

COMISION NACIONAL DE ENERGIA ATOMICA
DEPENDIENTE DE LA PRESIDENCIA DE LA NACION

PROGRAMA MULTINACIONAL DE METALURGIA
(Programa Regional de Desarrollo Científico y Tecnológico-OEA)

ESTUDIO DE SUPERFICIES, PROPIEDADES Y TECNICAS DE ANALISIS

Jesse R. Lumsden

Tercer Seminario Latinoamericano en el Nivel de Postdoctorado
Tema: CORROSION

Buenos Aires - Argentina
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THE ASPECTS OF SPUTTERING IN SURFACE ANALYSIS METHODS

G.K. WEINER

I. Introduction

Low energy electron diffraction (LEED) requires single crystal targets which are atomically clean and well ordered up to the outermost atomic layer. By heating, such perfectly clean surfaces can be obtained with only a limited number of materials. From many other materials, it is not possible to remove oxide, carbide, nitride, or other tenacious layers by heating without melting or subliming the sample.

Farnsworth et al. [1] introduced in situ sputtering for cleaning solid surfaces in LEED studies using argon ions of less than 500 eV energy. It was found that it is necessary to remove the bombardment damage and drive out the embedded argon atoms by annealing at elevated temperature.

In composition analysis of a surface or of the "selvedge" ("near-surface region which differs from the bulk by virtue of its proximity to the surface") [2], it is usually necessary to remove remnants of cleaning acids, solvents, polishing compounds or other impurities which are acquired from the environment during handling. Sputtering has turned out to be an indispensable tool for this purpose. Beyond that, sputtering plays an increasingly important role as an in situ microsectioning technique for determining composition versus depth profiles.

Table 1 gives in matrix form a survey of compositional analysis methods based on physical phenomena. Methods for which commercial apparatus is available are underlined. *Surface* analysis methods with a depth resolution of less than $\sim 100 \text{ \AA}$ are listed in the three heavily-lined quadrants $h\nu \rightarrow e$, $e \rightarrow e$, and ions $\rightarrow$ ions. Of those, only nuclear backscattering of MeV H^+ or He^+ ions is nondestructive and permits composition vs. depth analysis without substantial sputtering [3]. The ion microprobe or secondary ion mass analysis (SIMS) [4] and mass spectroscopy of sputtered neutrals [5,6] rely, of course, on sputtering. If a large analysis area is available ($> 0.1 \text{ cm}^2$) a complete mass spectrum with SIMS can be obtained with only 1/100 of a monolayer removed [7]. This "static" method then becomes nearly non-destructive. In low energy ion scattering spectroscopy (ISS) [8] sputtering of the surface is unavoidable. In fact, an initial sputtering dose is required for

TABLE 1

Survey of compositional analysis methods based on physical phenomena
(Methods for which commercial apparatus is on the market are underlined)

		Excitation →		
← Emission	$h\nu$	$h\nu$	e	Ions
	X-ray fluorescence	<u>Electron microprobe</u> X-ray appearance or disappearance spectroscopy (APS, DAPS)	Surface composition analysis of neutral and ion impact Radiation (SCANIR) Ion induced X-rays (IEX)	
	Electron spectroscopy for chemical analysis (ESCA) or soft X-ray photoelectron spectroscopy (XPS) UV photoelectron spectroscopy (UPS) Auger electrons	<u>Auger electron spectroscopy (AES)</u> Ionization spectroscopy	Ion neutralization spectroscopy (INS)	
Ions			Ion microprobe or secondary ion mass spectroscopy (SIMS) Mass spectroscopy of sputtered neutrals Ion scattering spectroscopy (ISS) Nuclear backscattering	Field ion mass spectrometry

removal of hydrogen and hydrogen-containing surface molecules which obscure the single collision events with target atoms heavier than the "probing" ion on which the interpretation of ISS spectra is based.

Whenever sputtering becomes involved in the analysis technique, a more intimate knowledge of the sputtering process and of the role which various parameters may play is often required or desirable. A wealth of sputtering data has been accumulated in the past 15 years for monoatomic metals. However, present knowledge is very meager for multi-component materials.

For instance, there has been considerable concern about how much the sputtering process may alter the composition at the sample surface. Erroneous composition analysis would occur in those methods in which the sample surface is analyzed (ESCA, ISS, AES) but not in those methods (provided equilibrium is established) which analyze the sputtered species (SIMS).

After summarizing what is presently known about the sputtering process, we will discuss the more specific role which sputtering plays in the various recently matured surface analysis methods. Wherever appropriate, only the most recent references are listed. The reader can from there, readily locate earlier, often voluminous literature on the particular subject matter.

II. The sputtering process

A. SURVEY

It has become well established that physical sputtering by noble gas ions is the result of independent binary collisions just as if the ion (or "neutralized ion", because close to a metal surface, the ion before impinging becomes neutralized by a field-emitted electron) had collided with the atoms of a gas. In this three-dimensional billiard game, the masses of the collision partners and the individual cross-sections (which depend upon the ion velocity and the electronic structure of the partners play a decisive role. Under oblique ion incidence the forward sputtered atoms can be ejected with high energy in a single collision event. Under normal ion incidence, the momentum vector for sputtering has to change in direction by more than 90° and this requires more than one successive collision. When the ion mass is lower than the target atom mass, the ion may be scattered backward in a single collision event. If its mass is higher, it can only be reflected backward as a result of multiple collisions. At kinetic energies in excess of ~ 100 eV, some ions begin to become embedded in the lattice. The penetration depth for a 1 keV Ar^+ -ion is roughly $10 \text{ \AA}$ in Cu. The crystal structure and orientation enter the picture via the total cross-section area (shadowing effects). Whenever the projection of lattice points in a plane perpendicular to the ion beam is high, one observes a high sputtering yield but a low collection rate for ions and vice versa. A sputtered atom has to receive an energy which is sufficient to overcome its surface binding energy. Clusters have frequently been observed but the sputtered species are predominantly single atoms [9]. The heat of sublimation provides a measure for the *average* binding energy. Many atoms may be found at sites with lower numbers of nearest neighbors such as at grain boundaries or dislocations or an atom may be sitting on top of a filled plane. Such exposed atoms have a lower binding energy and are more readily sputtered than those from filled planes. A rather poorly defined sputtering energy threshold suggests that sputtering may often involve a two-step pro-

cess where an atom is first lifted in one impact to a more exposed position and is subsequently sputtered in another collision event. In particular, ion bombardment-induced or -enhanced surface migration of atoms plays an important part in the sputtering of metals and alloys.

Measurements of the sputtering yield and the average velocity (which is much higher than those of evaporated atoms) of sputtered atoms, show that sputtering is a rather inefficient process. Usually not more than 5% of the incident ion energy goes into kinetic energy of sputtered atoms, and the remaining 95% appears partly as kinetic energy of backscattered ions but mostly as heat in the target. A most fortunate point for the use of sputtering as a microsectioning technique is the fact that the sputtering yields for different elements or their compounds rarely differ by more than a factor of 10. For instance, the sputtering rate for W (under Ar^+ -ion bombardment) is only a factor of 2 or 3 lower than that of Al, whereas the evaporation rate for these two metals differs by more than 9 orders of magnitude (at 2000°C).

Ion bombardment of a surface is always accompanied by emission of γ -electrons. One distinguishes between potential and kinetic γ -electron emission. The former is caused by an Auger process (radiationless transition) when the neutralization of the impinging ion provides the energy for the ejection of another electron from the solid. The γ -coefficient is of the order of 0.1 with Ar^+ -ions (15.6 eV ionization energy) and is fairly independent of the kinetic energy of the ion up to 1 keV. Kinetic γ -emission becomes superimposed when the ions impinge with velocities of greater than $\sim 10^5$ m/sec and this can result in much larger γ values [10]. The γ -coefficients have to be taken into account in plasma sputtering if one wants to distinguish the bombarding ion current from the measured target current accurately. The γ -coefficient plays an important role in the charging of insulating surfaces.

Sputtering can be accomplished either with an ion beam, or with a target operated as a cathode in an abnormal d.c. glow discharge or immersed like a large negative Langmuir probe in an independently created low-gas-pressure plasma (triode sputtering). In plasma sputtering, the strong electric field in the vicinity of the target causes sputtered positive ions to be turned back towards the target and negative ions (as well as the γ -electrons) to be propelled away from the target. Sputtering of insulators is no problem with ion beams if one provides electrons (from a nearby thermionic filament) for neutralizing the accumulating positive surface charge. Bulk insulator sputtering in plasmas requires rf methods.

Many billiard game aspects of sputtering can be demonstrated when metal single crystals are sputtered because atoms are preferentially ejected in closely packed crystal directions. The resulting ejection- or deposit-patterns have been the subject of many experimental as well as theoretical studies and have contributed much to present understanding of the basic sputtering process.

For a more detailed discussion, the reader may find the survey in ref. 11

useful. A thorough discussion of theoretical aspects can be found in articles by Harrison et al. [12] and by Sigmund [13].

B. SPUTTERING YIELDS

The essential parameters which determine sputtering yields (atoms or molecules per ion) are: the kinetic energy, mass, electronic configuration, and angle of incidence of the bombarding ion and the atomic mass, electronic structure, crystal structure, orientation, binding energy of surface atoms, and the surface roughness of the target. The target temperature plays only a minor role.

Sputtering under normal incidence with Ne, Ar, Kr, or Xe ions requires a kinetic energy of at least about 4 times the heat of sublimation of the target material. For Ar, this threshold ranges from 13 eV for Al to 33 eV for W. Above the threshold energy, the yield rises first exponentially then linearly with ion energy, reaches a flat maximum, and finally decreases again with increasing ion energy. The maximum is located at lower energies for lighter ions (H^+ at ~ 2 keV) than for heavy ions ($Ar^+ - Cu$ at ~ 30 keV). This is the result of deeper penetration of the low mass ions.

Sputtering yields show characteristic periodicities with the positions of ions and target atoms in the periodic chart. Noble gas ions which behave most closely like hard spheres in the billiard game provide the highest sputtering yields. The noble metals Cu, Ag, Au for the same reason have the highest yields among vacuum-compatible metals (Zn and Cd next to Cu and Ag have still higher yields due to their lower heat of sublimation but these are undesirable elements to have in an ultra-high vacuum system). The energy transfer factor which is proportional to $mM/(m + M)^2$ plays an important role in sputtering yields. Therefore, yields for H^+ - or He^+ -ions impinging on heavier metal targets become very low. In Rutherford scattering with MeV H^+ - or He^+ -ions, the sputtering yield becomes negligibly small due to the deep penetration and low energy transfer coefficient. For the same reason, true physical sputtering with electrons is negligible unless the electrons have energies in the MeV range. A wide range of ion energies and ion species is involved in the various analysis methods. Tables 2–4 give some indication of sputtering yield values which may be encountered for polycrystalline metals. More detailed data with source references are found in various sputtering surveys [10,14,15]. Yield values often show considerable scatter which is most likely due to undefined surface roughness, preferred crystallite orientation in a nominally polycrystalline target, or the buildup of impurity layers on the target during sputtering.

At 0.13 Pa (10^{-3} torr) gas pressure, the mean free path of atoms between collisions is of the order of 4 cm. At pressures smaller than this, gas scattering of sputtered atoms back to the target becomes negligibly small. In plasma sputtering, the ion accelerating distance (sheath thickness) is usually very

TABLE 2

Sputtering yields in atoms/ion for 500 eV ion bombardment

	He	Ne	Ar	Kr	Xe
Be	0.2	0.4	0.5	0.5	0.4
C	0.07		0.12	0.13	0.17
Al	0.16	0.7	1	0.8	0.6
Si	0.13	0.5	0.5	0.5	0.4
Ti	0.07	0.4	0.5	0.5	0.4
V	0.06	0.5	0.65	0.6	0.6
Cr	0.17	1	1.2	1.4	1.5
Fe	0.15	0.9	1.1	1.1	1.0
Co	0.13	0.9	1.2	1.1	1.1
Ni	0.16	1.1	1.45	1.3	1.2
Cu	0.24	1.8	2.4	2.4	2.1
Ge	0.08	0.7	1.1	1.1	1.0
Y	0.05	0.5	0.7	0.7	0.5
Zr	0.02	0.4	0.7	0.6	0.6
Nb	0.03	0.3	0.6	0.6	0.5
Mo	0.03	0.5	0.8	0.9	0.9
Rb		0.6	1.2	1.3	1.2
Rh	0.06	0.7	1.3	1.4	1.4
Pd	0.13	1.2	2.1	2.2	2.2
Ag	0.2	1.8	3.1	3.3	3.3
Sm	0.05	0.7	0.8	1.1	1.3
Gd	0.03	0.5	0.8	1.1	1.2
Dy	0.03	0.6	0.9	1.2	1.3
Er	0.03	0.5	0.8		
Hf	0.01	0.3	0.7	0.8	
Ta	0.01	0.3	0.6	0.9	0.9
W	0.01	0.3	0.6	0.9	1.0
Re	0.01	0.4	0.9	1.3	
Os	0.01	0.4	0.9	1.3	1.3
Ir	0.01	0.4	1.0	1.4	1.6
Pt	0.03	0.6	1.4	1.8	1.9
Au	0.07	1.1	2.4	3.1	3.0
Th		0.3	0.6	1.0	1.1
U		0.5	0.9	1.3	

small and ion collisions within the sheath can be neglected. Under these conditions, the sputtering yield becomes independent of gas pressure. In ion beam sputtering where longer distances of travel are involved, the kinetic energy of the ions can be scattered over more atoms (including neutrals) and more directions. Accordingly, in ion beam sputtering, the gas pressure may already become important when it exceeds 10^{-2} Pa.

Much more stringent requirements exist with respect to the background pressure of reactive gases. With about one equivalent monolayer per second

TABLE 3

Sputtering yields in atoms/ion for 1 keV ion bombardment

	Ne	Ar	Kr	Xe
Fe	1.1	1.3	1.4	1.8
Ni	2	2.2	2.1	2.2
Cu	2.7	3.6	3.6	3.2
Mo	0.6	1.1	1.3	1.5
Ag	2.5	3.8	4.5	
Au		3.6		
Si		0.6		

TABLE 4

Sputtering yields in atoms/ion for 10 keV ion bombardment

	Ne	Ar	Kr	Xe
Cu	3.2	6.6	8	10
Ag		8.8	15	16
Au	3.7	8.4	15	20
Fe		1.0		
Mo		2.2		
Ti		2.1		

arriving at a surface at 10^{-4} Pa gas pressure, the competition between surface layer formation and sputtering becomes serious at sputtering rates of 100 Å/min which is often used in profiling. If the sample provides a high sticking coefficient to the reactive background species, the background pressure should be at least down to 10^{-6} Pa. The removal of only 1/100 of a monolayer in a static SIMS scan requires background pressures better than 10^{-10} Pa at which reactions with background gases should become negligible.

Commercially available sputter-ion guns for profiling are usually operated with Ar^+ ions at energies of 1–5 keV. Little reliable yield data are available in this energy range. If the thickness of a thin film is known, profiling provides an excellent means for calibrating sputtering rate vs. sputtering time under the actual operating conditions. As determined with AES profiling with an Ar^+ ion beam of 2 keV with $150 \mu\text{A}/\text{cm}^2$ ion current density, the sputtering rates for stainless steels, Ta, SiO_2 , Ta_2O_5 , etc. lie in the range 70–130 Å/min, for Pt at 230 Å/min, and for Cu, Ag, and Au, at 300–400 Å/min. Such rates are adequate for most profiling tasks.

The question of whether it would be better to switch to a heavier noble

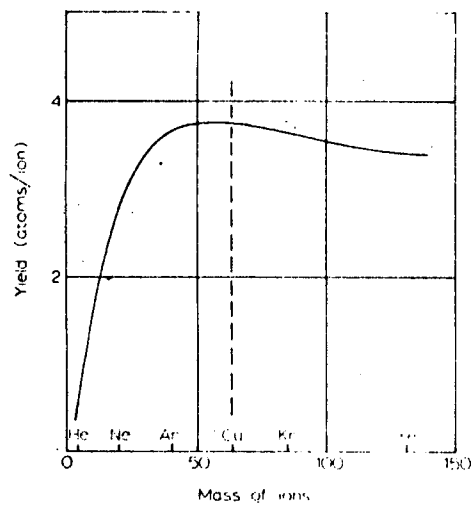


Fig. 1. Sputtering yield of Cu bombarded with 1 keV noble gas ions under normal incidence [16].

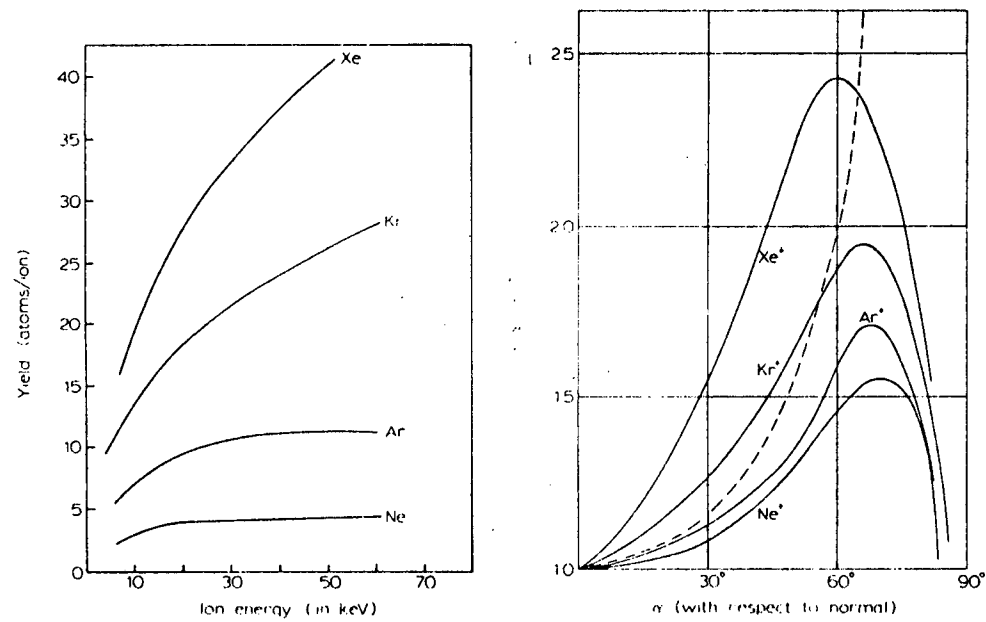


Fig. 2. Sputtering yield of Au vs. ion energy for various noble gas ions [17].

Fig. 3. Sputtering yield increase of Cu for bombardment by various noble gas ions under oblique incidence. The broken line is the $1/\cos\alpha$ curve which separates rate increase from rate decrease [16].

gas for achieving higher sputtering rates sometimes arises. Taken from recent measurements by Oechsner [16], performed with normal incident 1 keV He, Ne, Ar, Kr, Xe ions, Fig. 1 shows that Ar is the best choice for Cu and probably for most medium atomic weight target materials. At higher bombarding energy or higher mass materials, the sputtering yields for Xe^+ become considerably higher than for Ar^+ as shown in Fig. 2 [17].

Oechsner [16] recently reported a wealth of improved data on the influence of the angle of incidence of the ions on sputtering yields. At 60–70° from the normal, the yields in the energy range 0.5–2 keV rise to maximum values which are 1.5–2.8 times higher for high mass ions (Fig. 3) and higher for the low sputtering yield metals. With an ion beam, the ion current density decreases with the cosine of the angle α between beam and the normal to the surface, i.e. the sputtering rate-increase, if any, is much less than the yield increase. The broken curve in Fig. 3 shows the reciprocal of the $\cos \alpha$ dependence of $Y(\alpha)/Y(0)$. Only above this curve does one achieve in a beam a higher sputter removal rate. It would, of course, be erroneous to conclude that the sputtering at a target under normal ion incidence should increase with increased surface roughness. The reverse is true because sputtered atoms are preferentially ejected in a forward direction and atoms sputtered from a micro-slope are mostly ejected towards the target and not away from it. Under very oblique incidence, the sputtering yield can decrease drastically with increased sputter etch roughening of the surface due to shadowing effects. Unless the target is bombarded simultaneously with several ion guns from different directions or rotated during bombardment, it is advisable in profiling to ion-bombard the target as nearly as possible under normal incidence, even though this causes more pronounced “knock in” effects as described below.

Little yield data are available which show the influence of crystal structure and crystallite orientation. The latter subject, of course, is of much importance in etching and profiling. In the medium ion-energy range, from several 100 eV to 1 keV, the yield differences between different low index planes of a single crystal rarely exceed 50%. Even in such an extreme case as a metal in its polycrystalline or its liquid state (Sn, Al), the sputtering yield was found to differ not much more than 50%. At higher energy, channeling of ions in “open” crystal directions causes the yields to differ more substantially. In Cu at 5 keV Ar^+ -ion bombardment, for instance, the sputtering yield of a (111) surface is nearly double that of a (110) surface.

As already mentioned, the target temperature seems to play no major role in the sputtering yields of metals. At low bombarding energy (<1 keV) the sputtering yields tend to decrease with increasing temperature due to the annealing of more loosely bound atoms on the surface (such as created in a previous ion impact) to positions of stronger binding. At high bombarding ion energies (>10 keV) when metals are heated to within 250°C of their melting point, “thermal sputtering” becomes superimposed on binary colli-

TABLE 5

Sputtering yields of oxides and their metals under 10 keV Kr⁺-ion bombardment [19]

Oxide	Y (total atoms/ion) for oxide	Y (atoms/ion) for metal
Al ₂ O ₃	1.5	3.2
MgO	1.8	8.1
MoO ₃	9.6	2.8
Nb ₂ O ₅	3.4	1.8
SiO ₂	3.6	2.1
SnO ₂	15.3	6.5
Ta ₂ O ₅	2.5	1.6
TiO ₂	1.6	2.1
UO ₂	3.8	2.4
V ₂ O ₅	12.7	2.3
WO ₃	9.2	2.6
ZrO ₂	2.8	2.3

sional sputtering so that the apparent sputtering yield increases with temperature [18].

It should be emphasized again that only few reliable sputtering yield data of alloys or compounds exist. Some recent data on oxide yields obtained by Kelly and Lam [19] for 10 keV Kr⁺-ions are listed in Table 5. They found that, contrary to widespread belief, oxides have little effect as protective barriers to metals. A careful study of the sputtering yield of two phase Ag—Ni and Ag—Co alloys by Dahlgren and McClanahan [20] revealed that the low yield component, if present in an amount exceeding 10% (by volume), has the determining influence on overall yield.

With a primary ion current density J^+ [$\mu\text{A}/\text{cm}^2$], a sputtering yield Y (atoms/ion), an atomic or molecular weight A of target atoms or molecules (g/mole) and the specific weight δ [g/cm^3] of the target material, one calculates a removal rate $\dot{S}$ [$\text{\AA}/\text{min}$] of

$$\dot{S} = 0.06 Y J^+ A / \delta$$

In profiling applications, a uniform, layer-by-layer microsectioning is usually much more desirable or important than an accurate knowledge of the sputtering rate. Uniformity is more readily obtained if the analyzed area is much smaller than the sputtered area. AES but not ESCA can meet this goal very simply by making the electron beam at least 2 orders of magnitude smaller than the sputter ion beam (which has usually mm size dimensions) and to aim with the analyzing beam towards the center of the sputtering crater. It is desirable to achieve a beam which causes a flat bottom sputtering crater. Wobbling or scanning of the ion beam can produce craters of any desired flatness and uniformity.

In AES, if the crater has a peaked shape, the alignment of the electron and the ion beam is important for achieving the maximal and reproducible sputtering rate. Deflection plates for the ion beam in combination with a Faraday collector are convenient for the alignment procedure. An occasional profile of a Ta sample which has been anodized to a known thickness is a simple way for checking that the sputtering rate has remained unchanged. A crystal oscillator film thickness sensor mounted close to the target for receiving part of the sputtered material is often a useful addition for monitoring relative sputtering rates. The sensor receives material from the whole sputtering crater but only in a certain direction of ejection. This scheme does not provide sufficiently accurate results for converting the sputtering time into a sputtered thickness scale because the crater walls are included and the angular distribution of sputtered atoms can be different for different materials.

C. SPUTTER ETCHING

Sputtering provides universal and well-reproducible etching because it is applicable to all materials. However, many details of etching are still unexplained or unpredictable even in such a supposedly simple case as that of a monoatomic metal.

The sample surface should be smooth otherwise, with a monodirectional ion beam, the etch rate will be different at differently inclined microslopes.

Sputter-etched polycrystalline metal targets show that grain boundaries or dislocations (often created by the bombardment) become delineated as furrows or pits. Differently oriented crystallites are attacked with different rates and each grain shows characteristic fine etch features (facets) which reveal the crystallite orientation.

The sputtering rate of a high-yield crystallite becomes lower as it recesses deeper below its surroundings because fewer atoms are able to clear the surface. Accordingly, the degree of surface roughness reaches a steady-state value. A single crystal or an amorphous target are etched more uniformly. The different sputtering rates of differently oriented crystallites or of grain boundaries are a disturbing fact in profiling because an interface deep below the surface appears to be broadened. The ratio of average crystallite size to film overlayer thickness plays an important role in the obtainable depth resolution at an interface.

Ion bombardment causes considerable bombardment damage and has a tendency to convert a material to the amorphous state. Well-defined ejection patterns are obtained in sputtering from metal single crystals even when they are kept at room temperature. This indicates that the surface retains, or at least resembles, its single-crystal structure under the bombardment. This fact is somewhat surprising in a material such as W which has a recrystallization temperature much above room temperature. The damage created by an ion impact must obviously anneal out so fast that the next ion which strikes

there encounters a somewhat ordered surface again. This situation is different in semiconductors or insulators. When the bombardment is performed below a characteristic annealing temperature [Ge 550°K and Si 700°K for Ar⁺-ion bombardment] [21], the surface layer becomes and stays amorphous and ejection patterns can no longer be observed. It is interesting to note that a 1 keV Ar⁺-ion impact on Ge displaces about 50 surface atoms while only 1.7 atoms/ion are being sputtered [22]. Although this has not been demonstrated yet, one should expect the same amorphization phenomenon to occur in metals much below room temperature. Cooling of the target to liquid nitrogen temperature may provide a possible method for achieving more uniform, less orientation-dependent etch rates in polycrystalline materials.

Aside from singular features such as the often-observed cones, even an amorphous surface develops undulating features after long sputtering in the form of rilles or bumps [23] or shows the so-called "lemon-peel" pattern. The reasons for this are still poorly understood. Sputter etching of a single-crystal surface is governed by a complicated interplay between creation and movement of dislocations, surface migration of atoms, and the tendency of the surface to achieve its lowest free-energy configuration. Considerable effort has been spent in developing theories for predicting the evolution of surface topographies of impurity-free amorphous solids under ion bombardment [24–28]. The dependency of the sputtering rate on the angle of incidence of the ions plays an important role in these theories. If secondary effects such as redeposition of sputtered atoms, sputtering by sputtered atoms, bombardment-induced directional surface migration of atoms etc. are negligible, planes on a surface which are parallel to the ion beam or inclined at the angle of maximum sputtering attack would be stable and become the dominant features on an amorphous surface. Ion beam polishing has been attempted with varying degrees of success [29–32]. Oblique ion incidence, sample rotation and fairly low ion energy [33,34] seem to be beneficial for obtaining a good polishing action. Under favorable conditions, profiles with a remarkable depth resolution can be obtained. For instance, Fig. 4 shows an AES profile of a twenty-five layer (each layer 50 Å thick) single-crystal epitaxially grown periodic thin film structure (Esaki tunneling device) [35].

An extreme case of surface roughening by sputtering can arise when a minority metal species is difficult to sputter from its host metal. For instance, rather small amounts (<0.1%) of Mo, W, or Cr, etc. in Al, Au, Ag, Cu, etc. can give rise to the formation of cones which make sputtering a rather poor micro-sectioning technique. For example, Fig. 5 shows what happened to an Au surface which was seeded with a rather small flux of Cr atoms during sputtering. The Cr atoms can be furnished either as an internal impurity or deposited from another Cr source during the sputtering of a pure Au target [36]. It is obvious that such a surface exhibits a rather low sputtering yield and any interface must become washed out because atoms

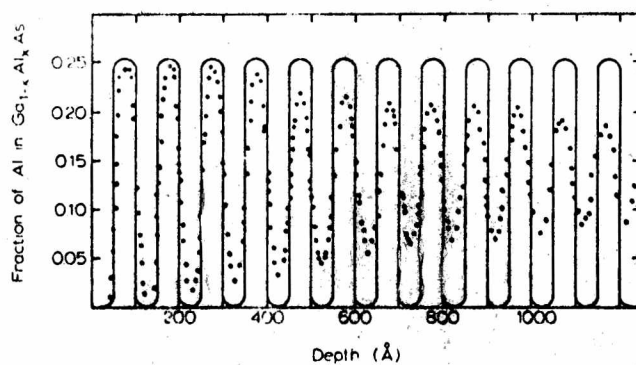


Fig. 4. Composition vs. depth profile of a superlattice structure $GaAs-Ga_{1-x}Al_xAs$ obtained with AES [35].

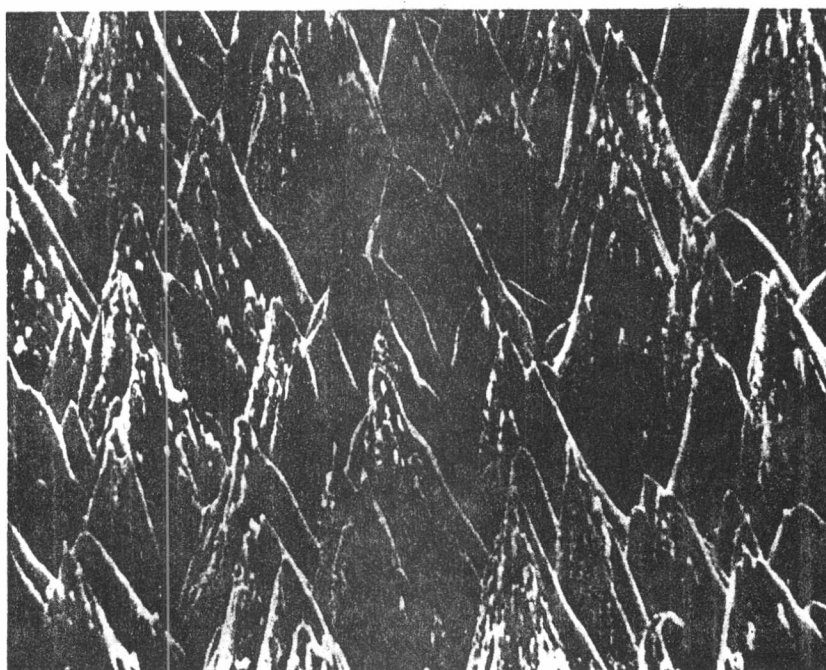


Fig. 5. SEM picture of sputtered Au target onto which a small amount of Cr was deposited during sputtering. The cone height is several microns.

sputtered back and forth between the cones can linger on the surface for a long time. The angles of incidence of the ion beam and analyzing beam on such a surface have a large influence on the results. Surface migration of the low sputtering yield species seems to play an essential part in the formation of cones and this cone formation can be avoided if the sample is kept below a critical temperature during sputtering. It is unlikely that cone formation is a problem in profiling of thin, smooth films in which only hundreds of Å thickness are involved. But the fact that certain atomic species are more difficult to sputter from a substrate of other atoms than from their own may give erroneous composition results as discussed in the next section. Of interest is the fact that pillars with a very narrow apex angle are produced at the surface of organic materials like Teflon, blood cells, etc. as observed under ion or neutral atom bombardment in the SEM [37].

D. COMPOSITION CHANGES CAUSED BY ION BOMBARDMENT

Composition changes of a monoatomic metal surface bombarded by noble gas ions at a low impurity background pressure are confined to the implantation of the noble gas ions. Incorporation of noble gas is more pronounced at a rough surface because gas atoms may become buried underneath other sputtered and redeposited atoms. Since the sputtering yield is usually above unity and the implantation depth is so shallow, little noble gas can accumulate on the surface in profiling with ion beams in the keV range. Any embedded noble gas is readily detectable with AES or ESCA. With ISS (90° scattering) analysis, however, detection is possible only if a lighter noble gas than the embedded species is used. If noble gas peaks cause interference with AES analysis peaks, a rather infrequent occurrence, it is always possible to switch to another noble gas for bombardment.

Any metal surface, except possibly Au, becomes very reactive and acquires a high sticking coefficient for impurity atoms after cleaning by ion bombardment. Therefore, the impurity background pressure requirements become very stringent for keeping the surface clean after bombardment.

A much more complicated situation arises in multi-component materials. For instance, if such a sample is cleaved in UHV in the analysis apparatus, the topmost surface composition will most likely be different from that of the bulk, even without any ion bombardment. If the samples cleave intergranularly, the new surface consists of the original grain boundaries which have a composition which is often different from the bulk. But even if the sample cleaves intragranularly, different thermodynamic driving forces arise for different constituents because the surface tries to achieve its lowest surface-free energy.

An answer to the question of what the ion bombardment does to the surface composition of a multi-component sample is of much wider interest. This is particularly true in those methods in which the sample surface is

analyzed (as in AES, ISS, ESCA) instead of the sputtered material (SIMS). In the absence of significant bulk thermal diffusion, it is obvious that the material which is sputter-removed from a multi-component target must have the same composition as the bulk target, once equilibrium is established. However, the high-sputtering yield elements must become depleted at the target surface.

It should take very little sputtering (only some tens of monolayers) of a compound or a one-phase alloy to establish the new sputter-equilibrated surface layer which then recedes with an unaltered composition different from the bulk material. In multiphase materials in which the components exist as separate crystallites, the time for reaching equilibrium can be much longer because topographical changes at the surface become important. For example, high-yield crystallites become recessed until their sputtering rate is reduced to the point that the constituents leave in the same ratio as they exist in the bulk.

Any composition change caused by different sputtering rates of different species in a one-phase alloy or in a compound is most pronounced in the outermost layers from where the vast majority of sputtered atoms are ejected. Thus ISS, which analyzes only the topmost layer, should be most seriously concerned with this problem. In AES and ESCA, the information is gathered from a layer which is between 4 and 20 Å thick depending on the energy of the ejected electrons. For many elements, the latter two methods offer the possibility of comparing analysis peaks which originate at different average depths. The composition changes at the sample surface are of no concern in bulk analysis with SIMS or in glow discharge mass spectrometry after equilibrium conditions are established.

Experimental data show that the bulk-sputtering yield values of the components are not useful for predicting the composition of the altered surface. Aside from the ion energy and the masses of the collision partners, the phase diagram of the material, the "surface phase diagram" [38], the directionality of bonds and the sample temperature (which determine surface migration) become additional important factors. At this stage, the situation becomes so complicated that one has to depend largely on experimental evidence.

An important difference exists between bombardment in a plasma or with an ion beam. A much lower electric field exists at the target surface in ion-beam sputtering than in plasma sputtering where the ion sheath adjacent to the sample surface creates a strong electric field. Atoms sputtered as positive ions are more likely to be pulled back to the negative target surface in a plasma than in ion-beam sputtering while negative ions are accelerated away from the sample. This should lead to enrichment of the sample surface with electropositive atoms.

Changes in composition can also arise at the surface of an insulator film from charging and subsequent induced motion of impurities. Some interesting studies on this were recently performed by McCaughan and Kushner

Review: Sputtering mechanisms for amorphous and polycrystalline solids

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In this article the latest developments in the theory of sputtering of amorphous and polycrystalline targets are reviewed and comparison is made with available experimental data. Special attention is given to differences in the various theoretical approaches to the sputtering yield problem and the conclusions derived therefrom.

1. Introduction

The phenomenon of atomic ejection from solid surfaces under bombardment by energetic ions is known as "sputtering". The sputtering yield, S , is defined as the number of target atoms ejected per incoming ion. For some time, the sputtering process was thought of as an evaporation process which implied that sputtering was due to very high local temperatures created at or very near the surface by the bombarding ions. Later, however, measurements of the dependence of sputtering yield on the angle of incidence of the bombarding ions established that sputtering is really a momentum transfer process rather than an evaporation process. In the past decade various successful theories have been developed based on the model of atomic collision cascades generated inside the solid target by the bombardment ion. An incoming ion penetrates the surface and strikes a target atom. This atom is usually not itself sputtered, (at least in the case of perpendicular incidence, a struck atom always has a velocity component in the direction away from the target surface), but in its turn, collides with neighbouring lattice atoms producing secondary displacements. Some of these recoil atoms have the possibility of getting scattered back towards the surface with sufficient energy to collide with and liberate surface atoms. Meanwhile, the incident ion describes a random path within the solid, losing energy by nuclear collisions and electronic excitation and finally either comes to rest or leaves the surface as a sputtered atom. Thus sputtering is a typical multiple collision process involving a cascade of moving target atoms.

In the present article we shall consider only the

sputtering of amorphous and polycrystalline solids. By confining ourselves to random targets we avoid other processes such as channelling, focused collisions and anisotropy of sputtering yield which are generally associated with the regular lattice structure of single crystals. In a polycrystal where any anisotropy of the ejection pattern which could be caused by regular lattice structure is small, we can assume these lattice effects can be averaged out and therefore can be treated the same way as amorphous materials. We shall review the more recent and more important theories on sputtering and make comparison with experimental data wherever possible. Generally speaking, the sputtering yield of amorphous solids is calculated under the assumption of random slowing down in an infinite medium. The steps taken are as follows: (1) to determine the energy loss in the collisions; (2) to determine the number of primary and secondary recoil atoms; (3) to find how many of these atoms arrive at the target surface; and (4) to find the atoms which have sufficient energies to overcome surface binding and appear as sputtered atoms outside the solid. In addition to consideration of the sputtering yield, we shall also discuss the sputtering efficiency of amorphous materials, γ , defined as the fraction of bombarding ion energy leaving the target surface via sputtering.

2. Sputtering yield theory

There are three recent important theories on the sputtering of amorphous and polycrystalline solids, all of which have been successful to some extent in explaining experimental observations. They are due to Thompson [1], Sigmund [2] and

Brandt and Laubert [3]. We shall endeavour to reproduce these three theories here in a condensed form so that we can compare their different approach to the sputtering yield problem. In doing so, we try to adhere as closely as possible to the symbols used by the respective authors so that readers can easily refer to their original papers if necessary.

2.1. Thompson's theory (1968)

Consider an interaction between a bombarding particle and an infinite solid, leading to atoms recoiling from their lattice sites with energy E_2 . This is called the primary event.

The density of atoms recoiling in the energy range between E_2 and $E_2 + dE_2$

$$= q(E_2) dE_2. \quad (1)$$

Each of the primary recoils generates a secondary collision cascade in which energy is shared by a series of two-body collisions. For one recoil at E_2 , the number of atoms slowed down through E' is given by a function $v(E_2, E')$.

Density of atoms slowed down through E' in 1 sec

$$= \int_0^\infty q(E_2) v(E_2, E') dE_2. \quad (2)$$

We can write the flux of atoms in the energy range between E' and $E' + dE'$ crossing any internal surface and travelling into a solid angle $d\Omega'$ in direction $\mathbf{r}'$ as:

$$\Phi'(E', \mathbf{r}') dE' d\Omega' = \int_0^\infty q(E_2) \frac{v(E_2, E')}{dE'/dx} \frac{\cos \theta d\Omega' dE'}{4\pi} \quad (3)$$

where dE'/dx is the energy loss per unit path length of the atoms in the secondary cascades.

It can be shown [4] that for a random cascade

$$v(E_2, E') = \eta E_2/E' \quad (4)$$

where η is of order unity and is equal to 0.52 assuming an inverse square form of potential between colliding atoms.

For the term dE'/dx we neglect energy loss due to electronic excitation (true for ion energy below $\sim M_2$ keV [5]), and consider only energy transfers in elastic collisions between target atoms (mass M_2). Then

$$dE'/dx \sim E'/D \quad (5)$$

where D is the nearest neighbouring spacing.

Substituting Equations 4 and 5 into Equation 3, we obtain

$$\Phi'(E', \mathbf{r}') dE' d\Omega' = \frac{\eta D}{E'} \int_0^\infty q(E_2) E_2 dE_2 \frac{\cos \theta d\Omega' dE'}{4\pi} \quad (6)$$

provided E' is small compared to E_2 and can be brought out of the integral.

Now we have to find $q(E_2)$, the function which determines the density of recoil atoms. Let us assume the incident ion has mass M_1 and energy E_1 and target atoms mass M_2 and energy E_2 . Their interaction is characterized by the Screened Coulomb potential, sometimes called Thomas-Fermi potential,

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \exp(-r/a) \quad (7)$$

where $a = Ca_0/(Z_1 Z_2)^{1/6}$, C is a constant of the order unity and e is the electronic charge. For a limited range of r , one can fit an inverse square function to the screened Coulomb potential [5] and obtain

$$V(r) = \frac{2E_R}{e} (Z_1 Z_2)^{5/6} (a_0/r)^2 \quad (8)$$

where $E_R = e^2/2a_0 = 13.6$ eV; $a_0 = 0.53$ Å and $e = 2.718$.

Equation 8 is applicable to ion energy range from 10^3 to 10^5 eV. For lower energies the Born-Mayer potential

$$V(r) = A \exp(-r/b)$$

has to be used.

From $V(r)$ one can calculate $d\sigma/dE_2$, the differential cross section for producing a primary event [5], and using the fact that

$$q(E_2) = n\Phi_1 \cdot d\sigma/dE_2$$

where n = density of target atoms, Φ_1 = flux of bombarding ion crossing unit area normal to their path, we find:

$$q(E_2) = \frac{\pi^2 a^2 n E_a A^3 \Phi_1}{8 E_1^3 E_2^{3/2}} \text{ for } E_2 < AE_1 \quad (9)$$

where AE_1 = maximum recoil energy =

$$\frac{4M_1 M_2}{(M_1 + M_2)^2} E_1; \quad a = \text{screening radius} = a_0/(Z_1 Z_2)^{1/6}; \quad E_a = \text{the value of } E_1 \text{ which gives the distance of closest approach } a, \text{ in a head-on collision} = 2E_R(Z_1 Z_2)^{5/6} (M_1 + M_2)/eM_2.$$

To transform $\Phi'(E')$, the flux inside the solid.

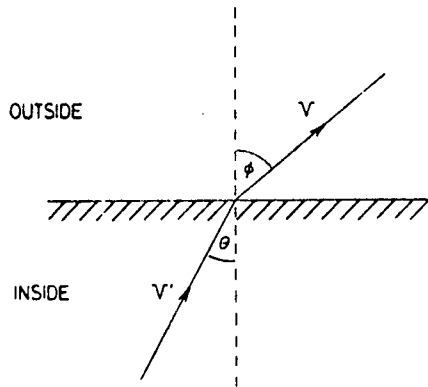


Figure 1 Change in magnitude and direction of the velocity of an atom leaving a target surface.

into $\Phi(E)$, the flux which can be measured outside the surface, a simple assumption is made of a binding force normal to the surface. So when an atom leaves the surface, its velocity component parallel to the surface will be unaffected but the normal component of its kinetic energy will be reduced by E_b .

This means that parallel to the surface (see Fig. 1), we have

$$v' \sin' \theta = v \sin \phi$$

and normal to the surface

$$E' = E + E_b.$$

From these two equations we can transform Equation 6 into:

$$\Phi(E, \phi) d\Omega dE = \frac{\eta D \cos \phi}{4\pi(1 + E_b/E)^3 E^2} \int_{E+E_b}^{\infty} E_2 q(E_2) dE_2 d\Omega dE. \quad (10)$$

If we consider the spectrum as a function of E at a fixed angle ϕ , then at energies where $E_b \ll E \ll E_t$, we see that approximately

$$\Phi(E) \propto 1/E^2.$$

Thompson [1] has shown experimentally that the energy spectra of ejected Au atoms under bombardment by Ar^+ and Xe^+ ions exhibit this E^{-2} dependence, and indeed the main purpose of Thompson's theory was to predict the shape of the energy spectrum.

Now if we substitute Equation 9 into Equation 10 and integrate first over $d\Omega$ with Φ going from 0 to $\pi/2$ and then over dE with E from 0 to $1/E_t$ and finally divide throughout by $\Phi_1 \cos \psi$ where

ψ is the angle of ion incidence, we obtain the sputtering yield in atoms/ion:

$$S = \frac{\pi^2 a_0^2 n^{2/3}}{8e} \frac{E_{11}}{E_b} \frac{M_1 (Z_1 Z_2)^{3/4}}{M_1 + M_2} \sec \psi \quad (11)$$

where we have put $D = n^{-1/3}$ and $\eta = \frac{1}{2}$.

The important points in this expression are that: (1) S is proportional to a function of the atomic masses and atomic numbers of the bombarding ion and target atom; (2) S is independent of E_1 , the energy of the bombarding ions in the range $E_b \ll E_t \ll E_a$. E_b = sublimation energy ≈ 3 to 5 eV for metals, $E_a \approx 1$ to 100 keV; (3) S is proportional to $\sec \psi$.

2.2. Sigmund's theory (1969)

The target surface under bombardment is assumed to have a planar surface. Consider a collision cascade initiated by an ion which starts its motion in a plane $x = 0$ at a time $t = 0$. The distribution function

$$G(x, v_0, v, t) d^3 v_0 dx \quad (12)$$

defines the number of atoms which, at time t , are moving in a layer between x and $x + dx$ and have velocities lying within a velocity-space element $d^3 v_0$ about v_0 .

The sputtering yield for backward sputtering of a target with a plane surface at $x = 0$ can be written as

$$S = \int d^3 v_0 |v_{0x}| \int_0^\infty dt G(0, v_0, v, t) \quad (13)$$

where

$$\frac{dx}{dt} = v_{0x}.$$

Now we write

$$F(x, v_0, v) = \int_0^\infty G(x, v_0, v) dt \quad (14)$$

$F(x, v_0, v) |v_{0x}| d^3 v_0$ is the total number of atoms that penetrate the plane x with a velocity $(v_0, d^3 v_0)$ during the period of the collision cascade.

We then introduce the function

$$H(x, v) = \int d^3 v_0 |v_{0x}| F(x, v_0, v) \quad (15)$$

which in fact represents the sputtering yield for the case where the starting point of the cascade is at $x = 0$ and the sputtered surface is in the plane x . Thus $H(x, v)$ is measurable in principle for $x < 0$ for backward sputtering.

Next we replace velocity variables with energy variables and write the sputtering yield as

$$S(E, \eta) = H(x=0, E, \eta) \quad (16)$$

where E = energy of the impinging particle and η = direction cosine relative to x -axis.

Finally, the Boltzmann transport equation is formulated in terms of $H(x, E, \eta)$ and solved using the Legendre polynomial expansion

$$H(x, E, \eta) = \sum_{l=0}^{\infty} (2l+1) H_l(x, E) P_l(\eta) \quad (17)$$

where $P_l(\eta)$ are Legendre polynomials.

To solve the Boltzmann equation, other input quantities such as electronic stopping cross section, the differential cross section for elastic collisions and the surface binding force have to be specified.

(a) For electronic stopping power, Lindhard's expression is used:

$$S_e(E) = KE^1 \quad (18)$$

The constant K depends on the atomic numbers and masses of the ion and target.

(b) For the collision cross section, the power potential approximation to the Thomas-Fermi cross section for elastic scattering described by Lindhard *et al* [7, 8] is chosen. So we have:

$$d\sigma = CE^{-m} T^{-1-m} dT \quad (19)$$

where E = projectile energy; T = recoil energy; $m = 1$ for Rutherford scattering ($= \frac{1}{2}$ for energy from 10^3 to 10^5 eV (corresponds to the case of an inverse square potential), $= \frac{1}{3}$ for energy from 10^2 to 10^3 eV, $= 0$ for energy less than 10^2 eV).

These values of m hold true for interaction between ions and atoms of medium masses.

The constant C is given by [8]:

$$C = \frac{1}{2} \pi \lambda_m a_{22}^2 (2Z_2^2 e^2/a_{22})^{2m} \quad (20)$$

for ion and atom with equal masses

$$C = \frac{1}{2} \pi \lambda_m a_{12}^2 (M_1/M_2)^m (2Z_1 Z_2 e^2/a_{12})^{2m} \quad (21)$$

for ion and atom with unequal masses, where Z_1 and Z_2 are atomic numbers, a_{12} and a_{22} are Thomas-Fermi screening radii, and λ_m are dimensionless constants equal to

$$\lambda_1 = 0.5, \lambda_2 = 0.327, \lambda_{1/3} = 1.309 \quad (22)$$

For collisions in the eV range, $m = 0$ and we have, from Equation 19:

$$d\sigma = C_0 T^{-1} dT \quad (23)$$

where

$$C_0 = \frac{1}{2} \pi \lambda_0 a^2 \quad (24)$$

and $\lambda_0 = 24$, $a = 0.219 \text{ \AA}$.

The stopping power for elastic collisions is given by:

$$S_n(E) = \int_0^E T d\sigma = \frac{1}{1-m} CE^{1-m} \quad (25)$$

(c) The surface binding force which affects the ejection of a surface atom is chosen to be that of a spherically symmetric potential barrier type, i.e.

$$U(\eta_0) = U_0 \quad (26)$$

U_0 is of the order of a few eV for most metals.

With these three input quantities the Boltzmann equation is solved using the Legendre polynomial expansion (Equation 17) to give the sputtering yield

$$H(x, E, \eta) = \frac{3}{4\pi^2} \frac{F(x, E, \eta)}{NC_0 U_0} \quad (27)$$

where $F(x, E, \eta) dx$ is the amount of energy deposited in a layer (x, dx) by an ion of energy E starting at $x = 0$ and by all the recoil atoms. N is the atomic density of the target.

We can rewrite Equation 27 in the form

$$H(x, E, \eta) = \Lambda F(x, E, \eta) \quad (28)$$

where

$$\Lambda = \frac{3}{4\pi^2} \frac{1}{NC_0 U_0} \quad (29)$$

In the elastic collision region where electronic stopping is unimportant, the distribution $F(x, E, \eta)$ is approximately Gaussian and can be approximated by the Edgeworth expansion [9, 10] in terms of the moments $\langle x^n \rangle$:

$$F(x, E, \eta) = \frac{\nu(E)}{\langle \Delta x^2 \rangle^{1/2}} \left[\psi_0(\xi) - \frac{1}{6} \Gamma_1 \psi_3(\xi) - \dots \right] \quad (30)$$

where $\nu(E)$ is the amount of energy deposited in the target in the form of atom motion.

$$\langle \Delta x^n \rangle = \langle (x - \langle x \rangle)^n \rangle \quad n = 2, 3, \dots$$

$$\psi_n(\xi) = (d^n/d\xi^n) (2\pi)^{-1/2} \exp(-\xi^2/2) \quad n = 0, 1, 2, \dots$$

$$\xi = (x - \langle x \rangle) / \langle \Delta x^2 \rangle^{1/2}$$

$$\Gamma_1 = \langle \Delta x^3 \rangle / \langle \Delta x^2 \rangle^{3/2}$$

For backward sputtering at a surface at $x = 0$, we can obtain Equations 28 and 30 to give the sputtering yield

$$S(E, \eta) = \frac{AE}{\langle \Delta x^2 \rangle} [\psi_0(\xi_0) - \frac{1}{2} F_1 \psi_1(\xi_0) - \dots] \quad (31)$$

where $r(E) = E$ in the elastic collision region and $\xi_0 = -\langle x \rangle / \langle \Delta x^2 \rangle^{1/2}$.

For the power cross section (Equation 19), the moments $\langle x^n \rangle$ have the general form [11]:

$$\langle x^n \rangle = (E^{2m}/NC)^n h_n(\eta) \quad (32)$$

where $h_n(\eta)$ is some function of η . This means that ξ_0 and the contents of the square brackets in Equation 31 are independent of ion energy. The factor in front of the brackets is proportional to NCE^{1-2m} , which is essentially the stopping power (Equation 25). Hence the sputtering yield is a product of the stopping power and some function of the angle of ion incidence which may depend on m and the mass ratio M_2/M_1 .

We note that for medium mass ions and atoms, in the energy range from 10^3 to 10^5 eV, $m = \frac{1}{2}$, which makes the sputtering yield $S(E, \eta)$ independent of ion energy. This finding agrees with that of Thompson (Equation 11).

The angular dependence of the sputtering yield is given by Sigmund as

$$\frac{S(E, \eta)}{S(E, 1)} = \eta^{-f} = (\cos \theta)^{-f} \quad (33)$$

for not-too-oblique incidence, where $S(E, 1)$ is the yield for perpendicular incidence, $f \approx 5/3$ for mass ratios $M_2/M_1 \lesssim 3$ and Sigmund also shows that f is nearly the same for $m = \frac{1}{2}$ and $m = \frac{1}{3}$, indicating in the energy range from 10^2 to 10^5 eV the angular variation of the yield is not sensitive to ion energy.

2.3. Theory by Brandt and Laubert (1967)

This theory is based on the concepts advanced by Lindhard *et al* [6, 7] on the energy loss by an ion travelling in a solid. A comprehensive sputtering yield curve is derived which is valid for a wide range of ion-target combinations and for all ion energies large compared with the energy required to displace a lattice atom.

Consider an incoming ion of atomic number Z_1 , mass M_1 and initial energy E_1 colliding with a random target whose atoms have atomic number Z_2 , mass M_2 and average density N_2 . The ion loses energy by nuclear collisions and electronic excitation. After it has travelled a distance r , it displaces an atom from its lattice position and this atom recoils with energy E_2 . This primary recoil atom creates a secondary cascade of

displaced atoms. On average $dn_2(E)$ secondary recoil atoms are created in the energy range between E and $E + dE$.

Integrating over the whole distance travelled by the incoming ion, we can write the total number of atoms escaping from the target surface due to the atom motion caused by this ion, i.e. the sputtering yield, as

$$S = \gamma N_2 \int_{E_1} dq_{12}(E_2) \int_{E_1} dn_2(E) l_2(E_2 - E) \quad (34)$$

where $\gamma = (\cos \theta)^{-1}$ and θ is the angle between the direction of the ion beam and the normal to the target surface; $q_{12}(E_2)$ = cross section for energy transfer between the ion and target atom; and $l_2(E_2 - E)$ = the path length of the cascade, i.e. the distance away from the site of the initial event where $dn_2(E)$ atoms are dislodged. If the ion energy is large, then we have:

$$\frac{dn_2(E)}{dE} = \frac{1}{U_2} (1 - d_k(E)) \quad (35)$$

where U_2 = energy required to displace an atom from its rest position (about 20 to 30 eV for metals) and $d_k(E)$ = a numerical factor which accounts for the energy lost to electronic excitations.

Let E_c denote the energy at which electronic stopping power becomes comparable with nuclear stopping power, i.e. at ion energies $\geq M_2$ keV. For $E \ll E_c$, we have:

$$d_k(E) = \frac{3}{2} \alpha (E/E_c)^{\frac{1}{2}} + \dots \quad (36)$$

The constant α is slightly larger than unity. The stopping cross section of the target for the bombarding ions is given by

$$S_{12}(E_1) = \int_{E_1} E dq_{12} \quad (37)$$

According to Brandt and Laubert, $l_2(E)$ can be written as:

$$l_2(E) \approx l_0 [1 - \exp(-L(E)/l_0)] \quad (38)$$

where l_0 is a constant characteristic to the target material, and $L(E)$ the path length of energy propagation in the cascade.

Putting Equations 35, 37 and 38 into Equation 34, the sputtering yield becomes:

$$S = \gamma (E_1/U_2) N_2^{-1} [\phi(x) - \Lambda_k] \quad (39)$$

where x is a dimensionless variable given by:

$$x \equiv L_1 / \{l_0 N_2 S_{12}(E_1)\} \equiv \epsilon / \{\lambda_0 (l_{12} \sigma(\epsilon))\} \quad (40)$$

in which

$$\lambda_0 = 3.25 \times 10^{-3} \quad \text{for most metals} \quad (41)$$

$$\epsilon = E_1/\epsilon_{12} \quad (42)$$

where

$$\epsilon_{12} = Z_1 Z_2 \epsilon^2 (M_1 + M_2) / (a_{12} M_2) \quad (43)$$

$$a_{12} = (9\pi^2/2)^{1/3} a_0 (Z_1^{2/3} + Z_2^{2/3})^{-1} \quad (44)$$

$$a_0 = \hbar^2/mv^2 = \text{Bohr radius} \quad (45)$$

and

$$f_{12} = \{8M_1 M_2 / (M_1 + M_2)^2\} Z_2^{2/3} / (Z_1^{2/3} + Z_2^{2/3}) \dots \dots (46)$$

$\sigma(\epsilon)$ = the scaled nuclear stopping power

$$= (\mathcal{L}_{12}/\epsilon_{12}) N_2 S_{12} \quad (47)$$

where

$$\mathcal{L}_{12} = (M_1 + M_2)^2 / (4\pi a_{12}^2 M_1 N_2 M_2) \quad (48)$$

$\sigma(\epsilon)$ has been calculated by Lindhard *et al* [7] for the Thomas-Fermi approximation of the scattering potential (Equation 7).

Having defined x in Equation 39, Brandt and Laubert find, using Thomas-Fermi potential [8]:

$$\varphi(x) = 1 - \{2x - 1 + \exp(-2x)\}/2x^2 \quad (49)$$

and

$$\Delta_k = \alpha(x/x_c)^{1/2} \psi(x) \text{ for } \epsilon \ll \epsilon_c \quad (50)$$

where

$$x_c \equiv (\epsilon_c/\epsilon)x \quad (51)$$

$$\psi(x) = \frac{1}{2} \{1 + (3/2x^3)$$

$$[1 - x - (1 + x) \exp(-2x)]\}. \quad (52)$$

At high ion energies, we can rewrite Equations 49 and 52 as:

$$\varphi(x) = 1 - x^{-1} + (2x^2)^{-1} \quad (53)$$

$$\psi(x) = \frac{1}{2} [1 - (3/2x^2) + (3/2x^3)]. \quad (54)$$

If electronic stopping can be neglected, i.e. $\Delta_k = 0$ in Equation 39, Brandt and Laubert show that at high ion energies ($E_1 \gg 1$ keV) the sputtering yield can be written as:

$$S = (\gamma\epsilon_{12}/U_2) f_{12} \lambda_0 \sigma(\epsilon). \quad (55)$$

This means that the sputtering yield is proportional to a function of the atomic numbers and masses of the particles, proportional to the nuclear stopping power and its angular dependence goes as $\sec \theta$. In the energy range 10^3 to 10^5 eV where the Thomas-Fermi potential can be approximated to an inverse square type (see Equations 7 and 8), Lindhard [7] shows that

$\sigma(\epsilon)$ becomes independent of ion energy; hence S is independent of ion energy. These conclusions reached by Brandt and Laubert are largely similar to those of Thompson and Sigmund.

3. Comparison of experimental data of sputtering yield with theory

The sputtering yield of solids has been measured by various different methods. The simplest method is the determination of mass difference of the target before and after sputtering by weighing. Another simple way sometimes favoured is by measuring the eroded volume with interference microscopy, but this method requires a smooth and reflecting surface in order to achieve reasonable accuracy. Other novel techniques of yield measurements include one of spectroscopic detection [12] in which the intensity of the emission lines of the sputtered particles as a function of ion beam current and energy is calibrated using the weight loss method. While this technique does not appear to offer any immediate advantage over the former two, its use may be more appreciated when the different sputtering yields of the various components in an alloy or a multiphase material are required since different components can be distinguished by their characteristic emission lines [13]. It is perhaps worth mentioning here that work of this kind on multiphase materials is virtually nonexistent and it is highly desirable to carry out such studies because of its practical importance.

Sputtering yield measurements on amorphous and polycrystalline solids have been widely carried out in the past 15 years or so. To interpret the experimental results in terms of the above three theories we are interested in the sputtering yield expressed as (i) a function of the ion energy, (ii) a function of angle of ion incidence and (iii) a function of masses of the incident ion and target material. However, the sputtering yield data given in terms of the ratio of atoms/ion is misleading in the majority of investigations because the parameters of the incident ion beam were not well defined. For example, most experiments were carried out without using any mass analysing attachment. This means the ion beam probably contained energetic doubly or even triply charged ions of the species under study plus a host of other impurity ions such as H^+ , H_2^+ , N^+ , O^+ , HO^+ , H_2O^+ etc, due to contamination of pump vapours and degassing of the apparatus etc [14]. This puts the energy and mass of the incident ions in doubt. If the pressure in the

apparatus is high, then the energetic ions will have the probability of colliding with the neutral gas atoms giving rise to a neutral component in the ion beam. This causes an uncertainty in the determination of the number of ions arriving at the target surface. Also, back diffusion due to high pressure near the target surface will cause redeposition of particles sputtered from the target.

In view of the uncertainties which exist, exacting experimental requirements must be satisfied for reliable sputtering yield data to be obtained. It is therefore essential to use: (1) ions of definite energy, (2) ions of definite mass and charge, (3) ions with a definite angle of incidence, (4) a low pressure in the apparatus. Much of the earlier work was not performed under well-defined experimental conditions. In the following sections, we shall only discuss work in which most of the parameters have been brought under control.

3.1. Variation of sputtering yield with ion energy

Figs. 2 and 3 show the yield of polycrystalline copper as a function of Ar^+ ion energy. The yield of amorphous targets such as fused silica, Ge and Si are shown in Figs. 4 and 5. Although Ge and Si are essentially single crystals, they can be treated as amorphous under ion bombardment at room temperatures [15, 16] due to randomization of the lattice within collision cascades. From these curves it can be seen that the sputtering yield increases rapidly in a linear

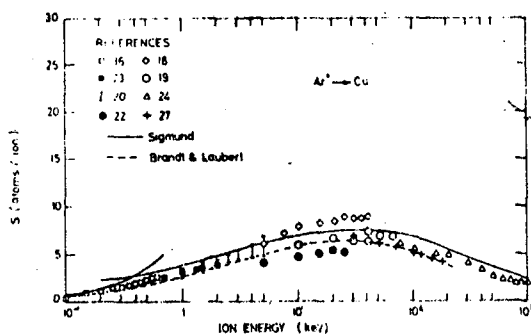


Figure 3 Comparison of theoretical sputtering yield with experimental data of Ar^+ on polycrystalline Cu at normal incidence over a wide range of ion energies.

fashion once the ion energy reaches a threshold value which is characteristic of the particular ion-target combination. Somewhere between 1 and 10 keV the curve shows a slowing-down in the rate of increase of sputtering yield, finally reaching a maximum. After this, the yield stays approximately constant in the region between 10 and 100 keV, and at higher energies the yield begins to decrease due to the ions penetrating more deeply below the target surface and very few of the atoms ejected from their lattice sites as a result of the collisions finding their way to the surface. One significant fact emerging from this curve is that the yield is virtually independent of ion energy in the range 10 to 100 keV, as predicted by all three theories. The majority of the sputtering experiments (on a variety of ion-

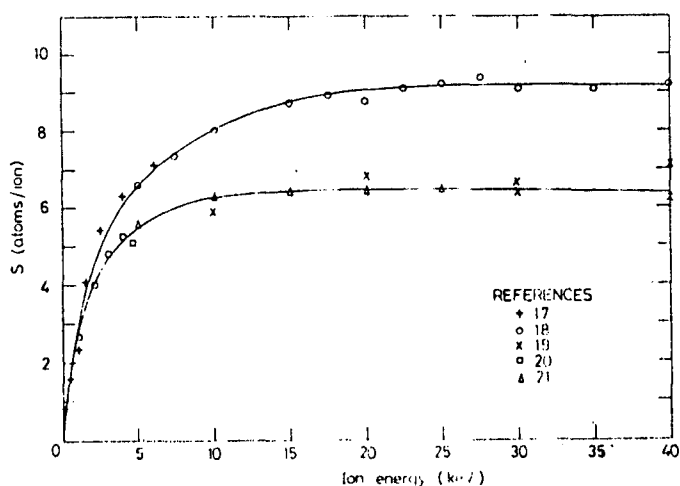


Figure 2 Variation of sputtering yield with ion energy up to 40 keV for polycrystalline Cu bombarded with Ar^+ ions at normal incidence.

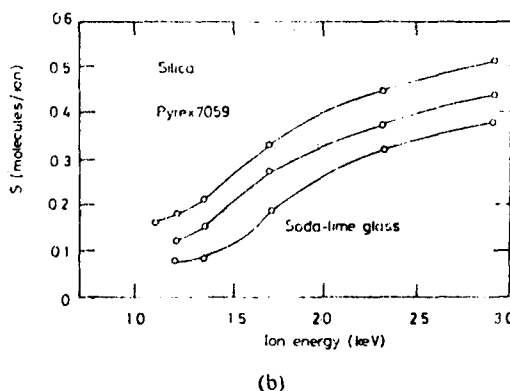
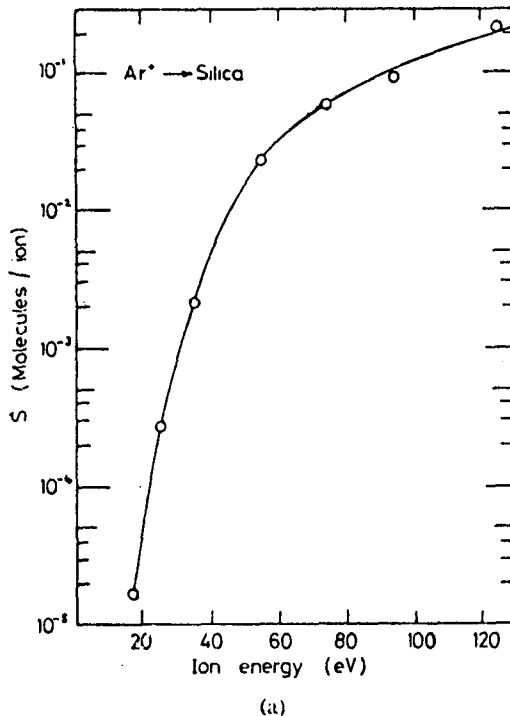


Figure 4 (a) Variation of sputtering yield with ion energy for Ar^+ on fused silica according to Jorgensen and Wehner [25]. The yield is expressed in molecules/ion despite the fact that sputtered particles mostly appear as single atoms.

Figure 4 (b) Variation of sputtering yield with ion energy on fused silica, Pyrex 7059 and soda-lime glass. Davids and Maissel [26].

target combinations) have been carried out in this ion energy range and most of them tend to confirm the theoretical prediction of invariance. In addition, both the theory of Sigmund and that of Brandt and Laubert show reasonably good agreement over the entire range of ion energies from 0.1 to 10^3 keV.

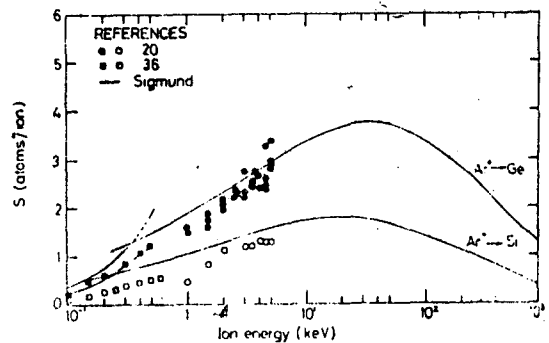


Figure 5 Sputtering yield for Ar^+ on "amorphous" targets of Si and Ge as a function of ion energy.

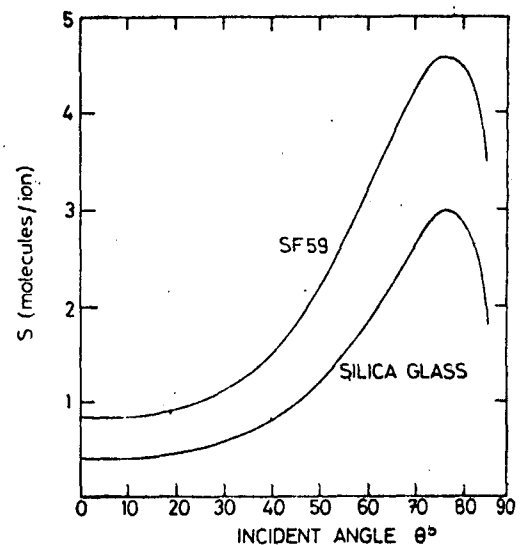


Figure 6 Variation of sputtering yield with incident angle of Ar^+ ions at 5.6 keV on Schott lead glass SF59 and silica glass. Buch [28].

3.2. Variation of sputtering yield with angle of ion incidence

Nearly all the curves of sputtering yield as a function of the angle of ion incidence display similar behaviour to that shown in Fig. 6, which describes the sputtering of silica glasses. The yield increases rather slowly in the beginning, then increases rapidly beyond about 30° (we take 0° as perpendicular incidence), finally passes through a maximum at grazing incidence and falls towards zero at $\theta = 90^\circ$. The maximum and the falling-off can be explained by the fact that as θ increases, the incident ion has an increasing probability of being reflected without traversing

the effective surface layer because of the repulsive action of the potential barrier associated with the surface plane of atoms. Lindhard [29] shows that the critical angle for such reflection is given by:

$$\frac{\pi}{2} - \theta = \left[\frac{5\pi a_0^2 n^{2/3} Z_1 Z_2 E_R}{(Z_1^{2/3} + Z_2^{2/3}) E_1} \right]^{1/2} \quad (56)$$

When $\theta > \theta_c$, penetration of the potential barrier is not possible. Hence θ_c corresponds to the angle where the sputtering yield, S , reaches its maximum value.

In polycrystalline solids the sputtering yield can be regarded as a summation of S from all the possible orientations of individual grains and the angular dependence of S is expected to vary much the same way as that for amorphous solids shown in Fig. 6. Recently, however, Evdokimov and Molchanov [30] have observed line structures in the sputtering curves of Kr^+ , Ar^+ and Ne^+ on polycrystalline Cu and Mo thought to be due to a certain amount of close-packing at the target surface. Fig. 7 shows the variation of the yield with angle of incidence for Ar^+ ions on polycrystalline copper, together with curves calculated according to Sigmund and the $\sec \theta$ relationship. Fig. 8 shows the angular dependence of the yield for self-sputtering of Nb [34].

Sigmund finds that the $\sec \theta$ dependence, favoured by Thompson and Prandtl and Laubert, and derived from a simple path-length consideration for an ion travelling in a solid, does not fit

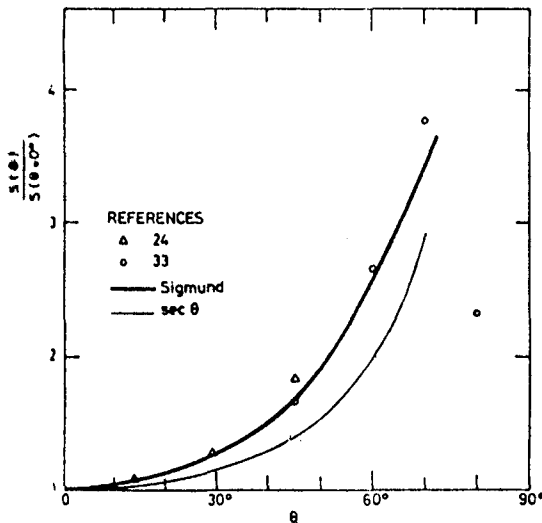


Figure 7 Comparison of calculated sputtering yield as a function of incident angle with experimental data of Ar^+ on Cu.

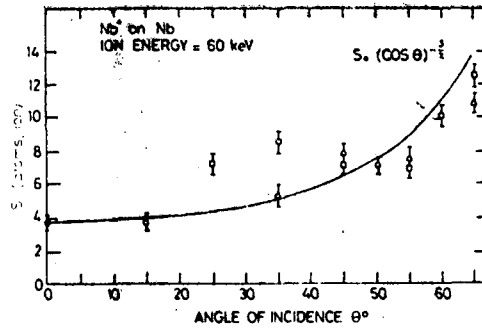


Figure 8 Variation of Nb self-sputtering yield with incident angle according to Summers *et al.* [34]. Empirical relationship $S(\theta) = S(\theta = 0) \cdot (\cos \theta)^{-1.6}$ is very close to the $(\cos \theta)^{-1.6}$ dependence predicted by Sigmund.

experimental values well except for $M_1 \ll M_2$. The agreement between experimental results and Sigmund's theoretical prediction, based on calculations of the spatial distribution of the energy deposited by the bombarding ion, is generally quite good. Other forms of angular dependence of sputtering yield have been found by various workers [21, 27, 35], the details of which will not be dealt with here.

3.3. Variation of sputtering yield with the atomic numbers and masses of incident ion and tangent atom

All three theories predict complex variations of sputtering yield with the atomic numbers and masses of the incident ion and target atom. The experiments of Almen and Bruce [19] and Rol *et al* [21] appeared to confirm this. Their results are shown in Tables I and II and Fig. 9. Gener-

TABLE I Sputtering yield for Ne^+ , Ar^+ , Kr^+ and Xe^+ ions at 45 keV on different polycrystalline target materials. Almen and Bruce [19].

Target material	Sputtering yield (atoms/ion)			
	Ne	Ar	Kr	Xe
V	0.3	1.0	1.7	1.9
Fe	1.3	2.3	4.0	4.9
Ni	1.4	3.5	5.6	7.6
Cu	3.2	6.8	11.8	19.0
Mo	0.6	1.5	2.7	3.8
Pd	2.5	5.3	10.5	14.4
Ag	4.5	10.8	23.5	36.2
Sn	1.8	4.3	8.5	11.8
Ta	0.7	1.6	3.1	4.0
W	1.0	2.3	4.7	6.4
Pt	1.9	5.3	11.3	16.0
Au	3.6	10.2	24.5	39.0
Pb	3.6	10.5	24.0	44.5

TABLE II Sputtering yield expressed in atoms/ion for polycrystalline copper bombarded with the following ions at 15 keV. Rol *et al* [21].

Ion	N	Ne	Na	Si	P
yield	2.0	3.2	2.7	3.9	4.7
Ion	S	Cl	Ar	K	Cu
yield	3.8	5.2	6.3	5.2	6.8
Ion	Zn	Cd	I	Hg	Tl
yield	7.1	10.5	11.0	11.2	13.1

ally speaking, the sputtering yield tends to increase with increasing ion mass for the same target material, whereas the same cannot be said for increasing target mass for the same incident ion. Sigmund [2] has calculated the yield for various target materials bombarded by 400 eV Xenon ions and obtained reasonable agreement with experimental data [36]. The sputtering yield for a variety of amorphous targets bom-

barded by 5 keV Ar⁺ ions has been measured by Bach [37] and compared with theoretical values according to Brandt and Laubert. Good agreement was obtained for SiO₂, TiO₂ and ZnS. More recently Bach [38] has reported the sputtering yield of silica glass bombarded by Ne⁺, Ar⁺ and Xe⁺ ions and reasonable agreement between experimental and calculated values was again achieved.

Andersen and Bay [39] have performed sputtering experiments in ultrahigh vacuum conditions to measure the yield of copper bombarded by 21 different ions at 45 keV. It was found that the measured sputtering yield depended sensitively on the previous irradiation history of the target which changes the ejection conditions at the surface. This is thought to be due to volume diffusion (possibly damage-enhanced) or surface diffusion, giving rise to a

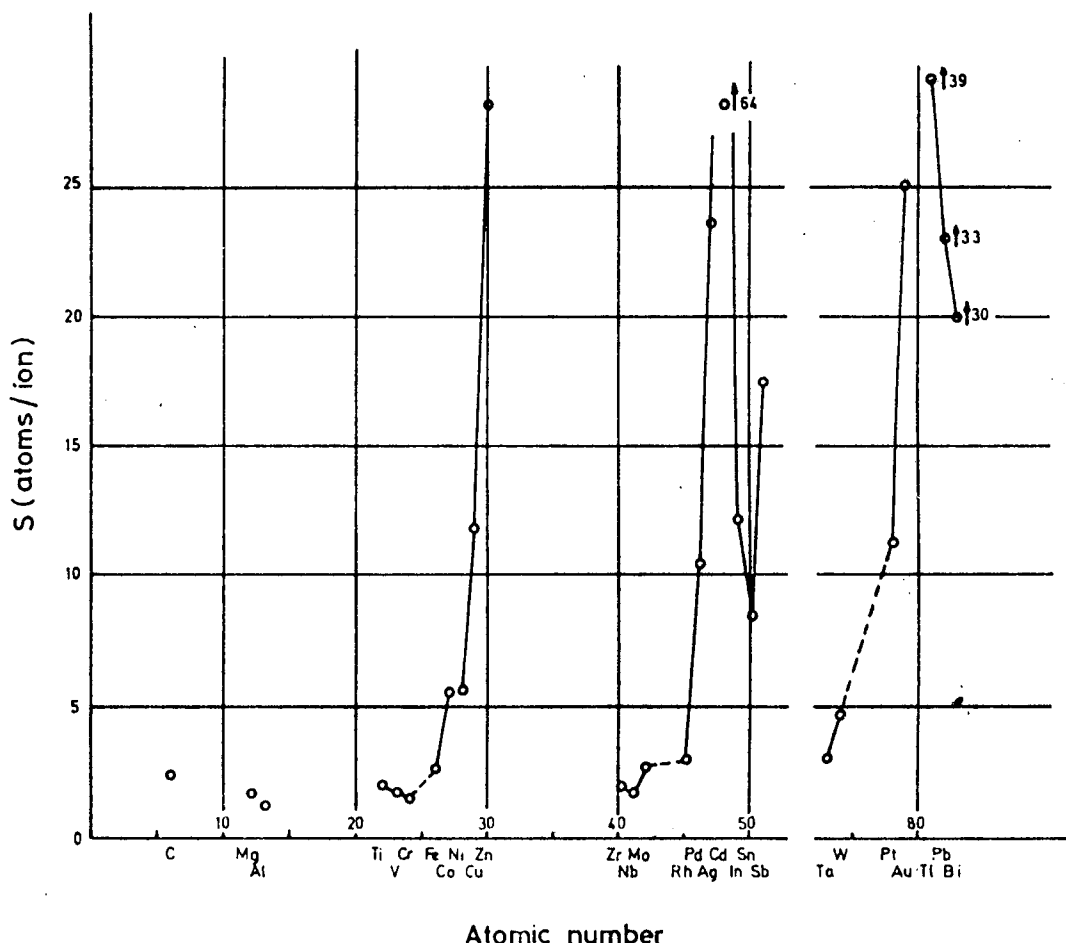


Figure 9 Sputtering yield for 45 keV Kr ions bombarding different target materials. Almen and Bruce [19].

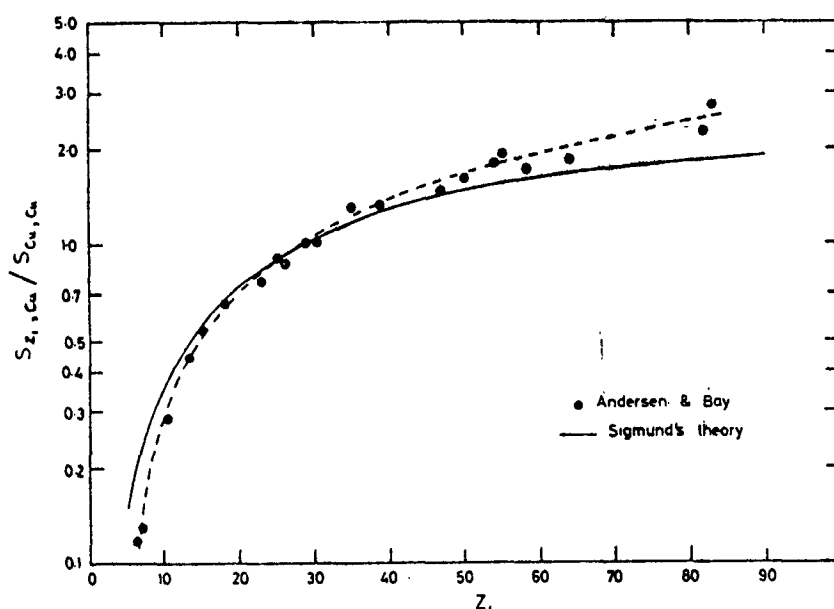


Figure 10 Sputtering yield ratio of copper for 21 different 45 keV ions together with the theoretical prediction of Sigmund.

clustering of projectile atoms with a low yield on the target surface. These effects make it difficult to define an absolute yield for many systems. The sputtering yield at perpendicular incidence from Sigmund's theory (Equation 31) can be written as

$$S = \text{Const.} \propto S_n(Z_1, Z_2)/U_0 \quad (57)$$

where $S_n(Z_1, Z_2)$ is the nuclear stopping power for the ion-target combination Z_1, Z_2 ; α is a factor depending only on m and M_2/M_1 , but for most purposes can be taken to be independent of m ; and U_0 is the surface binding energy. Equation 57 therefore suggests that the ratio

$$\frac{S_{Z_1, Z_2}}{S_{\text{self}}} = \frac{S_n(Z_1, Z_2) \cdot \alpha(M_2/M_1)}{S_n(Z_2, Z_2) \cdot \alpha(1)} \quad (58)$$

should be independent of surface saturation effects if it is assumed that U_0 remains the same for both projectiles at the moment of change. Andersen and Bay [39] found experimentally that this ratio is insensitive to previous bombardments of the target surface and agrees reasonably well with Sigmund's theory. Fig. 10 shows a plot of this sputtering yield ratio as a function of the atomic number of the incident ion. The smooth curve indicates that the nuclear stopping power in copper exhibits no oscillations as a function of Z_1 .

4. Sputtering efficiency

We have seen that sputtering is a typical multiple collision process involving a cascade of moving target atoms. Obviously in the sputtering process, not all the energy of the incoming ion is deposited within the target. Some of it will be contained in sputtered and backscattered particles leaving the surface. Sigmund [10] defines sputtering efficiency, γ , as the fraction of bombarding ion energy leaving a crystal via sputtering and backscattering:

$$\gamma = \frac{E_{\text{out}}}{E_{\text{in}}} \quad (59)$$

He has calculated this quantity for the case of perpendicular incidence on a random medium with a plane surface and shown that, unlike the sputtering yield, the sputtered energy is much less sensitive to surface conditions as reflected by variations in the surface binding force. Thompson [1] has measured the energy spectrum of polycrystalline gold bombarded by 41 keV Ar^+ ions and 45 keV Xe^+ ions using a time-of-flight technique. His results show that the number of particles ejected from the surface is determined by the dense low-energy part of the spectrum and is therefore very sensitive to the surface binding energy, while the total energy depends much more on the few high energy particles in the spectrum.

which are influenced relatively little by the surface. Sigmund has shown in his calculations of sputtering efficiency, γ , that the effect of surface binding can be neglected as long as the ion energy is over 1 keV. It thus appears that a direct measurement of γ will give possibly even more reliable information in the sputtering phenomenon than, say, measurements of the sputtering yield which have been widely carried out in the past decade.

In his calculations Sigmund makes use of the spatial distribution of energy deposited by ion bombardment determined previously [11]. He defines $f_D(x) dx$ as the average energy deposited in a layer of thickness dx at depth x from the starting point. The assumptions made are that: (i) the target medium is random and infinite; (ii) the collisions are elastic, and (iii) the scattering cross section is given by that derived by Lindhard *et al* [7, 8] (see Equation 19). Then for the target surface at 0, we have:

$$\gamma = \frac{1}{E} \int_{-\infty}^0 f_D(x) dx. \quad (60)$$

To calculate $f_D(x)$ Sigmund makes use of Edgeworth's expansion in terms of spatial moments over the energy distribution. He puts

$$\frac{1}{E} f_D(x) dx \equiv f_D(\xi) d\xi \quad (61)$$

where

$$\xi = (x - \langle x \rangle) / \mu_2^{1/2} \quad (62)$$

is a dimensionless variable which eliminates the energy dependence, and

$$\mu_n = \langle (x - \langle x \rangle)^n \rangle \quad n = 2, 3, 4 \dots \quad (63)$$

$\langle x \rangle$ is given by Equation 32, $f_D(\xi)$ can then be approximated by N terms in Edgeworth's expansion

$$f_D(\xi) \simeq f_N(\xi) = \sum_{n=2}^N a_n(\xi). \quad (64)$$

The expansion on the r.h.s. is convergent.

The sputtering efficiency can now be redefined as:

$$\gamma = \frac{1}{E} \int_{-\infty}^0 f_D(x) dx \equiv \int_{-\infty}^{-\langle x \rangle / \mu_2^{1/2}} f_D(\xi) d\xi. \quad (65)$$

Values of γ calculated from Equation 65 show that: (i) γ is essentially independent of ion energy in the range above 1 keV, and (ii) γ depends on the ion-target combination through the mass ratio M_2/M_1 . One striking result is that γ tends to increase with decreasing ion mass, though it is

known from experiment that sputtering yield tends to show the opposite behaviour.

The only investigation of sputtering efficiency so far has been that by Anderson [40] using a rather complicated calorimetric method. He measured γ for graphite, aluminium, silicon, copper, silver, tantalum and lead with 30 to 75 keV He^+ , C^+ , Ne^+ , Ar^+ , Cu^+ , Kr^+ , Xe^+ and Pb^+ ion at perpendicular incidence, to an accuracy of $\pm 15\%$. The results obtained were in good agreement with Sigmund's theoretical prediction.

Acknowledgement

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drogen atom will have a larger energy barrier to overcome. Presumably because of its small size the hydrogen atom moves interstitially in the nickel lattice, escaping relatively easily, however.

Nitrogen on the other hand, which does not chemisorb on nickel because of the high energy required to dissociate the N_2 molecule, does form a stable compound when driven into the lattice. Thus nitrogen is not evolved until a relatively high temperature is reached.

The unusual effect of enhancing hydrogen uptake by previous nitrogen adsorption is due no doubt to a specific chemical attraction. Much as a hydroxide radical can occupy a lattice position of an oxide ion in many oxides, an NH radical will be bound with some stability at a nitrogen site. However, this radical is not very stable, decomposing to give off H_2 at not much higher temperatures than that of the hydrogen alone driven into the lattice.

Surface Composition Analysis by Binary Scattering of Noble Gas Ions

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Measurement of the energy distribution of backscattered noble gas ions yields information regarding the elemental composition of the first atomic surface layer. An instrument based on this principle and designed for routine surface analysis will be described. This flange-mounted device is comprised of an electron bombardment ion source, an electrostatic energy analyzer, a channel electron multiplier, and a multiple sample holder. Primary ion beam energies range from 100–2000 eV at current densities up to $50 \mu A/cm^2$. A depth profile of the surface constituents is obtained by utilizing the probe beam to selectively sputter clean the surface. Observations show the ability to resolve elemental isotopes, such as Cu^{63} from Cu^{65} . Surface analyses are shown for 304 stainless steel, Cu, Ni, and ZnTe.

Introduction

The phenomenon of ion scattering from solid surfaces has recently been shown to be particularly sensitive to the composition of the first monolayer of atoms.^{1–3} This paper describes a new miniaturized ion scattering instrument designed to utilize the binary elastic collision process for routine surface analysis.

Briefly, the technique consists of bombarding the sample with a beam of noble gas ions, of energy preferably less than about 3 keV. Energy measurements of the ions scattered from the surface at a particular scattering angle produce a distribution comprised of a number of peaks at various energies. The number of peaks is related to the number of surface constituents and the energy of each peak corresponds uniquely to the mass of each constituent. In particular, when E_0 is the kinetic energy of the primary ion mass M_1 and E_1 is its kinetic energy after being scattered at an angle of 90° during an elastic binary collision with a surface atom of mass M_2 , the following relation has been found to be valid

$$E_1/E_0 = (M_2 - M_1)/(M_2 + M_1). \quad (1)$$

Thus, by selection of the primary ion M_1 and measuring

the scattered ion energy ratio E_1/E_0 , one can calculate M_2 .

1. Description of the Improved Ion Scattering Instrument

The instrument design was a compromise between sensitivity and resolution with the intent to make it compatible with most ultrahigh vacuum systems. The main components necessary for performing ion scattering surface analysis are: an ion gun capable of producing a monoenergetic and stable ion beam of high purity and intensity, a high resolution energy analyzer which defines a precise scattering angle, a low-noise efficient ion detector, and an accurately positioned sample. The resolving power of the instrument is primarily dependent upon the first two components—namely the ion gun and analyzer design. Figure 1 shows the instrument mounted on a standard ultrahigh vacuum flange (8-in. o.d.).

The ion gun consists of a cylindrical grid with an external filament. Ions formed inside the grid are extracted axially from one end and focused on to the target by an electrostatic five-element aperture lens system. The ion gun produces a nominal 1-mm-diam He^+ beam throughout an operating range of 300–3000 eV; by additional focusing adjustments current densities of from 1 – $50 \mu A/cm^2$ are obtained. Independent measurements of the He^+ and Ar^+ beam energy spread

¹ D. P. Smith, J. Appl. Phys. 38, 340 (1967).

² D. P. Smith, 13th Nat. Vac. Symp. Am. Vac. Soc., San Francisco (1966).

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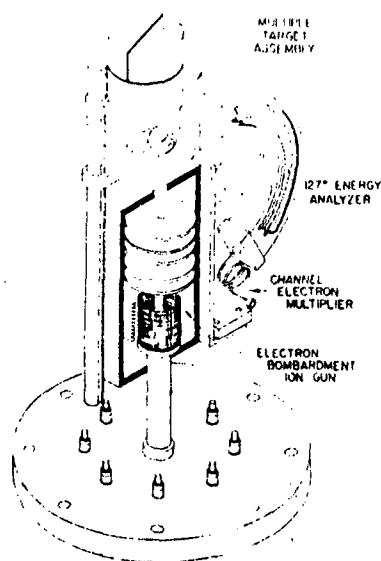


FIGURE 1. Schematic cutaway diagram of the flange mounted 90° ion scattering instrument.

revealed less than 0.5% (FWHM) of primary beam energy. Under normal operating conditions (electron ionization current of 10 mA at 125 eV) a 1500-eV He^+ ion beam yields a target current of 150 nA at an indicated He pressure of 5×10^{-5} Torr (Bayard-Alpert gauge reading). The ion beam consists of predominantly singly ionized He^+ as monitored directly from scattering measurements. By the same method approximately 10% doubly charged Ar^{++} ions are found when Ar is used as a probe gas.

Energy analysis is made by means of a standard 127° electrostatic energy analyzer⁴ having a mean radius of 2 in. and designed to accept only scattered ions having a narrow angular spread about the 90° scattering angle. The entrance and exit slit widths are 0.005 in. corresponding to an energy resolution of 0.5%. Positive biasing of these slits has proven to be effective

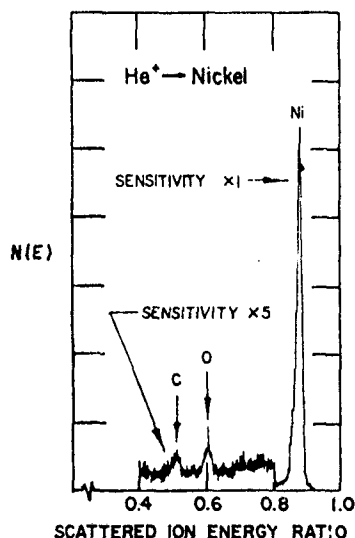


FIGURE 2. Plot of scattered ion current $N(E)$ vs scattered ion energy ratio E_1/E_0 for 1500-eV He^+ scattered from polycrystalline Ni contaminated with C and O.

in suppressing the extraneous background ion spectrum resulting from the sputtered ions, resulting in improved sensitivity. Ion detection is accomplished by the use of a continuous channel electron multiplier^{5,6} mounted directly behind the exit slit of the analyzer. The multiplier is operated in the pulse counting mode.

A multiple target holder capable of selecting any one of eight samples is actuated by an in-vacuum solenoid.⁷ The use of such a solenoid drive eliminates the need for a rotary motion feedthrough-gearing assembly and assures accurate target selection. The angle of incidence is fixed at 45° from the incident ion beam.

II. Experimental Method and Sample Preparation

Instrument operation requires no elaborate sample preparation or special vacuum conditions. The ultra-high vacuum system is given a mild 150°C bake and pumped to the low 10^{-9} Torr region. A Ti getter is flashed and the ion pump shut off. The noble gas to be ionized is admitted into the system to about 5×10^{-5} Torr (Bayard-Alpert gauge reading). No special gas cleanup is required other than that supplied by the active getter surfaces in the vacuum system. Beam purities of approximately 0.01% are thus obtained. The above static gas conditions eliminate the need for the difficult, dynamic pumping of high-pressure inert gases during ion scattering measurements.

Samples are normally ultrasonically cleaned in high-grade methanol and dried prior to mounting on the multiple target holder. The sample is then controllably cleaned during the analysis measurements by the action of the probe ion beam. In such a manner, "real" surfaces are examined without the necessity of high temperature treatments or other severe etching-polishing-sputtering procedures.⁸

III. Surface Analysis by Ion Scattering

The examples presented here are intended to exemplify the method of ion scattering surface analysis using the improved instrument on a variety of materials rather than be a complete study of a particular surface. Generally, He^+ ions are used as a probe since the lower atomic mass materials can be examined, and surface conditions are disturbed less than by the other noble gas ions. When increased resolution for higher atomic mass materials or a greater surface cleaning rate is desired, a more massive noble gas ion is used, generally Ar^+ .

A typical spectrum is shown in Fig. 2 which is the scattered ion energy distribution obtained when a poly-

⁵ K. C. Schmidt and C. F. Hendee, IEEE Trans. Nucl. Sci. NS 13, No. 3, 100 (1966).

⁶ Bendix Model CEM-1028.

⁷ Vid-E-Solenoid TM, Mfg. by Dividean, Inc.

⁸ R. W. Roberts, Brit. J. Appl. Phys. 14, 537 (1963).

⁴ A. L. Hughes and V. Rojansky, Phys. Rev. 34, 284 (1929).

crystalline nickel sample was bombarded with 1500-eV He^+ ions. Only the energy range corresponding to scattered primary ions is displayed; the low-energy sputtered ions are excluded.⁹ In addition to the peak due to scattering from Ni atoms, one also obtains two additional peaks at 0.5 and 0.6 scattered ion energy ratio. These are ascribed to scattering from surface atoms of C and O, respectively, according to Eq. (1). The contaminants are believed to be adsorbed hydrocarbons or CO, possibly in combination with a surface oxide. The contamination level associated with these data is estimated to be a fraction of a monolayer based on auxiliary measurements in conjunction with earlier studies of the effect of adsorbed CO on He^+ ion scattering from Mo.²

An important feature of this method is the unambiguous spectrum interpretation. Once confident that the binary-elastic collision model is applicable for the energies and materials of interest, Eq. (1) reduces the identification of surface species to a simple calculation. In our search for a possible failure of this simple collision model due to binding effects at the surface, extensive experimentation showed that the binary-elastic model was valid for primary ion energies down to less than 100 eV.¹⁰

Successive measurements of the scattered spectra using controlled probe beam dosages enable one to perform a depth profile analysis of practical surfaces. The primary ion beam not only serves as a probe for

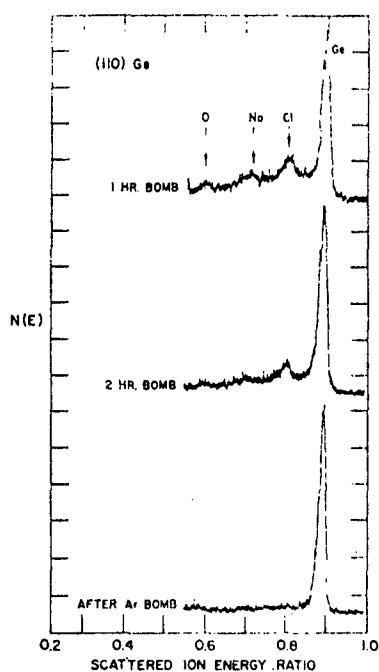


FIGURE 3. Time sequential ion scattering energy distributions for 1500-eV ($10 \mu\text{A}/\text{cm}^2$) He^+ scattered from (110) Ge surface. Upper curve—after 1-h bombardment. Middle curve—after 2-h bombardment. Lower curve—after Ar^+ bombardment (1500 eV, $10 \mu\text{A}/\text{cm}^2$, $\frac{1}{2}$ h).

⁹ In general, we have found that the number of low-energy sputtered ions depends on the degree of surface contamination and is virtually zero for the case of a clean surface.

¹⁰ D. P. Smith and R. F. Goff, 29th Ann. Phys. Electron. Conf., Yale, (1969). [Bull. Am. Phys. Soc. 14, 788 (1969)].

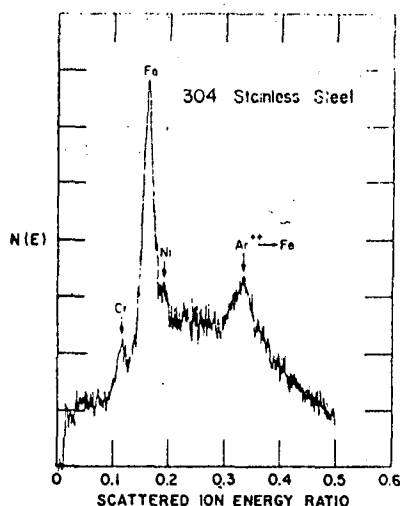


FIGURE 4. Spectrum of 1500-eV Ar^+ scattered from 304 stainless steel. Major constituents are shown to be Cr, Fe, and Ni.

the detection and identification of surface atoms, but also provides selective *in situ* cleaning by sputtering. Three such time-sequence He^+ ion scattering spectra are shown in Fig. 3 for a (110) Ge sample which received no special cleaning treatments other than described in Sec. II. Each spectrum required about 3–4 min to record. The presence of O, Na, Cl, and Ge is clearly seen on the upper spectrum recorded one hour after bombardment at $10 \mu\text{A}/\text{cm}^2$ was started. After an additional hour bombardment under the same conditions, the middle spectrum shows that Cl still appeared to be a major surface contaminant. After 30 min Ar^+ bombardment (1500 eV, $10 \mu\text{A}/\text{cm}^2$) the lower spectrum was obtained, again using He^+ probe ions. The absence of any impurity peaks indicated that the surface Cl contaminant had indeed been removed. The Ge peak height increase due to sputter cleaning of contaminants is similar to observations made on other surfaces, namely, in the study of CO absorption on Mo.²

Quantitative analysis with ion scattering depends on the ability to relate scattered ion peak heights to surface coverages. Evidence that this is indeed possible was shown earlier¹¹ for a thin film of Al_2O_3 on aluminum. However, additional work on other surfaces is necessary to ascertain the applicability to quantitative analysis in general.

Increased resolution, i.e., the ability to resolve scattering signals due to atoms which have comparable masses, can be obtained by choosing a heavier primary ion. For example, the analysis of stainless steel when bombarded with He^+ ions revealed the low atomic mass contaminants, primarily O, together with a broad unresolved peak around Fe. However, if one bombards with Ar^+ ions, the dispersion in scattered energy due to a small change of target mass is sufficient to be resolved experimentally. The spectrum shown in Fig. 4 was

¹¹ D. P. Smith, 15th Ann. Conf. Mass Spectrometry Allied Topics, Denver (1967).

obtained using Ar^+ ions to probe 304 stainless steel. Peaks are indicated for the major constituents of stainless steel, namely, Cr, Fe, and Ni. After continued bombardment of the surface, the Ni peak disappeared, probably due to complex preferential sputtering.¹² Also shown is the peak resulting from Ar^{6+} (approximately 10% of ion beam) impacting on Fe.¹³ The presence of the multiply charged species has presented no problem in spectrum identification.

A direct measure of the mass resolution of this instrument is shown in Fig. 5 depicting a partial ion energy spectrum obtained when clean polycrystalline Cu was bombarded by 1500-eV Ar^+ ions. The asymmetric peak demonstrates that scattering from the isotopes Cu^{63} and Cu^{65} are readily distinguishable. Superimposed on the data is a plot of the expected curve shape derived from the natural Cu isotopic abundances and gaussian peak shapes. Similar isotopic data were obtained by others, but only for high energy scattering (60 keV) from single crystals at precise beam orientations.¹⁴

Further evidence of the sensitivity of ion scattering to the composition of the first monoatomic layer was

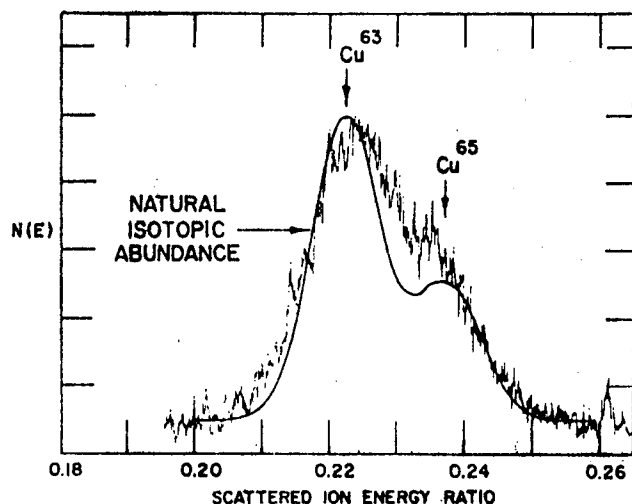


FIGURE 5. Observations of scattering from isotopes Cu^{63} and Cu^{65} by 1500-eV Ar^+ . The smooth curve is a calculated distribution using naturally occurring isotope abundance ratios and assuming gaussian peak shapes.

¹² G. S. Anderson (private communication); J. Appl. Phys. 40, 2884 (1969).

¹³ Since the electrostatic energy analyzer used here measures kinetic energy per unit charge, we conclude that the charge exchange reaction $\text{Ar}^{6+} + e \rightarrow \text{Ar}^+$ is the mechanism responsible for this peak.

¹⁴ S. Datz and C. Snook, Phys. Rev. 134, A347 (1964).

recently reported.¹⁵ The polar faces of CdS , a noncentrosymmetric crystal with the Wurtzite crystal structure, were found to have significantly different ion scattering spectra. Figure 6 shows similar data for the two polar (111) faces of a ZnTe crystal, which has a zinc blend crystal structure, also a noncentrosymmetric structure. Since only the polar faces have different elemental surface compositions, it is concluded that the detected ions are scattered from the first atomic layer and that neutralization processes prevent deeply penetrating ions from interfering with this measurement method.

IV. Conclusions

Selected examples show that low energy ion scattering surface analysis can be performed with simplified apparatus. Scattering spectra, in conjunction with the established validity of the binary-elastic collision model, permit one to unambiguously identify surface atoms without the need for special sample preparations or complex signal processing techniques. Since the scattering process is mass sensitive, surface isotopes can be identified.

Acknowledgments

It is a pleasure to acknowledge the assistance of J. W. Salo, G. P. Fandel, and F. L. Lessar in the design and construction phases of this work.

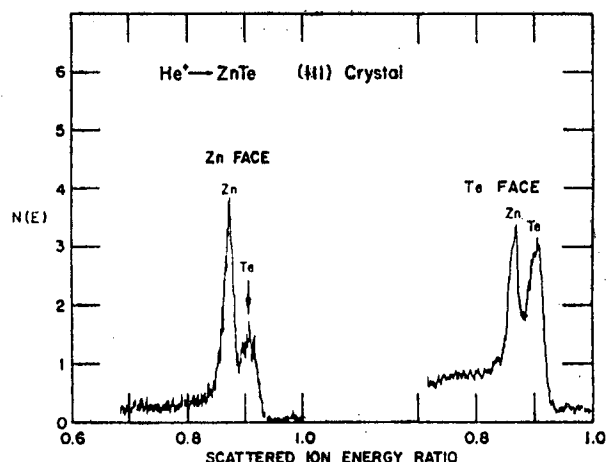


FIGURE 6. Ion energy distributions for 1500-eV He^+ ions scattered from the polar faces of ZnTe demonstrating the polarity effect.

¹⁵ W. H. Streblow and D. P. Smith, Appl. Phys. Letters 13, 34 (1968).

Energy dependence of scattered ion yields in ISS

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Scattered ion yields as a function of primary ion energy in the range from 200 to 2500 eV have been measured for He^+ , Ne^+ , and Ar^+ scattering from a variety of solid surfaces. The energy dependence of these yield curves contains information about the electronic states of surface atoms which complements normal ISS data. In addition, changes in the surface-atom chemical environment can be manifested as changes in the yield curve. A preliminary classification of yield curve shapes is proposed based on two considerations. First, does the target atom have an electronic state with a binding energy within approximately ± 10 eV of the bombarding species' first ionization potential? Second, if the first criterion is satisfied, what are the orbital symmetries of this electronic state and the vacant ionic state?

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INTRODUCTION

Ion scattering spectrometry (ISS) utilizes the energy distribution of scattered noble gas ions to characterize the composition of solid surfaces. For a given primary ion mass and energy, peaks in the energy distribution can be used to infer the masses of atoms constituting the target surface.¹

Recent work by Erickson and Smith² has shown that the dependence of the He scattered-ion yield on primary ion energy contains significant information about the electronic states of surface atoms which complements normal ion scattering data. This paper presents results for the scattering of Ne^+ and Ar^+ , as well as He^+ , and proposes a preliminary classification of the results.

EXPERIMENTAL PROCEDURE

The measured elastically-scattered ion yield Y_i from the i th surface constituent can be expressed as³

$$Y_i(E_0, \theta) = k N_i I_0 T D \Delta \Omega \sigma_i(E_0, \theta) [1 - P_n(E_0, \theta)], \quad (1)$$

where E_0 is the primary ion energy, θ is the laboratory scattering angle, N_i is the concentration of the i th constituent, I_0 is the primary ion current, T is the analyzer transmissivity, D is the detector sensitivity, $\Delta \Omega$ is the analyzer acceptance angle, $\sigma_i(E_0, \theta)$ is the differential scattering cross section, $P_n(E_0, \theta)$ is the ion neutralization probability, and k contains the appropriate conversion factors. For a given experimental configuration, $\Delta \Omega$ is constant and the energy dependencies of T , D , and I_0 are measurable. When using elemental samples, the value of N_i should be independent of E_0 . Hence, if the yield is normalized with respect to these factors,

$$Y_i(E_0, \theta) \propto \sigma_i(E_0, \theta) [1 - P_n(E_0, \theta)], \quad (2)$$

and the energy dependence of the normalized scattered ion yield represents the energy dependence of the product $\sigma_i[1 - P_n]$.

The ion scattering system has been previously described by Smith.¹ A primary ion angle of incidence of 45° and a laboratory scattering angle of 90° were used for all measurements. The system electronics have been modified as shown schematically in Fig. 1 to allow the primary ion energy and the analyzer pass energy to be synchronously scanned.

To track the scattered ion signal of interest, a selected fraction of the primary ion accelerating voltage was applied to the energy analyzer. An offset voltage was also applied to the analyzer to compensate for a reduction in primary ion energy below eV_p (e times the applied primary voltage) which is thought to result from space-charge effects in the ion source. The adjustment of this offset voltage was critical to properly tracking the scattered ion signal at primary ion energies less than 500 eV. It should be noted that the

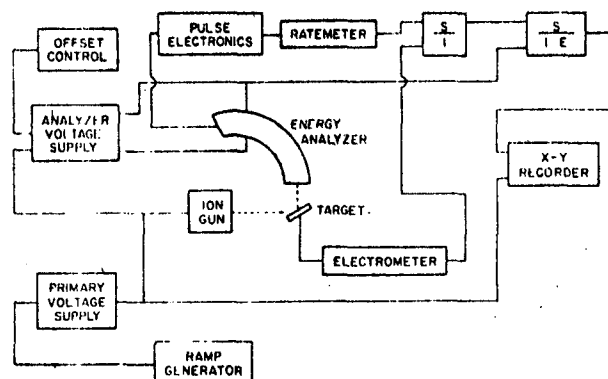


FIG. 1. Schematic diagram of the electronics used to synchronously scan the primary ion energy and the analyzer pass energy, and to normalize the scattered ion yield.

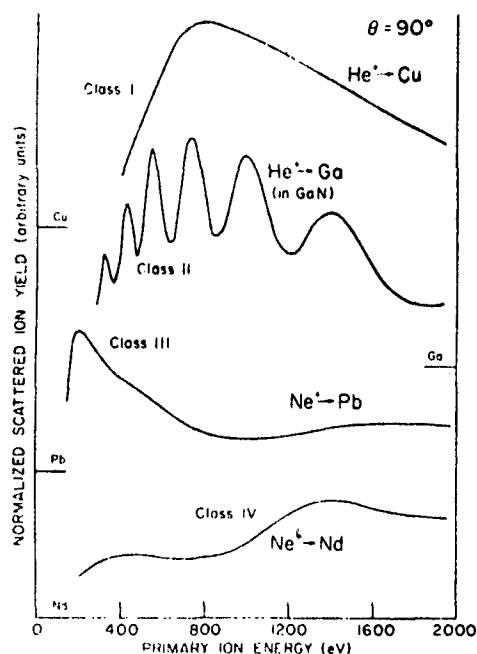


FIG. 2. Representative normalized yield curves illustrating the four general classes which have been observed for He^+ , Ne^+ , and Ar^+ scattering.

abscissae of all ion yield curves are in units of eV_p , hence, the actual primary energy is 20–30 eV less.⁴

The scattered ion signal was normalized with respect to primary ion current and analyzer transmissivity using analog division circuitry.⁵ The primary ion current was not corrected for secondary ion and electron emission, and the analyzer transmissivity was assumed to be proportional to the positive portion of the symmetrically applied analyzer voltages. The two-step division sequence was chosen to maximize the accuracy of the normalization. Referring to Eqs. (1) and (2), this normalization allows the product $\sigma_s[1 - P_n]$ to be plotted directly. Comparison with data accumulated point-by-point verified that the scanning and normalization electronics did not introduce artifacts into the data.

Because the ions which pass through the analyzer are preaccelerated to 3 keV before entering the multiplier, the detector sensitivity D should be a slowly varying function of scattered ion energy.⁶ The energy variation of D does remain as a systematic error in the scattered ion yield curves.

RESULTS AND DISCUSSION

The scattered-ion yields as a function of primary ion energy for He^+ , Ne^+ , and Ar^+ scattering from elements and compounds in selected regions of the

periodic table have been found to exhibit four general shapes (Fig. 2). However, the yield for each ion-target atom combination has its own distinct energy dependence within these broad classes. Also, as reported previously,² changes in the chemical environment of the target atom have been found to affect the energy dependence of the scattered ion yield.

The occurrence of a particular class of yield curve appears to correlate with two criteria. First, does the target atom have an electronic state with a binding energy within approximately ± 10 eV of the first ionization potential of the bombarding species? Table I lists the outer shell configurations for He^+ , Ne^+ , and Ar^+ , and the first ionization potentials of the corresponding atoms. Second, if the first criterion is satisfied, what are the orbital symmetries of this target atom state and the vacant ionic state? Several specific examples will be used to discuss these criteria in more detail.

If the first criterion is not satisfied yield curves of Class I (Fig. 2) are observed. These are considered to have the "classical" shape, i.e., a broad maximum followed by a monotonically decreasing yield. Examples of Class I yield curves are presented in Fig. 3 for He^+ and Ne^+ scattering from polycrystalline Cu. The outermost states of Cu are the $3p$ and $3d$ states having energies⁹ of 78 and 6 eV, respectively. (It should be noted that a 4-eV work function is used to refer the tabulated binding energies to the vacuum level.) As discussed by Smith,¹ this class of yield curve can be explained using a monotonically decreasing differential scattering cross section and a monotonically increasing probability of the scattered ion remaining ionized. Class I yield curves have been observed for He^+ scattering from Al, Si, Cu, Zn, Zr, Nb, Ag, Cd, Ta, and Tl, and Ne^+ scattering from Cu and Zn.

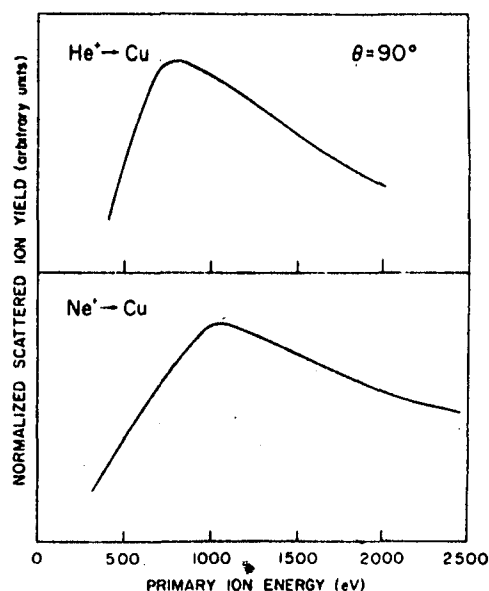


FIG. 3. "Classical" yield curves for He^+ and Ne^+ scattering from polycrystalline Cu ($\theta = 90^\circ$).

TABLE I. Ground-state characteristics of noble gas ions.

Atom	Outer shell configuration of ion	First ionization potential of atom
He	1s (Ref. 1)	24.580 eV (Ref. 7)
Ne	2p (Ref. 5)	21.559 eV (Ref. 7)
Ar	3p (Ref. 5)	15.68 eV (Ref. 8)

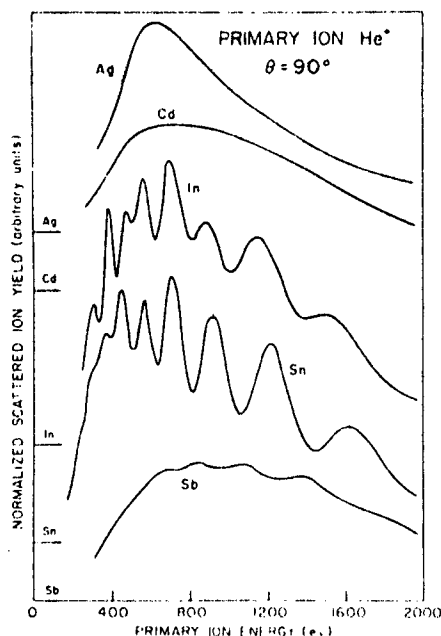


FIG. 4. Yield curves for He^+ scattering from a sequence of elements which illustrates the effect of shifting d -electron energy on the presence of oscillatory structure.

When the first criterion is satisfied, then the symmetries of primary ion and appropriate target atom states appear to influence the shape of the yield curves. Curves of Class II are observed when He^+ scatters from target atoms having energetically favorable d electron states.

For the sequence of five adjacent elements Ag, Cd, In, Sn, and Sb, the d -electron binding energies⁹ are 7, 13, 20, 28, and 35 eV, respectively. As the d -electron energy approaches 24.58 eV, pronounced oscillations in scattered ion yield are superimposed upon a Class I curve (Fig. 4). As the d -electron energy exceeds 24.58 eV by increasingly greater amounts, the oscillations subside. Erickson and Smith² have attributed this oscillatory structure to resonant or quasi-resonant charge exchange between the vacant He 1s state and the target atom d states. Class II yield curves have been observed for He^+ scattering from Ga, Ge, In, Sn, Sb, Pb, and Bi.

When Ne^+ or Ar^+ , having vacant p states, are scattered from target atoms having d or f states satisfying the energy criterion, yield curves of Class III are observed. Neon scattering from Si, S, Ge, In, Sn, Sb, Hf, and Pb, and Ar^+ scattering from In, Tl, and Pb exhibit this type of yield curve. In addition, Ne^+ scattering from Ga (in GaN) exhibits a yield curve with characteristics of both Classes II and III.

The Class III curves appear to contain broad oscillatory structure in addition to the peak at primary energies less than 1 keV. Because resonant or quasi-resonant charge exchange is a velocity-dependent phenomenon, an increased period of the oscillations is to be expected for primary ions with larger masses.¹⁰ Figure 5 illustrates this type of behavior for Ne^+ and Ar^+ scattering from In foil.

For the occurrence of Class IV yield curves, the

energy criterion is satisfied by at least one target atom state but the role of orbital symmetry is less clear. These yield curves have the general characteristic of slowly varying or increasing yield with increasing primary ion energy. Subtle oscillatory structure or other irregular structure as illustrated in Fig. 2 is observed. If the range of primary ion energy is increased, Class IV may well be an extension of Class II. Helium and Ne^+ scattering from La, Ce, Nd, Sm, Gd, Dy, Er, and Yb exhibit Class IV yield curves as do He^+ scattering from S (in CdS) and Hf, Ne^+ scattering from Cd and Tl, and Ar^+ scattering from Ge, Cd, and Sn.

A further illustration of the sensitivity of scattered ion yield to target atom electronic structure is provided by Ne^+ scattering from Yb and Hf (Fig. 6), at the transition from the Lanthanide series back into the sixth row of the periodic chart. The energy criterion is satisfied for Yb by a $5p$ state with a 27-eV binding energy and for Hf by a $4f$ state with a 21-eV binding energy. Similar yield curves were observed for Ne^+ scattering from the rare earths listed above, yet for Yb and Hf, separated by only one element, the yield curves at low primary energy are quite dissimilar.

As noted in Eq. 2, the energy dependence of the scattered ion yield is related directly to the energy dependence of the product $\sigma_i[1-P_n]$. Classical scattering calculations using the Bohr, Born-Mayer, and Thomas-Fermi interaction potentials indicate that σ_i is a structureless, monotonically decreasing function of primary ion energy.^{14,15} It is concluded that the structure in the yield curve results from the energy dependence of the ion neutralization probability P_n . In the Class II yield curves, the envelopes of the oscillations have Class I shapes suggesting that the neutralization argument advanced previously¹ is appli-

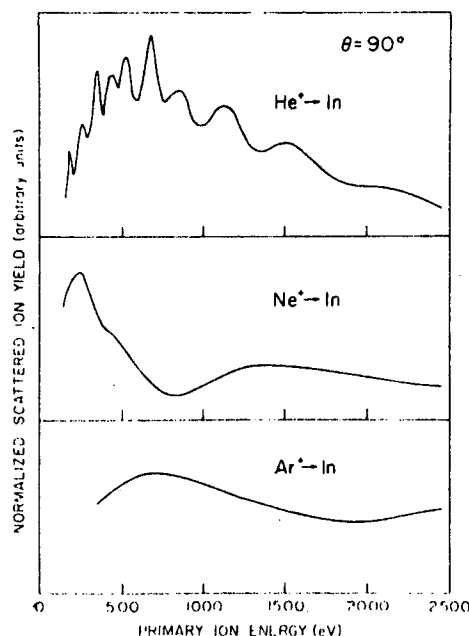


FIG. 5. Yield curves for He^+ , Ne^+ , and Ar^+ scattering from elemental In.

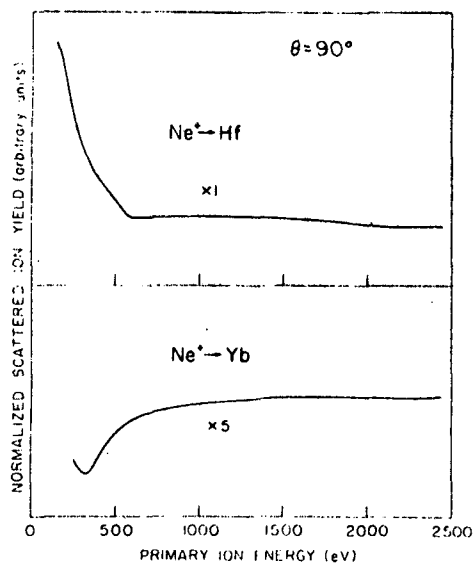


FIG. 6. Yield curves for Ne^+ scattering from Yb and Hf illustrating the effect of changing the electronic structure of the target atom.

cable with the oscillatory structure occurring as a second component of P_n .

One additional mechanism for producing structure in the yield curves is inelastic scattering of the primary ions. For Class II yield curves, such a mechanism is probably not important since no consequential variations of inelastically scattered ions are observed. However, for ion-solid combinations in which subtle structure is observed, inelastic effects cannot be ruled out.

Yield curves for He^+ scattering from a series of In and Ga compounds have supported the assertion by Erickson and Smith² that the oscillatory structure is sensitive to the chemical environment of the target atom. Figure 7 presents yield curves for He^+ scattering from In in elemental In, InP, and ZnIn_2S_4 .

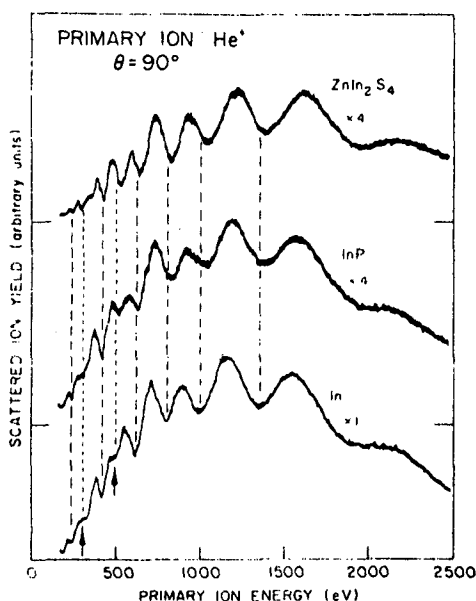


FIG. 7. Yield curves for He^+ scattering from In in elemental In, InP, and ZnIn_2S_4 illustrating the effect of changing the chemical environment of the target atom. (These curves have not been normalized with respect to analyzer transmissivity.)

crystals. (These curves have been normalized with respect to primary ion current but not analyzer transmissivity.) Although the yield curves are similar, two notable differences exist: the oscillatory structure in the compound curves is shifted to higher values of primary ion energy, and shoulders in the elemental In curve at 300 and 600 eV are distinct minima in the compound curves.

The effect of chemical environment can be qualitatively understood using theoretical models of charge exchange in gas-phase ion-atom scattering.¹⁰⁻¹² As the electronic states of the target atom shift due to changes in their chemical environment, both the period and the phase of the oscillations could change with respect to primary ion energy.¹³ Because the scattered ion signal is sensitive to the outer 1-2 atomic layers, the scattered ion yield curves provide a probe of changing chemical environment with a depth resolution of that order.

SUMMARY

The dependence of scattered ion yield on primary ion energy has been measured for a variety of ion-solid combinations. A preliminary classification of yield curve shapes has been proposed based on two considerations. First, does the target atom have an electronic state with a binding energy within approximately ± 10 eV of the first ionization potential of the bombarding species? Second, if the first criterion is satisfied, what are the orbital symmetries of this electronic state and vacant ionic state. The scattered ion yield curves also can be used to probe changes in the chemical environment of the target atom.

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Quantitative Aspects of Ion Scattering Spectrometry

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In ion scattering spectrometry, as with all surface analytical techniques, there is a great deal of interest in obtaining quantitative information. There have been a number of recent papers pointing out the information which is needed to make ISS quantitative (1-3).

There are two approaches to achieve this end. The more fundamental one is to relate the scattered ion intensity to the number of atoms present per cm^2 (N) through the differential scattering cross section (σ_0), the probability the ion escapes neutralization (P) and a geometric factor (G), i.e., scattered peak area $\propto N\sigma_0PG$. The classical differential cross sections based on the screened Coulomb potential have been tabulated by Bingham (4) and a more complete table based on Bingham's calculation for 90° scattering has been prepared by Nelson (5). The geometric factor is interpreted as the partial masking of atoms of species A. by atoms of species B. Very little is theoretically known about the probability for escaping neutralization in the region of interest here (300 to 3000 volts) except that it appears to be a function of the ion velocity. This is in agreement with data obtained at higher energies (6). It has previously been shown that for some binary compounds such as Al_2O_3 or SiO_2 one can obtain good results by using the classical scattering cross sections and assuming the neutralizing factors are the same for the two elements (2, 3). However, since this does not work for other systems, one wonders if these results may be fortuitous.

The more direct approach to quantitative measurements is to use standards. Since there is a lack of good surface standards, the approach which has normally been taken is to use pure materials and scale the peak heights to determine the composition. In addition to possible problems with variation in surface roughness between standard and sample, there is a question of variation of the neutralization probability in going from a pure material to a compound. This type of variation has been observed by Leys (7) for Zn in pure Zn and ZnO. Using $^3\text{He}^+$, Leys observed that the Zn peak height decreased in intensity by a factor greater than two in going from Zn metal to ZnO while the Zn peak decreased by a factor of two when $^{20}\text{Ne}^+$ was used as a probe gas. He interpreted the $^3\text{He}^+$ results as a variation in the neutralization probability as a function of the form of the Zn.

EXPERIMENTAL RESULTS

The goal of the present studies is to try to determine the probability of the ion escaping neutralization as a function

of energy and atomic environment. For these measurements, a commercial ion scattering spectrometer was used. This apparatus has been described elsewhere (8, 9). In these measurements, two assumptions were made. The first was that the area under the scatter peak divided by the beam current and corrected for efficiency of the detector is related to the cross section. The efficiency values of Burrous *et al.* (10) were used. While they may not be completely correct, the maximum correction is on the order of 10% for He ions at 300 volts. The second assumption was that the experimental differential scattering cross section is given by $\sigma = \sigma_0 P$ where σ_0 is the screened Coulomb value and P is the probability of not being neutralized. In these measurements, the variation in the energy pass band of the electrostatic analyzer has been neglected. This was done because the widths of the peaks are considerably greater than the analyzer energy pass band and it was unclear how to unfold this contribution. The factor P was determined by dividing σ by σ_0 . The probability of not being neutralized, P , has been reported (3) to have the form $P = e^{-C/v}$ where v is the ion velocity and C is a constant characteristic of the ion-atom interaction. This has been interpreted in terms of resonance and Auger neutralization processes. The exponential nature of P was tested by plotting the experimentally determined values as a function of $1/v$ where v was the incident ion velocity.

A typical plot of σ as a function of energy for $^3\text{He}^+$ scattered from Cu is shown in Figure 1. Also plotted in Figure 1 are the σ_0 values of Bingham as a function of energy. It should be pointed out that the vertical scales are not the same for these two curves and only the shapes of the curves are of interest here. As can be seen, there are gross differences between the shape of the measured cross section and the screened Coulomb values. These differences are attributed to neutralization. The factor P for $^3\text{He}^+$ scattered from Cu is plotted against $1/v_{\text{initial}}$ in Figure 2. The vertical scale is arbitrary. The solid line is a least-squares fit to the data points. As can be seen, the fit is quite good and confirms the exponential variation of P with velocity. The slope of the line in Figure 2 gives the constant C . These results can easily be interpreted in terms of the final velocity by multiplying the constant C by a factor of 0.954, 0.939, and 0.722 for $^3\text{He}^+$, $^4\text{He}^+$, and $^{20}\text{Ne}^+$ scattered from Cu. Similarly, they can be displayed in terms of the normal component of the velocity by multiplying C by 0.707. One of the goals of the present experiments was to study the variation of P with the form of the material. This has been done by studying Cu and Cu_2O using $^3\text{He}^+$, $^4\text{He}^+$, and $^{20}\text{Ne}^+$ as the probe gases. The results of these measurements reconfirm the exponential variation of P with $1/v$. In addition, no mass dependence was found for He, i.e., the $^3\text{He}^+$ and $^4\text{He}^+$ results were the same within experimental error. However, when the species of the probe gas was changed, e.g., He^+ to Ne^+ , the characteristic constant, C , also changed. In addition, a matrix effect was observed for He^+ scattered from Cu in Cu_2O . In this case, the character-

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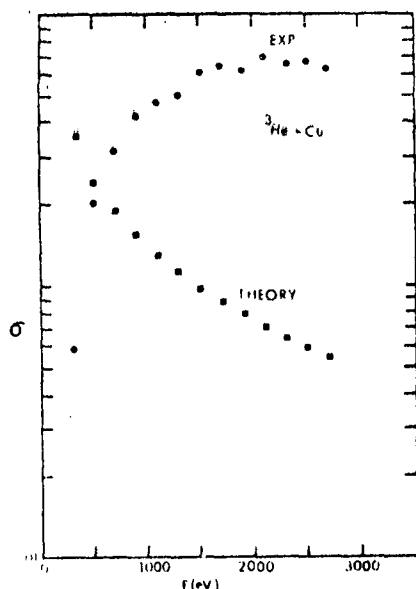


Figure 1. Experimental and theoretical differential scattering cross sections as a function of energy for $^3\text{He}^+$ scattered from Cu. The vertical scale is arbitrary

istic constant had a value of 11.1×10^7 cm/sec as opposed to a value of 8.8×10^7 cm/sec for pure Cu. No matrix effect was observed when $^{20}\text{Ne}^+$ was used as the probe gas, i.e., the slope was 6.2×10^7 cm/sec for Cu_2O as well as Cu. These data confirm the Zn data of Leys. The increase in slope when He is used as the probe gas means that the neutralization is higher for Cu in Cu_2O than for pure Cu. This implies that the Cu peak height should decrease by a factor greater than 0.66 in going from pure Cu to Cu_2O .

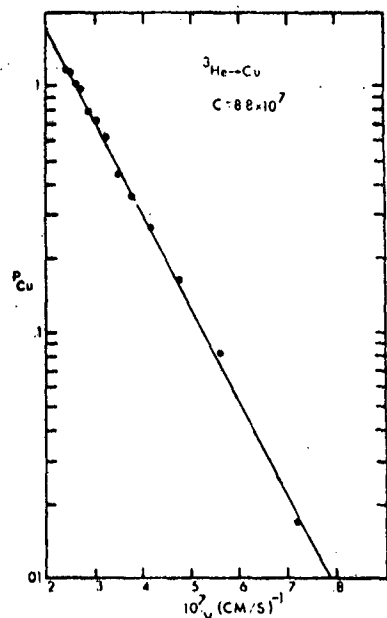


Figure 2. Probability of an ion remaining an ion as a function of the ion velocity for $^3\text{He}^+$ scattered from Cu. The vertical scale is arbitrary

. How general these effects are and what effect the geometrical factors have on peak intensities will be determined in future studies.

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Investigation of Surface Topography of Oxygen on Nickel Single Crystals by Helium Ion Backscattering*

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In an experiment which combines low energy noble gas ion backscattering with LEED the sorption of oxygen on the (110) face of a nickel single crystal is investigated. The energy of the backscattered He^+ ions is governed by binary collisions whereas the intensity of the spectrum is given by the cross sections, the concentration of surface atoms, the neutralization probabilities and the geometry. The spectra obtained by varying the angle of incidence relative to the surface and the crystal orientation, can be explained by the assumption that in the case of the (2×1) structure every second place in the top $[110]$ rows of Ni is occupied by an oxygen atom. From a shadow effect observed at small angles of incidence it can be estimated that the adsorbed oxygen protrudes beyond the plane of the Ni atoms by about 0.4–0.8 Å.

Introduction

Backscattering of low energy noble gas ions can be used for the analysis of a solid surface. At primary energies below a few kiloelectron volts the scattering process is determined by the binary collisions between the ions and the surface atoms and by the neutralization of all particles backscattered from deeper layers of the solid. Therefore, energy analysis of the backscattered ions gives an insight into the surface composition of the target.¹ It is the aim of this work to demonstrate for the case of oxygen adsorption on nickel that the structure of a surface can also be investigated by this method, which thus provides valuable information in addition to LEED experiments.

I. Experiment

The experimental device combines ion scattering and LEED; the scheme is shown in Fig. 1. The ion source was operated between 25 and 1000 eV. For He^+ , Ne^+ , or Ar^+ the maximum current densities at the target (focus diameter 3 mm) are $30 \mu\text{A}/\text{cm}^2$ between 300 and 1000 eV and somewhat less at lower energies; the measurements were generally made at lower current densities. The target goniometer allows control of the incidence angle ψ and the azimuthal angle φ with a reproducibility better than 1° . The

energy of the backscattered ions is measured with a 127° electrostatic analyzer with a resolution of 3%; the scattering angle θ can be chosen by rotating the analyzer. For target processing ion bombardment, heating by electron bombardment and chemical reactions with oxygen or hydrogen can be applied. The ultimate pressure is approximately 2×10^{-10} Torr.

II. Method

For the investigation of surface structures, e.g., of adsorbed layers, besides the energy distribution it is necessary to consider the intensities of the ions backscattered from different kinds of atoms. In this way it should be possible to determine the relative number of scattering atoms of either species which can be hit by the ion beam impinging at different angles. The dependence on the crystal orientation can be used to check the assumed structure model. The relative intensity I scattered into the solid angle $\Delta\Omega$ is given by

$$I \sim N_j P_j (d\sigma_j/d\Omega)(\theta) \Delta\Omega, \quad (1)$$

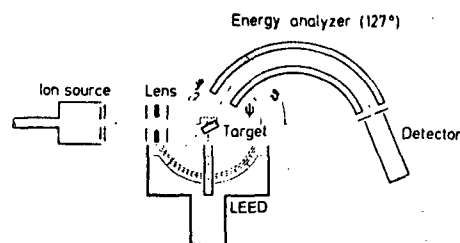


FIGURE 1. Scheme of the experiment.

* This work was performed under the terms of the agreement on association between the Max-Planck-Institut für Plasmaphysik and Euratom.

where N_j is the density of one kind of atoms which contribute to the scattering, $1 - P_j$ is the neutralization probability for the ion in this process and $d\sigma_j/d\Omega$ the differential scattering cross section. Here we are interested in the determination of N_j for different sets of ψ and φ . The neutralization probability is unknown and depends on a number of experimental parameters. It will be different for the scattering from an Ni or O atom, for example, but the dependence on the angle of incidence for these two cases should not be very different. So the assumption that the ratio P_{Ni}/P_O does not vary with ψ in a limited angular region seems reasonable. Hence, following Eq. (1), the measurement of the ratio of intensities I_{Ni}/I_O for different ψ or φ is proportional to N_{Ni}/N_O , the ratio of the number of atoms that can contribute to the scattering under the given experimental conditions:

$$(I_{Ni}/I_O)\psi_{k,\varphi,l,\vartheta} \sim (N_{Ni}/N_O)\psi_{k,\varphi,l,\vartheta}. \quad (2)$$

From a clean Ni (110) surface backscattering spectra can result that depend not only on the atomic masses and the scattering angle, Fig. 2. Besides the binary collision peak, given by

$$\frac{E_1}{E_0} = \frac{M_1^2}{(M_1 + M_2)^2} \left[\cos\vartheta \pm \left(\frac{M_2^2}{M_1^2} - \sin^2\vartheta \right)^{1/2} \right], \quad (3)$$

peaks due to multiple scattering are observed with Ar^+ and Ne^+ . These depend essentially on the size of the impact parameter relative to the lattice constant.^{2,3} For the case of He^+ backscattering, single binary collisions are the dominating process for energies above 150 eV. This energy range, together with a low current density, also affords the possibility of avoiding desorption by the primary ions. He^+ are therefore the appropriate ions for the investigation of sorption on monocrystals.

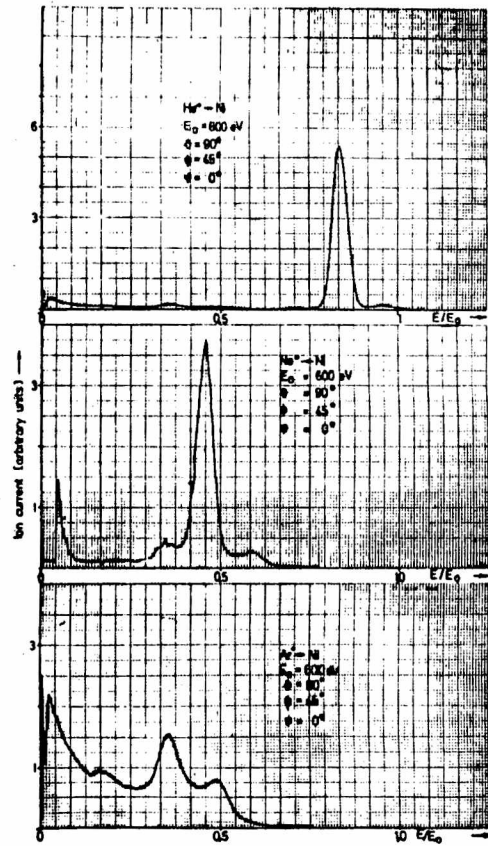
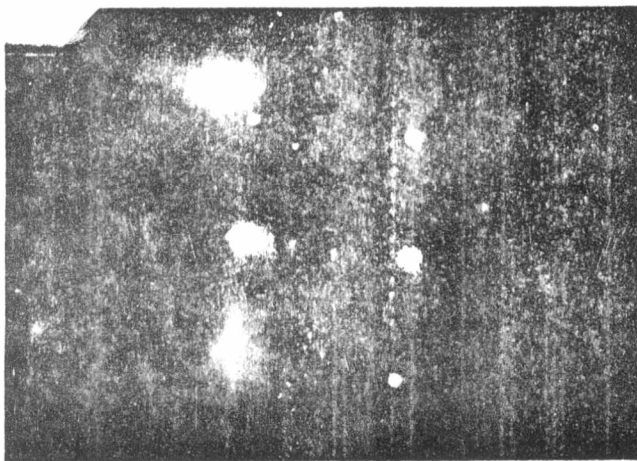


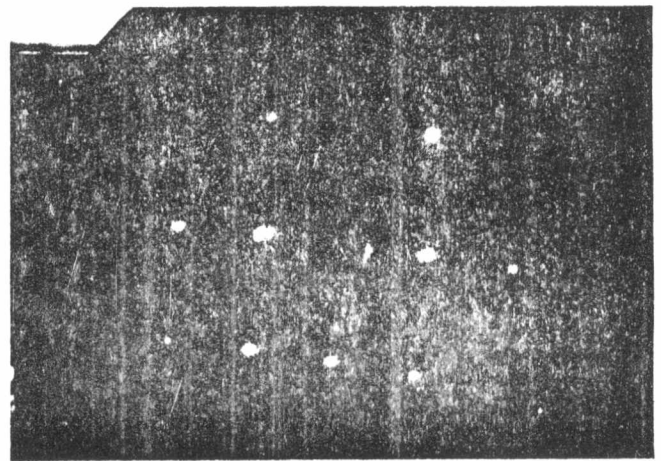
FIGURE 2. Backscattering spectra for He^+ , Ne^+ , and Ar^+ from a clean Ni (011) surface.

III. Sorption of Oxygen on Nickel

For the sorption experiment we started with a Ni (110) surface, which gave a sharp LEED pattern [Fig. 3(a)], and whose He^+ backscattering spectrum showed no peaks due to foreign atoms. It was then assumed that the target surface was clean. (A "good" LEED picture alone is no sufficient criterion; ion scattering often reveals residual surface contamination.)



(a)



(b)

FIGURE 3. (a) LEED pattern from a (011) Ni surface; (b) LEED pattern from a Ni-O surface with (2×1) structure. Primary electron energy 154 eV.

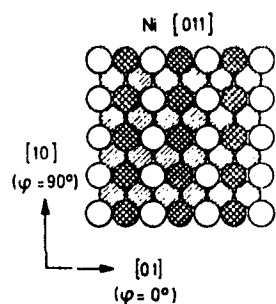


FIGURE 4. Model of the Ni-O (2×1) structure. Open circles: sites of the Ni atoms in the first layer; hatched circles: sites of the Ni atoms in the second layer; cross-hatched circles: sites of the oxygen.

tion.) After exposure to about 10^{-5} Torr·sec of oxygen, the formation of the Ni (2×1) structure can be observed on the LEED picture, Fig. 3(b).

The arrangement of the atoms in the surface cannot be derived unambiguously from the LEED pattern and different structures have been proposed.⁴⁻⁶ The He^+ backscattering experiments are suitable for testing the surface structure and supporting the model suggested by Germer and McRae,⁴ Fig. 4. The Ni atoms in the surface layer have double spacing in the [01] direction and normal spacing in the [10] direction. It is probable that the oxygen atoms are situated in the [01] rows between the Ni atoms, giving the same arrangement as the Ni atoms.

IV. Results and Discussion

Figures 5 and 6 show the energy distribution of He^+ ions backscattered from the (011)Ni surface with (2×1) structure. The primary energy is 600 eV, the current density less than 5×10^{-8} A/cm², so that there is no detectable change in the surface structure during the experiment. All spectra show the expected peaks from Ni and O, according to Eq. (3). For quantitative measurement of the intensities the area under the peaks has been integrated. The relative intensities $I_{\text{Ni}}/I_{\text{O}}$ are listed in Table I. The azimuthal angle $\varphi = 0^\circ$ means that the scattering plane is a (100) plane of the crystal, which contains a [011] row, i.e., a [01] chain in the surface. Correspondingly, $\varphi = 90^\circ$ means a (011) scattering plane containing a [100] row, i.e., a [10] direction.

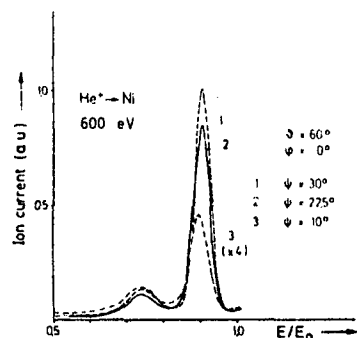


FIGURE 5. He^+ backscattering spectra from a Ni-O surface with (2×1) structure. Plane of incidence parallel to the [01] surface direction ($\varphi = 0^\circ$). The low energy peak corresponds to scattering from oxygen.

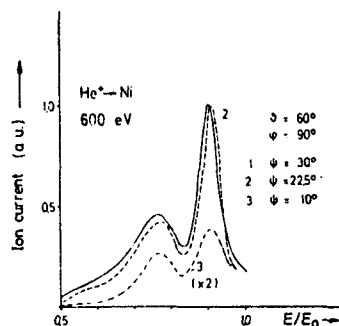


FIGURE 6. He^+ backscattering spectra from a Ni-O surface with (2×1) structure. Plane of incidence parallel to the [10] surface direction ($\varphi = 90^\circ$).

The intensity ratio $I_{\text{Ni}}/I_{\text{O}}$ for $\varphi = 0^\circ$ has about three times the value of $I_{\text{Ni}}/I_{\text{O}}$ for $\varphi = 90^\circ$. In accordance with our model the Ni atoms of the second surface layer contribute to the scattering for $\varphi = 0$ since they lie in the open [01] channels. For $\varphi = 90^\circ$ this second layer of atoms cannot be hit by the ion beam incident at $\psi = 30^\circ$ and below. Any model in which the oxygen covers the open channels cannot explain the observed intensity ratios.

For $\varphi = 0$ the intensity ratio drops by about a factor of two between $\varphi = 22.5^\circ$ and $\varphi = 10^\circ$. This indicates that the oxygen atoms partially shadow the Ni atoms in the surface rows (protruding about 0.4 to 0.8 Å). For $\varphi = 90^\circ$ the shadowing is at most 30%, though here the experimental error is large this would confirm our model, as in this case Ni and O form two different sets of rows.

Finally, we consider the ratio of the probabilities that the incident ion is reflected as an ion after impact with a Ni or O atom, $P_{\text{Ni}}/P_{\text{O}}$. Under the assumption of our model this can be calculated from the intensity ratio if the cross section ratio $d\sigma_{\text{Ni}}/d\sigma_{\text{O}}$ is known. Using a Born-Mayer interaction potential^{7,8} we get $d\sigma_{\text{Ni}}/d\sigma_{\text{O}} = 9$. Inserting this and the value of Table I into Eq. (1) our result is $1/4.5 < P_{\text{Ni}}/P_{\text{O}} < 1$, for all angles of ψ and φ .

The evaluation of the ion scattering experiment was facilitated by the fact that the periodic structure of the surface is known from the LEED experiment. In principle it should be possible to deduce the total structure from ion scattering experiments if the surface coverage is known. Combining LEED and ion scattering the structure and the coverage (0.5) of the

TABLE I. Relative intensities $I_{\text{Ni}}/I_{\text{O}}$ of He^+ ions backscattered from (2×1) Ni-O surface. Scattering angle $\vartheta = 60^\circ$, primary energy 600 eV. $\varphi = 0^\circ$: plane of incidence parallel to [01] surface direction. $\varphi = 90^\circ$: plane of incidence parallel to [10] surface direction. ψ : angle of incidence relative to the surface.

$\varphi \backslash \psi$	10°	22.5°	30°
0°	3.2	6.2	5.0
90°	1.4	1.7	1.8

(2×1) Ni-O surface was determined. The structure model which was used here has been disputed,⁶ but our results obviously favor this model.

Acknowledgments

The authors are indebted to the late Dr. E. W. Blauth for encouragement and many discussions at the beginning of this work. We are grateful to Franz Schuster for technical assistance.

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Direct comparison of low-energy ion backscattering with Auger electron spectroscopy in the analysis of S adsorbed on Ni

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A comparison was made between low-energy ion backscattering and Auger electron spectroscopy (AES) in the analysis of various coverages of sulfur on a nickel (111) crystal plane. For the intensity ratios S/Ni a linear relationship between both techniques was found for submonolayer coverage. Using the calibration of Perdereau for AES, ion scattering intensities are calibrated and relative values are obtained for the neutralization probabilities of Ne^+ and He^+ scattered from Ni and S. For 1-keV Ne^+ ions neutralization is about a factor of 7 lower for scattering from S than from Ni. Ion scattering is more sensitive to the position of adsorbed atoms than AES; a shadowing effect shows that the S atoms sit on top of the Ni surface layer. Both effects result in a high sensitivity of Ne^+ scattering for adsorbates such as S or O, the detection limit being some 10^{-4} of a monolayer.

For the elemental analysis of solid surfaces a number of techniques have been developed in recent years which probe different physical properties of the surface. Therefore, comparisons of different methods at the same surface are necessary, in particular if quantitative results are concerned. In this paper *in situ* comparison of low-energy ion backscattering and Auger electron spectroscopy (AES) from a Ni(111)-S surface is reported.

Backscattering of low-energy noble gas ions has been found to be particularly sensitive to the topmost atomic layer of a solid surface.¹ The intensity of the backscattered ions is determined by the scattering cross section σ , the probability P that the ion escapes neutralization, and the surface density N of the considered species of atoms

$$I \propto \sigma P N.$$

I can be approximately calculated on the basis of interaction potentials determined by theory² or experiment.³ P depends on the surface condition and is not very well known. Although P does not change the backscattered ion yield for different surface contaminations by orders of magnitude⁴ (as the ionization probability for secondary ions), it constitutes the main problem for quantitative surface analysis by low-energy ion backscattering. If surface concentrations of different constituents are determined by intensity ratios, mutual shadowing of surface atoms, depending on the surface structure and the experimental geometry, have to be taken into account.^{5,6}

The problems of quantitative surface analysis with AES⁷ are partly overcome by using appropriate standards. For the quantitative analysis of S adsorbed on Ni Perdereau⁸ used the Ni signal as a standard and calibrated the system with a radioactive tracer method. The peak-to-peak intensity ratio $S(150 \text{ eV})/Ni(62 \text{ eV})$ increases linearly with coverage up to a saturation level of the order of a monolayer. This Ni-S system has been used to compare surface composition data from ion scattering and AES and also to give some qualitative data on ion backscattering yield.

The experimental setup⁹ contains ion scattering equipment and a Varian 4-grid LEED system. The beam of the additional electron gun strikes the surface at

an angle of about 15° with respect to grazing incidence (target in LEED position). The target is a Ni(111) single-crystal surface; it is cleaned by ion bombardment and heating.

By heating in UHV (5×10^{-10} Torr) to about 800°C sulfur diffuses from the bulk to the surface and is detected by ion scattering and AES, Fig. 1. The sulfur can be removed by ion bombardment. A 1-keV Ne^+ beam of $7 \times 10^{-7} \text{ A/cm}^2$ desorbs about 14%/min of the S coverage at a coverage of $\frac{1}{20}$ monolayer. The backscat-

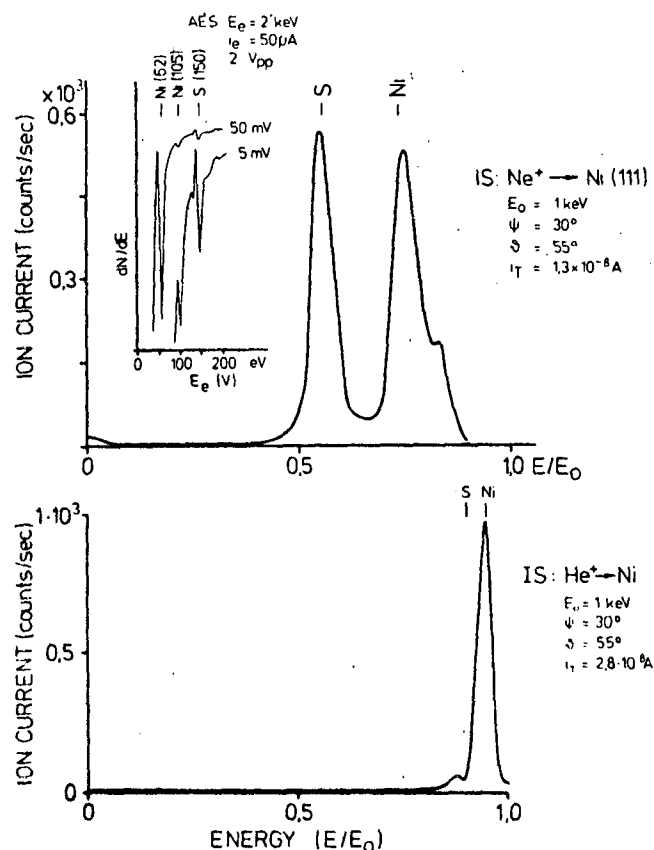


FIG. 1. Comparison of AES and ion backscattering with Ne^+ and He^+ for sulfur on a Ni(111) surface under equal conditions. ψ is the angle between the incoming beam and the surface, θ is the scattering angle. Coverage is about 1.8×10^{14} S atoms/cm². The high-energy shoulder of the Ne^+ -Ni peak is due to multiple scattering (Ref. 11).

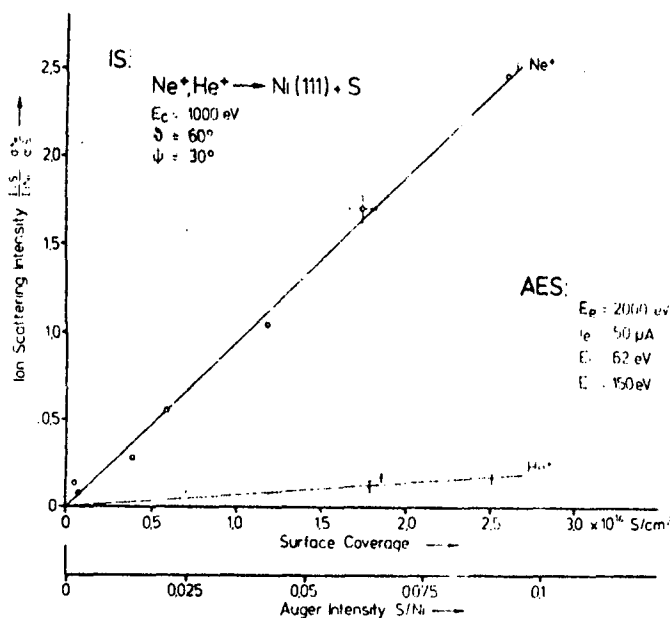


FIG. 2. Relative ion scattering intensities $(I_S/I_{Ni})\sigma_{Ni}/\sigma_S$ as a function of the Auger peak-to-peak intensities $S(150 \text{ eV})/Ni(62 \text{ eV})$. The Auger intensities are converted to absolute coverage using the calibration of Perdreau (Ref. 9). The scattering cross sections are calculated with Born-Mayer potentials.

tering measurements were made with a much lower current density of about $9 \times 10^{-8} \text{ A/cm}^2$. To make sure that the ion beam and the electron beam hit the same spot on the surface, the ion beam focus spot, i.e., a clean Ni area in an otherwise S-covered surface, can be traced by the electron beam. The surface concentration of sulfur is readily controlled by alternately heating and bombarding the surface.

In the coverage range below one monolayer which we examined, we find a linear relationship between the S/Ni intensity ratios from ion scattering and from AES. From this result it can be concluded that the neutralization probability is independent of the coverage in the observed range. Using the calibration of Perdreau⁹ we can plot the ion scattering intensity as a function of absolute surface coverage, Fig. 2. The linear relationship is better established for Ne^+ than for He^+ ions because we observe much higher sensitivity for S with Ne^+ , see also Fig. 1.

From Fig. 2 we obtain the probability that an ion is backscattered as an ion from a S atom compared with backscattering from a Ni surface atom. In the case of Ne^+ we get a factor of 15. This is due to the different probability of escaping neutralization, P , and a shadowing effect of the S atoms on top of the Ni surface. The cross section ratio is already taken into account by multiplying the intensity ratios with $\sigma(Ni)/\sigma(S)$ (1 keV, $\theta = 55^\circ$) = 0.63 for Ne^+ and 0.3 for He^+ in Fig. 2. The shadowing effect is reduced for higher angles of incidence and scattering angles θ up to $\theta = 90^\circ$ where the intensity ratio becomes independent of θ , Fig. 3. In our case evaluation of Fig. 3 yields a reduction factor from shadowing of about 2.2 between $\theta = 60^\circ$ and $\theta = 120^\circ$. So the ratio of the neutralization escape prob-

abilities finally obtained for 1-keV Ne^+ is $P_S/P_{Ni} = 6.8$. Similar behavior has been observed with submonolayer oxygen coverage,¹⁰ so that one could speculate that neutralization of the scattered Ne^+ ions is less for electronegative adsorbates compared with the Ni substrate. This effect together with the shadowing effect results in a very high sensitivity of the Ne^+ scattering for the adsorbed S. For small scattering angles of for example 30° , coverages of some 10^{-4} of a monolayer (about $3 \times 10^{11} \text{ atoms/cm}^2$) are readily detected and 10^{-3} of a monolayer are easily detected also for larger scattering angles. In this experiment the sensitivity with Ne^+ scattering for small scattering angles is about one order of magnitude higher than with AES. It is also confirmed that the ion scattering technique is much more sensitive to the topmost atomic layer than AES, owing to the different processes which are used for the analysis. With Ne^+ scattering the Ni signal decreases by about the same amount as the surface is covered with S atoms, whereas the Ni signal from AES, depending on the electron escape depth, shows a relatively small decrease with increasing S signals, even for monolayer coverage. Therefore, the curve of Fig. 2 can only be linear as long as the S coverage is well below one monolayer. The shadowing effect can be utilized for the analysis of surface structure, i.e., the position of adsorbed atoms. This has been accomplished before for other systems.^{5,6} In our case it demonstrates that the S atoms which diffuse to the surface come to a position above the layer of Ni atoms.

A few remarks can be made on He^+ scattering although our data are less complete in that case. For the same primary energy we get roughly the same backscattered intensity from Ni with He^+ as with Ne^+ . That is, the smaller scattering cross section is compensated by the lower neutralization probability for He^+ ions with higher

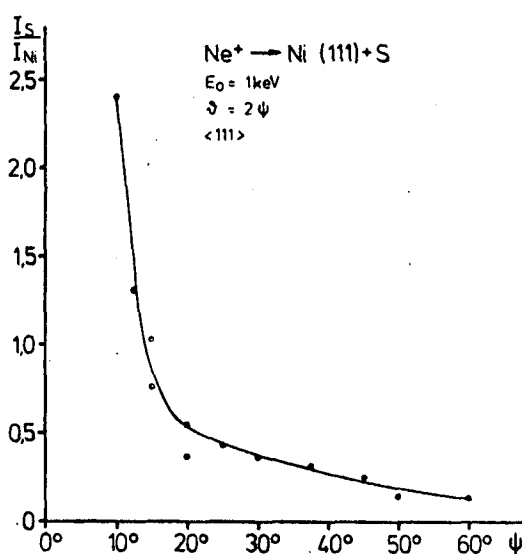


FIG. 3. Relative sulfur peak height I_S/I_{Ni} from Ne^+ backscattering as a function of the impact angle ψ . The scattering angle is $\theta = 2\psi$. The sulfur coverage is about $6 \times 10^{13} \text{ S atoms/cm}^2$. (I_S/I_{Ni} is not corrected for the θ dependence of the scattering cross sections.)

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Secondary Ion Mass Analysis: A Technique for Three-Dimensional Characterization

Secondary ion mass spectrometry with the ion probe technique can provide comprehensive elemental and isotopic detection, extremely high sensitivity, and three-dimensional resolution in a single instrument

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AN INCREASING INTEREST in the analysis of surfaces and the need for three-dimensional characterization of materials have led to the development of secondary ion mass analysis or ion microprobe mass spectrometry. The "ion probing" of a material is accomplished by bombarding the sample to be analyzed with a beam of 1-20 keV ions. These primary ions cause the upper atomic layers to be "sputtered" or stripped off. Most of the material leaves as neutral atoms or molecules, but a small fraction is ejected as positive or negative ions. These secondary ions are then extracted into a mass spectrometer for mass/charge separation to provide an analysis of that portion of the material sampled by the primary ion beam. A full mass spectrum can be taken, or an individual secondary ion mass can be monitored as the primary ions erode the sample. The analytical sample volume at any moment is bounded by the primary beam periphery and extends to a depth of 5-50 Å depending on the kinetic energy of the primary ions. Thus, by continuous monitoring of one or a few masses, the analyst can examine isotopic and concentration in-depth profiles with 50-100 Å resolution. Alternatively, complete mass spectra can be obtained every 25-2500 Å, depending on instrumental operating conditions.

The combination of sputtering and mass spectrometry forms an extremely powerful analytical technique. Control and localization of the sputtering process permit chemical analyses with x,y resolutions of approximately 1 μm ,

the examination of fractional surface monolayers, an in-depth analysis with 50-100 Å resolution, and the acquisition of secondary ion images. The mass spectrometer provides elemental coverage from hydrogen to uranium, isotopic characterization, and sensitivities of 10^{-15} to 10^{-19} gram, depending on the element under consideration. There is probably no other instrumental analytical technique that can make these claims.

Ion Production

The processes involved in the production of secondary ions are quite complex, and there are several postulated mechanisms. The following discussion will attempt to provide a simple, unified picture of the two essential ionization processes, "kinetic" (1) and "chemical" (2, 3). The kinetic process occurs when chemically uncombined elements are bombarded by ions which are chemically inert. The primary ions penetrate to a mean depth in the bombarded material. During penetration they transfer energy to the matrix atoms, causing lattice bonds to be broken and some atomically bound electrons to be ejected into the conduction band of the material. The vast majority of these ions are neutralized before departing from the sample surface, since the band electrons have a much higher velocity than the departing ions. However, these neutralized ions can retain significant energy in a metastable state. Once the neutralized atom has left the surface, an electron can be ejected by Auger or quantum deexcitation processes to produce the

ion for mass analysis. In this circumstance, most of the analytically important ions are produced exterior to the sample surface.

The "chemical" ionization process depends on the presence of a chemically reactive species which reduces the number of conduction electrons available for neutralization of the ions produced in the highly agitated solid. As an example, the presence of oxygen in the ion-producing volume causes compounds to be formed which render that region nonconducting. This oxygen can be previously in the sample as with a bulk or surface oxide, introduced by using oxygen ion bombardment, or accommodated from residual vacuum species. This reduction in ion neutralization causes such a dramatic increase in the number of ions emitted from many materials that the chemical mechanism predominates over the kinetic process.

The operation of these two mechanisms of ion production can result in analytical problems when ion intensities are evaluated. An example is the bombardment of aluminum. When bombarded with argon ions, the oxidized surface will give an Al^+ intensity much larger than when the superficial oxide layer is sputtered away and only pure metal is bombarded. In this and similar instances, the presence of a higher ion intensity would not mean a higher concentration.

The currently widespread use of oxygen ion bombardment to force the predominance of the chemical process has dramatically improved the ability to obtain quantitative ion intensity

For the adsorbed S we get approximately the S/Ni ratio if we assume $P_S = P_{Ni}$. In that case it may be possible to get surface concentration ratios and calibration for P . On the other hand, He^+ back-scattering is less sensitive to the sulfur coverage, as can clearly be seen in Figs. 1 and 2. Moreover, it is useful to take advantage of the shadowing effect because of the lower mass separation with He^+ , especially at small scattering angles. Decrease of the surface area because of sputtering was not observed with these experiments.

Skilful technical assistance of Franz Schuster is gratefully acknowledged.

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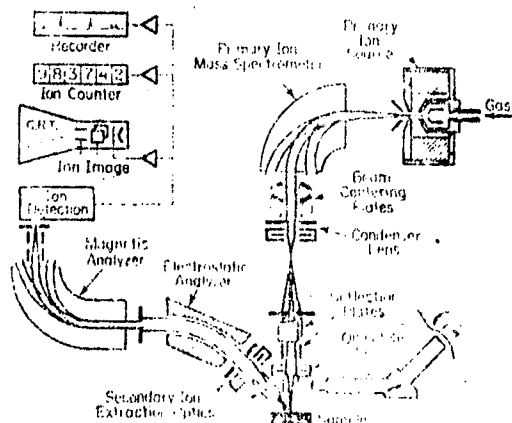


Figure 1. Schematic representation of ARL ion microprobe mass analyzer (not to scale)

on surfaces, oxygen impurities in copper, and innumerable thin films.

Ion Microprobe Mass Spectrometers. The ion microprobe mass spectrometer is the ion analog to the electron microprobe. In the ion microprobe, a finely focused beam of primary ions bombards the sample, and the secondary ions are extracted into a double-focusing mass spectrometer. The primary ions are produced by a high-intensity duoplasmatron ion source fed by a gas such as argon, nitrogen, or oxygen. The ions are extracted from the ion source with 1–20 keV of kinetic energy. Some workers pass the primary ions through a low-resolution mass spectrometer so that only a given ionic species bombards the sample, rather than the full ion output of the duoplasmatron. This primary mass spectrometry can reduce spurious effects owing to the duoplasmatron feed gas impurities or impurities introduced from the walls of the ion source. The primary ions are then focused or “demagnified” by two electrostatic lenses. Two sets of mutually opposing electrostatic deflection or scanning plates are also placed in the primary ion column so that the primary ion spot can be moved about the sample surface. Generally a 1–2- μm diameter spot of $\leq 1 \times 10^{-9}$ A ion current is formed at the sample with about a 300- μm x,y deflection capability.

The secondary ions produced by this “ion microprobe” are extracted into a double-focusing mass spectrometer or spectrograph for mass/charge separation. This type of mass spectrometer is advantageous because it accommodates the comparatively high initial kinetic energy spread of the secondary ions. Ion detection is accomplished by electrical and/or photographic means.

The ion microprobe produces a magnified image of the distribution of a given element or isotope in a manner similar to that of the electron probe. The primary ion beam is scanned about the sample surface in a raster pattern (much as the electron beam in a TV set), causing sputtering of the sample surface. The mass spectrometer is tuned to the desired mass/charge, and the appropriate ions are detected by an electron multiplier. The multiplier output is amplified and used to modulate the intensity (z axis) of an oscilloscope whose x,y deflection is synchronized to the primary ion raster. Thus, when the primary ions sputter an area containing the element of interest, the secondary ions pass the mass spectrometer, are detected, and increase the oscilloscope intensity at a position corresponding to the relative location of that element. The image magnification is simply the ratio of the oscilloscope raster area to the area scanned on the sample surface. By continuing to bombard and remove material, the analyst can obtain successive images which provide three-dimensional characterization of one or more elements in the sample.

There are two commercial ion microprobe mass spectrometers presently available. The first of these is based on a design by Liehl (11) and is sold by Applied Research Laboratories. This is a complete instrument designed for ion microprobe mass spectrometry and includes many sophisticated features. Figure 1 schematically diagrams this instrument. A hollow cathode duoplasmatron is used for ion production. The primary ion optics include a mass spectrometer to provide a bombarding ion beam composed of a single ion species. The ion probe diameter is

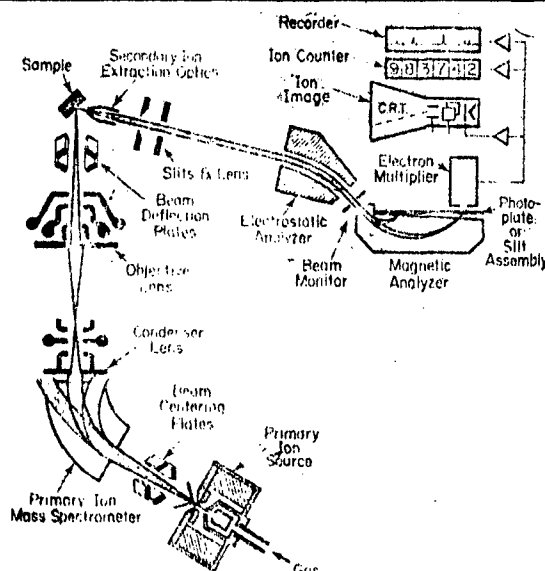


Figure 2. Schematic representation of AEI ion microprobe mass spectrometer (not to scale)

variable from 2–300 μm and can be rastered for imaging purposes. The primary column will provide both negative and positive ion bombardment capability. The sample handling facilities include a digitally controlled precision stage, a four-sample carousel to reduce sample turn-around time, and a microscope for sample viewing. A high-efficiency lens extracts the secondary ions into a modified Mattauch-Herzog, double-focusing mass spectrometer. The mass spectrometer provides a mass resolution of about 600 on a 10% valley definition. The detector-video system provides for mass scanning, ion counting, rapid peak switching for isotopic analysis, and a variety of imaging modes.

The second commercially available ion microprobe mass spectrometer is produced by AEI Scientific Apparatus. The AEI instrument is based on a modular concept and on their MS-702R spark source mass spectrometer. The ion probe column is similar to the design of Drummond and Long (12, 13). The basic primary ion column employs a hollow cathode duoplasmatron and electrostatic lenses for producing a 2–300- μm ion probe. This column is attached to the MS-702R, as shown in Figure 2, to provide a microanalytical capability. A primary ion mass spectrometer, as well as the rastering electronics required for ion imaging, is available for inclusion at the analyst's discretion. Light optical viewing of the sample is incorporated into the sample chamber. A one- or seven-position sample carousel is available.

The secondary ions are extracted into a Mattauch-Herzog double-focusing mass spectrometer with a mass resolution of 10,000 on a 50% valley definition (about 5000 on a 10% def-

relationships. Andersen (2, 3) has developed a quantitative model for the production of secondary ions by reactive ion bombardment. The model is based on the establishment of a surface plasma by the ion bombardment. The Saha-Eggert ionization equation is employed to calculate the ion yield for each of the species of interest. Before the ions produced in this surface plasma can be analyzed, they must escape the solid and survive the possibility of neutralization by electrons at the sample-vacuum interface. The probability of ion neutralization is dependent on the Fermi distribution of electrons in the material. The extent of this phenomenon can be calculated from the surface barrier potential, Boltzman's constant, and the absolute temperature of the surface electrons.

Andersen has had good success in calculating relative sensitivity coefficients for impurities in metals, alloys, and geological matrices. In most of the published examples, the accuracy of the final analysis has been $\pm 10\%$. For these calculations Andersen requires the spectral intensities, tabular values for a variety of physical constants, and an internal standard. The matrix element or elements serve quite satisfactorily as the internal standard. The implication of Andersen's work is quite far reaching: if one knows the matrix composition, a complete quantitative analysis can be performed without a comparative standard.

The excellent gram detectability of the secondary ion mass analysis technique results from the efficient ion production process and the high efficiency of collection and detection of these ions. If one assumes an average atomic weight of 100, a high ionization efficiency of 20% (ion/atom), a mass spectrometer efficiency of 10%, and 6 ions over a few-second period required for detection, the widely touted 10^{-19} gram detection limit is obtained. Ionization efficiencies of this order are obtained for positive ions of the alkali metals and negative ions of the halogens. A 10% mass spectrometer collection and transmission efficiency can be realized under low mass resolution conditions. The gram detectability decreases from this 10^{-19} gram level as one progresses to elements with ion yields of 10^{-2} down to 10^{-3} . Granted, these detection limits are optimistic and are not normal working regions, but they represent what can be achieved under optimum conditions.

A variety of ionic species are produced by the ion bombardment process. Generally, the most intense ion species from inorganic materials are the singly charged, monoatomic ions of the ele-

ments present. This is particularly the case for oxide matrices or for reactive gas ion bombardment employed as described above. The production of multiply charged ions is quite inefficient, and the doubly charged ions typically constitute between 0.1–0.01% of the corresponding singly charged ions. The +3 ions are even less intense. No multiply charged negative ions have ever been reported. Thus, multiply charged positive ions from highly concentrated species such as the matrix do not cause severe spectral interferences, and multiply charged negatives are never of concern.

On the other hand, polymer and interelement molecular ions are much more abundant. Singly charged dimer ion intensities can range from 0.1 to 20% of the parent atomic ion even if reactive ion bombardment is employed to increase atomic ion intensities. Interelement combination ions can be quite numerous; they are dependent on the abundance of the elements in the sample as well as on "chemical" considerations and can be quite numerous. Thus, the high mass region of a spectrum from a multicomponent matrix, such as a mineral or alloy, can be quite complex. In addition, "hydrocarbon" ions are produced if organic material is present in or on the sample. The production of these molecular species is probably the most significant limitation to sensitivity of the ion probe technique. Thus, in complex matrices the analyst must employ both instrumental and interpretive resources to fully utilize the technique's capabilities.

Instrumentation

The instrumentation employed for secondary ion mass analysis ranges from custom-designed, laboratory-constructed units to several commercially available ion probe instruments. The basic instrumental components include: an ion source and focusing optics for the primary ions, a sample chamber for holding and manipulating the material to be analyzed, a mass spectrometer for mass/charge separation, and a detection system for actual ion detection as well as image display. There are three basic types of ion probe instruments: the secondary ion mass analyzers which provide an analytical capability with no imaging facility, the "probe imaging" ion microprobe mass spectrometer (analogous to the electron microprobe), and the direct imaging mass analyzer. The term "ion probe" is used to describe the general technique or instrumentation involving ion sputtering and mass spectrometry, as is "secondary ion mass analysis." The terms "ion micro-

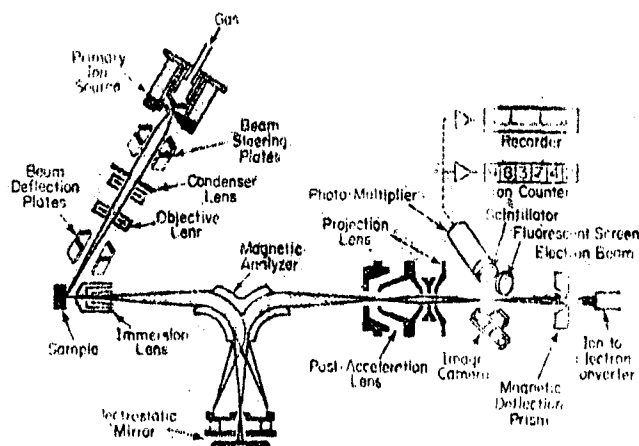
probe," "probe imaging," and "direct imaging" refer to specific instrumental concepts as described below.

Secondary Ion Mass Analyzers. The instruments in this category are generally of the laboratory-constructed type. They provide a facility for obtaining general analysis of the sputtered secondary-ions and depth profiling of elements and isotopes with a primary beam diameter (and consequently x,y resolution) of $\geq 300 \mu\text{m}$. A unique instrument of the secondary ion mass analyzer type is used by Benninghoven and Loebach (4, 5). Benninghoven and Loebach employ ultrahigh-vacuum techniques (10^{-10} to 10^{-11} torr.) and a quadrupole mass filter to provide an excellent system for surface and depth profiling analysis. They combine the ultrahigh vacuum in the sample region with low primary ion current densities to study surface monolayers. The high vacuum reduces surface contamination from the residual gas to the extent that they can take 10^3 or 10^4 sec to sputter away the equivalent of one monolayer. Once the surface at a given depth is characterized, the primary ion current density is increased to rapidly sputter down to the next region of interest.

To obtain the desired sensitivity, this technique employs a primary ion beam diameter of 1–5 mm. Thus, one is limited to x,y spatial resolutions of this amount. The other limitation of this technique is the limited resolution and abundance sensitivity of a quadrupole mass filter as compared to a double-focusing mass spectrometer. This technique would appear to have great value for the study of surface reactions, catalysis, surface contamination, and thin films. It is certainly complementary, perhaps even competitive, to Auger electron spectroscopy and ion scattering spectroscopy as a surface analytical tool. Balzers Aktiengesellschaft of Liechtenstein is currently marketing an instrument based on this design.

The two other main contributors in the field of secondary ion mass analysis have been Werner of Phillips-Eindhoven, using a laboratory-constructed instrument (6), and those workers using the instrument marketed by GCA Technology Division (two of these groups are Herzog, Poschenrieder, Ruedenauer, and Satkiewicz of GCA (7) and Evans and Pemsler and Pawel (8–10) of Kennecott Copper). These workers have employed conventional vacuum systems (10^{-6} to 10^{-7} torr.), medium-to-high primary ion currents, and magnetic deflection mass spectrometers to study a wide variety of systems. The samples studied include surfaces, gases condensed

Figure 3. Schematic representation of Cameca direct imaging mass spectrometer (not to scale)



trometry of the secondary particles. Nondispersive X-ray analysis could be easily added to provide nondestructive electron probe analysis as well as the destructive ion probe analysis.

Direct Imaging Mass Analyzer. The direct imaging mass analyzer developed by Castaing and Slodzian (16) is unique in the instrumentation employed for secondary ion microchemical analysis. In the Castaing-Slodzian design (Figure 3), commercially available from Cameca Instruments, an area of 10–300- μm diameter is bombarded by the primary ions. The secondary ions are extracted by an electrostatic immersion lens which maintains a point-to-point location image of the origin of each secondary ion. The secondary ion image then traverses a magnetic sector, an electrostatic mirror, and a second magnetic sector. This system provides for mass and energy separation as well as magnification. This prism-mirror-prism geometry accomplishes many of the same functions as the double focusing employed in ion microprobes as well as providing for image magnification. This results in a mass-resolved image of the secondary ions from the bombarded area.

This unique double-focusing mass spectrometer has a mass resolution of up to 1000 on a 10% valley definition. The ion image is converted to an electron image which can then be focused on a variety of detection systems. The electron image can be focused on a fluorescent screen and visually observed

in). The MS-702R normally employs photographic detection with electrical detection facilities added if desired. The photographic detection allows the maximum resolution to be obtained and permits simultaneous collection of the entire mass spectrum. Electrical detection is employed to perform quantitative analyses, to obtain scanning mass spectra, and to produce secondary ion imaging. The high-resolution mass spectrometer should be particularly valuable when examining samples containing hydrocarbons, such as biological materials or complex samples which produce many polymeric and molecular ions. The normal MS-702R spark source ionization capability is also available when it is more appropriate to an anal-

ysis than the ion sputtering technique.

Two other ion microprobes have been constructed and described but are not yet commercially available. Workers at Hitachi in Japan (14) have built an instrument similar to the ARL unit but without many of the sophisticated features. The missing capabilities include primary mass analysis, a finely controlled sample stage, and versatile readout devices. The second laboratory-constructed ion probe was designed by Liebl (15), now at the Institute für Plasmaphysik, Munich-Garching. This unit is actually a combined electron and ion microprobe. The instrument provides for alternate or simultaneous electron and ion bombardment with electron or mass spec-

Table I. Instrumental Features

Instrument	1° Ion species	PRIMARY ION SYSTEM		1° Ion mass analyzer	SAMPLE CHAMBER		MASS SPEC.
		1° Spot diam	Raster 1° spot		Ultimate sample chamber pressure	Light optics	Mass spectrometer
SIMA							
GCA	Rare gas	300 μm-3 mm	No	No	1 × 10 ⁻⁷ Torr.	Yes	DF ^a
Werner	Rare gas	~1 mm	No	No	2 × 10 ⁻⁷ Torr.	Unpublished	SF ^b
Fogel	Rare gas	~1 mm	No	No	1 × 10 ⁻⁹ . 1 × 10 ⁻¹⁰ Torr. (estimate)	Unpublished	SF
Benninghoven	Rare gas	~1 mm	No	No	1 × 10 ⁻¹⁰ . 1 × 10 ⁻¹¹ Torr.	No	Quadrupole
Ion microprobes							
Liebl/ARL	Reactive and rare gas	2-300 μm	Yes	Yes	1 × 10 ⁻⁷ . 1 × 10 ⁻⁸ Torr.	Yes	DF
AEI	Reactive and rare gas	2-300 μm	Yes (optional)	Yes (optional)	1 × 10 ⁻⁹ Torr. (estimate)	Yes	DF
Liebl/Munich	Rare gas	Unpublished	Yes	Yes	Unpublished	Yes	DF
Tamura/Hitachi	Reactive and rare gas	2-300 μm	Yes	Optional	5 × 10 ⁻⁷ Torr.	Yes	DF
Direct imaging analyzers							
Castaing-Slodzian/Cameca	Reactive and rare gas	10-300 μm	Yes	No	1 × 10 ⁻⁸ Torr.	Yes	Prism-mirror-prism

^a Ions to detector/ions produced from sample. ^b DF = double focusing. ^c SF = single focusing.

on a photographic film to produce a permanent record. Alternatively, the image can be focused on a scintillator for electrical measurement by a photon counting system. In addition, the analyst can quantitatively measure the ion intensity from a portion of the image by placing a mechanical aperture in the secondary image plane and allowing only a selected portion of the electrons to fall on the electrical detection system. Thus, the Cameca instrument acquires all points in the secondary ion image *simultaneously* rather than *sequentially* as in the probe imaging instruments.

The x,y resolution of the direct imaging instrument is limited by the quality of the ion optical devices rather than by the diameter of the primary ion beam as in the probe imaging instruments. Presently, the quality of the immersion lens limits the resolution to 0.6–0.75 μm , whereas the best resolution obtained with an ion probe is about 1.5–2 μm . However, Drummond and Long have reported 0.2–0.3 μm when their column is operated in what has been called the scanning ion microscopy mode. They anticipate obtaining similar beam diameter and resolution in the secondary ion analysis mode. Table I provides a summary of some of the instrumental features of secondary ion mass analyzers.

Since the Castaing-Slodzian direct imaging concept is unique in ion optical devices, it offers distinctly unique capabilities as compared to a conventional

ion microprobe. One major difference is in the acquisition of secondary ion images. As mentioned above, the direct imaging instrument acquires the image data *simultaneously* over the entire viewed area, whereas the probe imaging instruments acquire data sequentially. Thus, a direct image can be obtained in a much shorter time than a probe image for a species at a given concentration. This time advantage can vary from a factor of 10 to 10^4 , depending upon instrumental conditions and the area and element (chemical) to be imaged.

The other major difference between direct imaging and the probe imaging concepts is related to the effects of residual vacuum species. Since no instrument has a perfect vacuum, the analyst must consider the results of reactions between the surface being analyzed and the residual vacuum species. The direct imaging technique is constantly bombarding the entire area and removing surface contaminants. In addition, the constant bombardment produces a surface agitation, much like thermal heating, which prevents accommodation or reaction of the surface with the residual gas species.

On the other hand, an ion microprobe is removing material from one spot at a time during imaging, and the remaining area to be imaged is reacting with residual vacuum species. Therefore, hydrogen, carbon, nitrogen, and oxygen from the residual vacuum components are sputtered and analyzed just as if

they were in the actual sample. Thus, the ion microprobe is detrimentally affected to an extent determined by the quality of the vacuum and the effective average primary ion current density over the area imaged. A somewhat similar effect is noticed when using a static ion probe. Since the current density and, consequently, the rate of removal are quite low at the primary beam edge, there is sufficient time for residual vacuum species to react with the surface before being sputtered and to enter into the analysis. In the direct imaging technique an analysis can be performed only on the central part of the bombarded area by simply using the appropriate aperture to reject the ions from the beam periphery.

One of the limitations of present direct imaging instruments is that the primary beam diameter is 10–20 μm . Thus, if one wishes to examine an area of smaller dimension with the electrical detection system, an aperture must be used, but material from the entire bombarded area is removed. Another limitation is related to the inability to directly view the sample during bombardment in the direct imaging instrument. It would appear that this problem could be remedied easily by an immersion lens and vacuum housing modification.

These are only some of the relative merits of the two imaging concepts. The relative importance of these and others must be considered for different analytical applications. Obviously, the

Secondary Ion Mass Spectrometers

INSTRUMENT

Max estimated spectrometer transmission ^a	Max mass resolution	Detection	Imaging (?) and type	x,y Resolution	Commercially available (?) and approx base price
10^{-4} – 10^{-6}	1000	Electrical	No	300 μm	On special order \$100,000–\$125,000
Unpublished	Several hundred	Electrical	No	~ 1 mm	No
Unpublished	Several hundred	Electrical	No	~ 1 mm	No
0.1–0.5	200	Electrical	No	~ 1 mm	Yes, \$40,000–\$60,000 (estimate)
0.1	600	Electrical	Yes, probe	2 μm	Yes, \$240,000
0.01–0.1	3000 Electrical 10,000 Photographic	Electrical and/or photographic	Yes, probe (optional)	2 μm	Yes, price varies with options, \$215,000 (min)–\$280,000
Unpublished (estimate 0.1)	600 (Estimate)	Electrical	Yes, probe	Unpublished	No
Unpublished	300	Electrical	Yes, probe	2 μm	Yes, \$175,000 (rough estimate)
0.08–0.1	1000	Electrical for ion current measurement and images viewed visually and recorded photographically	Yes, direct	0.6–0.75 μm	Yes, \$225,000

relative merits will change as improvements are made in ion source intensities, vacuum capabilities, mass spectrometer resolutions, etc., and from one analytical problem to another. Thus, the potential user must closely examine his particular analytical problems and critically evaluate the two concepts before proceeding. It is also important for the potential user to understand that he may not be able to realize all combinations of the above capabilities simultaneously. Thus, an analytical situation which requires 1- μm lateral resolution, 10–40 Å depth resolution, and a ppm sensitivity may prove too exacting even for an ion probe.

Analytical Applications

Although secondary ion mass spectrometry is a relatively new field, and the majority of the literature deals with instrumentation, the technique has been applied to a wide variety of systems. The applications can be roughly divided into surface studies, x,y microcharacterization, and in-depth profiling.

Surface Studies. Since the secondary ions are produced in the few atomic layers nearest the surface, the ion probe (referring to the general technique, not necessarily to the ion microprobe) provides valuable surface characterization. The sampling depth can be controlled by varying the primary ion kinetic energy; all the elements as well as hydrocarbon type material can be detected; isotopic labeling and exchange studies can be performed, and surface and bulk can be compared by sputter removal of the surface. In addition to the broad elemental coverage, the ion probe technique provides detection limits of 10^{-15} to 10^{-19} for most elements. On a relative basis this is of the order of 1 atom in a million. This can be 1 atom in a million (1 ppm atomic) comprising a surface contaminant or 1 ppm dispersed throughout a bulk region.

Benninghoven and Loebach (4, 5) have studied the kinetics and products of gas-solid reactions by the "static" mode of secondary ion mass analysis. Others have examined the impurities on metal, semiconductor, and mineral surfaces. Other workers have used the imaging capability to examine the x,y distribution of surface contaminants on deposited thin films and tungsten surfaces. Hernandez and coworkers (17) used a high-resolution mass spectrometer to study the hydrocarbon, oxide, and elemental ions sputtered from a surface. Although of preliminary nature, this study indicates the value of high spectral resolution when molecular ions are encountered during an analysis. Recently, Fogel (18) re-

viewed the study of surface processes with an emphasis on the work performed in his and other Russian laboratories.

x,y Microcharacterization. As described above, the ion probe technique can provide x,y distributional characterization by either the probe imaging or the direct imaging instrumentation. The resolution one can obtain is limited only by the instrumentation used for the analysis. The sensitivity, broad elemental coverage, and isotopic capability of this technique provide many advantages over the classic electron probe. The importance of the ability to perform microanalyses for the light elements (H–Na) cannot be over emphasized. This is particularly true for the study of the "gaseous" or interstitial elements such as hydrogen, carbon, nitrogen, and oxygen in metallurgical and geological matrices. Preliminary work has used the ion probe technique to study oxygen concentrations, gradients, and oxidation processes in metals (19, 20) and surface corrosion (21). The majority of the microchemical ion probe work has been performed by Andersen and coworkers (22, 23). These authors have studied impurity distributions in both geological and lunar materials. They also performed in situ, localized geologic dating of these materials.

Previous studies have shown the ion probe to be a valuable microanalytical technique for inorganic materials. With this proven capability in inorganic systems, it seems reasonable that secondary ion microanalysis could make significant contributions to the study of biological systems. The first two biological applications of secondary ion microanalysis (24, 25) demonstrated the excellent sensitivity of the technique (10^{-20} gram of Na) and the ability to examine concentrational distributions in biological materials with minimal sample preparation. Since biological systems have defied study with the electron probe, the successful application of secondary ion microanalysis to these systems will be extremely valuable.

Figures 4a and 4b are secondary ion images obtained with a direct imaging instrument. Figure 4a is the $^{27}\text{Al}^+$ image from a Cr–Al microcircuit test pattern. The sample was prepared by first laying down sets of Cr lines in a chevron pattern. The lines in the most closely spaced set are 1.5 μm wide and 1.5 μm apart. These lines were then overlaid with about 1500 Å of Al. To obtain this image, the sample was bombarded by the primary beam until the Cr lines were reached, and a $^{27}\text{Al}^+$ image was taken. From an image such as this, a lateral (x,y) resolution of 0.6–0.75 μm can be estimated. Figure

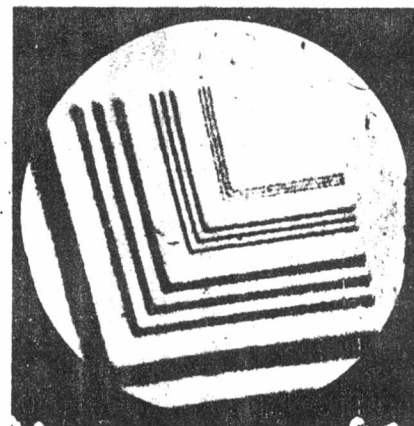


Figure 4a. $^{27}\text{Al}^+$ image from chromium lines in aluminum matrix

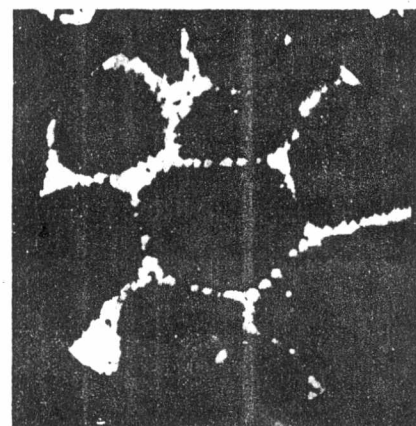


Figure 4b. $^{56}\text{Fe}^+$ image illustrating grain boundary precipitation in Al–Fe alloy

4b is a $^{56}\text{Fe}^+$ image from a sample containing 1.5 wt % of iron in aluminum. The image shows the high Fe concentration at the grain boundaries owing to an Fe-rich eutectic precipitate. Some of the precipitates are less than 0.7 μm in diameter; however, no image appears smaller than this value, owing to the limitations of the immersion lens discussed above.

In-Depth Profiling. As a result of the sputter removal of material by the primary ion bombardment, the ion probe provides concentration and isotope profile characterization. This profiling can take the form of surface monolayer characterization by use of the techniques of Benninghoven or continuous monitoring of one or more masses by use of the ion microprobe or direct imaging instruments. Depending on the information desired and the depth resolution needed, the analyst can repeatedly monitor a few masses or the entire spectrum as the sample is penetrated and removed.

The realization of maximum depth resolution by ion probe techniques requires that serious consideration be given to several instrumental operating conditions. One of these is the kinetic energy of the primary ions. During the bombardment process, the primary

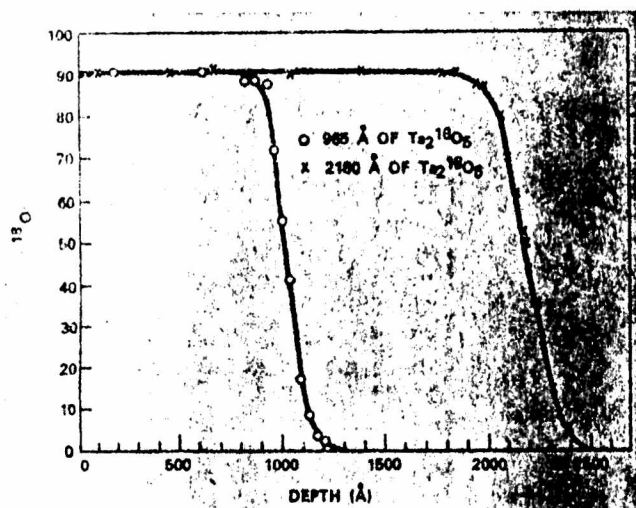


Figure 5a. Percent ^{18}O vs. depth for Ta_2O_5 anodized in H_2^{18}O followed by D_2^{18}O

ions penetrate and "stir" the upper atomic layers as they collide and dissipate their kinetic energy. Thus, the high kinetic energy (20 keV) normally used to obtain optimum focusing and ion yields would lead to poorer depth resolution than a lower kinetic energy, say 2–5 keV. A second point to consider is the shape of the crater formed from the eroding action of the primary beam. Since the crater produced by a stationary beam is hemispherical in shape, ions are being produced from a variety of depths in the sample rather than at one specific depth.

Three different methods have been employed to obtain what is generally called a flat-bottomed crater. The first is simply to defocus and aperture the primary ion beam to produce a flat-bottomed, vertical-sided crater (8–10). The second method uses partial defocusing of the primary beam and the direct-imaging concept. The defocusing produces a crater with a flat bottom over the center of the crater. One then simply places any of a variety of mechanical apertures in the focal plane and measures only those ions from the flat area. The third method employs primary beam rastering and electronic gating of the detection system. The rastering produces a flat region in the crater and is synchronized with electronics which allow data to be collected from only that central region. These last two methods are employed with the direct imaging and the probe imaging instruments, respectively.

A variety of materials have been examined for depth-profile characterization, including In in Ge, and impurity and isotopic gradients in Ta_2O_5 thin films (8–10). Figures 5a and 5b illustrate both P and O isotopic gradients in Ta_2O_5 thin films. These data

are examples of profiles obtained during an extended study of the relative transport numbers of Ta and O during the formation of anodic Ta_2O_5 films. The $^{31}\text{P}^+$ profile illustrates the detail one can obtain with the in-depth profiling mode of operation. The sharpness of the $^{18}\text{O}/^{16}\text{O}$ deviates only a few tens of angstroms from theoretical at the 2000 Å depth. The reader is referred to References 8–10 for detailed discussions of these data.

Summary

The ion probe technique provides a unique analytical system in its ability to perform three-dimensional micro-analysis. Although other techniques can provide some of the ion probe's capabilities, none can provide the comprehensive elemental and isotopic detection, the high sensitivity, and the three-dimensional resolution in a single instrument. In only a few years of application, the technique has demonstrated its capabilities on a wide variety of materials, and it is anticipated that secondary ion mass spectrometry will continue to be an extremely valuable analytical tool.

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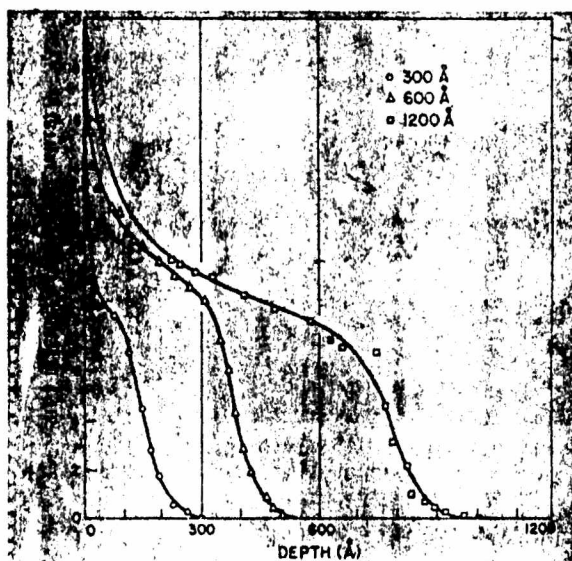


Figure 5b. $^{31}\text{P}^+$ vs. depth for 300, 600, and 1200 Å thin films of Ta_2O_5

Ion Microprobe Mass Analyzer

C. A. Andersen and J. R. Hinthorne

The ion microprobe mass analyzer is an instrument that has been developed to provide an in situ mass analysis of a microvolume of the surface of a solid sample. It accomplishes the analysis by bombarding the surface with a high-energy beam of ions, which causes the atoms at the surface to be sputtered away. A fraction of the sputtered particles is electrostatically charged, and these sputtered ions are collected, and analyzed according to their mass-to-charge ratio in a mass spectrometer. The instrument complements other microanalytical techniques, such as the electron microprobe x-ray analyzer, by providing information about the concentrations and distribution of the isotopes of the elements in the surface of the solid. The technique permits isotope ratios to be measured, makes it possible to detect the very light elements, and generally extends spatial microanalysis into the range of trace elements. In addition, a highly sensitive analysis can be made of the sample in depth as successive atomic layers of the surface are sputtered away by the impinging ion beam.

The general concept of producing a spatially resolved mass analysis of the surface of a solid by bombarding it with a beam of primary ions and analyzing the secondary ions sputtered from

the sample was introduced by Castaing and Slodzian (1). Their work has resulted in the production of an ion microanalyzer, which has been described by Rouberol *et al.* (2) and Socha (3). Other sputtering-ion mass spectrometers with varying degrees of microanalytical capability have been described by Barrington *et al.* (4), Tamura *et al.* (5), and Nishimura and Okano (6). An ion microprobe design was proposed by Long (7), and a scanning ion microscope based on the design was built and demonstrated by Drummond and Long (8). The present article deals with the ion microprobe mass analyzer basically designed by Liebl (9). This instrument is parallel in design concept to the electron microprobe x-ray analyzer in that a heavy-ion beam has been substituted for the electron beam and a mass spectrometer for the x-ray spectrometer. This analogy permits a similar microanalytical methodology to be applied in both instruments.

Instrumentation

Figure 1 is a schematic diagram of the instrument. The ions used for sample bombardment are generated in a hollow-cathode duoplasmatron ion source that is capable of producing ions of a wide variety of gases, including those of a highly electronegative char-

acter. The ions, which can be either positively or negatively charged, are accelerated to energies ranging from 5 to 22.5 kilovolts and passed through the primary mass spectrometer. This spectrometer permits the analyst to select and purify by mass separation a specific chemical species from those produced in the ion source. The purified ion beam is focused to a small probe in an electrostatic lens column consisting of a condenser lens and an objective lens and allowed to impinge on the surface of the sample. The diameter of the ion probe can be varied continuously from about 2 to 500 micrometers. The sample and the point being analyzed can be viewed through an optical microscope while under bombardment.

The sputtered ions are collected and their masses analyzed in a double-focusing mass spectrometer generally similar to the Mattauch-Herzog type, in which the velocity dispersions of the magnetic and electric sectors are matched to permit the acceptance of a wide range of initial energies of the sputtered ions. No entrance slit is used, and the bombarded area is stigmatically focused directly onto the resolving slit. A retrofocal lens is used before the mass spectrometer to increase the solid angle of acceptance of the instrument. Because of the stability of the duoplasmatron ion source and the resulting continuous generation of sputtered sample ions, electrical detection and mass scanning can be used to good advantage.

The ion beams are then detected with a high-gain device of the Daly type (10) that permits single-ion counting. Both positive and negative sputtered ions can be detected when the potentials of the conversion electrode and the scintillator are suitably arranged. Sputtered ions from the sample eject secondary electrons at the conversion electrode, and

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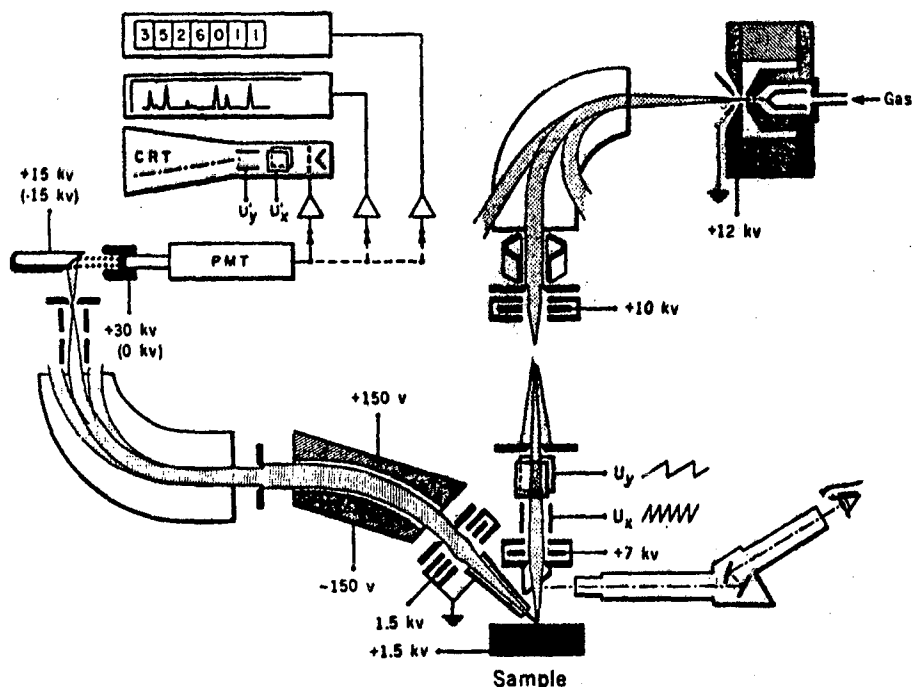


Fig. 1. Schematic diagram of the ion microprobe mass analyzer, Applied Research Laboratories, Sunland, California. (PMT) Photomultiplier tube; (CRT) cathode-ray tube; (U_x , U_y , U_x' , U_y') sweep voltages in x and y directions.

these are accelerated toward the scintillator of a photomultiplier tube, where the light produced by their impact is detected. The resolved ion signals can be read as count rates from scalers, which can accommodate rates in the megacycle range with insignificant dead-time losses, or as direct currents on chart recorders. In the scaling mode no mass-discrimination effects are noted; both heavy and light ions are counted with the same efficiency. To increase

the precision of isotope ratio measurements over that obtained by simple mass scanning and counting the ion peaks of interest, the detector assembly has been designed to automatically yield the isotope ratios for isotopes whose mass ranges are within 15 percent of each other. This is accomplished by electrostatically switching the appropriate ion beams in and out of the resolving slit and detector by means of two pairs of electric deflection plates

positioned before the slit. The ion beams are switched at a rate of 500 times per second and are recorded separately by the scaling units. A blanking pulse is used between counting intervals to eliminate interference from ion peaks that might fall between the two isotopes of interest. The method has been produced, for both metal alloys and noninsulators, isotope ratios measured with precisions essentially defined by counting statistics down to a practical limit of about 0.1 percent (11).

In addition to bombarding a fixed point, the impinging ion beam can be swept over a selected area of the surface of the sample to form a raster by means of the sweeping plates in the primary lens column. The sputtered ions generated by this process are analyzed for mass, and the ion signals can be viewed as a television-like image on a cathode-ray tube. The image gives the two-dimensional distribution of the sputtered element in the selected area. (An example of such a scanning micrograph is given in Fig. 9, which will be discussed in a later section.)

Analytical Method

The analytical method applied with this instrument is based on the observation that the yields of sputtered ions are greatly affected by the surface chemistry of the sample. The sputtered-ion yields of many pure elements have been studied, and the behavior

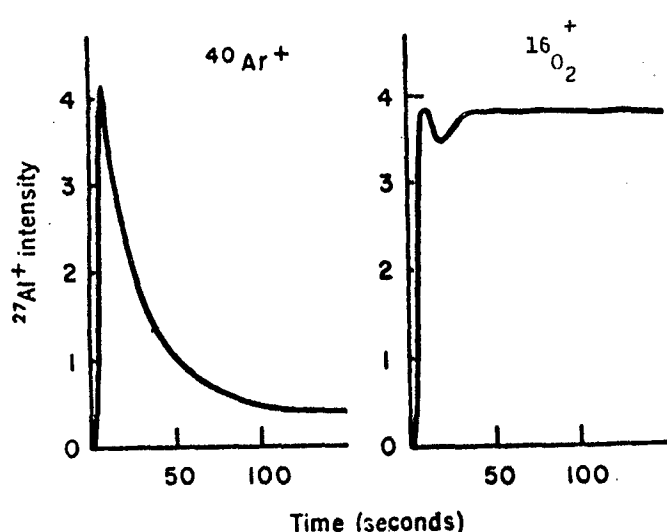
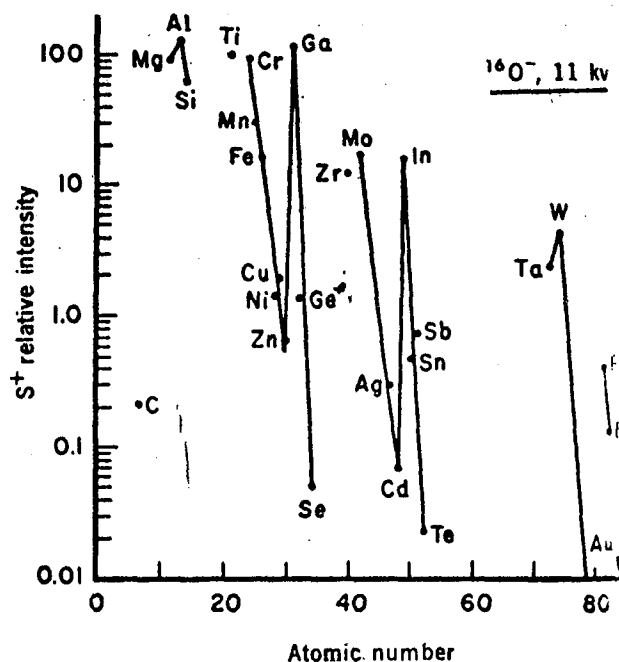


Fig. 2 (left). The variation with time of the intensity of positive Al ions sputtered from pure Al bombarded with Ar ions and with O ions. The sample current is the primary bombarding current measured at the sample. In these experiments, the accelerating potential was 11 kv, the sample current 4×10^{-9} amp, and the probe size $20 \mu\text{m}^2$. Fig. 3 (right). The relative intensities of sputtered positive ions (S^+) for pure elements bombarded with O ions. The intensities have been corrected for natural isotopic abundances.



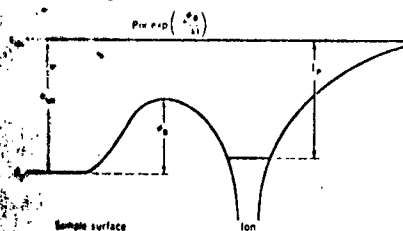


Fig. 4. Probability for neutralization of a positive ion in close proximity to the surface of the solid. The symbol ϕ_n denotes the surface barrier, ϕ_{sto} is the electronic work function of the surface, E_F is the Fermi energy level for electrons in the solid, E_{vac} is the energy level for electrons in a vacuum, and I_p is the ionization energy of the sputtered ion.

illustrated in Fig. 2 (12) is typically observed experimentally. When a metal such as aluminum is bombarded with ions of an inert gas such as argon, which has been the common practice, the yield of positive Al ions falls exponentially with time. The ability of the sample to yield positive ions is progressively destroyed by the bombardment. On the basis of the similar behavior of many metals under bombardment by inert gases, it was postulated that the production of sputtered ions is a function of the electronic properties of the surface. The ability to extract positive ions from the sample diminishes as the strongly bonded compounds formed on the surface of the sample through the chemisorption of reactive gases are removed by the eroding action of the bombarding ion beam. In the case of Al it is most likely due to the destruction of the oxidized phase known to exist on its surface. We have shown that the production of positive ions can be maintained at a higher level by controlling the surface chemistry through a proper selection of the species of bombarding ion. Instead of employing the necessary chemical compounds with an inert gas, it is possible to reconstitute them by bombarding with a reactive gas. The results of bombarding Al with oxygen are also shown in Fig. 2. The yield of Al⁺ ions rose to a maximum similar to that observed with Ar bombardment, but instead of decaying exponentially it suffered only a small variation and recovers quickly to maintain a high, stable output of ions. The experimental results indicate that it is possible to manufacture a suitable surface compounds at the time at which they are destroyed by the sputtering process, if the primary ions are a reactive species. This is not a specific effect of oxygen but has been demonstrated to be a general effect of

all electronegative gases. Enhanced, stable yields of sputtered positive ions of many pure elements have been produced by bombarding with beams of carbon, nitrogen, oxygen, fluorine, chlorine, and iodine ions (12).

Figure 3 (13) illustrates the relative sputtered-ion intensities of some pure elements subjected to bombardment by oxygen ions, $^{16}\text{O}^-$. The relative intensity for each isotope has been corrected only for its natural abundance. It can be seen that the intensities vary markedly. Those elements that have a high affinity for oxygen (that is, the heat of formation of the metal oxide is large and exothermic) also have the highest sputtered-ion yields. The observed exponential variation in positive-ion emission suggests that the ion yield of a sample is a function of the availability of electrons at the surface.

Electron availability at the surface can be understood, to a first approximation, in terms of the thermionic electron emission of the bombarded surface. In this simple model, illustrated in Fig. 4 (13), the probability that an electron will have sufficient energy to be above the surface barrier, ϕ_n , and available for neutralization of the escaping ion is determined by the Fermi distribution of electrons in the material. The probability for neutralization is given by

$$P \propto \exp(-\phi_n/kT)$$

where ϕ_n is the energy barrier, k is Boltzmann's constant, and T is the absolute temperature of electrons at the surface. At a given temperature corresponding to a given set of bombardment conditions, the number of electrons with sufficient energy to surmount the energy barrier decreases exponentially as the height of the surface barrier increases. The probability of ion neutralization, therefore, decreases as the electronic work function, ϕ_{sto} , of the surface increases. This increase occurs when strongly bonded chemical compounds are formed on the surface because of the chemisorption of electronegative gases. The experimental results indicate that similar types of compounds can be manufactured by bombarding with reactive gases. It should be noted that the ionization potential of the escaping ion, I_p , has no direct influence on the probability of neutralization.

The model proposed for interpreting the emission of sputtered positive ions suggests a method of producing enhanced yields of sputtered negative

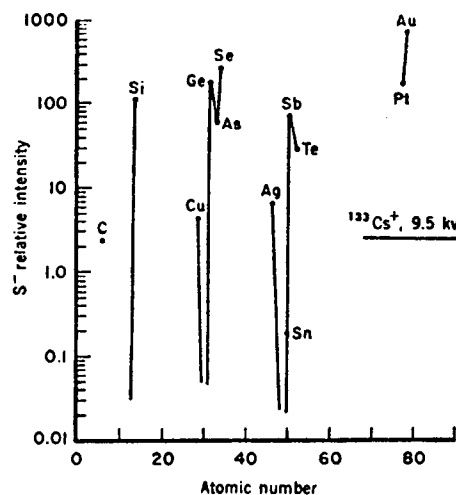


Fig. 5. Relative intensities of sputtered negative ions for elements bombarded with Cs. The intensities have been corrected for natural isotopic abundances.

ions. Positive-ion emission is decreased by electron transfer from the sample surface to the escaping ion. This transfer becomes increasingly prevalent as the energy barrier of the surface decreases. The neutral atoms of many of the most affected elements have large electron affinities. It is possible to take advantage of this fact and produce negative ions by optimizing the conditions for electron transfer from the surface to the sputtered atom. This can be done by reducing the work function of the surface by bombarding it with an electropositive element such as cesium. The relative yields of negative sputtered ions for many elements bombarded with cesium are plotted against atomic number in Fig. 5 (13). The yields have been corrected for isotopic

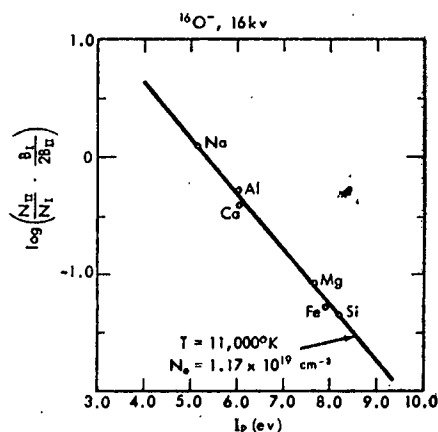


Fig. 6. Saha-Eggert ionization plot of the observed intensities of sputtered ions from a well-characterized mineral standard, clinopyroxene (AC-362-C1). The term ΔE_i , which is a constant for all the elements, is not indicated on the abscissa as it produces only a constant scale change in I_p . In this case ΔE_i is 0.66 electron volt.

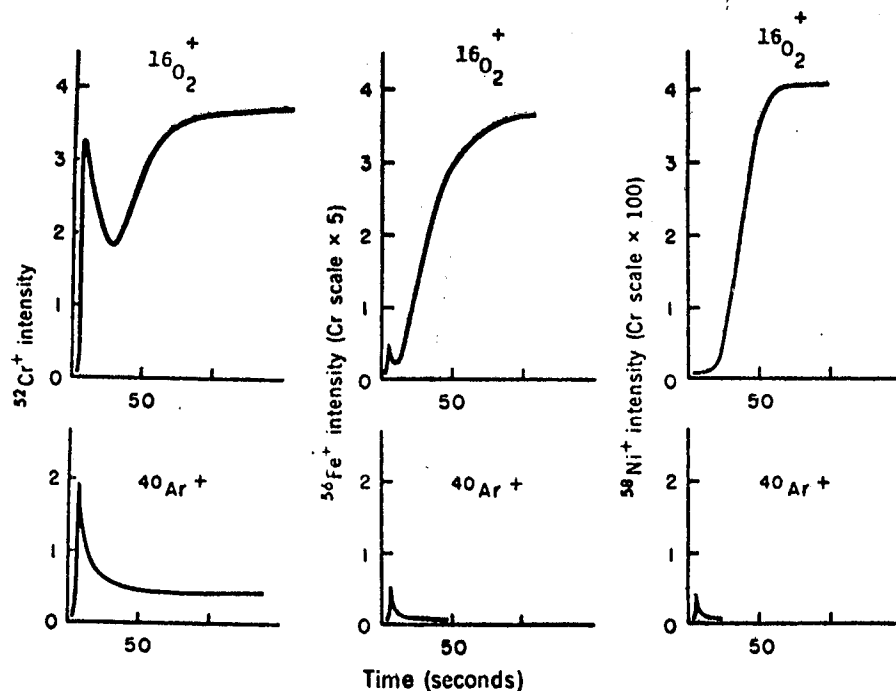


Fig. 7. The variation with time of the intensities of sputtered positive ions of Cr, Fe, and Ni from 304 stainless steel bombarded with oxygen and argon. The sample current is the primary bombarding current measured at the sample. In these experiments, the accelerating potential was 11 kv, the sample current approximately 5×10^{-6} amp, and the probe size approximately $20 \mu\text{m}^2$.

abundance and are plotted on the same intensity scale as the yields for positive ions in Fig. 3. It should be noted that the elements shown in Fig. 5 are generally those of low positive-ion yield and high electron affinity. The yield from gold, for example, has increased by six orders of magnitude from its positive-ion yield under oxygen bombardment.

It has been established that sputtered-ion emission from solids can be enhanced and controlled by the proper chemical selection of the primary bombarding ion beam. The model indicates that the attachment of thermionic electrons does not alter the relative ion yields of the elements of a given sample because the common surface barrier of the sample affects all the constituent elements equally. It has also been established that the number of sputtered atoms of a given element is related only to its atomic concentration in the sample (13). It appears, therefore, that the only factors that alter the relationship between the relative sputtered-ion yields of the elements and their atomic concentrations in a given sample are those that are related to the excitation and ionization of the sample atoms in the atomic collisions caused by the ion bombardment. In this respect our experiments have indicated that an equilibrium partition-

ing of excitation energy exists between the atoms in the bombarded region (14). Therefore, the energy states of all the particles within the excited volume can be described thermodynamically (15) and the ion-to-atom ratio of each element calculated with the Saha-Eggert ionization equation (16).

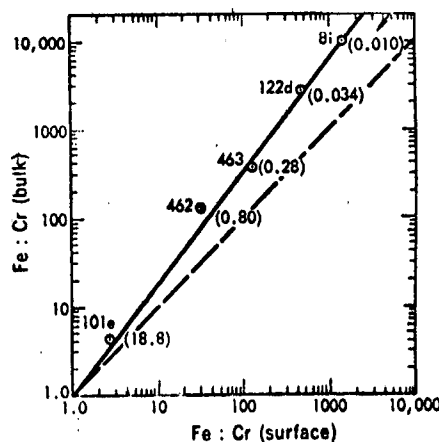


Fig. 8. The measured Fe/Cr ratio of the surface of some Fe alloys as a function of the Fe:Cr ratio of the bulk material, as given by the National Bureau of Standards. The bulk Cr concentration of each sample is given in atomic percent in parentheses. The numbers next to the sample points designate National Bureau of Standards standard reference materials. (81) Bessemer steel, (122d) cast iron, (463) low alloy steel, (462) low alloy steel, and (101e) 304 stainless steel.

The Saha-Eggert ionization equation gives the ratio of the number of atoms in one charge state to the number of atoms of the same element in the next lower charge state in terms of Boltzmann distribution functions. A practical logarithmic form of the equation is

$$\log \frac{N_{i+1}}{N_i} = 15.38 + \log \frac{2B_{i+1}}{B_i} + 1.5 \log T - \frac{5040(I_i - \Delta E_i)}{T} - \log N_e$$

where N_{i+1} and N_i are the number of atoms in the two charge states, B_{i+1} and B_i are the partition functions of these charge states; I_i is the ionization potential of the lower charge state; ΔE_i is the depression of the ionization potential due to Coulomb interaction of the charged particles; T is the absolute temperature of the electron gas and atom assemblage in degrees Kelvin; and N_e is the number of electrons per cubic centimeter. It can be seen that the partition functions and ionization potentials are known, the ratio of the number of singly charged ions to the number of neutral atoms of an element is determined by the effective electron temperature and electron density of the assemblage.

Figure 6 (15) illustrates the application of this approach to the data for sputtered positive ions from a well characterized mineral standard. In the case the temperature and electron density of the sputtering assemblage was obtained by solving the Saha-Eggert ionization equation for the best fit of the observed intensities of singly charged ions to the known concentration of the elements in the sample. The fit of the data indicates that the singly charged ions are in thermal equilibrium with the neutral atoms and the equation can be used to predict their ratio. This is the basis for a quantitative method since the singly charged ions are directly observed in the mass spectrum. Therefore, from the predicted ratio of singly charged to neutral atoms, the total number of atoms of an element present in the sputtering assemblage can be calculated. If all elements observed in the mass spectrum are treated in this way, atomic composition of the sample is derived.

The sputtering assemblage is basically a dense plasma of coexisting positive and negative atomic and molecular ions, electrons, and neutral atoms and molecules. Under the present experimental ion-bombardment conditions

most of the particles are neutral atoms and singly charged positive ions. There are, however, for elements of high electron affinity and high oxygen affinity, significant numbers of negative ions and oxide molecules in equilibrium with the positive ions and neutral atoms. The equilibrium concentrations of these species can be calculated with the appropriate Saha equations (16) and the intensities of the positive ions corrected for their abundance. All the observed intensities of singly charged positive ions in the mass spectrum are corrected in this way to give the total atomic composition of the sputtering plasma, which is directly related to that of the solid. A computer program entitled Carisma (corrections to Applied Research Laboratories ion-sputtering mass analyzers) has been developed to perform these computations.

The accuracy of the correction procedure is illustrated in Table 1, where analyses for well-characterized, homogeneous mineral standards are given. In each case Carisma was used to find the values of T and N_p , consistent with the observed ion intensities, that gave an absolute atomic composition that best matched the known concentrations of two of the elements in the standard. The observed intensities of all the other elements in the sample were then corrected at the same T and N_p to give the tabulated results. With this method and two internal standards, the concentrations of the major elements are generally within 10 percent of the values determined by wet chemistry. Carisma also contains provisions for using one or two internal standards, but the accuracies of these procedures have not yet been fully evaluated.

Table 2 is a comparison of analyses of major and trace elements in two well-characterized mineral specimens. The comparative analyses for the major and minor elements were performed with an electron microprobe (EMX) using well-analyzed mineral standards for calibration (17), and the analyses for the trace elements were performed with a spark-source mass spectrometer for solids (AEI Scientific Apparatus, Ltd., model MS-7), with the Geological Survey geochemical standards G1 and W1 for calibration (18). The ion microprobe analyses were made with the method of two internal standards. The applicability of the method to the analysis of metals is illustrated in

Table 3, where the ion microprobe analyses of National Bureau of Standards steel samples are compared to optical-emission and wet-chemical analyses. The ion microprobe results are based on the method of two internal standards. The lower accuracies here may result from local inhomogeneities in depth as well as inhomogeneities on the surface of the sample.

Applications

Ion-sputtering mass spectrometry has been applied to several problems in the analysis of solids, with various types of instruments. These include studies of oxygen concentrations and concentration gradients and of processes of oxidation in a variety of metals (19), a study of some catalytic and corrosion

Table 1. Comparison of ion microprobe and wet-chemical analyses of mineral standards. The numbers AC-362, AC-362-Cl, and AC-362-Or are intralaboratory sample reference numbers.

Element	Plagioclase AC-362		Clinopyroxene AC-362-Cl		Orthopyroxene AC-362-Or	
	Ion	Wet	Ion	Wet	Ion	Wet
Na	3.15	3.14	0.22	0.27	0.054	0.076
Mg			6.39	6.69	9.14	9.03
Al	11.90	11.97	1.07	0.97	0.64	0.66
Si	18.77	18.77	19.56	19.30	19.60	19.60
K	0.16	0.08	0.01	0.02		
Ca	4.30	4.29	8.56	8.54	0.31	0.35
Fe	0.17	0.11	3.98	4.09	9.89	10.0

Table 2. Comparative mineral analyses of Camperdown peridotite. Electron microprobe (EMX) and mass spectrometer (MS-7) analyses were made by the Department of Mineral Sciences of the Smithsonian Institution, Washington, D.C. The analyses labeled IMMA were made with the ion microprobe mass analyzer. The abbreviation n.d. means not determined.

Element	Orthopyroxene			Olivine		
	IMMA	EMX	MS-7	IMMA	EMX	MS-7
<i>Major elements (atomic percent)</i>						
Si	19.22	19.22		14.21	14.21	
Al	1.42	1.22		n.d.	n.d.	
Mg	17.37	17.58		26.64	25.80	
Fe	1.29	1.72		2.70	2.89	
Ca	0.40	0.31		0.018	0.025	
<i>Trace elements (atomic parts per million)</i>						
Ti	150		160	77		64
V	45		24	23		4
Cr	1120		1180	195		160
Mn	350		320	340		320
Co	16		19	32		78
Ni	n.d.		240	520		750

Table 3. Comparison of ion microprobe (IMMA) and National Bureau of Standards (NBS) analyses of steels. Concentrations are in atomic percent.

Element	NBS 462 low alloy steel		NBS 101c stainless steel	
	IMMA	NBS	IMMA	NBS
B	0.013	0.0025		
C	1.83	1.83	0.15	0.25
Si	0.60	0.55	0.90	0.84
P	0.012	0.08	0.006	0.044
Ti	0.034	<0.042		
V	0.031	0.063	0.058	0.047
Cr	0.95	0.78	19.17	19.04
Mn	1.44	0.94	2.08	1.77
Fe	93.73	94.43	68.73	68.17
Co	0.10	0.10	0.17	0.17
Ni	0.63	0.65	7.28	8.89
Cu	0.20	0.17	0.67	0.31
Zr	0.032	0.038		
Nb	0.042	0.057	0.0088	0.0077
Sn	0.017	0.031	0.068	0.009
Pb	0.0010	0.0016		

Table 4. Abundances of trace elements in Apollo 11 fines material and the crust glass of a breccia. All concentrations are given in atomic parts per million. The abbreviations are M (major element) and n.a. (not analyzed).

Element	Olivine 10085,17-28	Clinopyroxene -26	Plagioclase -25	Ilmenite -28	Crust glass -17
Li	<3	12	17	9	31
B	<12	11	12	<1	26
Na	24	312	3000	18	3800
Mg	M	M	988	18000	M
Al	390	15200	M	1600	M
Si	M	M	M	852	M
P	43	33	32	1.5	130
K	9	14	108	3.5	666
Ca	1230	M	M	<475	M
Ti	475	5200	498	M	M
V	19	69	<0.5	120	45
Cr	680	1340	<2	3300	858
Mn	980	505	42	1600	795
Fe	M	M	1450	M	M
Ni	<45	<1	n.a.	<2	15
Co	17	7	n.a.	11	16
Sr	1.2	4	68	<4	70
Y	0.9	8	<1	5	21
Zr	<1.0	4	<1	36	61
Ba	<0.9	<0.4	<1	n.a.	29
Pb	<1.0	<0.7	<0.5	<1.0	<0.8

processes on metals (20), and a study of the chemistry of trace elements in geologic specimens (21).

An example of the application of the ion microprobe mass analyzer to surface analysis is the analysis of a polished section of 304 stainless steel (12). The intensities of positive sputtered ions of chromium, iron, and nickel were studied as a function of bombardment time and are shown in Fig. 7. As sputtering continues, deeper layers of the sample are exposed and analyzed. The intensity of Cr ions de-

cays at first but then, when oxygen is the bombarding ion, recovers to a high, stable level. According to the proposed model, the original intensity peak indicates that there is a layer of Cr oxide on the surface of stainless steel. This oxide layer is at first destroyed by the eroding action of the sputtering process but is soon reconstituted when oxygen is used in the bombarding beam. As noted earlier, the final level reached in the case of Ar bombardment is a dynamic equilibrium between the cleaning action of the bombarding beam and

the recontamination of the surface by the ambient gases in the instrument. A large primary peak is observed in the case of Cr, a much smaller one in the case of Fe, and practically none in the case of Ni. Each curve represents bombardment of a fresh surface spot. This is interpreted to indicate that few Fe atoms and practically no Ni atoms participate in the oxidized phase on the surface of 304 stainless steel.

The Fe/Cr ratio in the surface layers of several steel samples was studied by measuring the intensities of the ion peaks corresponding to the original surface layers in a time study such as those presented in Fig. 7. The measured Fe/Cr ion ratios were quantitatively corrected to yield atom ratios which are plotted as a function of the Fe/Cr ratio of the bulk material, as given by the National Bureau of Standards, in Fig. 8. A regular dependence of the surface chemistry on the bulk composition is noted, but with the surface layers enriched in Cr over the bulk composition. (As shown in Table 3, the ion microprobe analyses of Fe and Cr in the bulk material of two of these steels, after the surface layer had been sputtered through, compared favorably with those reported by the National Bureau of Standards.) The dashed line indicates a one-to-one correspondence between the Fe/Cr ratios of the bulk and surface layers. The measured ratio deviates from this line in a regular way. As the amount of Cr in the bulk sample decreases, the difference between the surface and bulk Fe/Cr ratio increases, which indicates that a larger relative proportion of the Cr in the bulk of the sample is entering into the surface layers. This apparently indicates that the surface prefers some minimum number of Cr atoms and that these can readily be obtained from the existing reservoir in the bulk of the sample.

The techniques discussed above have been applied to the study of the distribution of trace elements in lunar rocks (21). Phenocrysts of the major mineral phases were analyzed in situ in polished thin sections, and quantitative measurements were made of the contents of the major and trace elements. Five thin sections of fragments of four types of Apollo 11 rocks were investigated. The samples were (i) type A basalt (10085,17-25), (ii) type B basalts (10085,17-26 and 17-28), (iii) a type C breccia with

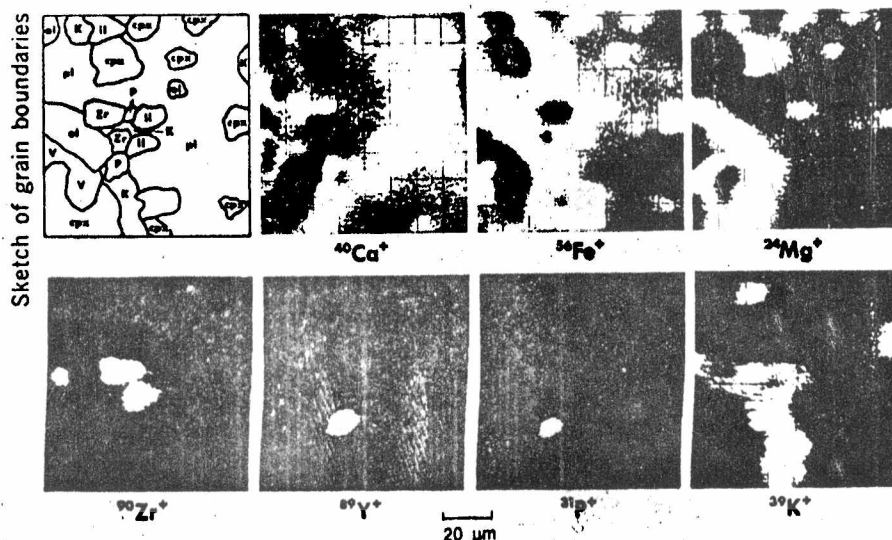


Fig. 9. Scanning-ion micrographs showing the distribution of Ca, Fe, Mg, Zr, Y, P, and K in a type B lunar basalt (10085,17-26). A sketch of the mineral grain boundaries gives the relative positions of the minerals in the scanned area. The abbreviations are ol (olivine), cpx (clinopyroxene), pl (plagioclase), il (ilmenite), Zr (zirconium oxide), p (apatite), K (potassium-rich glass), and V (void).

glasses and a partial rim of crust glass (10085,17-17), and (iv) an anorthosite-like fragment (10085,7-6).

Table 4 contains typical ion microprobe values of the concentrations of trace elements in all the major mineral phases of Apollo 11 fines material and in the crust glass of a breccia sample that generally represents the bulk chemistry of the rock fines. Several of the elements are more concentrated in the glass than in any of the major mineral phases by about a factor of 2 or more. These are zirconium, yttrium, potassium, phosphorus, barium, lithium, and boron. The data indicate that these elements must be concentrated to a large degree in minor mineral phases not included in this table. A search of the intergranular areas for localized concentrations of these elements was made, and several minor mineral phases were found. The minor phases were tentatively identified as a hafnium-bearing zirconium oxide; a calcium, iron, yttrium, fluorine, rare earth phosphate; a titanium, zirconium, yttrium, rare earth silicate; and a potassium-rich glass phase.

Several of these phases are seen in scanning-ion micrographs in Fig. 9, which show the distribution of seven elements in a type B lunar basalt (10085,17-26). The distribution of Zr identifies the Zr oxide; that of Y and P the Ca, Fe, Y, F, rare earth phosphate; and that of K, the glass phase. The phases coexist in a matrix of clinopyroxene, plagioclase, ilmenite, and olivine, as shown in a sketch of the mineral grain boundaries determined from the distribution of the major elements. The Ca, rare earth phosphate is probably a fluorapatite, and the Zr oxide is probably a grain of baddeleyite. The potassium-rich glass and the Ti, Zr, Y, rare earth silicate are similar to associations described by Ramdohr and El Goressey (22).

Figure 10 shows a partial mass spectrum of the heavy isotopes in the Ti, Zr, Y, rare earth phase. This phase was found as an inclusion in a plagioclase phenocryst in the anorthosite-like fragment 10085,7-6. The mass spectrum shows Ba; abundant rare earths represented by both atomic and molecular monoxide ions; thorium and uranium, represented by molecular monoxide ions; and radiogenic lead. The baddeleyite and apatite phases shown in the micrographs of Fig. 9 also contain abundant Th, U, and radiogenic Pb.

Table 5. Thorium- and uranium-bearing minor mineral phases in Apollo 11 lunar material. The concentration ranges for total Pb are given in atomic parts per million.

Sample number	Phase	Th/U	Total Pb	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
10085,17-26	Zr oxide	0.49	100-1000	0.13	0.45
10085,7-6	Ti, Zr, Y, rare earth silicate	2.16	1000-2000	0.59	0.40
10085,17-25,26	Fe, Y, rare earth apatite	5.54	10-50	1.78	0.73

Apparently major portions of the Th, U, and Pb reported on a bulk chemical basis for the Apollo 11 fines material are heterogeneously distributed throughout the rocks in minor mineral phases such as those described here. Finding that Th, U, and their Pb daughter isotopes are concentrated in accessory phases raises the possibility that the separate phases might be radiometrically dated. Such information could be very helpful in understanding the apparently greater age, as determined by $^{207}\text{Pb} : ^{206}\text{Pb}$ dating (23, 24), of the breccia and fines than of the coexisting, coarser crystalline rock.

Table 5 (25) is a summary of the Th/U ratios and the Pb isotopic data for the three minor mineral phases found here. The potassium-rich phase contained no apparent Th, U, or Pb. The isotopic data are preliminary in nature and have an accuracy of only about 10 percent. The Th/U ratio in the three phases varies by more than a factor

of 10, and, as expected, the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio increases linearly with the Th/U ratio. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the baddeleyite from the type B basalt (10085,17-26) and in the Ti, Zr, Y, rare earth silicate from the anorthosite-like fragment are about the same, within experimental error, and give an apparent age of about 4.1×10^9 years. These ratios correlate with the ratios given by Silver (23) for the crystalline rocks. The ratios given in Table 5 for these phases have been corrected for molecular ion interferences, which in both cases are very slight. The apatite phase has a very large $^{207}\text{Pb}/^{206}\text{Pb}$ ratio, and a large correction for molecular ion interferences was applied in this case. Lead-204 could not be detected in any of the phases, and the common Pb correction was not applied. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios reported here, even with relatively large errors, imply that there are individual mineral phases within the fines material that

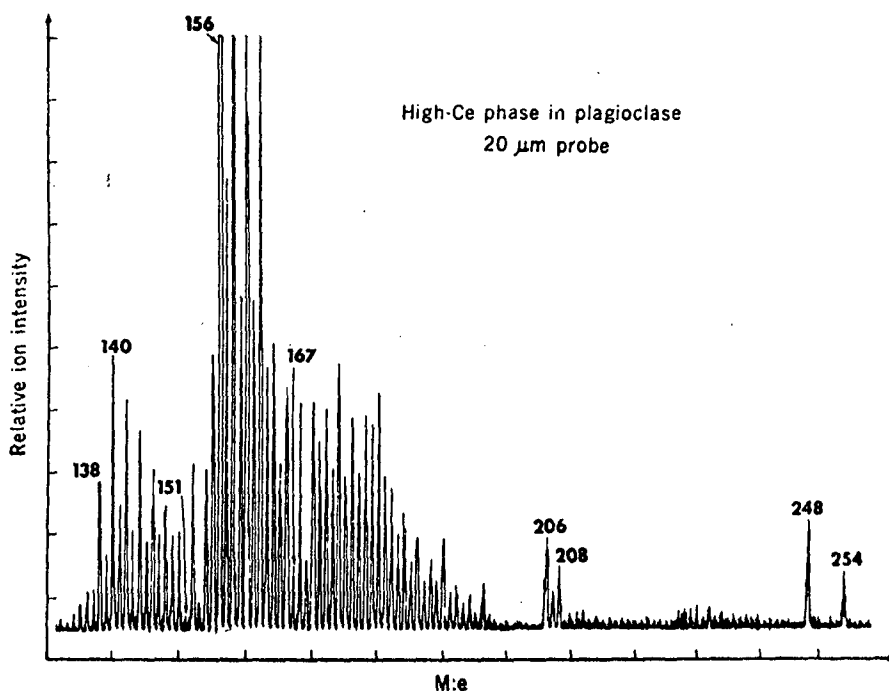


Fig. 10. Partial mass spectrum of the heavy isotopes in the Ti, Zr, Y, and rare earth phase included in a plagioclase in sample (10085, 7-6). The abbreviations are M/e (ratio of mass to ion charge), 138 (Ba), 140 (Ce), 151 (Eu), 156 (CeO), 167 (EuO), 206 and 208 (Pb), 248 (ThO), and 254 (UO).

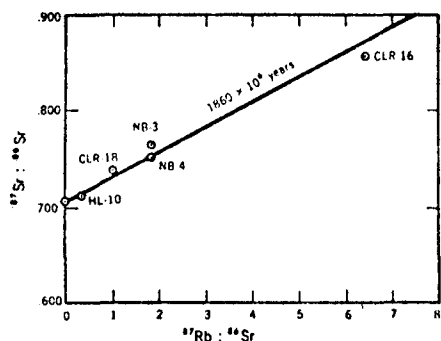


Fig. 11. The ratios $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ determined by ion microprobe mass analysis for five separate feldspar grains. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the isochron of 1860×10^6 years were determined by Tilton and Sinha (26) for bulk specimens, with isotope dilution. The numbers next to the sample points are intralaboratory sample reference numbers.

are of the same approximate age as the coarser crystalline rocks.

The ion microprobe has also been applied, in a preliminary fashion, to the rubidium-strontium dating technique. Potassium feldspar crystals selected from five mineral separates prepared by Tilton and Sinha (26) were analyzed with the ion microprobe. Tilton and Sinha determined, by mass spectrometry involving double-filament ionization and isotope dilution, that the ages of all the samples are nearly the same and that they fit an isochron of 1860×10^6 years. The position of this isochron is shown in Fig. 11. Each of the points in the figure represents an ion microprobe analysis of a single 50- μm area on an individual crystal selected from one of the five mineral separates. The relative amounts of ^{87}Sr and ^{87}Rb were determined by measuring the ion intensity of the stable ^{86}Rb isotope and using the known isotopic abundances to predict the intensity of ^{87}Rb . The latter was then subtracted from the intensity observed at mass 87 to yield the ion intensity of ^{87}Sr . The intensities of ^{87}Rb and ^{86}Sr were quan-

titatively corrected according to the methods proposed in the previous section. The correlation of the ion microprobe results with the independently determined isochron indicates that it may be possible to obtain useful results, for samples on a micrometer scale, from this dating technique.

Conclusion

The quantitative analyses and other applications described in this article indicate a useful future for the ion-microprobe mass analyzer in many areas of the science of solid materials. It should be possible to analyze all the elements quantitatively, but detection sensitivities will vary depending on the matrix, the element, and the polarity of the sputtered ion being studied. Most elements will have optimum yields in the spectrum of positive sputtered ions, and will be detected in concentrations of parts per million in micrometer-sized sampling areas. Electronegative elements will be detected with similar sensitivities in the spectrum of negative sputtered ions, but inert gases, which are ionized with difficulty and have small electron affinities, will be detected with considerably poorer sensitivities. In general, it will be possible to measure isotope ratios without chemical separation of the constituent elements of the sample. The precision of an ion microprobe isotope ratio measurement depends basically on the counting rates involved, and its accuracy can approach its precision if auxiliary standards are used. The isotope ratios of different elements can be compared readily because of the small mass-discrimination effects of the system. Surface layers can be quantitatively analyzed in depth with a resolution of tens of angstroms; hence, it should be possible to study the migration of atoms.

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Thermodynamic Approach to the Quantitative Interpretation of Sputtered Ion Mass Spectra

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An analytical method has been developed for quantitative sputtered ion mass analysis with the ion microprobe mass analyzer. The method involves the use of reactive gases in the primary bombarding ion beam to enhance and control the emission of sputtered ions from the sample and the use of a theoretical correction procedure to convert the sputtered ion intensities to quantitative elemental analyses. The correction procedure is based on a thermal equilibrium model of the sputtering ion region that permits the relative numbers of positive and negative ions, of neutral atoms, and of oxide molecules to be calculated using simple dissociation reactions and the well established Saha relationships. The theoretical correction procedure has been tested as a practical method with favorable results on the analyses of over one hundred standard reference materials ranging from insulators to metals for over thirty elements spanning the major to trace element concentration range.

The ion microprobe mass analyzer is one of a new class of instruments that have been developed to provide an *in situ* mass analysis of a microvolume near the surface of a solid sample. The instruments which have been described in general by Robinson (1) and Skogerboe (2) accomplish the analysis by bombarding the surface with a high energy beam of ions that causes some of the atoms at the surface of the sample to be sputtered away. A fraction of the sputtered particles is electrically charged and these sputtered ions are collected and analyzed according to their mass to charge ratio in a mass spectrometer. An understanding of the relationship between the intensities of the sputtered ions and the elemental composition of the bombarded sample is required for the quantitative analysis of the sample using this analytical technique. These relationships have been discussed by many authors (3-13) with varying degrees of success in practical application. This paper describes and thoroughly tests a theoretical correction procedure developed to produce quantitative elemental analyses from sputtered ion intensities. The method discussed was developed over the past several years using the ion microprobe mass analyzer basically designed by Liebl (14). This instrument, the analytic methods, and their practical application have recently been discussed by Andersen and Hinthorne (15).

ANALYTICAL METHOD

The analytical method utilized with this instrument is based on the observation that the yield of sputtered ions from the sample is greatly affected by the surface chemistry of the sample. On the basis of experimental observations, it is postulated that the production of sputtered sample ions is a function of the electronic properties of the surface which are related to the surface chemistry. We have demonstrated that it is possible to control the electronic properties of a surface and enhance the yield of either positive or negative sputtered sample ions through control of the surface chemistry by the proper chemical selection of the primary bombarding ion beam (16). The emission of positive ions is enhanced and stabilized by the increased electronic work function created by bombardment with an electronegative gas such as oxygen, while the emission of negative ions is enhanced and stabilized by the decreased work function created by bombardment with an electropositive gas such as cesium (17). These experimental results can be understood in terms of a simple thermionic emission model (17). This model states that the electronic work function of the surface affects only the absolute ion yield of the sample and does not alter the relative ion yields of the different elements from the sample.

The quantitative model used to convert the sputtered ion intensities to atomic concentrations, therefore, can be simplified to one that is concerned only with the relative numbers of ions of the different elements generated in the sample by the ion bombardment. Quantitative interpretation of the sputtered ion yields from a small spot on a sample, therefore, reduces to calculating, for each element in the sample, the initial number of ions generated. This calculation and the testing of the correction method based on this assumption are the main subjects of this paper.

In this respect, our experiments (18) indicate that the sputtering region (*i.e.*, the collection of excited atoms and ions that are being sputtered from the surface) resembles a dense plasma in local thermal equilibrium. This indication is given by the fit of the experimental data to validity criteria established for local thermal equilibrium as will be demonstrated shortly. A correction procedure based on this assumption that produces generally accurate and useful results, can be justified on practical grounds at least.

With this in mind, we may start by noting that the total number of atoms of some element, M , is given by

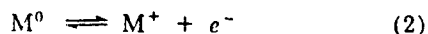
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the sum of all the atoms of M that are present in the sputtering region as positive ions, as negative ions, as neutral atoms, or are present as part of a molecule, since molecules are also observed in the mass spectrum. For the sake of practicality, we will consider only monoxide and dioxide molecules at present. A justification of this position will be given later in this paper. The total number of atoms of element M, to a first approximation, is given by:

$$n_M = n_{M^+} + n_{M^-} + n_{M^0} + n_{MO} + n_{MO_2} \quad (1)$$

where n_M , n_{MO} , and n_{MO_2} refer to the total number of particles in all charge states of the atom and monoxide and dioxide molecules, respectively; and n_{M^+} , n_{M^-} , and n_{M^0} refer to the number of positive and negative ions and of neutral atoms, respectively. If the element in question is oxygen, then the fourth term on the right hand side of Equation 1 is multiplied by two and the last term by three. Each of the parts of Equation 1 will now be examined in turn.

Positive Ions. Under the assumption of thermal equilibrium, the ionization process can be written as a dissociation reaction:



where the dissociation constant of this reaction is given by:

$$K_{n^+} = \frac{n_{M^+} n_{e^-}}{n_{M^0}} \quad (3)$$

n_{M^+} , n_{M^0} , and n_{e^-} represent the concentrations per unit volume of the singly charged positive ions and atoms of element M and of the electrons, respectively. Under equilibrium conditions, the energy states of all the particles within the excited volume can be described thermodynamically and the ion to atom ratio of each element calculated using the Saha-Eggert ionization equation (19-21)

$$K_{n^+} = \left(\frac{2\pi m_{M^+} m_{e^-}}{h^2} kT \right)^{3/2} \frac{B_{M^+} B_{e^-}}{B_{M^0}} e^{-E/kT} \quad (4)$$

where h is Planck's constant, k is Boltzman's constant, T is the absolute temperature in °K, m is the mass, B the internal partition function, and E the dissociation energy of the species in question, in this case it is the first ionization potential of the atom. Equations 3 and 4 can be combined to give the ratio of the numbers of positive ions to neutral atoms in terms of the temperature and the concentration of free electrons. A practical logarithmic form of this combined equation reads:

$$\log(n_{M^+}/n_{M^0}) = 15.38 + \log 2(B_{M^+}/B_{M^0}) + 1.5 \log T - \frac{5040(I_p - \Delta E)}{T} - \log n_{e^-} \quad (5)$$

where n_{M^+} and n_{M^0} are the number of atoms of element M in two adjacent charge states, B_{M^+} and B_{M^0} are the internal partition functions of these charge states, 2 is the partition function of a free electron, I_p is the ionization potential of the lower charge state, ΔE is the ionization potential depression due to coulomb interactions of the charged particles, and n_{e^-} is the number of electrons per cm³. The ratio of the mass of the ion to atom is essentially one. It can be seen that if the partition functions and ionization potentials are known, the ratio of the number of singly charged ions to neutral atoms of an element is determined by the electron temperature and the electron density of the assemblage.

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ΔE is calculated according to the Debye-Hückel model (22):

$$\Delta E \cong \gamma(r + 1)e_0^2/\rho_D \quad (6)$$

where $\gamma = 1.2 \pm 20\%$, r refers to the ionization state of the test particle with the lower charge state (in this case it is the neutral atom and $r = 0$). e_0 is the electronic charge, and ρ_D is the Debye radius.

$$\rho_D = \left(\frac{kT}{4\pi e_0^2 (1 + Z)n_{e^-}} \right)^{1/2} \quad (7)$$

where Z represents the mean electric charge number of the plasma and in this work is set equal to one. We use a value of $\gamma = 0.68$, however, in order to produce a value of ΔE that is equal to the average value calculated by Sparks and Fischel (23) for a series of elements in the temperature and electron density regime that pertains to this work.

Equation 5 was developed to describe thermal ionization and is taken as one of the validity criteria for the establishment of local thermal equilibrium (24). An example of the application of this equation taken from the optical emission literature (25) is given in Figure 1 where experimentally observed ratios of the numbers of ions to atoms, n_i/n_a , modified by the appropriate partition functions, B_a/B_i , of eleven elements in the Cu arc are plotted vs. their ionization potential. The line was calculated from the Saha-Eggert equation for the conditions of temperature and electron density indicated in the figure.

Figure 2 illustrates the application of this approach to sputtered positive ion data obtained from a well-characterized mineral standard. In this case, the effective temperature and electron density of the sputtering region were obtained by solving the Saha-Eggert ionization equations for the best fit of the observed singly charged ion intensities to the known concentrations of the elements in the sample. The symbols II and I refer to the singly charged ion and neutral atom, respectively. ΔE in this case is 0.66 eV. Equation 5 is basically a linear equation in two unknowns, T and n_{e^-} . Two observed singly charged to neutral atom ratios, therefore, permit a solution for the temperature and electron density of the sputtering region. In practice, the neutral atom intensities are not observed but the composition of the sample is known and the ratio of the corrected ion intensities, thereby, established. This will be discussed in more detail later in this paper. The fit of the data to the Saha-Eggert ionization equation indicates that the singly charged ions in the sputtering assemblage are in thermal equilibrium with the neutral atoms and that the equation can be used to predict this ratio.

The apparently better fit of the sputtering data relative to the optical emission data should not be misconstrued to imply that the sputtering region is in a more perfect state of equilibrium. The better fit of the data more likely reflects the increased accuracy of the intensity measurements in the ion microprobe mass analyzer because of its electrical detection capabilities. The optical emission data are taken from photographic plates and must be converted to absolute numbers of ions and atoms through the transition probabilities of the appropriate emission lines.

Negative Ions. As stated above, the sputtering region

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(23) W. M. Sparks and D. Fischel, NASA SP-3066, Scientific & Technical Information Office, NASA, Washington D.C., 1971.

(24) P. W. J. M. Boumans, "Theory of Spectrochemical Excitation," Plenum Press, New York, N.Y., 1966, p. 80.

(25) C. H. Corliss, *J. Res. Nat. Bur. Std., Sect. A*, **66**, 169 (1962).

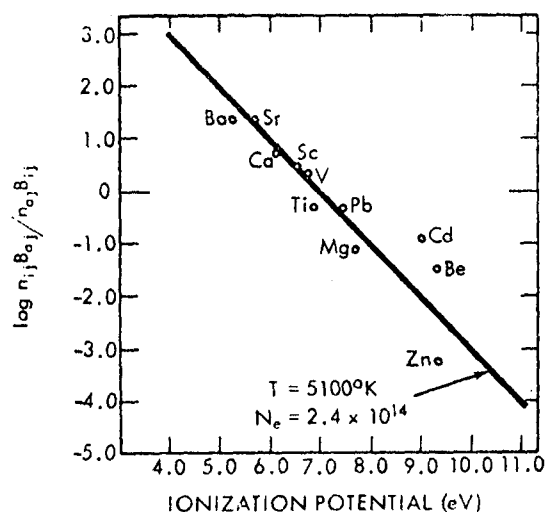
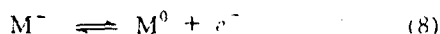


Figure 1. Saha-Eggert ionization equation applied to optical emission data from the Cu arc, after Corliss (25)

appears to be a dense plasma of co-existing positive and negative atomic and molecular ions, of electrons, and of neutral atoms and molecules. Under the present experimental ion bombardment conditions (e.g., primary ion beam accelerating potential on the order of 10 to 20 keV, bombardment current density of several milliamperes per square centimeter, analyzed sample regions on the order of 100 μm in diameter or less, and an oil free ion pumped vacuum system with a liquid nitrogen cooled cold plate above the surface of the sample), most of the particles are neutral atoms and singly charged positive ions. Some of the elements of high electron affinity, however, have significant numbers of negatively charged ions. The electron attachment process under equilibrium conditions can be written as:



where the dissociation constant of this reaction is given by:

$$K_n = \frac{n_M n_e}{n_{M^-}} \quad (9)$$

n_M , n_{M^-} and n_e represent the concentration per unit volume of the negative ions and neutral atoms of element M and of the electrons, respectively. The equilibrium number of negative ions relative to the number of neutral atoms of element M can be predicted by a Saha equation similar to Equation 4:

$$K_n = \left(\frac{2\pi m_M m_e}{h^2} kT \right)^{3/2} \frac{g_{M^-} g_e}{g_M} e^{-E_{\text{aff}}/kT} \quad (10)$$

where the symbols are as before except that the term g represents the statistical weight of the ground state of the atom, negative ion, or electron, and E , in this case, is the electron affinity of the atom. A practical logarithmic form of the combination of Equations 9 and 10 reads (26):

$$\log(n_{M^-}/n_M) = -15.38 + \log(g_M/2g_{M^-}) - 1.5 \log T + \frac{5040 E_{\text{aff}}}{T} + \log n_e \quad (11)$$

where E_{aff} is the electron affinity of the neutral atom of element M. This relationship permits the equilibrium concentration of negative ions of an element to be calculated at a given temperature and electron density. Experimental confirmation that sputtered negative ion yields fit such

(26) H. R. Griem, "Plasma Spectroscopy," McGraw-Hill, New York, N.Y., 1964, p 119.

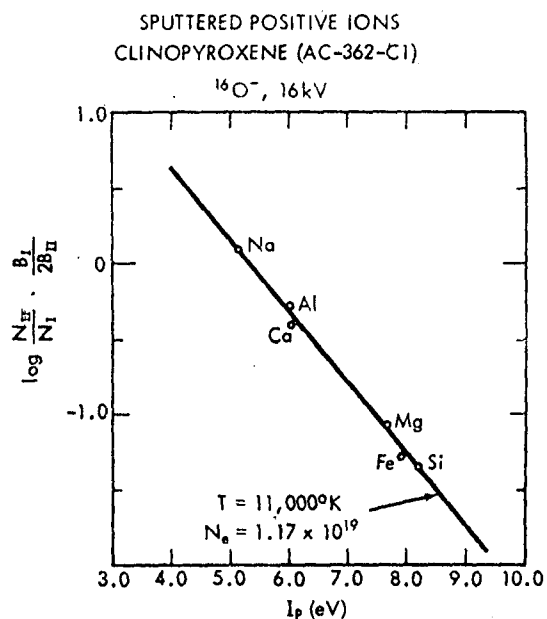


Figure 2. Saha-Eggert ionization equation applied to sputtered positive ion data from a mineral standard bombarded with $^{16}\text{O}^-$ at 16 kV

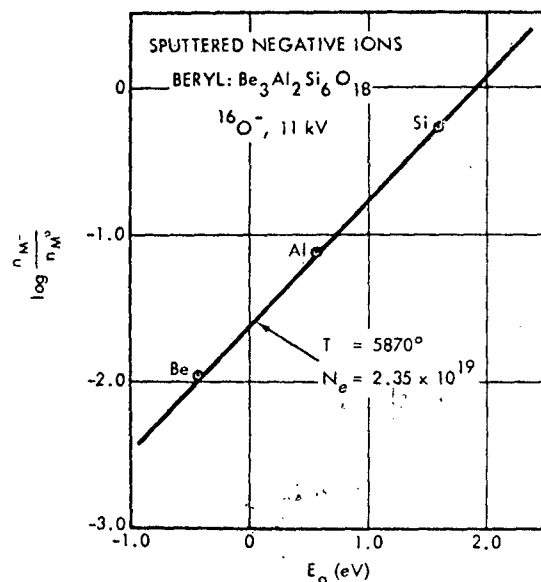


Figure 3. Saha equation applied to sputtered negative ion data from a mineral standard bombarded with $^{16}\text{O}^-$ at 11 kV

a relationship at elevated temperatures is given in Figure 3. Here the ratio of the number of negative ions to neutral atoms for three elements from a mineral standard are plotted vs. the electron affinity of the atom. The statistical weights of the ions and atoms have not been included because they are unknown. This simplification will be discussed later in this paper. The effective temperature and electron density were obtained from the experimental data using Equation 11, setting the statistical weights equal to one, and the known atomic concentrations of the elements in the sample. Note that Be which has a negative electron affinity (27-30) under standard conditions is

(27) V. I. Vedenev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Ltd., London, 1966.

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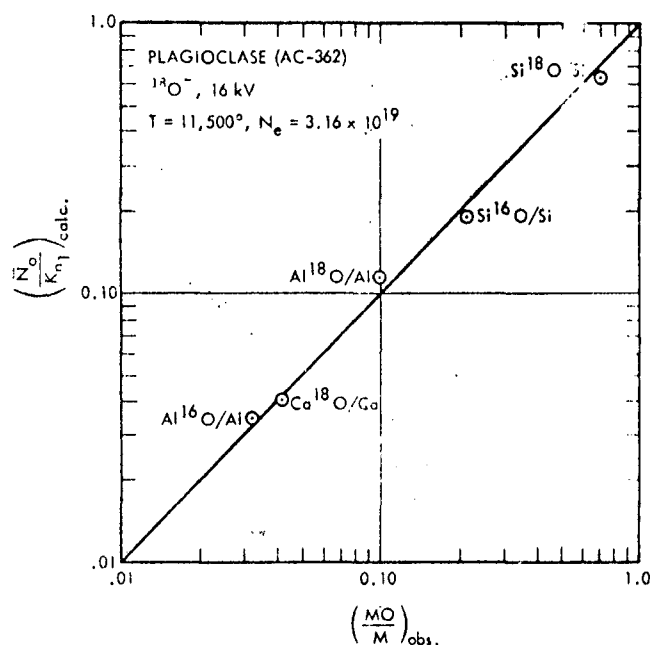


Figure 4. Observed positive atomic and monoxide ion intensities (corrected for degree of ionization) as a function of the calculated dissociation constant and the average concentration of free oxygen. Data from a mineral standard bombarded with $^{18}\text{O}^-$ at 16 kV

correctly predicted to yield negative ions, as observed, under these conditions of elevated temperature and electron density.

Molecular Ions. The molecular and atomic species under conditions of local thermal equilibrium are related through dissociation reactions such as:



where the superscript refers to neutral particles. Similar equations could be written for the dissociation of charged molecules to charged atoms.

The dissociation constant of the reaction written in Equation 12 is given by:

$$K_{n1} = \frac{n_{\text{M}^0} n_{\text{O}^0}}{n_{\text{MO}^0}} \quad (13)$$

where the n 's represent the concentrations per unit volume of the neutral atoms and molecules. Similar dissociation constants can be written for the dissociation of charged molecules and would be designated as K_{n1+} and K_{n1-} etc. The subscript 1 refers to the monoxide molecule. The dissociation constant can be calculated with the Guldberg-Waage equation (31):

$$K_{n1} = \left(\frac{2\pi}{h^2} \frac{m_{\text{M}} m_{\text{O}}}{m_{\text{MO}}} kT \right)^{1/2} \frac{B_{\text{M}^0} B_{\text{O}^0}}{B_{\text{MO}^0}} e^{-E/kT} \quad (14)$$

where the symbols are as before and E in this case is the dissociation energy of the diatomic gaseous molecule. B_{MO^0} is the partition function of the neutral molecule which includes vibrational, rotational, and electronic terms. Herzberg (32) has given an approximate solution for the partition function of one electronic state of a diatomic molecule. Since it generally suffices to consider the lowest electronic level of a diatomic molecule, this leads to the following equation for calculating the dissociation constant (33):

(31) S. M. Glasstone, "Physical Chemistry," D. Van Nostrand, New York, N.Y., 1946, p 817.

(32) G. Herzberg, "Molecular Spectra and Molecular Structure. I, Spectra of Diatomic Molecules," D. van Nostrand, Princeton, N.J., 1950, pp 123, 125, 467.

$$K_{n1} = 2.70 \times 10^{20} \frac{B_{\text{M}^0}}{g^0} \left(\frac{m_{\text{M}} m_{\text{O}}}{m_{\text{MO}}} \right)^{1/2} \times B_{\text{M}^0} B_{\text{O}^0} T^{1/2} \left(1 - 10^{-\frac{0.625 \omega^0}{T}} \right) 10^{-\frac{5.010 V_d^0}{T}} \quad (15)$$

where B_{M^0} and B_{O^0} are the internal partition functions of the neutral atoms and m_{M} , m_{O} , and m_{MO} are the masses of the atoms and molecule, respectively. B_{M^0} is the rotational constant for the electronic state referred to a vibrationless condition, ω^0 is the vibrational constant, g^0 is the statistical weight of the electronic ground state, and V_d^0 is the dissociation energy of the neutral molecule. It can be seen that Equation 15 and the definition of the dissociation constant (Equation 13) can be used to determine the neutral molecular monoxide to metal atom ratio if the concentration of neutral free oxygen is known. In practice, the concentration of neutral free oxygen is experimentally determined from the observed sputtered ion intensities of a single monoxide-metal ion pair and the calculated neutral molecule dissociation constant, K_{n1} , (the observed positive ion intensities are first corrected to yield neutral particle concentrations through Equation 5). This free neutral oxygen concentration is then used with calculated dissociation constants to predict all other neutral monoxide to metal atom ratios of interest.

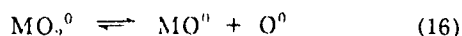
The accuracy of this approach is illustrated in Figure 4 where data obtained from a silicate mineral standard bombarded with a pure beam of $^{18}\text{O}^-$ are shown. The observed positive atomic and molecular ion intensities of both M^{16}O and M^{18}O have been corrected for their degree of ionization and plotted (abscissa Figure 4) as a function of the calculated neutral molecule dissociation constant and average concentration of neutral free ^{16}O or ^{18}O (ordinate Figure 4) in the sputtering region. $\bar{n}_{\text{O}^0}$, the average concentration of neutral free oxygen, was determined from the experimental data to be the average of the neutral free oxygen concentrations calculated according to Equations 13 and 15 using the observed MO^+/ M^+ intensity ratios, corrected for their degree of ionization (Equation 5) to yield neutral particle concentrations, of each of the molecule and atom pairs illustrated in Figure 4. The $^{40}\text{Ca}^{16}\text{O}/^{40}\text{Ca}$ pair was not used because of a ^{56}Fe interference in this sample. The fit of the data demonstrates that the molecular ions observed in the mass spectrum are the products of equilibrium reactions and that their relative concentrations can be calculated with Equations 15 and 13. The internal consistency of the data for molecules formed from metal atoms from the sample with both natural ^{16}O from the sample and with bombardment introduced ^{18}O demonstrates that (under these experimental conditions) the molecules observed in the mass spectrum are not directly related to the molecular structure of the solid but are the reaction products of a collection of implanted atoms and sample atoms interacting at an elevated temperature.

In principle, the equilibrium number of molecular species in the sputtering region of a compound sample would be difficult to predict because of the great variety of molecules possible in a multicomponent sample. When bombarding with oxygen, however, our experimental results indicate that the dominant molecular species are monoxide molecules. Oxygen behaves in this manner because, by experimental determination, it represents 50% or more of the total number of atoms in the sputtering region and because the oxide molecules have a generally stable nature and long lifetime in the sputtering region as reflected by their high dissociation energies. In many min-

(33) P. W. J. M. Boumans, "Theory of Spectrochemical Excitation," Plenum Press, New York, N.Y., 1966, p 327.

eral standards, for example, it is observed that the concentration of bombardment introduced ^{18}O exceeds that of the natural ^{16}O in the sputtering region by factors of about 2.5. This large concentration of oxygen acts as a chemical buffer by moderating the formation of molecules in the sputtering region and, thereby, simplifies the mass spectra. The concentration of simple metal oxides is increased and that of complex metal-metal molecules is reduced. Oxygen is a particularly convenient bombarding gas in this respect because the monoxides have been studied rather thoroughly and it is possible to find many of the required physical constants in the literature (34).

Dioxide molecules are also considered in terms of thermal equilibrium dissociation reactions. The dioxide dissociation constant can be written in terms of the monoxide dissociation constant through the relationships:



where the superscript again refers to neutral particles, see Equation 12.

The dissociation constant of this reaction is given by:

$$K_{n^0_2} = \frac{n_{\text{MO}^0} n_{\text{O}^0}}{n_{\text{MO}_2^0}} = \frac{n_{\text{M}} (n_{\text{O}})^2}{K_{n^0_1} n_{\text{MO}^0}} \quad (17)$$

where $K_{n^0_1}$ is the dissociation constant of the monoxide reaction and the n 's represent the concentrations per unit volume of the neutral atoms and molecules. The subscript 2 refers to the dioxide molecule, $K_{n^0_2}$ is calculated according to Equation 15 but, of course, using the constants, molecular weights and dissociation energies appropriate to the dioxide molecule. The sputtering ion mass spectra generally confirm an equilibrium behavior of the dioxide molecular ions, at least for the lighter elements, and the operation of the above equations. The experimental data, however, are not presented here because of a general lack of the physical constants required to accurately interpret the observed data. The error generated by the lack of physical constants will be discussed further later in this paper. Use of the relationships given above permits the observed positive or negative atomic ion yield of an element to be corrected for the equilibrium concentration of monoxide and dioxide molecules of that element.

CARISMA

The mathematical method used to calculate the composition of the sputtering region at the surface of the bombarded solid, assuming thermal equilibrium, is given as follows. As stated, the majority of the atoms of a given element, M, are present in the sputtering region either as positive atomic ions, negative atomic ions, neutral atoms, or as part of monoxide or dioxide molecules. The total number of atoms of that element, to a first approximation, is then given by the sum of these parts; Equation 1. When positive sputtered ion spectra are analyzed, the ratio of the number of observed positive ions to the total number of atoms of that element can be obtained from:

$$\frac{n_{\text{M}^+}}{n_{\text{M}}} = \frac{n_{\text{M}^+}}{n_{\text{M}^0} + n_{\text{M}^-} + \frac{n_{\text{M}^+}}{K_{n^0_1}} + \frac{n_{\text{M}^+}}{K_{n^0_1} K_{n^0_2}} + \frac{n_{\text{M}^+}}{K_{n^0_1} K_{n^0_2}} n_{\text{O}^0}} \quad (18)$$

where each term in Equation 1 has been divided by the concentration of neutral atoms of M, n_{M^0} . In this form, it is possible to recognize the Saha equations for singly charged positive and negative ions in the numerator and denominator.

The molecular oxide terms, $n_{\text{MO}}/n_{\text{M}^0}$ and $n_{\text{MO}_2}/n_{\text{M}^0}$, are calculated through a simplification which assumes that the dissociation constant of the neutral molecule applies to the dissociation of all charge states of the molecule to all charge states of the atom (i.e., $K_{n^0_1} \sim K_{n^+1_1} \sim K_{n^-1_1}$). Another statement of this simplification is that the ratio of the concentration of positive or negative molecular ions to neutral molecules is given by the ratio of the concentration of positive or negative atoms to neutral atoms, respectively (e.g., $n_{\text{MO}^+}/n_{\text{MO}^0} = n_{\text{M}^+}/n_{\text{M}^0}$). The consequences of this simplification will be discussed later. For the moment, the simplification permits us to proceed with a practical calculation by combining it with:

$$\frac{n_{\text{MO}}}{n_{\text{M}^0}} = \frac{n_{\text{MO}^+}}{n_{\text{M}^0}} + \frac{n_{\text{MO}^-}}{n_{\text{M}^0}} + \frac{n_{\text{MO}^0}}{n_{\text{M}^0}} \quad (19)$$

through Equation 13 to yield:

$$\frac{n_{\text{MO}}}{n_{\text{M}^0}} = \frac{n_{\text{O}^0}}{K_{n^0_1}} \left(\frac{n_{\text{M}^+}}{n_{\text{M}^0}} + \frac{n_{\text{M}^-}}{n_{\text{M}^0}} + \frac{n_{\text{M}^0}}{n_{\text{M}^0}} \right) \quad (20)$$

and

$$\frac{n_{\text{MO}_2}}{n_{\text{M}^0}} = \frac{(n_{\text{O}^0})^2}{K_{n^0_1} K_{n^0_2}} \left(\frac{n_{\text{M}^+}}{n_{\text{M}^0}} + \frac{n_{\text{M}^-}}{n_{\text{M}^0}} + \frac{n_{\text{M}^0}}{n_{\text{M}^0}} \right) \quad (21)$$

where $K_{n^0_1}$ and $K_{n^0_2}$ are calculated with Equation 15.

The total number of atoms of element M is then given in terms of the observed positive sputtered ion intensity of that element by the following equation:

$$n_{\text{M}} = \frac{n_{\text{M}^+}}{n_{\text{M}^+}/n_{\text{M}^0}} \left[\left(1 + \frac{n_{\text{M}^+}}{n_{\text{M}^0}} + \frac{n_{\text{M}^-}}{n_{\text{M}^0}} \right) \left(1 + \frac{n_{\text{O}^0}}{K_{n^0_1}} + \frac{(n_{\text{O}^0})^2}{K_{n^0_1} K_{n^0_2}} \right) \right] \quad (22)$$

A similar equation can be written in terms of negative sputtered ions intensities by changing the first term on the right side to read the observed negative ion intensity over the equilibrium ratio of negatives to neutrals (i.e., $n_{\text{M}^-}/n_{\text{M}^0}$).

This is the basis for a quantitative method since the singly charged ions are directly observed in the mass spectrum. If the temperature and electron density are given, the singly charged positive ion intensities of all the elements observed in the mass spectrum of a sample can be corrected with Equation 22 to give the total number of atoms of each element present. This calculation produces, within the limits of error of the model, the total atomic composition of the sputtering region which is directly related to that of the sample. A computer program entitled CARISMA (Corrections to Applied Research Laboratories Ion Sputtering Mass Analyzers) has been developed to perform these computations (35).

CARISMA contains several options for establishing the temperature and electron density of the sputtering region at the surface of the sample. The most straightforward procedure and the one which is tested in this paper is based on knowing the atomic concentrations of two of the elements in the sample. This two internal standard approach permits the two variables of temperature and electron density to be obtained from a pair of the above equations, 22, written for the two known elements. In practice the computer searches $T - n_e$ space to find a set of values for these two parameters which on the basis of the observed sputtered ion intensities gives an absolute atomic composition that best matches the known concentrations of the two elements selected to be internal standards in the specimen. The best match is taken as the smallest

(34) D. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, N.Y., 1970.

(35) J. R. Hinthorne and C. A. Anderson, "Ion Microprobe Mass Analyzer Operation Manual," Applied Research Laboratories, Sunland, Calif., 1972, sec. 3, p. 44.

Table I. Silicate Analysis at Different Primary Accelerating Potentials. Sample: Andesine AC-362 (NaCa) (AlSi)₄O₈

	WET CHEMICAL ANALYSIS	ATOMIC PERCENT			
		IMMA			
		keV (Primary Ions: ¹⁸ O ⁺)			
		18	16	14	11
Na	3.14	3.08	3.03	3.14	3.32
Al	11.97	11.93	11.96	11.95	11.86
Si	18.77	18.73	18.77	18.73	18.77
K	0.08	0.18	0.17	0.22	0.19
Ca	4.29	4.31	4.38	4.28	4.22
Fe	0.11	0.22	0.14	0.12	0.09

Table II. Silicate Analysis Using Different Primary Beam Ions. Sample: Clinopyroxene AC-362-CI (CaMgFe)₂Si₂O₆

	WET CHEMICAL ANALYSIS	ATOMIC PERCENT		
		IMMA		
		Primary Ion Species (16 keV)		
		¹⁶ O ⁺	¹⁸ O ⁺	³⁵ Cl ⁺
Si	19.30	19.31	19.24	19.26
Al	.97	1.17	1.11	.99
Mg	6.69	6.30	6.89	6.08
Fe	4.09	4.08	4.10	4.09
Ca	8.54	8.62	8.56	8.82
Mn	.10	n.a.	.094	.060
Na	.27	.24	.29	.17
K	.02	.010	.013	.008

sum of the percentage errors of the two standard elements.

The observed intensities of all the other elements in the sample are then corrected at these same T and n_e conditions to give the atomic composition of the sample. The sum of all the corrected element intensities is called 100% and each element is assigned a fractional value based on its proportionate share of the total corrected intensity. For this purpose the intensity of the bombarding gas is not included in the total corrected intensity. In the case of oxide specimens, such as silicates, for example, bombarded with oxygen, only the cations are considered and the total corrected intensity is equated to the known cation sum, typically about 40% in this example.

The results of over a hundred analyses of standard samples have indicated that a functional relationship exists between the temperature and electron density established in the sputtering ion region. This relationship which appears to be something like $\log T = 2.817 + 0.0638 \log n_e$ reduces the required number of known element concentrations to one and permits CARISMA to have a one internal standard option. The analyses have further indicated that similar samples analyzed under identical bombardment conditions appear to establish similar temperatures and electron densities. This permits CARISMA to have an option that requires no internal standards and the T and

n_e of the unknown sample are set from experience with similar standard samples. The accuracies of these approaches will be assessed at another time.

There are also certain diagnostics that are directly observable in the mass spectrum that appear to permit the temperature and electron density of the sputtering region to be established independently of any knowledge of the concentrations of the elements in the sample. One such temperature and electron density sensitive diagnostic is the observed ratio of doubly to singly charged ions of certain elements. These ratios can be described in terms of ionization equilibria as are singly charged ion to neutral atom ratios. Two such ratios coupled with Equation 5, appropriately written, should produce the same T and n_e as is obtained from the singly charged to neutral atom data, assuming thermal equilibrium. To date we have had a degree of success with this approach using ratios such as $\text{Ca}^{2+}/\text{Ca}^+$, $\text{Si}^{2+}/\text{Si}^+$ and $\text{Al}^{2+}/\text{Al}^+$ (i.e., the determined temperatures are within 10% of those obtained with singly charged and neutral atom data while the n_e is about a factor of ten smaller). Another set of temperature sensitive diagnostics directly observable in the mass spectrum are the ratios of MO/M for various elements. A pair of such ratios coupled with Equation 15 should also produce the same temperature obtained from singly charged to neutral atom data. Again we have had a degree of success (i.e., temperatures are essentially the same but n_e cannot be determined) using pairs of ratios such as SiO^+/Si^+ , AlO^+/Al^+ , CaO^+/Ca^+ , and O_2^+/O^+ (converted to neutral particle concentration). These competing methods of establishing T and n_e are still being evaluated and are not discussed further in this paper. They hold out the promise, however, of completely standardless analysis.

For the present, we will test the thermal model with the two internal standard option of CARISMA. In many of the results presented here, however, more than two internal standards were used when available. The additional internal standards were used only to reduce our dependence on the absolute accuracy of the concentration of any one element as supplied by the other analytical technique. The use of multiple internal standards also serves to reduce the requirements on microscale homogeneity of the sample, on the accuracy of the constants used in the program for any one element, and on the absolute accuracy of the observed ion intensities obtained in the ion microprobe mass analysis. CARISMA is a general program and contains the physical constants required to quantitatively correct all 92 of the elements of the periodic system. The accuracy of these data is not the same for all elements, however, and resulting errors will be discussed later in this paper.

RESULTS

The two internal standard option of CARISMA using Equation 22 has been tested as a practical method on as wide a variety of materials as it was possible to collect during the time span of this study. The range of materials includes insulators, semiconductors, and metals and the results reported here cover many of the materials commonly encountered in the fields of geology and metallurgy. Standard semiconductor materials containing more than two or three well-analyzed elements are difficult to acquire and, although the method has been found to produce generally satisfactory results with these samples, no comparison data are presented at this time. This is also the case for the carbonates, sulfates, phosphates, and borates we have analyzed.

The accuracy of the correction method in the analysis of a well-characterized, homogeneous, mineral standard

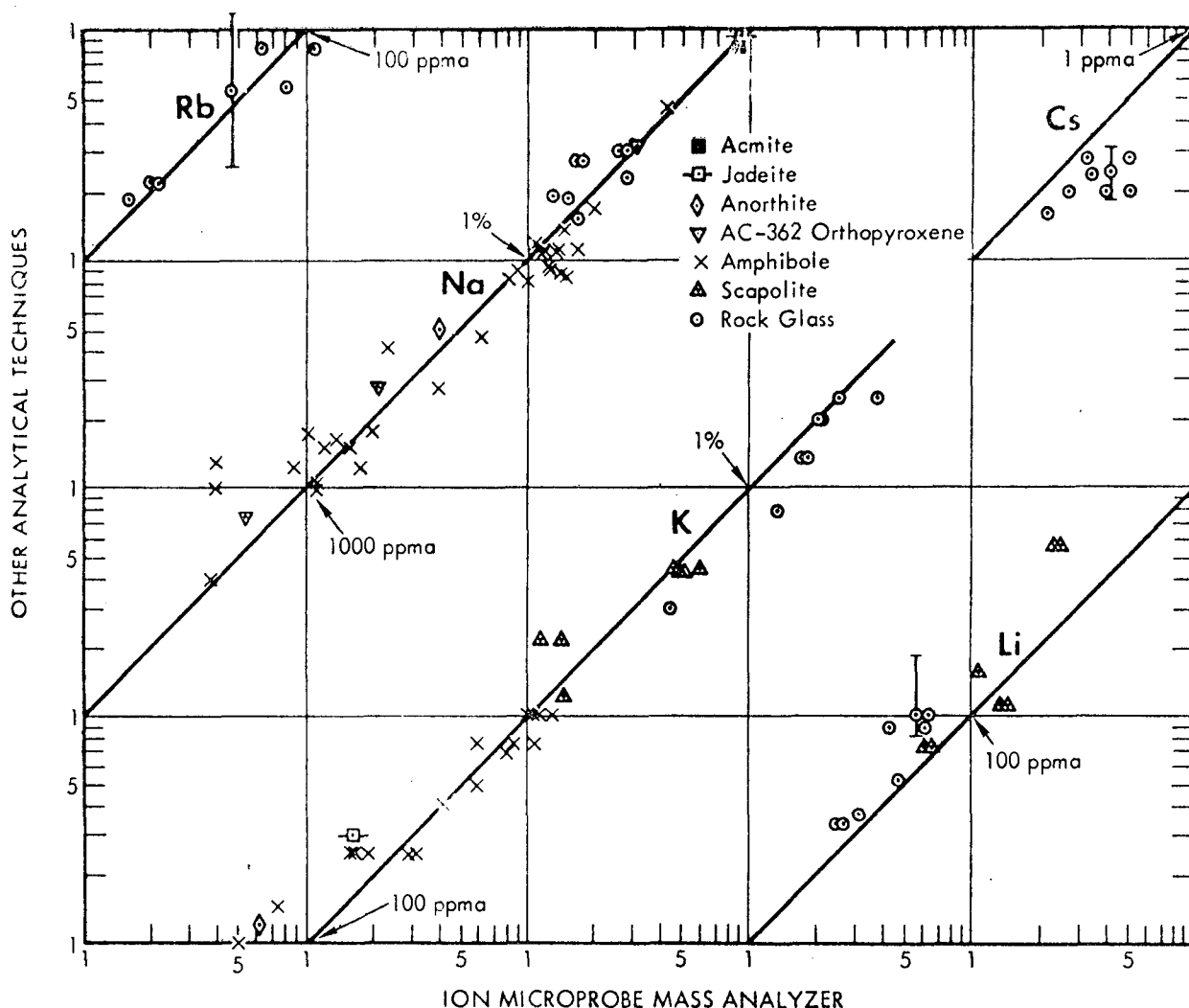


Figure 5. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for the alkali elements in silicate matrices

bombarded at different accelerating potentials (keV) of the primary ion beam is demonstrated in Table I. The major element determinations are generally within 10% relative error of the values determined by wet chemistry. The four analyses illustrate that the correction procedure gives generally the same results at several different accelerating potentials and is not, in this sense, restricted to a particular set of bombardment conditions. Although no specific precision tests were performed in this study, the four analyses illustrate the minimum reproducibility that can be expected. The apparently large error in the values for potassium is, we believe, at least partly the responsibility of the wet chemical analysis as will be demonstrated by the potassium analyses presented later in this paper. All four major elements were used as internal standards in these particular data reductions although the same general results are obtained by using any two, such as Ca and Si. The temperature and n_e change with keV and are in the range of 14000 °K and 10^{20} per cm^3 .

The accuracy of the correction procedure using different bombarding gases in the primary ion beam is illustrated in Table II. A well-characterized, homogeneous, mineral standard was bombarded with isotopically pure beams of $^{16}\text{O}^+$, $^{18}\text{O}^+$, and $^{35}\text{Cl}^+$. All three of these gases are negatively charged as required for the micro-point analysis of cations (36) and have an electronegative chemical char-

acter as required by the general analytical method for sputtered positive ion analysis (16). The major element determinations are again within 10% relative error of the values determined by wet chemical analysis. The errors are larger when using the Cl^- beam. This is to be expected because CARISMA, at this time, contains no provisions to account for the molecular chlorides that form as a result of Cl^- bombardment. Fortunately, the Cl^- molecules represent small corrections in this case. The data again demonstrate that the general thermal model used in the correction procedure is not tied necessarily to a particular set of bombardment conditions. The four major elements were used as internal standards although again the same general results are obtained with two internal standards, such as Fe and Si. The temperatures and n_e are in the range of 13000 °K and 10^{19} per cm^3 in these analyses.

The application of the correction procedure to a general range of elements and samples is given in the following set of figures and tables. The ion microprobe analyses were all performed with a negatively charged oxygen beam at about 16 kV accelerating potential under the general experimental conditions outlined. The data were collected as count rates on isotopes of each of the elements of interest in the sample. No detector or mass spectrometer correction factors were used, other than detector dead-time corrections where appropriate, and all data from all samples were taken using identical mass spectrometer instrument parameters. Only sputtered positive ion data are presented here, and it must be understood that many ele-

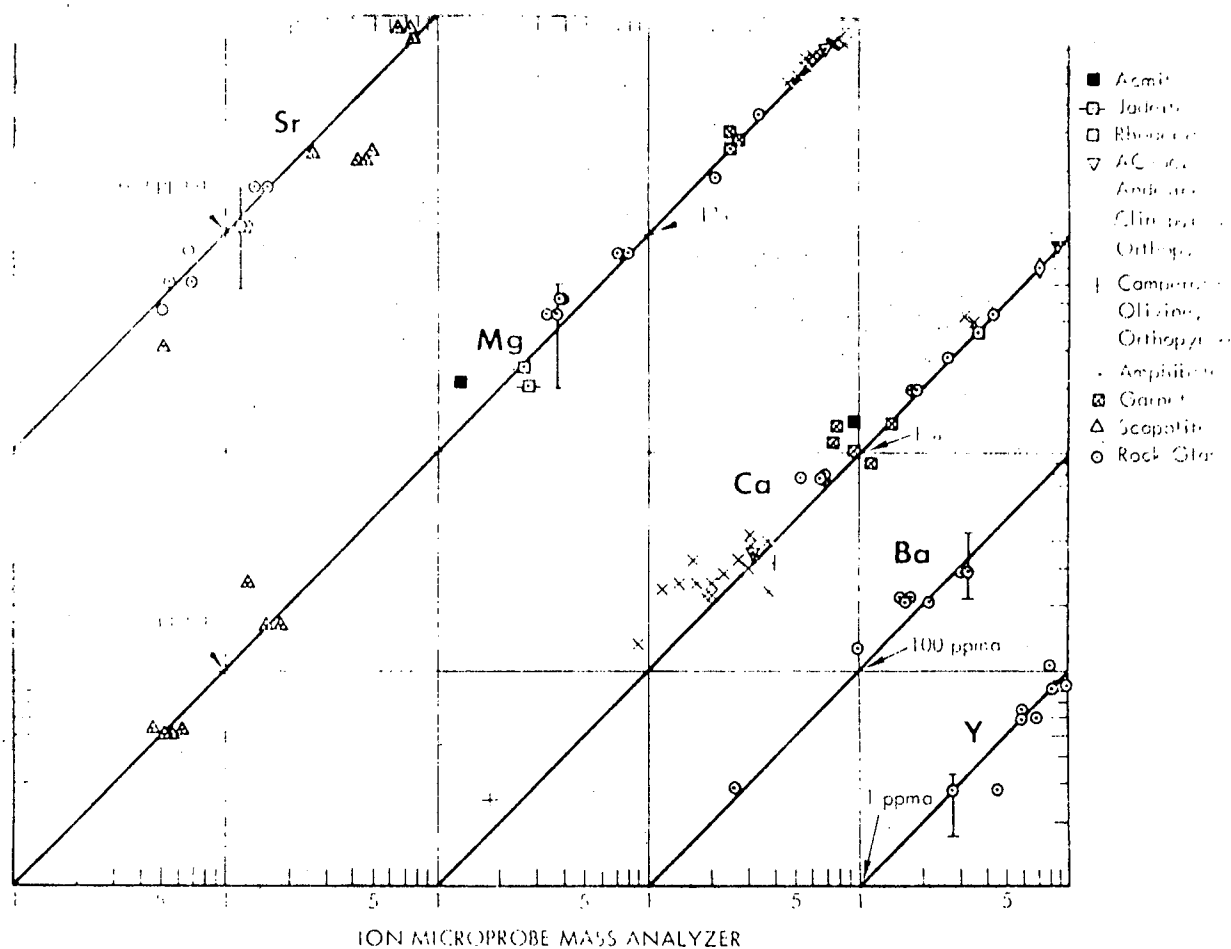


Figure 6. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for the alkaline earth elements plus yttrium in silicate matrices

ments are not optimized for either sensitivity or accuracy for this reason. The correction procedure was applied without alteration throughout the entire range of major to trace element concentrations. In some cases, it should be noted, the data cover six orders of magnitude. In each case, major element constituents were used as internal standards. The ion microprobe analyses are presented along the horizontal axis and the results of the other analytical techniques performed by other laboratories are presented along the vertical axis. The other analytical techniques include most viable techniques in use today including: wet chemistry, optical emission, atomic absorption, neutron activation, isotope dilution, X-ray fluorescence, electron microprobe, flame photometry, and spark source mass spectrometry among others. A complete reference list of the sources of the other chemical analyses and the types of materials analyzed is given at the end of this paper. In some cases the points represent, on the vertical axis, the average of several different laboratories' results. In the analyses of the fused rock powders (rock glass), the laboratory spread is indicated by a vertical bar for a representative sample (G 2). Homogeneity studies were not generally made in this work, although homogeneous standards were sought for analysis; and the ion microprobe analyses generally represent one point of an area on the order of $5000 \mu^2$ on each sample. Particular problems with the homogeneity of some of the metal alloys will be discussed below. Over thirty elements have been compared in this manner with, we believe, satisfactory results. It should be noted that the lines drawn on the figures are one to one perfect correlation lines and not the best straight lines through the data. Each line is labeled in terms of concentration, and all results are given in atomic

units. Representative analyses from the figures are given in the accompanying tables permitting direct comparison.

Figures 5 and 6 illustrate the comparative results for the alkali and alkaline earth elements plus yttrium in silicate matrices. In general, the analytical results show good correlation. The Cs values measured by the ion microprobe appear to be too large by about 50%. These concentration values are all below 1 ppm, however, and recent evidence suggests that the error is most probably due to an improper background correction (37). The Li values given by the ion microprobe appear to be too small by about 25%. This error does not presently have an obvious source but may be related to errors in the physical constants for Li used in CARISMA. This will be discussed later in this paper. We do not believe that the Li and Cs errors are related to a mass effect as demonstrated, for example, by the accuracy of the B and Ba analyses which span nearly the same mass range.

Figure 7 shows the transition metals Ti, Mn, Cr, and V in silicates plus B in silicates and metals. The analytical results again show good correlation in many different samples. We are able to obtain, for example, satisfactory results on B in both silicates and metals with the same theoretical program. Special attention should be paid to the good correlation shown by Ti and Mn for later reference. Si, Al, and Fe which are not illustrated on the graphs have usually been used as the internal standards in the silicate analyses and also show good correlation.

Figures 8 and 9 show the transition metals V, Cr, Fe, Co, Ni, and Cu plus C, Si, Sn, and Pb in metal alloys. Pb and Ni results from silicate analyses are also given. Note

(37) J. F. Lovering, Australian National University, personal communication, 1972.

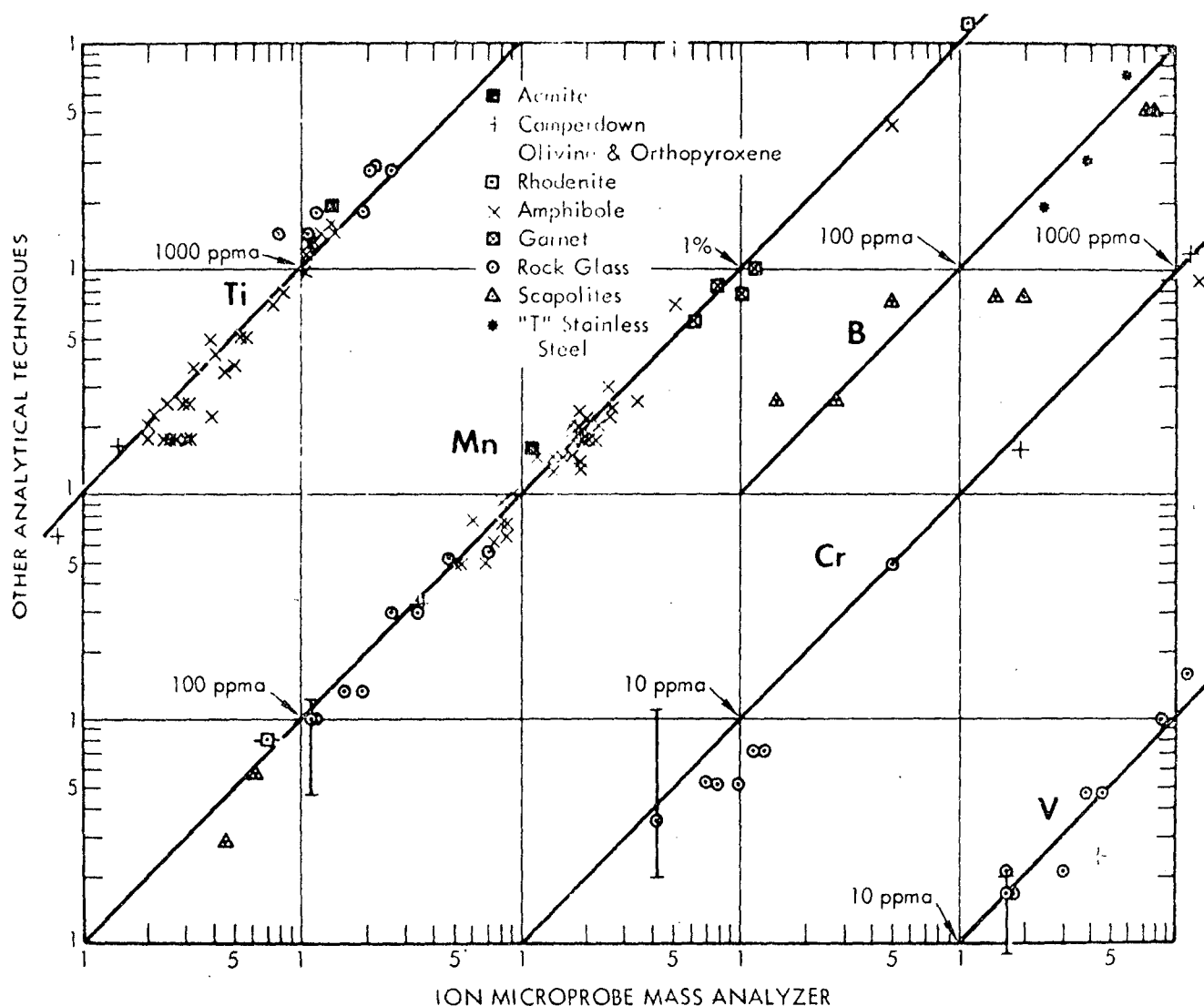


Figure 7. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for some of the transition metals in silicate matrices plus B in silicates and metals.

that the two lowest Ni concentration values have been plotted an order of magnitude too high for convenience of the graph. The ion microprobe analytical results for V and Sn appear to be too low. The reason for this is not known but it should be noted that in the silicates V showed good correlation. The Pb values from the metals show considerable scatter while those from the silicates look reasonably good. In general, we believe, the poorer results obtained from metals relative to the silicates reflect local inhomogeneities in the metal samples.

The inhomogeneity of the metal alloy standards is brought to attention by the results achieved on Al, Mn, and Ti in these samples as illustrated in Figure 10. The analytical results produced by the ion microprobe on Al and Mn generally give too high a concentration while Ti shows considerable scatter. Reference to Figure 7 demonstrates that, in silicates, the analyses of Mn and Ti are accomplished satisfactorily by the correction program. Since neither the instrumental parameters nor the program are altered for the analysis of different materials, the metal alloys themselves are suspect. Small inclusions can be observed with the microscope and microanalysis confirms the segregation of Ti, Mn, and Al. The errors produced by the local segregations indicate that the inclusions yield more or fewer ions per unit concentration than does the matrix. The increased or decreased ion yields probably reflect an increased or decreased electronic work

function on the surface of the inclusion, respectively, as compared to the matrix (17). It should be remembered that the correction procedure used here assumes that all sputtered ions pass through a common surface potential. This assumption leads to the recommended procedure of only using data collected from a single matrix. It is interesting to note, however, that the presence of the inclusions did not cause the degradation of the analytical results of the elements present in the matrix as can be seen by a study of Figures 7, 8, and 9. Bulk analysis for matrix elements of materials bearing minor segregations, therefore, appears to be possible if the compositions of the segregations are known.

Another type of error encountered in our analyses is illustrated in Figure 11. This error which is characteristic of a certain group of elements appears to be mainly the responsibility of the ion microprobe analysis. The elements shown in the figure belong to the group of elements that have large molecular oxide components. In fact, in many cases, the observed intensity of the monoxide ion in the mass spectrum is greater than that of the atomic ion of the same element. It is felt that the analytical error is related to this unusual circumstance. Possibly, the assumptions concerning the molecular oxide corrections contained in the general program are not good enough for these exaggerated cases or possibly the physical constants used in the program are in error. It should be noted, how-

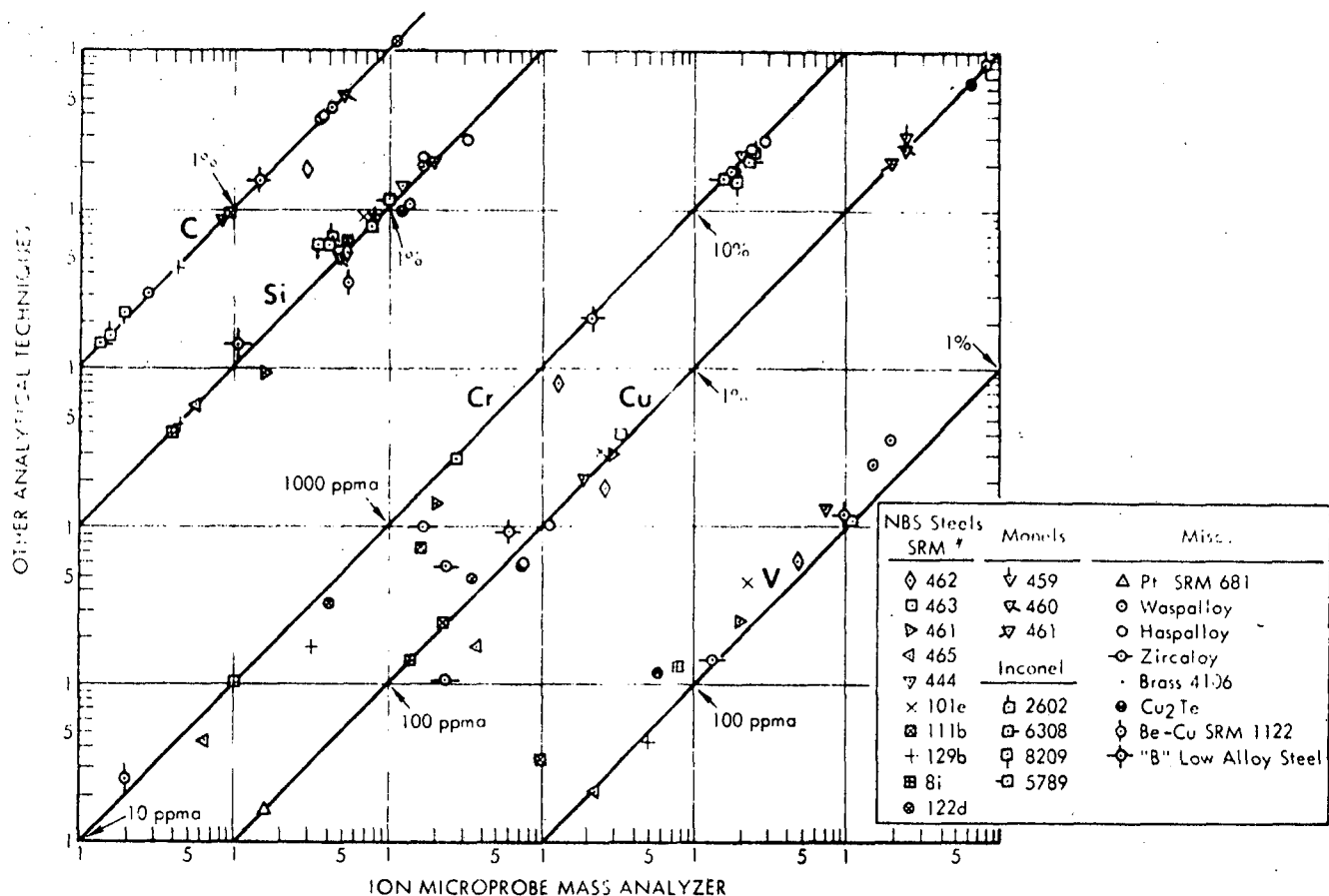


Figure 8. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for some of the transition metals plus C and Si in metal matrices

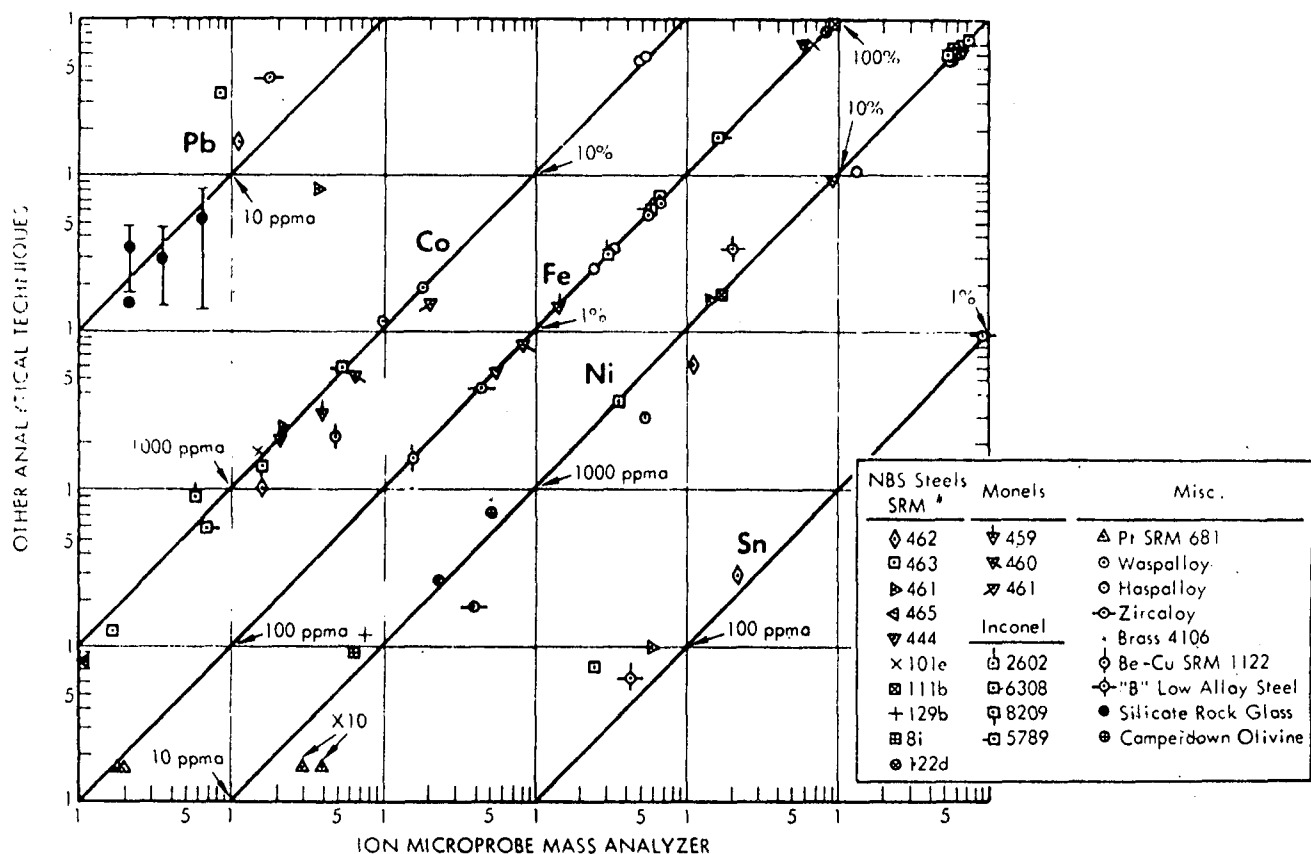


Figure 9. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for some of the transition metals plus Sn and Pb in metal matrices and Pb and Ni in silicates

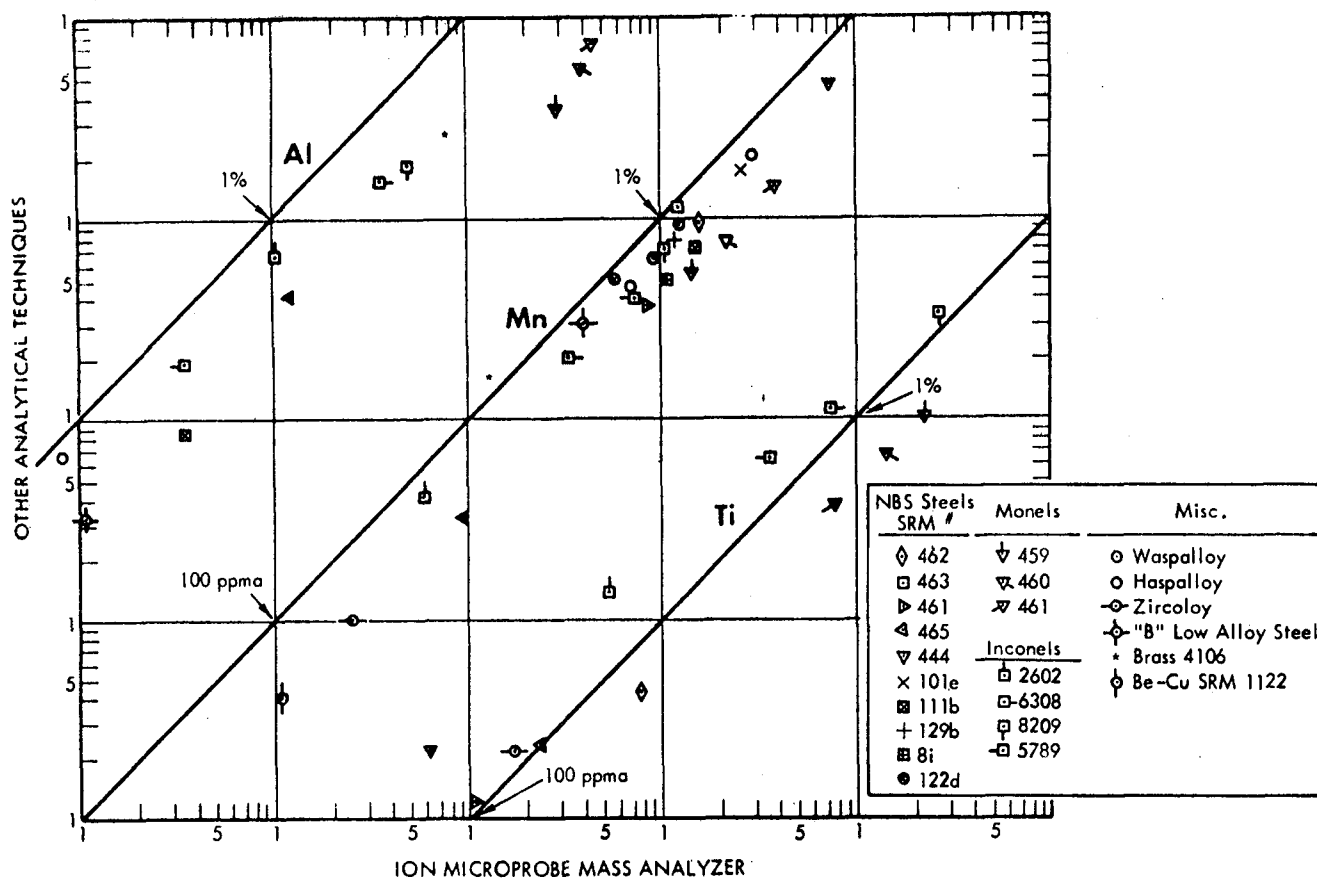


Figure 10. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for Al, Mn and Ti in metal alloys

ever, that the analytical errors observed appear to be nearly constant for each element in many different materials. This gratifying result points to some fundamental error and for the present, without understanding the problem further, to an extremely practical solution. The error can simply be corrected by multiplying the observed intensities of these elements by constant correction factors ($Zr \times 2.5$, $Mo \times 6.25$, $Nb \times 5.7$, $Ce \times 2.5$, $La \times 2.5$, $P \times 3.0$). This has not been done in the program, however, in order to keep it perfectly theoretical and to be able to study the errors without confusion. More will be said about this error below. W, Hf, Th, and U also belong to this group of elements but an insufficient number of analyses of these elements in standard materials have been accomplished at this time to establish reliable correction factors. The other rare earth elements are also almost certainly in this group and, considering the results on La and Ce, a correction factor of 2.5 is probably appropriate for all the rare earth elements.

We also have some data on a number of other elements some of which will appear in the following tables. In general we seem to get satisfactory results when analyzing for Be, S, Ru, Rh, Ag, Au, Ga, In, Sb, Te, and As. Arsenic may require a correction factor similar to P. We also get fair correlation with Zn, more will be said about this element later, but we appear to have an unresolved problem with Pd, Cd, Hg, Os, and Ir, at least in some matrices. The gases H, N, O, F, and Cl have not as yet been studied in detail in the positive ion spectrum. Preliminary data on some of these gases, however, look encouraging. We have little knowledge of most of the other elements of the periodic table at this time. It should be remembered that the analysis of many of the above elements, especially the gases and semi metals, is optimized in terms of sensitivity and accuracy in the negative sputtered ion spectrum (17).

Work in the negative spectrum will be presented at another time.

Comparative analyses of common rock forming feldspars, pyroxenes, and amphiboles are given in Tables III, IV, and V, respectively. The tables permit direct comparison with several analytical techniques and demonstrate that in most cases the ion microprobe results are within 10% relative error of the comparative technique for the major and minor elements. This is the most important concentration range for comparison because the competing techniques are often subject to error in the trace concentration range. If the competing technique is the electron microprobe, then it suffers error in the trace concentration range because of a general lack of sensitivity. If the competing technique is not a microanalytical technique, then it suffers possible error in the trace concentration range from the contamination of the analyzed mineral with small inclusions of other mineral phases. In the pyroxene, rhodinite, for example, the Zn value reported by the other technique may be a factor of two too large (38). Some of the ion microprobe results obtained on Al in the amphiboles may be too high because these samples were polished with Al_2O_3 which is possibly caught in micro-cracks in the surface of the mineral.

Table VI gives comparative analyses for three United States Geological Survey standard rock powders that were fused into glasses by two different laboratories. The ion microprobe is again compared through all concentration ranges against many different analytical techniques (the ion microprobe results for the two glasses are given in columns R and S). The analyses demonstrate the accuracy of the ion microprobe for a wide variety of elements within the context of the errors already discussed and also demonstrate the feasibility of producing a glass with the (38) B. Evans, University of Washington, personal communication, 1972.

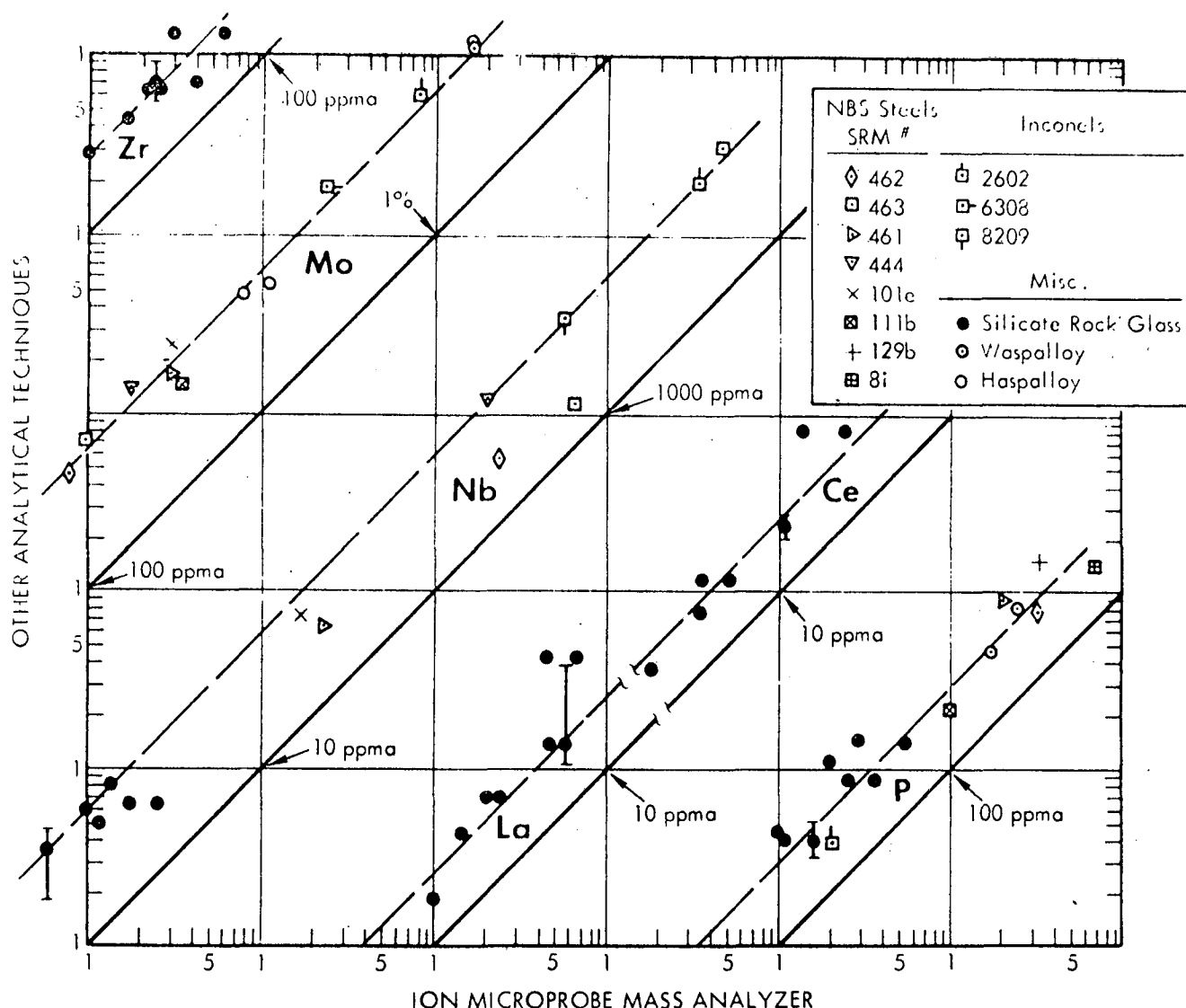


Figure 11. Comparison of the analyses of the ion microprobe mass analyzer with those of other analytical techniques for Zr, Mo, Nb, La, Ce, and P in metal and silicate matrices.

chemical composition of the original rock. The ion microprobe analyses given consumed only about 10^{-10} gram of material for each rock analysis. The increased B content found with the ion microprobe probably resulted during the glass manufacture. The generally low Na contents in the glasses prepared by both laboratories and the low Pb values found in the "S" prepared glasses may reflect volatile loss of these elements during glass manufacture. The analysis of alkalis in soft glasses is being studied further.

Table VII gives comparative analyses of several different natural oxides. These are interesting to compare with the metal alloys to be discussed next because the alloys are converted to oxides by the oxygen ion bombardment. The analyses generally show good correlation and demonstrate that it is possible to obtain satisfactory analyses for Ti and Mn in metal oxide matrices. The high Si and Al contents reported by the other analytical technique in the ilmenite are probably the result of foreign mineral inclusions (39). This may also be true of the Si and Na in the magnetite. In the chromites, the ion microprobe analysis shows the Al to be higher and the Cr and Ti to be lower in concentration than does the wet chemical analysis. This discrepancy is still to be resolved.

Comparative analyses of a wide variety of metal alloys are given in Tables VIII and IX. As mentioned above,

many of the alloys are not as homogeneous as we might like but it was desired to test the correction method against as many different materials as possible in order to understand the practical range of application of the method and to possibly uncover a flaw in the procedure. Representative data are presented for direct comparison. The ion microprobe again shows good correlation over the entire concentration range for many different elements within the context of the errors discussed above. Major elements and C and Si, where available, were generally used as internal standards. The analysis given for this particular brass is that obtained almost immediately upon initiation of ion bombardment. The analyses obtained on this sample at later times show a deficiency of Zn. Other brasses have not shown this peculiar tendency (40). These results are being studied further. The reported analyses and the wide range of alloys studied provides convincing evidence that the proposed quantitative procedure is of some practical use.

PROGRAM LIMITATIONS

As has been mentioned throughout this paper, the general theoretical correction procedure has certain limitations imposed by a lack of the required physical constants. The most important term in the correction applied

(39) K. Snetsinger, NASA, Ames Research Center, personal communication, 1972.

(40) D. J. Comaford, Applied Res. Labs., Sunland, Calif., personal communication, 1973.

Table III. Comparative Analyses of Feldspars (atomic per cent)

	Anorthite (Pacaya)		Labradorite (AC-362)		Oligoclase (A-220)		Albite (Amelia)		K-Feldspar (A-222)		Sanidine (Coi Tech)	
	IMMA	EMX	IMMA	EMX	IMMA	EMX	IMMA	OTHER	IMMA	WET	IMMA	OTHER
Si	15.88	16.02	18.76	18.77	20.59	20.53	23.01	23.08	23.50	23.03	22.99	22.55
Al	14.80	14.86	11.97	11.97	9.65	9.62	7.68	7.69	7.63	7.59	7.55	7.60
Ca	7.13	7.00	4.28	4.29	1.81	1.55	.060	-	.006	.032	-	-
Na	.41	.51	3.06	3.14	5.55	5.79	7.53	7.54	.39	.72	1.19	-
K	.0063	.054	.16	.08	.42	.53	.18	.12	6.38	6.33	6.47	6.50
Fe	.18	.12	.21	.11	.080	.084	-	-	.11	.29	-	-
Rb	.000028	-	-	-	-	-	-	-	.015	.025	-	-
Ba	-	-	-	-	-	-	-	-	-	-	.147	.15

Table IV. Comparative Analyses of Pyroxenes (atomic per cent)

	Orthopyroxene (Campeador)		Orthopyroxene (AC-362-Oi)		Clinopyroxene (AC-362-Cl)		Jadeite (A-208)		Acmite (A-206)		Rhodonite (P-179)	
	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER
Si	19.21	19.22	19.60	19.60	19.24	19.30	19.92	20.01	20.25	19.95	20.80	20.0
Al	1.58	1.22	.64	.66	1.11	.97	9.70	9.74	.44	.44	.012	.005-.035
Mg	17.59	17.58	9.14	9.03	6.89	6.69	.27	.20	.13	.21	.26	.25
Fe	1.73	1.73	9.89	10.00	4.10	4.09	.075	.083	8.93	8.82	4.04	3.89
Ca	.41	.31	.31	.35	8.56	8.54	.71	.28	.91	1.34	3.67	3.52
Na	.12	-	.055	.076	.29	.27	9.25	9.31	8.91	8.45	.018	-
Mn	.034	.032	-	-	.094	.100	-	-	.12	.16	11.05	11.74
K	.0040	-	-	-	.013	.020	.016	.030	.036	-	.022	-
Ti	.016	.016	-	-	-	-	.005	-	.014	.20	.0003	-
V	.0044	.0024	-	-	-	-	-	-	.0038	-	.0003	-
Cr	.143	.118	-	-	-	-	-	-	.0015	-	.0001	.0017
Co	.0015	.0019	-	-	-	-	-	-	-	-	.006	-
Zn	-	-	-	-	-	-	-	-	-	-	.041	.110

to the positive ion intensities of most elements is that given by Equation 5 which predicts the ratio of the number of singly charged positive ions to neutral atoms of an element. In fact for the purposes of illustration in Figure 2, the positive ion intensities corrected for the atomic concentration of the elements have been plotted as a function of Equation 5 only, and the molecular oxide and negative ion contributions of Equation 22 have been neglected. Generally, the molecular oxide and negative ion corrections become significant at lower temperatures and at higher values of the electron density. Equation 5 depends on the internal partition functions of the singly charged positive ion and of the neutral atom. In this respect, the limitations imposed by the available physical constants

set the upper limit of our program at 17000 °K, mainly because of a lack of the partition functions of the neutral atoms of the elements at higher temperatures. We use partition functions that have been calculated as functions of ΔE by Drawin and Felenbok (41), wherever possible, and extrapolate their data to 17000 °K, if their data are not given in this temperature range. For most of the other elements we use partition functions from De Galan *et al.* (42). Their data stop at 7000 °K and we use the ratio of

(41) H. W. Drawin and P. Felenbok, "Data for Plasmas in Local Thermodynamic Equilibrium," Gauthier-Villars, Paris, 1968.

(42) L. De Galan, R. Smith, and J. D. Winefordner, *Spectrochim. Acta*, **23B**, 521 (1968).

Table V. Comparative Analyses of Amphiboles (atomic per cent)

	Cummingtonite STD 3		Actinolite Chester		Hornblende HP 2		Gedrite HPG-L2		Anthophyllite SE-2	
	IMMA	Wet Chem.	IMMA	Wet Chem.	IMMA	EMX	IMMA	EMX	IMMA	EMX
Si	20.01	20.02	19.70	19.64	16.90	16.30	16.64	16.65	20.66	19.15
Al	.066	.10	.94	.93	7.56	6.28	6.61	5.95	2.52	1.50
Mg	9.89	9.92	10.30	10.32	5.79	6.40	7.24	7.25	9.38	10.60
Fe	2.13	2.13	1.84	1.84	4.38	4.38	7.13	7.13	5.48	5.80
Mn	4.90	4.47	.081	.094	.082	.078	.20	.21	.148	.142
Co	.030	.040	5.17	4.60	3.84	3.78	.11	.20	.19	.23
Na	.048	.050	.27	.41	1.39	1.03	1.00	.81	.40	.28
K	.0019	-	.044	.043	.062	.048	.011	.030	.030	.013
Ti	.019	-	.04	.009	.106	.113	.044	.040	.049	.023

Table VI. Comparative Analyses of Fused Rock Powders

	G-2			AGV-1			GSP-1		
	STD. ¹	R ²	S ³	STD.	R	S	STD.	R	S
atomic percent									
Na	2.81	1.67	1.69	3.04	2.52	2.85	1.95	1.60	1.27
Al	6.29	6.62	6.48	7.26	7.74	7.21	6.22	5.38	4.58
Si	24.78	25.77	26.70	21.33	21.27	21.15	23.46	23.76	24.28
K	2.00	2.21	2.06	1.34	1.79	1.86	2.43	3.76	2.47
Mg	.42	.37	.34	.80	.72	.80	.50	.39	.48
Ca	.74	.63	.67	1.93	1.83	1.89	.76	.65	.52
Fe	.72	.72	.51	1.85	1.85	1.85	1.14	1.14	1.16
Ti	.14	.08	.11	.29	.21	.27	.18	.19	.12
atomic ppm									
Li	102	56	64	37	24	26	109	63	44
B	3.4	98	132	-	33	180	1.4	160	172
P	410	175	103	1500	300	550	880	250	338
V	17	17	18	47	47	38	21	29	17
Cr	3.6	4.2	11	7	8	13	5.3	7.1	10
Mn	100	116	120	320	328	260	130	156	199
Co	2	6	< 8	8	< 23	42	2.7	< 28	26
Rb	56	47	46	19	20	22	84	113	64
Sr	110	122	125	160	139	160	59	70	55
Y	2.9	2.8	4.6	6	6	7	8.6	8.4	9.9
Zr	71	24	41	60	23	24	125	30	60
Nb	3.6	.6	1.7	4	1.2	1.0	6.4	2.7	1.8
Cs	.23	.42	.34	.20	.40	.51	.27	.50	.33
Ba	290	337	327	210	185	165	208	210	173
La	16.5	6.8	5.8	5.4	5.5	2.1	42	5.5	7.8
Ce	24	11.5	11	12	5.3	3.6	83	13.5	24
Pb	3.0	3.3	.53	4.0	2.2	1.5	5.3	6.4	.23

¹ STD = Avg. of published values on rock powders. Flanagan, F.J. (1969) Geochim. Cosmochim. Acta, 33, 81-120.

² R = Glass obtained from J.C. Rucklidge, University of Toronto.

³ S = Glass obtained from R. Snetsinger, NASA, Ames Research Center.

Table VII. Comparative Analyses of Oxides (atomic per cent)

	Chromite 53-IN-8		Chromite 55-G-23ab		Ilmenite A-236		Magnetite 66-MAG-1	
	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER
Fe	11.51	11.25	11.39	11.38	19.51	19.22	42.34	41.99
Cr	16.94	18.49	14.22	16.46	.0014	-	.0034	-
Ti	0.42	0.57	0.18	0.27	19.88	19.55	.10	.10
Al	8.92	7.23	8.84	7.43	.007	.022	.18	.18
Mg	4.70	4.36	7.96	7.10	.025	-	.0035	-
Si	0.065	-	0.041	-	.002	.21	.11	.35
Na	0.027	-	.0017	-	.085	.078	.0074	.06
V	0.27	0.42	.050	.072	.004	-	.0052	-
Mn	0.10	0.13	.10	.072	.43	.45	.047	.050
Co	0.008	0.015	.012	.014	.0006	-	.0010	-
Ni	0.021	0.029	.053	.042	.0012	-	-	-

Table VIII. NBS Steels (atomic per cent)

SRM # ELEMENT	461		465		101e		111b		129b	
	Low Alloy A		Ingot Iron E		Stainless		Ni-Mo		High Sulfur	
	IMMA	NBS	IMMA	NBS	IMMA	NBS	IMMA	NBS	IMMA	NBS
Fe	96.0	96.4	99.2	99.2	69.2	68.2	94.7	95.7	98.2	98.2
Cr	.20	.14	.0066	.0043	19.34	19.04	.16	.075	.031	.017
Ni	1.52	1.65	-	-	7.31	8.89	1.72	1.73	.0074	.012
Mn	.87	.37	.097	.033	2.73	1.77	1.49	.72	1.22	.76
Cu	.30	.30	.037	.037	.26	.31	.024	.025	.016	.013
Si	.16	.093	.058	.058	.80	.84	.55	.60	.042	.042
C	-	-	-	-	-	-	.89	.90	.44	.44
Al	-	-	1.25	.40	-	-	.36	.085	-	-
P	.021	.096	-	-	.11	.044	.01	.02	.033	.15
S	-	-	-	-	-	-	-	-	.32	.38
Ti	.011	.012	.23	.23	-	-	-	-	-	-
V	.019	.026	.0022	.0022	.023	.047	.001	.033	.0049	.0044
C	.23	.25	.011	.008	.15	.17	.022	-	.0039	-
Zr	.0013	.003	-	-	-	-	-	-	-	-
Nb	.0023	.0066	-	-	.0016	.0077	-	-	-	-
Mo	.031	.175	.0009	.003	.030	.245	.035	.15	-	-
Sn	.0062	.010	.001	.0004	.049	.0093	-	-	-	-
Pb	.0037	.0008	-	-	-	-	-	-	-	-

the partition functions of the singly charged to neutral atom at this temperature for all higher temperatures. For some elements such as U and Th, we have to be satisfied with a single value for this ratio established at 5000 °K (43).

(43) C. H. Corlis, *J. Astrophys.*, 136, 916 (1962).

The most important term in the correction applied to negative ion intensities is given by Equation 11. Equation 11 depends on the statistical weights of the electronic ground states of the negative ions. These constants are generally unknown to the authors and, therefore, this term in Equation 11 is ignored in the correction program.

Table IX. Comparative Analyses of Assorted Metal Alloys (atomic per cent)

	Zircaloy		Waspelloy		Haspulloy		Monel		Inconel		Brass		Be Copper	
	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER	IMMA	OTHER
Be	-	-	-	-	-	-	-	-	-	-	-	-	10.76	11.10
B	.094	.0021	-	-	-	-	-	-	.0099	.0055	-	-	-	-
C	-	-	.29	.30	.36	.36	.529	.528	.15	.15	-	-	-	-
Si	1.32	.055	1.70	1.88	1.67	2.09	.526	.512	.44	.65	-	-	.57	.35
Ti	.018	.022	-	-	-	-	1.42	.651	.055	.14	-	-	-	-
V	.013	.014	.20	.37	.0007	-	-	-	.0007	-	-	-	-	-
Cr	.165	.097	18.10	18.60	24.14	23.95	-	-	26.46	23.59	-	-	.0025	.002
Mn	.026	.010	1.26	.94	2.93	2.03	2.26	.78	.060	.040	.13	.16	.011	.004
Fe	.442	.442	6.39	6.82	2.59	2.60	.824	.824	3.14	3.20	.17	.10	.16	.16
Co	.024	.0057	1.01	1.11	50.6	52.8	.68	.52	.061	.087	-	-	.49	.21
Ni	.039	.019	55.3	56.9	12.3	10.2	65.97	65.73	60.96	63.55	.052	.087	-	-
Cu	.024	.010	.073	.059	.076	.061	24.59	24.90	-	-	51.56	58.39	84.57	87.80
Zn	-	-	-	-	-	-	-	-	-	-	44.68	37.76	-	-
Nb	-	-	-	-	-	-	-	-	.35	2.00	-	-	-	-
Mo	.012	.0086	1.61	11.1	.081	.47	-	-	.80	5.94	-	-	-	-
Sn	.913	.984	-	-	-	-	-	-	-	-	.40	.58	-	-
Sb	-	-	-	-	-	-	-	-	-	-	.016	.0084	-	-
W	-	-	.027	1.23	.084	4.84	-	-	-	-	-	-	-	-
Pb	.0018	.0041	-	-	-	-	-	-	-	-	-	-	-	-

Figure 3 shows the negative ion intensities corrected for the atomic concentration of the elements plotted as a function of the right hand side of Equation 11 without the statistical weight term. The positive ion and molecular oxide terms of Equation 22 have again been neglected for the purpose of illustration. The electron affinities of the neutral atoms of the elements have generally been taken from Melton (44) with additions and substitutions from references 27-30.

As stated above, the molecular oxide terms are most important at lower temperatures and high concentrations of oxygen. This correction is mainly influenced by the exponential dissociation energy term of Equation 15. Fortunately, we have the dissociation energies and molecular constants of the neutral monoxide molecules of most of the elements and the dissociation energies of many of the important neutral dioxide molecules. The dissociation energies and the vibrational, rotational and electronic constants used in the program for the neutral monoxide molecules are generally taken from a compilation on diatomic molecules by Rosen (34) supplemented mainly by data from Gaydon (45). The dissociation energies of the important neutral dioxide molecules are from Vedeneyev (27). In general many of the ionization potentials and most of the electron affinities of the neutral monoxide and dioxide molecules are missing. To overcome this situation, Equation 22 has been written so as to be independent of the ionization potential and the electron affinity of the molecule. In order to accomplish this, however, Equation 22 makes the rather drastic approximation that the dissociation constants of the positive and negative molecular ions are equal to those of the neutral molecules. Also, because we do not have the molecular constants required to

calculate the partition function of the dioxide molecules, we substitute those of the monoxide molecule of the same element. This has the effect of approximating the monoxide to dioxide partition function ratio of an element with that of the atom to monoxide partition function ratio of the same element. The dissociation constant of the dioxide molecule is only calculated where we have actual data on the dioxide dissociation energy. The dioxide molecules of the other elements are ignored in the program. The lack of physical data also prevents the incorporation into the correction program of a general correction for the presence of molecular dimers of the metal atoms. These dimers are observed for certain elements in oxygen poor matrices such as those formed by the oxygen bombardment of the noble metals. Fortunately, the metal atom dimers usually represent a small correction in the other more frequently encountered matrices.

The concentration of free oxygen used in the correction program is calculated from a single set of experimentally observed monoxide to metal positive ion intensity ratio data, corrected to neutral particle concentrations, and the calculated dissociation constant, K_{n-1} , of that reaction as explained earlier (Equation 15). The temperatures and electron concentrations used in these calculations are, of course, the same as those used in the calculation of the singly charged to neutral atom ratios (i.e., Equations 5 and 11). In practice, we prefer to use the O_2^+/O^+ ratio because in this particular case we have the partition functions of both O_2^+ and O_2 (46) and also the electron affinity of O_2 (44) permitting a rather accurate correction of the raw data to O_2/O . Oxygen is also common to all the different samples analyzed because of the oxygen ion bombardment and, therefore, forms a convenient comparison parameter. If the intensity ratios of other monoxide to

(44) C. E. Melton, "Principles of Mass Spectrometry and Negative Ions," Marcel Dekker, New York, N.Y., 1970.

(45) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall, London, 1968.

(46) K. S. Drollishak, D. P. Aeschliman, and A. B. Cambel, *Phys. Fluids*, **8**, 1590 (1965).

metal ion pairs are used to establish the concentration of free oxygen as illustrated, for example, in Figure 4, then the partition function ratio of the molecule, B_{MO+}/B_{MO} , is approximated by the partition function ratio of the atom, B_{M+}/B_M , of the same element. The ratios of the partition functions are required, as in Equation 5, to convert the observed ion intensities to total molecule concentrations.

Considering the above approximations, it may seem surprising that the correction program produces quantitative results for as many different elements in as many different matrices as are illustrated in this paper. The correction method is able to accomplish this because the most important term in each part of the correction for most elements is known. The ionization potentials, electron affinities, and dissociation energies required by Equation 22 are known. The internal partition functions required by Equation 5, which is the most important term in Equation 22 for the correction of the positive ion intensities of most elements, are known exactly for many of the elements and approximately for the rest of the elements at temperatures appropriate to this work. We are not able to obtain the reported degree of accuracy over the range of elements and matrices analyzed here without the use of the partition function or for that matter without the use of the ΔE and n_e terms of Equation 5. The importance of the latter term argues against the effective use of the well-known Saha-Langmuir equation (47) for the general quantitative interpretation of our sputtered ion intensity data.

Equation 22 can be rewritten to eliminate the approximation concerning the dissociation constants of the molecular ions. In this form, however, in addition to the physical constants required for Equation 22, the ionization potentials of the monoxide and dioxide molecules, the partition functions of the neutral and charged states of the molecules and the observed intensities of the monoxide and dioxide ions are also required. This assumes the negative molecular ion contribution to be negligible. This modification will be tested in subsequent work where possible.

It may also be possible to achieve higher degrees of accuracy for the elements with large molecular oxide components, such as those illustrated in Figure 11, by correcting the intensity of the monoxide ion rather than that of the atomic ion as done in Equation 22. This procedure will at the very least, for those cases where the monoxide ion intensity is considerably larger than the atomic ion intensity, result in a more sensitive and statistically more precise analysis of the element concerned. It still will be required to know the physical constants necessary to Equation 22 plus the new information mentioned in the last paragraph. The increased accuracy can only be expected, therefore, if the errors noted in Figure 11 are not primarily the responsibility of the assumptions of Equation 22 but rather the result of some basic instrumental factor related to the formation of molecular ions. A possible source of such a factor may be found in the abnormally wide (several hundred electron volts) energy spread observed for the atomic ions of the elements that readily form oxide molecules. The reason for the increased energy spread is not known but appears to be related to the dissociation reaction itself. The wider than normal energy spread could be responsible for a systematic discrimination against the intensity of the atomic ions of an oxide-forming element relative to the elements that do not readily participate in oxide formation. This possible source of

error is being studied further. The wide energy acceptance of the ion microprobe mass analyzer (14) used in this study (typically ± 150 eV) undoubtedly enables us to apply the thermal model with the range of success noted. More restricted energy acceptance in the mass spectrometer will most likely lead to more restricted success of the proposed theoretical model.

CONCLUSIONS

It would appear from the results reported here that the thermal equilibrium model has some range of application as a practical procedure for converting sputtered ion intensities to atomic concentrations. As a minimum the method should be able to produce an analysis that is within a factor of two of the true concentration for almost any trace element in any solid matrix with a minimum of knowledge about the sample. This is an important capability considering the extremely small volumes of material analyzed and the difficulty of producing homogeneous external standards for microanalysis.

The model may also have applications in fundamental studies of sputtering theory and plasma physics (e.g., an approach similar to that presented here has been applied with some degree of success to the discharge created between metal electrodes with the low voltage arc (48)). Our studies have shown that the temperatures and electron densities, calculated from the experimental ion intensity data, range from about 5000 to 15000 °K and from about 1.5×10^{14} e-/cm³ at the lower temperature to about 1.5×10^{20} to 4.8×10^{21} e-/cm³ at the higher temperature under the bombardment conditions used in these analyses. This temperature and electron density range correspond to conditions resembling those of a dense arc (49). The high particle density experienced in the sputtering ion source at the surface of the solid, in fact, may be the primary factor responsible for the existence of local thermal equilibrium among the sputtering particles as required by the proposed model (50). In general the insulators attain the highest temperatures and the metals, the lowest temperatures with semiconducting materials intermediate. The results from the metal analyses also show the sputtering regions of these samples to have higher electron densities than do those of the insulators. The influence of the chemistry and bulk physical properties of the sample on temperature and electron density are being studied further. High speed accurate data acquisition will be an important aid in this investigation.

The investigative program will continue to explore the range of application of the equilibrium model. Obviously, logic dictates that a temperature gradient must exist between the hot ion-emitting sputtering region and the cold bulk of the sample. The steepness of the gradient, the areal extent of the cooler regions and their contribution to the sputtered ion yields are of interest. The large negative sputtered ion yields observed experimentally may arise from such cooler, more electron rich areas of the sputtering region. This is possibly illustrated, for example, by the cooler than normal temperature and the higher than normal electron density observed for the negative ion yields of the insulator shown in Figure 3. The influence of such a suspected cool region on molecular ion intensities must also be considered.

(48) J. Franzen and K. D. Schuy, *Proc. Intl. Conf. Phenomena Ionized Gases*, 7th, Belgrade; *Fresenius' Z. Anal. Chem.*, **225**, 295 (1967).

(49) M. Venugopalan, "Reactions Under Plasma Conditions," M. Venugopalan, Ed., Vol. 1, Wiley, New York, N.Y., 1971, p 8.

(50) H. W. Drawin, *Z. Phys.*, **228**, 99 (1969).

(47) Z. Jurela, *Radiation Effects*, **13**, 167 (1972).

Source of Analysis of Standard Materials

Sample	Source	Sample	Source
Minerals		Minerals	
1. Rhodinite, sanidine	A. Albee, California Institute of Technology	8. Amphibole, garnet	J. Stout, University of Minnesota
2. Albite	Deer <i>et al.</i> (51)	9. Cu ₂ Te	W. Wise, University of California, Santa Barbara
3. Rock glass (R&S)	Flanagan and Fleischer (52)		
4. Anorthite, olivine, orthopyroxene (camperdown)	K. Fredriksson and B. Mason Smithsonian Institution (53)		
5. Andesine, clinopyroxene, orthopyroxene (AC-362)	K. Kiel, University of New Mexico	Metals	
6. Scapolite	J. V. Smith, University of Chicago (54)	10. Brass	Applied Research Laboratories
7. Acmite, jadoite, oligoclase k-feldspar, chromite, magnetite, ilmenite	K. Snetsinger, Ames Research Center, NASA	11. Zircaloy	W. Elkington, Teledyne
		12. Monels, incopels	International Nickel Company
		13. All SRM samples	National Bureau of Standards (55)
		14. "T" stainless steel	A. P. von Rosentiel, TNO
		15. "B" low alloy steel, waspalloy, haspalloy	Source of analysis restricted

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Quantitative Analysis of Low Alloy Steels by Secondary Ion Mass Spectrometry

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Positive secondary ion currents from oxygen or argon ion bombardment of iron standards have been measured. In either case, the singly-charged monatomic ion currents I_{M^+} may increase when oxygen gas is introduced into the bombardment chamber, but both the amount of the increase and the oxygen pressure dependence can vary dramatically from one element to another in the same sample. When sufficient oxygen is present to saturate every I_{M^+} , these currents can be corrected by a simple procedure based on Andersen's approach to obtain the concentrations of most elements to within a factor of 2 of their actual values; deviations of the remaining elements are discussed and remedies proposed. The parameter T , needed for this correction procedure, is independent of primary ion current density and equals 6300 K for O_2^+ or Ar^+ bombardment at 5.5 keV in sufficient oxygen gas; this value apparently increases if only higher energy secondary ions are monitored. The meaning of this parameter and the origin of the oxygen enhancement effect are discussed.

Although the SIMS technique has strong potentialities for thin film and surface analysis, particularly with respect to its low detection limits, the major drawback is the difficulty of quantitative analysis without using external standards of similar chemical composition for establishing a calibration curve. This arises from the common observations that the ion yield from one element to another can vary by orders of magnitude, and that the ion yield of a given element can differ substantially from one compound to another (matrix effect) and be severely influenced by the chemical nature of the bombarding species (chemical effect) (1). Thus, the yield of positive secondary ions may be increased by orders of magnitude by bombarding with an electronegative gas or by merely adsorbing this gas onto the sample surface (2). Conversely, the choice of an electropositive bombarding species can dramatically increase the negative secondary ion yield (3). These effects may conspire to make the relative intensities of the singly-charged atomic ions, released by bombardment of a solid, a poor reflection of the actual composition of the solid. Further, although significant yields of multiply-charged ions are generally not observed, the presence of molecular (cluster) ions often leads to coincidences in the mass spectra, which can confound the measurements of atomic ion intensities, and may indicate that consideration of the atomic ions alone is insufficient for a quantitative analysis.

For our first investigations into these quantitative aspects, we chose an NBS low alloy steel standard (NBS 461) because it contains a large number of elements with an extended range of first ionization potentials. We have made attempts to relate the measured intensities of the positive, monatomic, singly-charged secondary ions to the known composition by means of an empirical correction procedure,

using spectra measured with various instruments, primary ion energies and current densities, bombarding species, secondary ion acceptance energies, and residual gas conditions. The conclusions thus derived were checked by measurements with other iron ingot standards (NBS 465 and 466).

PRINCIPLE OF QUANTITATIVE ANALYSIS

The ion current measured with the mass spectrometer (and corrected for isotopic abundance) I_{M^+} of positive, monatomic secondary ions M^+ of a certain element M present in a sample can be considered as the product of five parameters:

$$I_{M^+} = \eta_{M^+} \cdot I_p \cdot S \cdot c_M \cdot \beta_{M^+} \quad (1)$$

η_{M^+} is the overall instrumental efficiency (viz, the fraction of M^+ secondary ions that emerge from the sample which is actually monitored), I_p is the primary ion current and S is the sputter yield of the sample (total number of emitted particles per primary ion). From dimensional considerations, the next term should be the total number of all M -containing species emitted per unit time, n_M , divided by the total number of emitted particles per unit time, Σn . As shown in the Appendix, this ratio is the same, however, as the fractional concentration of element M present in the sample, c_M (number of atoms per unit volume divided by the maximum possible number per unit volume) even if selective sputtering should occur.

The final term, β_{M^+} , is the degree of ionization of the element, being the number of M^+ ions emitted from the sample per unit time, n_{M^+} , divided by n_M . This latter term is given by the sum of the numbers of all M -bearing species emitted (ignoring the relatively small number of multiply-charged ions),

$$n_M = n_{M^0} + n_{M^+} + n_{M^-} + n_{MM_1^0} + n_{MM_1^+} + \dots \quad (2)$$

i.e., considering the sputtering of all neutral, positive and negative monatomic, diatomic, etc. species; M_1 refers to a second element, either present in the solid or introduced by the bombardment. Thus

$$\beta_{M^+} = \frac{n_{M^+}}{n_M} = \frac{n_{M^+}}{n_{M^0}} \left(1 + \frac{n_{M^+}}{n_{M^0}} + \frac{n_{M^-}}{n_{M^0}} + \frac{n_{MM_1^0}}{n_{M^0}} + \frac{n_{MM_1^+}}{n_{M^0}} + \dots \right)^{-1} \quad (3)$$

For an initial evaluation of our data, we shall assume that

$$n_M \approx n_{M^0} \quad (4)$$

i.e., we shall consider only the first term inside the parentheses of Equation 3; the second term might become significant for easily ionizable elements or for ionic matrices, the third term for high electron affinity elements, the next terms for strong bonding between elements, etc.

Various models have been proposed for estimating β_{M^+} (4-12). We shall consider only the semi-empirical approach of Andersen (4, 5) since the values of the physical parameters

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entering into this calculation are fairly well established so as to offer the possibility of practical utilization of the method. The basic assumption is that the majority of singly-charged ions are actually generated *inside* the solid selvedge. Obviously, only a proportion, $p(M^+)$, of the total number of ions formed per unit time within the escape depth of the solid, $n'M^+$, may leave the solid without being neutralized:

$$n_{M^+} = p(M^+)n'M^+ \quad (5)$$

The escape probability of M^+ is otherwise assumed to be the same as for M^0 .

To calculate the probability of ion formation, we shall explore the use of the following expression which is similar to that utilized by Andersen and Hinthorne (4);

$$\frac{n'M^+}{n'M^0} = K \cdot \frac{Z_{M^+}(T)}{Z_{M^0}(T)} \cdot \exp(-E_M/kT) \quad (6)$$

where Z represents an internal partition function (which is a function of temperature), E_M is the first ionization potential of the element M , k is the Boltzmann constant, and T is a parameter (whose meaning will be discussed later) with the dimension of temperature (13). Use of this expression attributes variations in the secondary ion yields of the elements to differences in E_M and (to a lesser extent) in Z_{M^+}/Z_{M^0} , and allows for matrix effects through the parameter T . The proportionality constant K (which might also contain exponential terms involving kT) is assumed not to differ from one element to another; its value need not interest us here since we have not measured, and for the present purposes are not concerned with, absolute secondary ion yields. Andersen and Hinthorne (4) in fact specify a value for K by adopting the Saha-Eggert equation as the complete expression for the ion to neutral ratio; this equation pertains to equilibria of the form $M^0 \rightleftharpoons M^+ + e$ and also allows for matrix effects through an additional parameter, viz, the electron density.

Inserting Equations 3-6 into Equation 1, we arrive at

$$I_{M^+} = \eta_{M^+} \cdot I_p \cdot S \cdot c_{M^+} \cdot p(M^+) \cdot K \{Z_{M^+}(T)/Z_{M^0}(T)\} \exp(-E_M/kT) \quad (7)$$

We may write an analogous expression for the reference element R of the sample:

$$I_{R^+} = \eta_{R^+} \cdot I_p \cdot S \cdot c_{R^+} \cdot p(R^+) \cdot K \{Z_{R^+}(T)/Z_{R^0}(T)\} \exp(-E_R/kT) \quad (8)$$

To proceed further, we shall for simplicity adopt two further approximations.

1) The instrumental efficiency η_{M^+} is assumed to be element-independent. This quantity is determined in our apparatus (Cameca IMS 300) by three main factors: a) The filtering effect of the collecting optics, which depends on the initial energy and emission angle of a secondary ion. For initial energies below 1 eV, the collection efficiency is 100%, but, at higher energies, the collection is more and more restricted to ions emitted in directions nearer to the target normal. b) The energy bandpass of the mass spectrometer, which is generally limited to 20 eV to reduce peak broadening and, hence, to improve mass resolution. c) Possible mass discrimination by the spectrometer, due to transmission effects and to detection and measurement with an electron multiplier whose response in the DC mode utilized depends (14) somewhat upon the mass, energy, charge, and chemical nature of the impinging ion. In summary, we see that η can vary from one element to another, reflecting differences in atomic masses and in secondary ion energy distribution functions, but this variation will be ignored.

2) The escape probability of an ion $p(M^+)$ is also assumed to be the same for every element present in the solid. However, if neutralization is effected by Auger type transitions or by resonance tunnelling of electrons from the solid to the departing ion, then $p(M^+)$ is given (15) by $\exp(-A/av)$, where A is the transition rate at the surface, a is a characteristic distance from the surface, and v is the velocity of the ejected ion normal to the surface. This would mean that, for a given energy, lighter ions would have a greater escape probability than heavier ions. However, quantitative use of this formula would require knowledge of the energy distributions of the ions *within* the solid.

Therefore, dividing Equation 7 by Equation 8, and rearranging,

$$\frac{c_{M^+}}{c_{R^+}} = \frac{I_{M^+} \{Z_{M^0}(T)/Z_{M^+}(T)\} \exp(E_M/kT)}{I_{R^+} \{Z_{R^0}(T)/Z_{R^+}(T)\} \exp(E_R/kT)} \quad (9)$$

i.e., correction of the measured currents of singly-charged, monatomic, positive secondary ions by the amount $\{Z_{M^0}(T)/Z_{M^+}(T)\} \exp(E_M/kT)$ leads directly to relative elemental concentrations. It is our aim to test the overall validity of this equation by measuring I_{M^+} from a given standard under various bombardment conditions; a plot of $\log(I_{M^+} Z_{M^0}(T)/c_{M^+} Z_{M^+}(T))$ against E_M should then be a straight line whose slope would be determined by the parameter T . The physical constants $Z_{M^0}(T)$, $Z_{M^+}(T)$ and E_M may be found from the literature. We shall briefly recapitulate the factors which have been ignored in the derivation of Equation 9 and which may have to be considered since they may not be the same for every element in the standard; a) instrumental efficiency, b) escape probability of ions from the solid, and c) appreciable sputtered concentrations of atomic ions and polymeric species compared to atomic neutrals.

EXPERIMENTAL

The vast majority of the measurements were performed with the Cameca IMS 300 instrument (16). The primary ions used were either O_2^+ , Ar^+ or O^- . Their nominal energy at impact was 5.5 keV for the positive species and, although the normal operating mode leads to 14.5 keV for O^- , it was possible to adjust the primary ion accelerating voltage so that the latter energy could be varied between 10 and 15.2 keV. The nominal incident angle of 45° changes somewhat with the selected primary energy, leading to more normal incidence for 14.5 keV and to more glancing incidence for 5.5 keV primary ions. The maximum primary ion current density available was several mA/cm². The energy bandpass of the mass spectrometer was usually taken as 0-20 eV; increase of the upper energy limit had little effect on either the absolute or relative secondary ion currents. In addition, the position of a band of chosen width along the energy scale could be adjusted by means of the grid filter included in the instrument. The non-bakeable apparatus could be evacuated to the low 10^{-7} Torr range during bombardment. Oxygen gas could be introduced via a finely-controlled leak valve up to nominal pressures in the upper 10^{-6} Torr range; the actual pressure at the sample surface was probably somewhat higher since the gas was squirted directly onto the sample by means of a capillary tube.

Specimens were sliced from 5-mm diameter rods, polished and sputter-cleaned to remove polishing contaminants. Their compositions (atomic %), as determined by chemical and chemical spectrographic analysis, are shown in Table I. The secondary ion currents, measured by a dedicated computer (Philips P 9205) with 500 s sweeps of the 0-250 mass range, were corrected for isotopic abundances.

Mass number 28 was exclusively assigned to silicon, although this could not be confirmed at the higher residual oxygen pressures because of molecular ion contributions to masses 29 and 30. A sulfur analysis was not attempted because of coincidence with $^{32}O_2^+$. The slight contributions of $^{54}Fe^{13}H^+$ were distinguished from those of $^{55}Mn^+$ using known isotopic abundances; mass number 60 was used for nickel to separate this element from ^{60}Fe . Cu^+ was recorded after allowances for $^{47}Ti^{16}O^+$ had been made. The germanium

Table I. Composition of Spectrographic Iron Standards in Atomic Percent as Quoted by NBS

Element	461	465	466
B	~0.001	~0.0005	~0.001
C	0.69	0.17	0.30
O	0.07	0.01	0.002
Al	0.01	0.39	0.03
Si	0.093	0.057	0.050
P	0.095	0.01	0.022
S	0.04	0.02	0.02
Ti	0.01	0.23	0.066
V	0.026	0.002	0.008
Cr	0.14	0.004	0.012
Mn	0.36	0.032	0.11
Fe	96.06	99.01	99.23
Ni	1.64	0.025	0.048
Co	0.25	0.008	0.043
Cu	0.30	0.017	0.029
Ge	0.001	0.003	0.0023
As	0.021	0.0074	0.010
Zr	<0.003	0.001	<0.003
Nb	0.0066	0.0006	0.003
Mo	0.17	0.003	0.0064
Ag	0.0008	0.0001	0.0002
Sn	0.010	0.0005	0.002
Ta	0.0006	0.0003	0.0006
W	0.0036	0.0003	0.0018
Pb	0.0008	<0.0001	0.0003

and arsenic signals were masked by those from the oxides, hydroxides, etc. of (mainly) iron. Detection of zirconium was prevented by the predominance of $^{56}\text{Fe}^{16}\text{O}_2^+\text{H}_2^+$ at high oxygen concentrations. The small $^{93}\text{Nb}^+$ current was swamped by $^{56}\text{Fe}^{37}\text{Cl}^+$, arising from the Cl^- impurity present in the primary ion beam when using O^- bombardment. Molecular ions such as $^{56}\text{Fe}^{51}\text{V}^+$, $^{91}\text{Zr}^{16}\text{O}^+$ and $^{93}\text{Nb}^{16}\text{O}^+$ prevented monitoring of either isotope of silver. The trace amounts of tantalum and tungsten could not be detected in the positive secondary ion spectrum owing to coincidences with the Fe_2 oxides and their hydrides; however, these elements were clearly distinguishable in the negative ion spectra, occurring mainly as the MO_2^- ions, as previously noted (17). Isotopes 120 and 208 were tentatively assigned to tin and lead respectively, although the intensities of the remaining isotopes did not concur. The secondary ion currents quoted for these elements should therefore be regarded as upper limits.

RESULTS

One novel result from these studies should especially be borne in mind for what follows; not only the absolute but also the relative secondary M^+ ion currents from iron standards can be influenced drastically by the amount of oxygen available. Hence, as will be shown, it is this latter physical parameter which essentially determines the success or failure of an analysis based on Equation 9. Results with NBS 461 will be considered first.

Data will initially be presented in graphical form showing the logarithm of the reduced ion currents, $I_{\text{M}^+}\text{Z}_{\text{M}^0}(T)/C_{\text{M}}\text{Z}_{\text{M}^0}(T)$, in arbitrary units vs. E_{M} in eV; values of the latter parameter were taken from the tables published by Moore (18). The internal partition functions used were those of de Galan et al. (19) which extend to 7000 K; the partition function ratios for the atom and ion of those elements of interest do not in fact vary widely in this temperature range.

Ar⁺ Bombardment in Vacuum. Figure 1 shows that the majority of the reduced ion currents from Ar⁺ bombardment at a high current density of 1.4 mA cm⁻² in vacuum do not lie on a unique straight line. Reduction of the bombardment current density increased somewhat the oxygen surface content through residual gas adsorption, as indicated by the enhanced O^+ signal relative to, e.g., Fe^+ or Al^+ . The most noticeable effect was the relative increases in the V^+ , Cr^+ , and Nb^+ points.

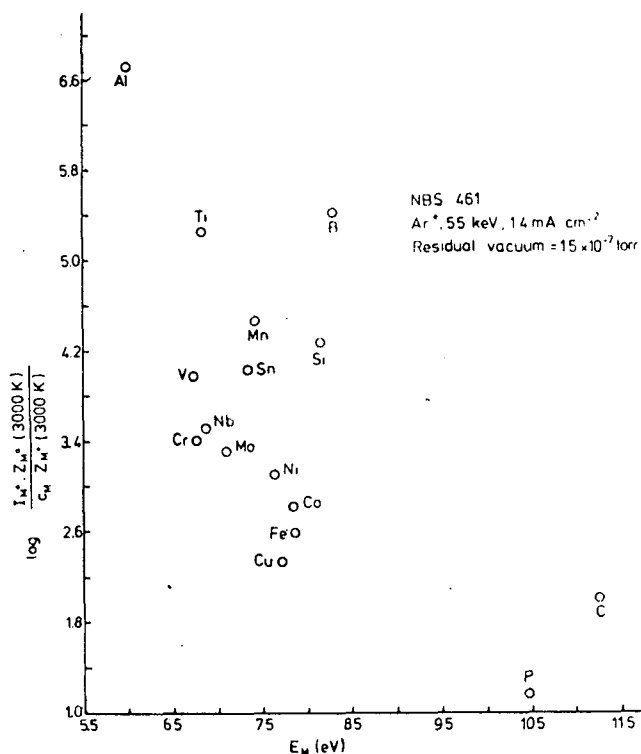


Figure 1. Plot of reduced ion currents $\log(I_{\text{M}^+}\text{Z}_{\text{M}^0}/C_{\text{M}}\text{Z}_{\text{M}^0})$ in arbitrary units vs. E_{M} (eV) for Ar^+ bombardment of NBS 461 in vacuum. The partition function ratios at 3000 K have been used

Measurements were also performed with UHV instruments utilizing quadrupole mass spectrometers with energy filtration, viz., the apparatus from Balzers with bombardment at 600 eV (0.004 mA cm⁻²) and 3 keV (0.04 mA cm⁻²), and from Atomika using 3 keV (0.03 mA cm⁻²), 10 keV (0.4 mA cm⁻²) and 13.5 keV (0.6 mA cm⁻²) bombardment. Apart from any current density influences as described above, all the resulting plots resembled Figure 1. The secondary ion currents from the Balzers equipment were approximately corrected for mass effects by multiplying by the mass number (20) since the quadrupole was not operated in the mass-independent transmission mode.

The apparent conclusion from Figure 1 that Equation 6 is not applicable to bombardment with Ar^+ primary ions cannot be drawn since, as will be demonstrated later, there is already enough oxygen present to influence some secondary ion current ratios. The successful analysis reported (21) for Ar^+ bombardment of a steel standard might well result from the limited number of elements (mainly the transition metals) considered.

O_2^+ Bombardment in Vacuum. We turn now to bombardment with O_2^+ ions, again in vacuum, and see (Figure 2) that an apparent better fit of the data to a straight line results. However, the secondary ion currents from B, Mn, Si, P, and C appear far too high while those for Mo, Nb, and Cu appear low. The last result can probably be attributed to a tenacious bonding of copper to iron, resulting in an appreciable concentration of sputtered FeCu^0 , since the observed intensity of the FeCu^+ signal was 2.4 times that of Cu^+ ; the remaining FeM^+ ions (including Fe_2^+) were less intense than the corresponding M^+ ion.

The slope of the line depended upon the oxygen surface content and varied between 2800 and 3600 K, the higher values being associated with increased oxygen content. This quantity was indicated by the O^+ to Al^+ ratio, the latter current being used for reference since it did not depend critically on oxygen content (see later). As discussed in a recent review (22), the amount of implanted oxygen does

not depend upon the primary ion current density since it is given by the reciprocal of the sputter yield (23). However, the concentration of oxygen in the surface region also depends upon the value of the residual gas pressure in relation to the primary ion current density. An increase of the latter diminishes residual gas adsorption due to the increased sputter rate.

Ar⁺ or O₂⁺ Bombardment in O₂. A dramatic increase in the Fe⁺ signal was effected by introducing oxygen gas while bombarding with either Ar⁺ or O₂⁺, Figure 3. The signal rises sharply, reaching a more or less saturated value at a given pressure. This pressure is lower, the lower the O₂⁺ current density (22) (or is lower for O₂⁺ than for Ar⁺ bombardment at the same current density). If the primary ion current density is too high, then Fe⁺ saturation is not achieved since the amount of oxygen gas that can be introduced is restricted. Note that the shape of the curve with Ar⁺ bombardment suggests that a further decrease in I_{Fe^+} would result if the residual vacuum could be improved to below 2×10^{-7} Torr.

Not all of the elements behave in the same way as iron, as is shown in Figure 4 (similar results were found with O₂⁺ bombardment). The secondary ion currents of most elements are increased by oxygen bleed-in, some by substantial amounts. However, for certain elements such as Al and Ti, the secondary ion currents even decrease slightly upon oxygen introduction; it is well known (2) that the secondary ion yields from Ar⁺ bombardment of these pure elements are significantly enhanced by the presence of oxygen. Thus, in a residual vacuum of 2×10^{-7} Torr, there is apparently enough oxygen available to guarantee saturation of the secondary ion currents from some elements. This oxygen could arise from residual gas adsorption, from impurities present in the primary Ar⁺ beam, and/or from the original oxygen content of the sample.

We thus see that the amount of oxygen required to saturate an M⁺ signal can vary from one element to another in the same sample, i.e., oxygen is preferentially attracted to those elements with high oxygen affinity and these elements require relatively lower pressures of oxygen for maximum enhancement of M⁺ currents. Also, by and large, less oxygen is required for saturation, the smaller the concentration of a particular element.

As the oxygen pressure increases, the apparent value of the parameter T increases. Figure 5, for instance, shows the plot derived from the data presented in Figure 4, at an intermediate oxygen pressure of 1×10^{-6} Torr. We should therefore be wary of any so-called temperatures reported from analyses of steel standards unless the oxygen content is also carefully controlled and specified.

Analysis with All M⁺ Signals Saturated. The best results were obtained by ensuring that at least enough oxygen was present so that the Fe⁺ signal (and hence those of the other metals) was more or less saturated. To achieve this condition, a certain loss in overall sensitivity had to be tolerated since it was not possible to utilize the maximum available bombardment currents on account of the restricted amount of oxygen gas that could be introduced (22). The results described in the following will pertain to this situation of saturated secondary ion currents.

Figure 6 illustrates the type of result found, which was independent of the primary ion current density and of whether the bombarding species was O₂⁺ or Ar⁺. A value from all analyses lying in the range of 6300 ± 200 K was found for the parameter T . The apparent high value for boron can perhaps be disregarded since the concentration of this element is given only approximately (see Table I), and, for both the iron ingot standards, the boron result fit-

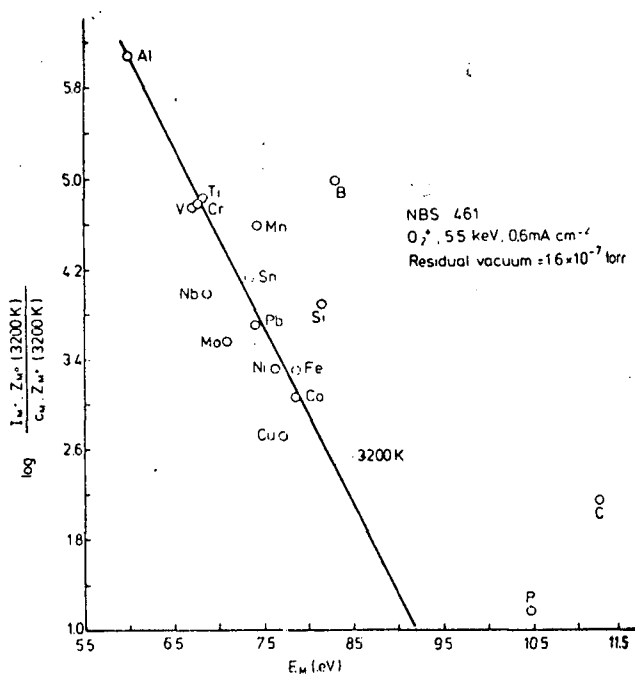


Figure 2. Plot of $\log(I_M + Z_M^0 / C_M Z_M^+)$ vs. E_M (eV) for O₂⁺ bombardment of NBS 461 in vacuum

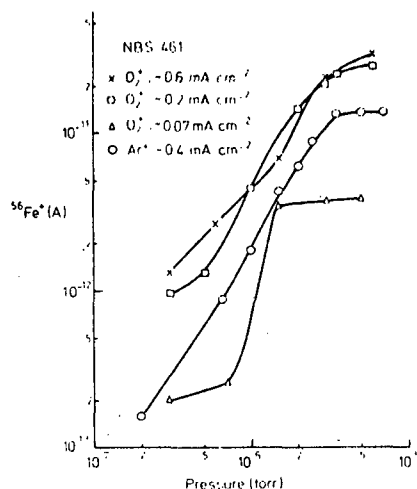


Figure 3. Increase of ⁵⁶Fe⁺ secondary ion current with residual pressure, when bleeding oxygen into the target chamber

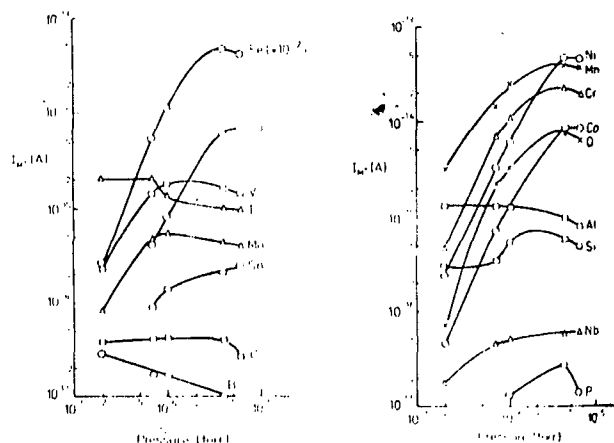


Figure 4. Effect of oxygen gas bleed-in on the secondary ion currents from NBS 461 when bombarding with Ar⁺, 5.5 keV, 0.1 mA cm⁻²

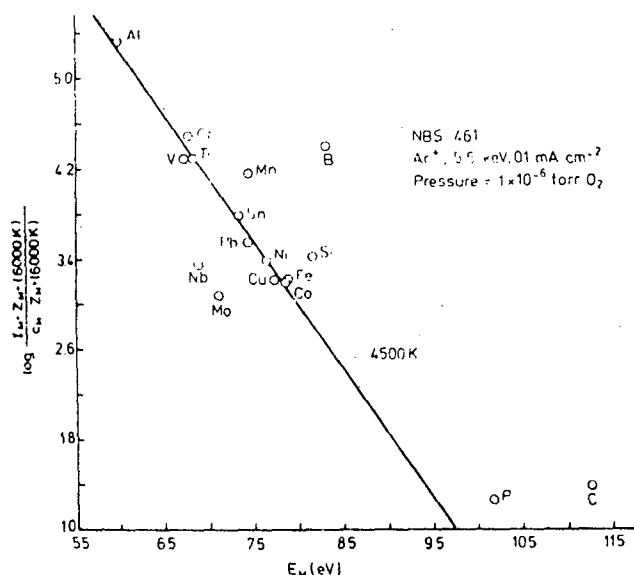


Figure 5. Plot of $\log(I_{M^+} Z_{M^+} / C_M Z_{M^+})$ vs. E_M for Ar^+ bombardment of NBS 461 in a pressure of 1×10^{-6} Torr oxygen

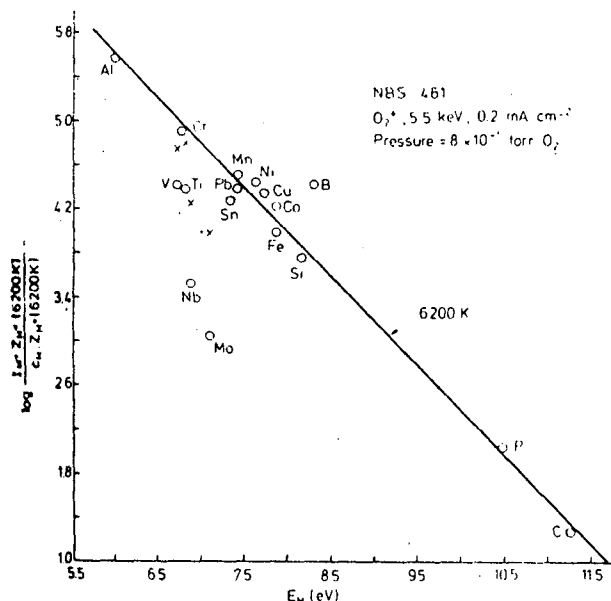


Figure 6. Plot of $\log(I_{M^+} Z_{M^+} / C_M Z_{M^+})$ vs. E_M when sufficient oxygen had been introduced to ensure that all secondary ion currents were saturated. Crosses are the results from 4 elements (V, Ti, Nb, Mo) when I_{MO^+} is added to I_{M^+}

led the straight line exactly. The reduced ion currents from all the remaining elements lie to within a factor of 2 (which will be considered as a satisfactory criterion for semi-analytical purposes) on a linear plot, except for V, Ti, Nb, and Mo whose measured ion currents are far too small. Why these four elements diverge and proposed remedies for analytical purposes will now be discussed.

One possible reason is suggested from an examination of Figure 7(a), which shows how the intensities of selected cluster ions change with oxygen pressure concurrently with the data given in Figure 4. The intensity increase of an MO^+ ion is even more than that of the corresponding M^+ ion when the oxygen pressure is raised. (This probably accounts for the slight decrease in an M^+ current, Figure 4, with further increase of the oxygen pressure above that required for saturation.) Further, the very elements that deviate from the linear plot have monoxide ion currents which are comparable to, or even greater than, the corre-

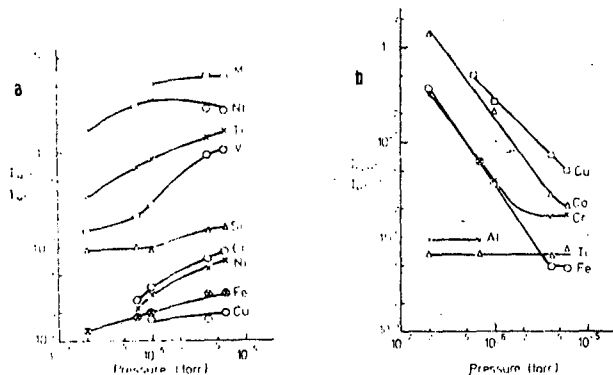


Figure 7. Variation of secondary ion currents of (a) MO^+ and (b) FeM^+ clusters relative to I_{M^+} caused by oxygen gas bleed-in during Ar^+ bombardment of NBS 461 at 5.5 keV and 0.1 mA cm^{-2}

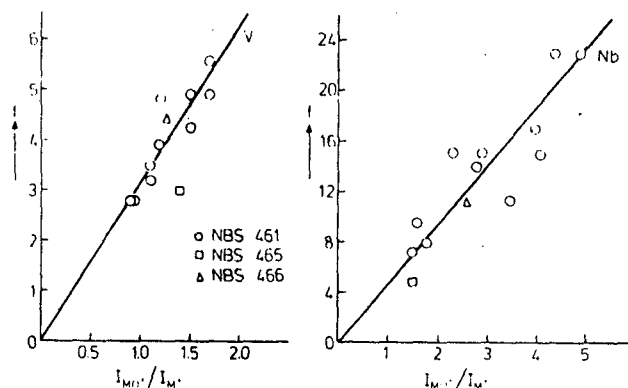


Figure 8. Fudge factor f (i.e., true concentration/measured concentration from Equation 9 with T between 6100 and 6500 K) for vanadium and niobium as a function of measured I_{MO^+} to I_{M^+} ratio; O_2^+ or Ar^+ primary ions at 5.5 keV with Cameca instrument accepting 0–20 eV secondary ions

sponding monatomic ion currents at those oxygen pressures required to saturate the latter currents. Figure 7(b) illustrates that, at these oxygen pressures, the fractional currents of the diatomic ions formed between iron and each of the elements (including the Fe_2^+ cluster) are very small. This is not necessarily true in the residual vacuum of 2×10^{-7} Torr for those elements found to have a low oxygen affinity. The absolute FeM^+ currents are in fact fairly insensitive to oxygen pressure.

For a given element, there appears to be a direct relationship between the measured I_{MO^+} to I_{M^+} ratio and the extent to which the reduced M^+ current appears too low relative to the majority of the elements (5), i.e., the fudge factor f by which a concentration derived from I_{M^+} via Equation 9 must be multiplied to obtain the true concentration. Figure 8 illustrates this for V and Nb where slopes of 3.1 and 4.7 are found, respectively, from measurements (with saturated signals) with O_2^+ or Ar^+ at various current densities and residual pressures of oxygen; the corresponding slopes for Ti and Mo were about 2 and 6, respectively. Peaks at mass numbers 67 and 109 were exclusively assigned to VO and NbO, respectively, although isotopic ratio checks are not available. The same minimum value for MoO^+ was obtained from masses 111 and 113, once corrections for Fe_2^+ had been made. If the oxygen pressure was much in excess of that required to saturate the ion currents, then first SiO^+ , and then CrO^+ , became relatively more significant (see Figure 7(a)), and the analyses for these elements also deteriorated somewhat. Therefore, an optimal overall analysis will be obtained by using the lowest oxygen pressure needed to saturate the secondary ion currents.

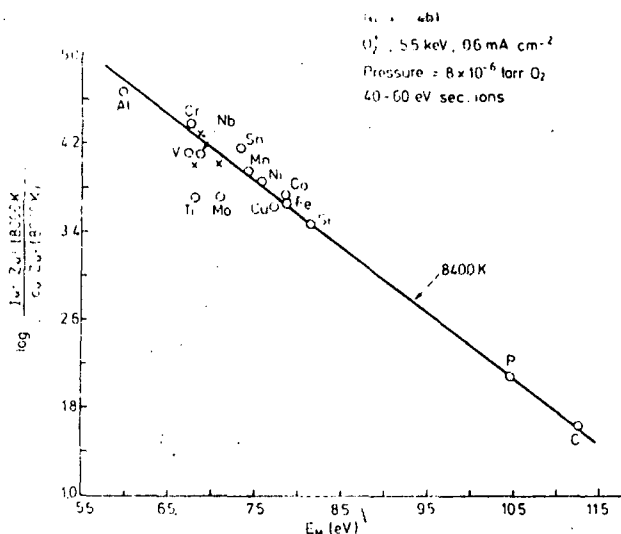


Figure 9. Plot of $\log(I_{M^+} Z_{M^0} / C_M Z_{M^+})$ vs. E_M for saturated signal condition when only those secondary ions with energies between 40 and 60 eV are monitored; crosses result when I_{MO^+} is included in the measurements

We have seen that by using calibration curves such as shown in Figure 8 in conjunction with measured I_{MO^+} to I_{M^+} ratios, it may be possible to analyze satisfactorily any "oxide elements". We shall now consider three alternative possibilities:

1) The MO^+ ions might arise exclusively from ionization of neutral monoxides. It has been our experience that an appreciable MO^+ signal generally correlates with a relatively low first ionization potential E_{MO} of the oxide. An intense MO^+ signal might indicate a significant concentration of MO^0 and, following Ref. (4) and (5), the 4th term in the parentheses in Equation 3 might have to be considered also (i.e., the approximation $n_M = n_{M^0}$ must be replaced by $n_M \approx n_{M^0} + n_{MO^0}$), in which case:

$$f = \left(1 + \frac{n_{MO^0}}{n_{M^0}}\right) \quad (10)$$

and, using Equation 6,

$$f - 1 = \left[\frac{Z_{M^+} \cdot Z_{MO^0}}{Z_{M^0} \cdot Z_{MO^+}} \right] \exp\left(\frac{E_{MO} - E_M}{kT}\right) \cdot \frac{I_{MO^+}}{I_{M^+}} \quad (11)$$

We are forced to ignore the partition-function term since Z_{MO^+} is unknown; also, E_{MO} is given in the literature for only a few of the elements (24, 25). Setting $T = 6200$ K for the experimental situation relevant to Figure 6, then the f values for Mo and Ti calculated from Equation 11 are 42 and 1.7, respectively, which are in good agreement with the values of 47 and 3.5 derived from Figure 6. However, Equation 11 leads to f values of 3.4, 16, and 1.9, respectively for Cr, Si, and Ni (the only other elements for which the data are available for calculation) which are not in accordance with Figure 6.

2) Alternatively, the deliberate build-up of appreciable concentrations of surface oxygen could mean that an MO^+ ion results mainly from the combination of an M^+ ion with a neutral oxygen atom present at the solid-vacuum interface. Then f would be simply equal to $1 + (I_{MO^+}/I_{M^+})$. We have tried this approach in Figure 6 by replacing I_{M^+} by $(I_{M^+} + I_{MO^+})$ for those elements with appreciable monoxide ion currents, and the results are shown as crosses. The analysis would now be satisfactory for V and Ti but, although improved substantially, still inadequate for Nb and Mo. However, it is obvious that this simple approach is better than nothing.

3) Another method found to improve the analysis for V, Nb, and Mo is to adjust the energy window of the mass spectrometer so that only relatively higher energy secondary ions are monitored. For O_2^+ or Ar^+ bombardment in oxygen (i.e., the type of analytical situation depicted in Figure 6) where acceptance of 0-20 eV secondary ions leads to a T value of 6300 K, alteration of the window to 20-40 eV improved the analysis somewhat for V, Nb, and Mo, while B and Ti remained the same. For Ar^+ bombardment, T had apparently increased to 7600 ± 500 K while remaining unaltered for O_2^+ . A good analysis for V and Nb resulted from the use of 40-60 eV secondary ions as can be seen from Figure 9 (partition functions extracted where possible from Ref. (26)). The analysis for Mo is much improved also, and becomes satisfactory with the $(I_{M^+} + I_{MO^+})$ oxide correction. The measured T value of 8400 ± 500 K is now comparable with the value of 8600 ± 500 K measured from Ar^+ bombardment. These results could imply that the high energy tailing in the energy distributions of Nb^+ , Mo^+ , and, to a lesser extent, V^+ secondary ions is more pronounced than for the other M^+ ions, and, hence, discrimination against higher energy secondary ions by the mass spectrometer collecting optics might also contribute to the measurement of relatively low M^+ currents for these elements (4). Alternatively, the results could simply mean that relatively fewer low energy ions of these elements are in fact generated, MO^+ ions being produced instead.

To check that our results are not confined to one type of instrument, measurements were also performed with other equipment. Remarkably similar plots to Figure 6 were obtained with data from both the Balzers equipment (Ar^+ , 3 keV, 0.05 mA cm^{-2} , 10^{-5} Torr O_2 , $T = 5900 \pm 100$ K, and corrections made for transmission effects) and that from Applied Research Labs (O_2^+ , 18.5 keV, several mA cm^{-2} , 0-150 eV secondary ions, no O_2 bleed-in, $T = 5600 \pm 100$ K). The reduced ion currents lay even closer to a straight line fit, except for B, V, Ti, Nb, and Mo which diverged from the line by comparable amounts to those found with the Cameca instrument. The ARL result is particularly interesting since the measurements were performed without deliberately introducing oxygen into the target chamber. However, the fact that a linear plot resulted, and that the O^+ signal relative to Fe^+ or Al^+ was similar to that found with the Cameca instrument under saturation conditions, suggests that (almost) enough oxygen had been brought into the sample. Presumably residual gas adsorption is responsible, a sufficient partial pressure of oxygen perhaps arising by leakage from the primary ion source into the target chamber. The lower T value might be due to the increased bombardment energy (5) or to slightly incomplete saturation of the secondary ion currents.

To investigate any influence of primary ion energy on the results, we undertook studies with our Cameca instrument using O^- bombardment since higher primary energies (similar results were obtained when using either 10 or 15 keV) could be utilized. Without deliberately introducing oxygen gas, results similar to those shown in Figure 2 were obtained even when using the highest current densities available (several mA cm^{-2}). By bleeding in enough oxygen, plots similar to Figure 6 were found with, if anything, slightly lower values for T lying in the range of 5800 ± 200 K. Somewhat different relationships between f and I_{MO^+}/I_{M^+} from those shown in Figure 8 were found; increased slopes resulted for V and Mo while a decrease was found for Ti (it was not possible to monitor Nb^+).

Results of the Analyses. The results for NBS 461 are finally summarized and presented in Table II. The quantity

Table II Ratios of Derived to Actual Concentrations of Elements in NBS 461 Using Fe as Reference Element: Concentrations Are Derived from I_{M^+} ^a

(1) Element	(2) From I_{M^+} using Ar^+ in vacuum	(3) From I_{M^+} using O_2^+ in vacuum	(4) From saturated I_{M^+}	(5) Col. 4 $\times \exp((E_M - E_{Fe})/kT)$	(6) Col. 5 $\times (Z_{Mo}/Z_{M^+})/$ (Z_{Fe}/Z_{Fe^+})
Li	~73	~6	~0.3	~0.6	~6
C	0.11	~0.02	0.0009	0.46	1.1
Al	1500	59	3.9	0.12	1.1
Si	19	1.6	0.20	0.34	0.86
	0.046	0.009	0.0071	0.86	0.68
Ti	750	68	3.2	0.46	0.41
	(1000)	(110)	(9.3)	(1.3)	(1.2)
V	14	26	1.5	0.19	0.31
	(15)	(29)	(3.4)	(0.43)	(0.72)
Cr	3.4	17	3.3	0.43	1.0
Mn	56	13	3.1	1.4	1.8
Fe	1	1	1	1	1
Ni	0.67	0.28	0.67	0.44	1.1
Co	0.92	0.50	0.91	0.89	1.5
Cu	0.18	0.12	0.63	0.49	1.7
Nb	7.9	3.6	0.31	0.049	0.090
	(21)	(18)	(1.3)	(0.20)	(0.37)
Mo	2.9	1.3	0.069	0.017	0.036
		(8.6)	(0.50)	(0.12)	(0.26)
Sn	13	3.5	0.85	0.32	0.81
Pb	...	2.9	2.0	0.88	1.2

^a Col. 2. Measured with Ar^+ , 5.5 keV, 1.4 mA cm⁻², vacuum of 1.5×10^{-7} Torr. Col. 3. Measured with O_2^+ , 5.5 keV, 3 mA cm⁻², 2×10^{-7} Torr. Col. 4. Averaged from 8 measurements with Ar^+ and O_2^+ in enough O_2 to obtain saturated values. Col. 5. Using values of col. 4) multiplied by $\exp((E_M - E_{Fe})/kT)$ with $T = 6300$ K. Col. 6. Using values of col. 4 in Equation 9 with $T = 6300$ K. Values in parentheses refer to use of $(I_{Mo} + I_{M^+})$ in place of I_{M^+} .

shown is the ratio of the derived concentration of a particular element c'_M , with Fe chosen as the reference element, to its actual concentration c_M (given in Table I). For columns 2-4, c'_M was obtained by using the measured ion currents alone, i.e., $c'_M = I_{M^+}/(I_{Fe^+} \cdot c_{Fe})$, the quantity $(I_{M^+}/c_{Fe})/(I_{Fe^+}/c_{Fe})$ (which is usually derived from a calibration curve) is commonly termed the relative sensitivity factor of the component M. Obviously if all of these factors would be equal to unity, a standardless analysis would be possible. Columns 2 and 3 list typical results found from Ar^+ and O_2^+ bombardment in vacuum (energy window of the mass spectrometer is 0 to 20 eV); the bracketed values for certain elements were obtained by including the MO^+ contributions. As can be seen, the derived concentrations (i.e., the magnitudes of the measured secondary ion currents) in general are not closely related to the actual sample composition. These values, being sensitive to oxygen content, will fluctuate somewhat, depending on the primary ion current density and residual gas pressure. However, column 4 shows that the saturated secondary ion currents (except for C and P) already give quite a good indication of the specimen composition. This implies that certain elements in iron matrices can be analyzed straightforwardly from saturated ion currents without the need of standards or of correction procedures.

Use of the full correction procedure however will improve an overall analysis, column 6; here c'_M was calculated from Equation 9, i.e., the saturated ion currents are multiplied by the terms $\{Z_{Mo}(T)/Z_{M^+}(T)\}$ and $\exp(E_M/kT)$ with T taken as 6300 K. For the majority of the components, inclusion of the partition function term is beneficial (cf. column 6 with column 5). It should be remembered that the results for Sn and Pb are provisional due to the tentative assignments of the mass peaks.

Reported analyses (27-29) of other low alloy steels using the Hitachi equipment (O_2^+ , 7 keV, 0.5 mA cm⁻², vacuum 1×10^{-6} Torr during bombardment) provide interesting

comparisons. A pressure of $\sim 5 \times 10^{-5}$ Torr was introduced (28) to maximize the secondary ion currents; however, the absolute currents were found to increase only a few times (no trace element analyses were attempted). Also, although the measured relative sensitivity factors change upon oxygen introduction in the same direction as we find for NBS 461 (cf., Figure 3 of Ref. (28) with columns 3 and 4 of our Table II), their changes are much less. These observations suggest that, as in the ARL equipment, residual gas adsorption under bombardment in vacuum is perhaps sufficient to maintain a high oxygen content in the sample. The Hitachi relative sensitivity factors at saturation are similar to ours, again demonstrating instrument independence and indicating that our correction procedure would again work satisfactorily. However, it would be difficult to determine a very accurate T value from their data since their relative sensitivity factors and E_M values (6.74 to 7.87 eV) only extend over a limited range (cf., our Figure 6). The quoted temperatures of 6000-7000 K have been derived from a correction procedure (27) using the approximation $n_M = n_{Mo} + n_{M^+}$.

In conclusion, the analytical results for the iron ingot standards are shown in Table III. Only the main divergences from NBS 461 will be mentioned. The boron results are in better agreement with the known (but also approximate) concentrations. The SiO^+ current relative to Si^+ is more appreciable, especially for NBS 465. The molybdenum reading is derived from $^{92}Mo^+$; interferences prevented a reasonable estimate of MoO^+ . Isotope 118 was used for Sn with NBS 465; however, for 466, the correct isotopic ratio was found at mass numbers 118 and 120 and, therefore, the Sn result is more definitive.

The relative sensitivity factors for NBS 465 alone were also measured in vacuum. Typical results for Ar^+ bombardment (1.8 mA cm⁻², 2×10^{-7} Torr) were 18 (Al), 43 (Ti), 20 (V), 2.5 (Mn), 1.7 (Co), and 14 (Ni). (The first four elements and iron now appeared to fit a linear plot of 3800 K

Table III. Ratios of Derived to Actual Concentrations of Elements in NBS 465 and 466 Using Fe as Reference Element^a

Element	NBS 465		NBS 466	
	(1) From saturated I_{M^+}	(2) From Eq. 9	(1) From saturated I_{M^+}	(2) From Eq. 9
B	~0.06	~1.2	~0.06	~1.1
C	0.00083	1.0	0.00099	1.2
Al	4.1	1.1	3.9	1.1
Si	0.14	0.60	0.15	0.64
	(0.25)	(1.1)	(0.19)	(0.81)
P	0.017	1.6	0.016	1.5
Ti	3.2	0.42	3.1	0.41
	(6.9)	(0.91)	(6.9)	(0.91)
V	2.2	0.46	1.1	0.23
	(5.2)	(1.1)	(2.5)	(0.52)
Cr	2.6	0.79	3.0	0.91
Mn	2.9	1.7	2.5	1.4
Fe	1	1	1	1
Co	1.2	2.0	1.2	2.0
Ni	0.81	2.0	0.61	1.5
Cu	...	...	0.50	1.4
Nb	0.86	0.25	0.31	0.091
	(2.1)	(0.62)	(1.1)	(0.32)
Mo	0.21	0.11	0.16	0.084
Sn	2.2?	2.1?	0.64	0.61
Pb	...	...	1.2	0.71

^a Col. 1. For each standard, concentrations are derived from saturated I_{M^+} measured for O_2^+ bombardment at 5.5 keV and 0.6 mA cm⁻² in 8×10^{-6} Torr oxygen. Col. 2. For each standard, concentrations are derived using these I_{M^+} values in Equation 9 with $T = 6300$ K. Parentheses refer to consideration of ($I_{MO^+} + I_{M^+}$).

slope). Comparing these values with those obtained with NBS 461 (column 2, Table II), it can be seen that, apart from Mn, an increase in the concentration of a given element results in a decreased relative sensitivity factor and vice versa. Thus, these factors for Ar^+ bombardment in vacuum not only vary widely from one element to another, but also depend critically upon the actual concentration of a given element (i.e., in relation to the oxygen content of the sample). This observation may help to explain the different results found with Ar^+ bombardment of steel samples (30).

DISCUSSION

Our experimental results suggest the feasibility of semi-quantitative analyses by means of SIMS. The physical processes, however, leading to the emission of secondary ions are not yet completely understood. We shall attempt in this discussion to indicate the trend of our thoughts in this direction.

When an ion of several keV energy impinges on a target surface and subsequently penetrates into the solid, a "collision cascade" is initiated (31) which, depending on the impact parameters, may extend over an approximately spherical region of about 100 Å in diameter. Within this volume, the projectile loses its kinetic energy by a series of collisions with the target atoms. These (recoil) atoms in turn transfer energy to other target atoms, displacing them also from their lattice positions etc., giving rise to several generations of collision branches. When such a branch intercepts the surface, an atom in the vicinity of the surface may have enough momentum in a suitable direction so as to be ejected from the target. This phenomenon is termed sputtering.

The average lifetime of a cascade (32) is much smaller (13) than the time between arrival of primary ions at that part of the surface disturbed by the cascade, even when using primary current densities of up to several mA cm⁻². Therefore, on the average, there is no overlapping of the cascade generated by one primary ion with that generated

by another (unless molecular ions are used for bombardment when closely-spaced cascades may result (33, 34)). The non-dependence of our results upon the primary ion current density (provided secondary ion currents are saturated with respect to oxygen), as already predicted (13), is in general agreement with this notion of individual cascades.

Each primary ion then is responsible for one individual, non-overlapping cascade. Not every cascade leads to the ejection of one or more sputtered particles, even fewer to the ejection of an ion. Further, very few atoms within an individual cascade are involved directly in particle ejection. From probability considerations alone, a sputtered particle has most likely been released by a collision with a matrix or an implanted projectile atom; with enough oxygen present, the collision partner in the ion formation process might be an oxygen atom.

If an atom near the target surface has received enough energy to overcome its binding energy E_B , then it may leave the target as a sputtered neutral. To generate a sputtered ion, additional energy must be available for ionization also, which will be related to the ionization potential E_M . The mechanism of this energy transfer is not known. The energy available for ion formation will vary from one cascade to another. Let E_C be the average energy available per individual cascade. The value of E_C which would be derived from SIMS measurements is in fact a statistical average in time and space across the individual cascades.

The degree of ionization β_{M^+} should thus be determined by E_C , E_M and perhaps E_B . The experimental results of Andersen (4) and our results (see also Ref. (13)) indicate an apparent exponential relationship of the form $\beta_{M^+} \propto [Z_{M^+}/Z_{M^0}] \exp(-E_M/E_C)$. The exponential term, the Boltzmann factor, relates the number of ions to neutrals if the average energy available for ionization is E_C and the ionization energy (energy difference between ground states of atom and ion) is E_M . The partition function ratio, Z_{M^+}/Z_{M^0} , (introduced by Andersen (4) through use of the Saha

Eggert equation) corrects for the different degeneracies of these states and allows for electronic transitions from excited atom levels to excited ion levels (35). An atom in the collision cascade volume might well be in an excited state before being struck by the ionizing recoil.

We can apparently ignore the quantity E_B . However, this parameter may make its presence felt (36) in determining the shape of the secondary ion energy distribution curves (as in the case of sputtered neutrals (31, 37)). A larger value of E_B for a particular element would then lead to relatively more higher energy ions.

Our results with various energy windows in the mass spectrometer indicate that the higher kinetic energy secondary ions are associated with higher E_C (or T) values. Also, E_C might well decrease with increasing primary ion energy (as reported by Andersen (5) and suggested by our results) since greater penetration depths might mean less energy loss in the target surface region and, hence, less average energy available for ionization. We have ascribed this energy E_C to individual cascades, rather than to the (ionization (13)) temperature (i.e., $E_C \propto kT$) of the complete bombarded region pictured as a plasma in local thermodynamic equilibrium. In either case, this quantity can be expected to be matrix-dependent and it was the pioneering work of Andersen (4, 5) which drew attention to this fact by revealing different values for different matrices.

Without oxygen present, it is apparently rather difficult to transfer enough energy for appreciable M^+ emission to occur. Our results have indicated that when oxygen is available, what is essential for the ionization process is not so much the total amount of oxygen present in the matrix but rather that this oxygen is in the immediate vicinity of the element to be ejected as an ion; with a limited concentration of oxygen, we have found preferential saturated enhancement of the secondary ion currents of certain elements in iron matrices (i.e., those with high oxygen affinity and/or weak bonding to Fe). The cause of this enhancement (chemical) effect cannot be due to any increase in the work function of the bombarded surface (and, hence, to a reduced probability of neutralization of the outgoing ion by electrons surmounting the surface potential barrier (38)) since any work function changes should affect all secondary ion currents equally. Also, this effect is difficult to envisage (15, 39) as an alteration of the (local) band structure of the bombarded solid, so as to inhibit the neutralization of the departing ion by resonance tunnelling of electrons from the solid. Since the preferential attraction of oxygen to certain components presumably implies that the (adsorbed) oxygen is initially bonded directly to that element, the ionization mechanism could be pictured in bond-breaking terms (2), $MO^0 \rightarrow M^+ + O^-$; i.e., to release an M^+ ion from the solid, M-O bonds must be ruptured rather than M-matrix element bonds, and the increased ionicity of the former leads due to electronegativity differences to enhanced ionization probabilities.

We wish, however, to consider other explanations for the chemical effect by postulating that immediately prior to ionization, an atom is not necessarily bound to oxygen, i.e., dissociation has already occurred, $MO^0 \rightarrow M^0 + O^0$. The ionization process then takes place essentially as in the absence of oxygen, $M^0 \rightarrow M^+ + e^-$. However, the nearby oxygen combines with the electron, $O^0 + e^- \rightarrow O^-$, preventing its recombination with the M^+ ion and thereby increasing the ion yield (13). This could be treated quantitatively using Andersen's formalism (1) as a change in the electron density, n_e , since the proportionality constant K of Equation 6 contains both $(n_e)^{-1}$ and an exponential term (ionization potential depression) involving $(n_e)^{1/2}$.

A more attractive description is that oxygen itself is di-

rectly involved in the collision process leading to the ionization of a nearby atom, i.e., $M^0 + O^0 \rightarrow M^+ + O^-$. The energy needed for this process is thus reduced by the electron affinity E_a of the oxygen atom, and the ionization potential is effectively decreased to $(E_M - E_a)$. The ionization probability β_{M^+} is now proportional to $\exp(-(E_M - E_a)/E'_C)$; the E'_C term might also be different (as might E_B) since we have changed from a pure metal (plus implanted argon) to a metal plus oxygen matrix. It is clear, however, that the enhancement effect is not necessarily synonymous with an increased value of the parameter T .

The formation of FeM^+ ions on the other hand is scarcely affected by the presence of oxygen. These currents relative to the corresponding M^+ current may, in fact, give a poor indication of the respective ratios of sputtered neutral molecules to sputtered neutral atoms. It is known, for instance, that whereas sputtered dimer and trimer neutrals amount to a few percent and to about 0.1%, respectively, of the number of monomer neutrals, the corresponding secondary ion ratios can be much greater (40, 41). The cluster ion may be more stable than the neutral cluster on chemical bonding grounds (40). Also, the cluster ion may still be formed even when the relative kinetic energy of the combining atoms is larger than the dissociation energy of the ejected neutral molecule, the excess energy being lost to ionization.

Appreciable MO^+ formation seems to occur (4, 5, 42) if apparently two criteria are satisfied:

1) M must be a heavy element. This probably ties in with the observation (40) of appreciable concentrations of sputtered heavy-metal monoxide neutrals whose generation can be attributed (43) to a collision of a heavy metal atom with the light oxygen (surface) atom.

2) The MO (strictly speaking, MO^+) bond dissociation must be large.

Collisions involving oxygen which could lead to M^+ production (as proposed above) may thus lead to MO^+ formation instead. However, the latter probability will be less likely, the larger the relative kinetic energy of the colliding partners. Thus, it is only from collisions which would have led to lower energy M^+ ions, that MO^+ formation may occur instead. Therefore, measurements with the energy filter restricted to higher energy M^+ ions would lead to more meaningful comparisons between elements and this may explain why any anomalies (e.g., with Nb^+ and Mo^+) then practically disappear.

An MO^+ current can only be related to n_{MO^0} via Equation 6 if these ions are formed solely by ionization of the neutral monoxide molecules. However, if for instance an MO^+ signal results from the loss of a previously-formed M^+ ion by combination with an oxygen atom, then Equation 11 is obviously not applicable; flooding the surface region with oxygen may, in fact, increase this probability. Statistical considerations (43, 44) (concerned only with binary collisions) indicate that the chance of a sputtered M^+ ion being able to combine with a simultaneously sputtered oxygen neutral atom is only a few percent. Thus if an I_{MO^+}/I_{M^+} ratio is of this order of magnitude (i.e., for most elements in the iron standards, see Figure 7(a)), then this statistical formation of MO^+ cannot be excluded. Formulas such as Equation 11 should therefore be applied cautiously. Similarly, the O^+ current (at saturation) if corrected via Equation 9 would imply an oxygen content of a few hundred times that of iron. Presumably then, the O^+ signal does not arise in the main from direct ionization of oxygen neutrals.

CONCLUSIONS

Relative sensitivity factors of elements in iron standards

are only meaningful and reproducible if enough oxygen is present to saturate all M^+ secondary ion currents. Under these conditions, the degree of ionization of a given element M is directly proportional to $[Z_{M^+}/Z_{M^0}] \exp(-E_M/kT)$. Satisfactory demonstrations of the validity of this formula and an accurate determination of the value of the parameter T require elements of appreciably different ionization potentials to be present in steel samples. Moreover, misleading T values may be obtained if saturation is incomplete.

The parameter T for iron matrices under saturation oxygen conditions equals 6300 K for bombardment with 5.5 keV Ar^+ or O_2^+ primary ions, independent of current density, in the Cameca instrument accepting 0 to 20 (or more) eV secondary ions. Whether the above formula applies also to Ar^+ bombardment alone, and whether the same T value then results, could not be answered owing to the trace amounts of oxygen present, which already affect the relative ion yields significantly. Once the value for T has been established, it should be possible to run essentially standardless analyses to obtain the concentrations of all elements in homogeneous steel samples to within a factor of 2.

The derived concentrations of those elements for which I_{MO^+} is significant compared to I_{M^+} , such as Ti, V, Nb, and Mo, will probably be too low, however, unless further steps are taken (besides introducing only just enough oxygen to saturate the M^+ currents). The apparent waywardness of these elements most probably arises from appreciable concentrations of sputtered monoxide species, and/or relatively fewer numbers of low energy M^+ secondary ions. Possible remedies for the analysis of these elements are to use: a) simply $(I_{MO^+} + I_{M^+})$ instead of I_{M^+} , b) previously-calibrated charts of fudge factors vs. measured I_{MO^+} to I_{M^+} ratio (5), and/or c) I_{M^+} from higher energy ions corrected with a different T value (e.g., 8500 K for 40–60 eV secondary ions).

Our findings with other metal alloys and insulators will be published elsewhere.

APPENDIX

Consider, for simplicity, a two-component sample

$$c_M + c_{M_1} = 1 \quad (A1)$$

We allow for selective sputtering by writing

$$S_M = x S_{M_1} \quad (A2)$$

$x \neq 1$ implies that the sputtering process will eventually establish a different concentration ratio at the sample surface

$$\frac{\theta_M}{\theta_{M_1}} = \frac{1}{x} \cdot \frac{c_M}{c_{M_1}} \quad (A3)$$

Remembering that $\theta_M + \theta_{M_1} = 1$, this means that

$$\theta_M = \frac{c_M}{x c_{M_1} + c_M} \text{ and } \theta_{M_1} = \frac{x c_{M_1}}{x c_{M_1} + c_M} \quad (A4)$$

The total number of particles emitted per unit time, Σn , will be

$$\Sigma n = (S_M \theta_M + S_{M_1} \theta_{M_1}) n_p \quad (A5)$$

where n_p is the number of bombarding particles per unit time. Substituting Equations A2 and A4 into Equation A5,

$$\begin{aligned} \Sigma n &= \left(S_M \frac{c_M}{x c_{M_1} + c_M} + \frac{S_M}{x} \frac{x c_{M_1}}{x c_{M_1} + c_M} \right) n_p \\ &= \frac{S_M (c_M + c_{M_1})}{x c_{M_1} + c_M} n_p \end{aligned} \quad (A6)$$

Therefore, the term

$$\frac{n_M}{\Sigma n} = \frac{n_p S_M \theta_M}{\Sigma n} = n_p S_M \frac{c_M}{x c_{M_1} + c_M} / n_p \frac{S_M (c_M + c_{M_1})}{x c_{M_1} + c_M} = \frac{c_M}{c_M + c_{M_1}} = c_M \quad (A7)$$

Similar considerations apply to multi-component systems.

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Theoretical and experimental aspects of secondary ion mass spectrometry

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Secondary ion mass spectrometry (SIMS) can be used to investigate the composition of solids in the following way: by means of an ion bombardment (energy 3–15 keV) the sample is sputtered away. The sputtered particles which are ejected immediately as ions (secondary ions) are characteristic for the composition of the sample. Separated in a mass spectrometer they can be used in principle for a quantitative analysis.

A short survey on the different models, proposed to explain the emission of secondary ions, will be given.

The experimental techniques, which have to be carefully chosen for each experiment, will be discussed in more detail, viz. (1) choice of the primary particle: state of charge, element, current-density; (2) selection of the secondary particles: positively or negatively charged, atomic or cluster ions, post-ionization of sputtered neutrals, high or low mass resolution.

The parameters which are important for solving practical problems, viz. element-dependent ionic field, quantitative analysis, limit of detection, material composition, resolution in depth, will be discussed.

Some examples from practice of SIMS will be used to illustrate the wide range of applicability of the method.

1. Introduction

Interest in secondary ion mass spectrometry (SIMS), a method which has been shown to be most useful for the analysis of solids, has strongly increased within the last few years. Although the principle is relatively simple, the large number of operational parameters available is often confusing to one who is not completely acquainted with this method.

It is the aim of this paper to give—for a better understanding—a review of the existing models which try to explain secondary ion emission, and further to give a survey on the choice of the different parameters, which have to be carefully selected when carrying out a SIMS analysis.

Other aspects of SIMS have been reviewed such as design aspects,¹ comparison with other methods² or application to the analysis of thin films or surface problems.^{3,4}

2. Principle of SIMS

The sample mounted in the mass spectrometer is bombarded with a beam of primary ions (see Figure 1) with an energy of about 3 keV. Due to this bombardment, particles are sputtered away from the sample. In general most of these sputtered

particles are neutrals, while only a small fraction, typical 1/1000, is emitted as positive or negative ions using Ar⁺ primary ions.

A subsequent analysis of these secondary ions in the analyser of the mass spectrometer, provides in principle quantitative information on the composition of the sputtered material. The ions are detected by suitable means and a mass spectrum is displayed on a recorder. In general the data are nowadays processed by means of a dedicated computer.

By continuously bombarding the sample and simultaneously monitoring the secondary ion current of certain pre-selected masses, the composition as a function of depth, i.e. an in-depth concentration profile can also be determined.

3. Quantitative aspects

The secondary ion current i_s of a given element M measured at the collector is proportional to the primary ion current i_p , the sputter yield S = number of atoms per primary ion, the degree of ionisation* $\alpha^+ =$ secondary ions/secondary neutrals, the concentration c_M of this element and the transmission η of the mass spectrometer:

$$i_s = i_p S \alpha^+ c_M \eta \quad (1a)$$

$$i_s = i_p S^+ c_M \eta. \quad (1b)$$

The product $S\alpha^+ = S^+$ we call ion yield = number of secondary ions/number of primary ions.

After measurement of the primary ion current and the transmission one could from the above equation calculate the concentration c_M provided $S\alpha^+$ is known.

The sputter yield S can be determined by experiment^{5,6} or theoretically. Many authors have contributed to the theory of sputtering. For a survey on the different theories of sputtering see, e.g. the works of Behrisch,⁷ Carter,⁸ Kaminsky⁹ and

*Similar relations hold for negative secondary ions.

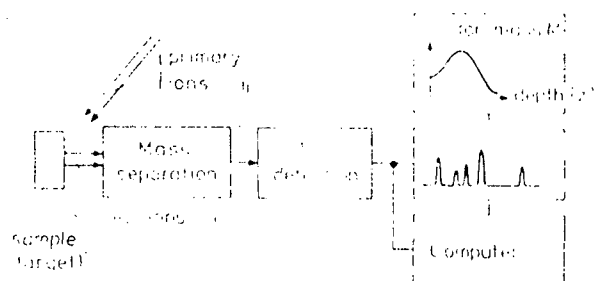


Figure 1. Principle of SIMS.

Oechsner.¹⁰ At the moment the theory of Sigmund¹¹ seems to give the best fit with experimental results. The anisotropy effect which has been found by Oechsner,¹² using oblique incidence of the primary ions, probably can be explained also with the aid of Sigmund's theory when terms including the momentum are taken into account.¹³

The determination of the degree of ionisation or of the ion yield either experimentally or theoretically is even more complex than the determination of the sputter yield.

We shall first discuss different models for the process of secondary ion emission and then discuss experimental methods, the latter being at the moment the safest method for the determination of α^+ and therefore for a quantitative analysis.

4. Models which describe the emission of secondary ions

As regards the models which try to explain the emission of secondary ions due to ion bombardment, the situation is as follows: a large number of models have been proposed. These models, however, either are only valid under certain assumptions or for certain materials. A theory, which covers all facts known up to now in secondary ion emission has not yet been given. Probably most of the processes described in the different models occur simultaneously during the emission of secondary ions. It is important therefore to know the cross-section for a given process, and its dependence on experimental conditions, before one starts to argue about the sole validity of one or the other theory. The dependence of these cross sections on the different experimental conditions probably also explains the contradictions, which are found to exist in the different models.

The existing models can basically be divided in two groups, viz. ions are generated outside or inside the target.

4.1 Ions are generated outside the target. In this model^{14,15} one considers a particle which is ejected from the target in a neutral metastable state due to the collision cascades initiated by the primary particles in the target (see Figure 2). De-excitation of this particle by means of an Auger process may take place near to the surface, outside the target, leading to the generation of an ion and the simultaneous ejection of an Auger electron.

Similar processes have been considered by Blaise^{16,17}, viz. the ejection of an atom in a super-excited state and its subsequent ionisation by an auto-ionisation process in vacuum immediately in front of the target.

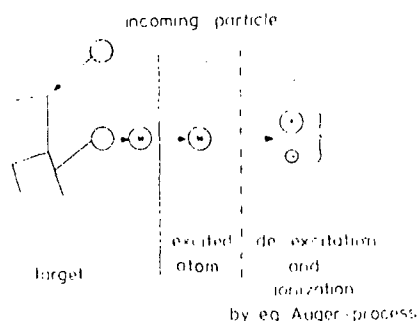


Figure 2. Model (schematic) assuming that the ions are generated outside the target.

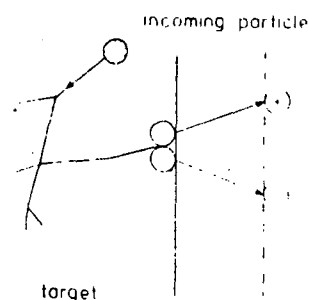


Figure 3. Model (schematic) assuming that the sputtered particles are already ejected as ions.

The processes mentioned up to now have been thoroughly studied by Castaing, Slodzian and co-workers. These processes are well understood, but not easily applicable to practical problems, as no simple relation has been given for the calculation of the ionic yield of an arbitrary element; moreover the data concerning the electronic structure of the elements, necessary for such a calculation, are not known for most of the elements.

Another approach using a simplified quantum mechanical model has been given by Schroeder.¹⁸ He has given a simple formula for the calculation of the ionic yield which is restricted to argon ion bombardment. His calculated values of the ionic yield agree with experimental values within a factor of 3 as has been shown by Schroeder¹⁹ and Rüdener.²⁰

4.2 Ions are generated within the target

4.2.1 Bond-breaking mechanism. When oxides are bombarded, particles are emitted directly as ions due to a breaking of the chemical bonds²¹⁻²⁶ (see Figure 3). The existence of such a mechanism has been suggested from the results shown in Figure 4: the logarithm of the positive copper ion current and the O^- ion current, originating from copper oxide layers of different thickness, is plotted as a function of depth. From the proportionality between the Cu^+ and O^- ion currents, it has been concluded that the Cu^+ and O^- ions originate from the same process,²⁶ i.e. originate by breaking the chemical bonds. The cross-section for the generation of ions by means of this bond-breaking mechanism is considered to be much larger than that for the generation of ions by one of the processes mentioned above thus explaining the increased positive ion yield of Cu^+ from Cu oxide. A similar increase of a factor of 10 for Ag^+ ions from Ag oxide have been reported.²⁶ Interpretation of the results from ion-induced photo-emission from oxides, led to the same conclusion.²⁷ Another explanation for the increased ion yield from oxides has been given by v.d. Weg²⁵ who assumed, that the probability for neutralisation of a generated ion is smaller in an oxide due to a forbidden zone.

Increase of the positive ion yield due to the presence of electro-negative elements. As has been discussed above, oxygen has a large influence on the positive ion yield. Due to a number of investigations^{14,28-30} we now know that the application of oxygen or other electro-negative elements increases the positive ion yield. The oxygen may be present in the target,²⁶ or one may use oxygen as primary ions^{26,31} or one may bleed in oxygen in the chamber in front of the target.³²

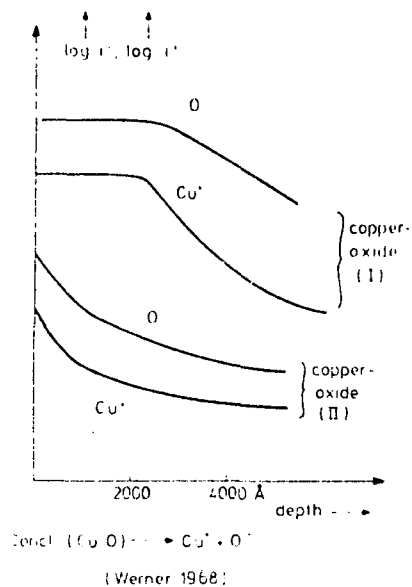


Figure 4. Cu^+ and O^- ion currents from two copper oxide samples with depth dependent oxygen concentration. From the proportionality between these two ion currents as a function of depth one may conclude that the ions originate from the same process viz: $\text{CuO} \rightarrow \text{Cu}^+ + \text{O}^-$, $\text{Cu}_2\text{O} \rightarrow 2\text{Cu}^+ + \text{O}^-$, giving in total: $\text{CuO} \rightarrow \text{Cu}^+ + \text{O}^-$.

Increase of the negative ion yield S^- by the presence of electro-positive elements. In a similar way, the negative ion yield is influenced by the presence of electro-positive elements.^{31,33} One may either use Cs^+ as primary ions or may adsorb Cs on the surface.

4.2.2 Creation in the target of a plasma in local thermal equilibrium (LTE). Another explanation for the increased positive ion yield from oxides, which has been much criticized by Blaise and Slodzian,³⁴ has been given by Andersen.³⁵ Andersen assumed, that in the metal oxide generated due to the use of oxygen in one of the above described forms, the work function and the potential barrier are high. Therefore the probability P_1 that an electron may surmount this barrier and neutralize an ion just in front of the target is practically zero and the same for all elements. Hence the probability for an ion, generated inside the target, to remain as such is high and therefore also the ion yield is high (Figure 5). Based on this idea, Andersen put forward a quantitative method to convert sputtered ion intensities into atomic concentrations.

His model, restricted to the presence of oxygen is based on the following idea (Figure 6): as a consequence of the neutral-

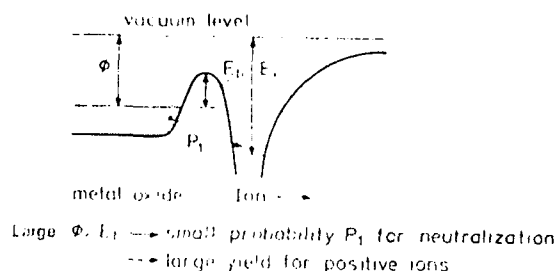


Figure 5. Model (schematic) proposed to explain the increased positive ion emission from metal oxides.

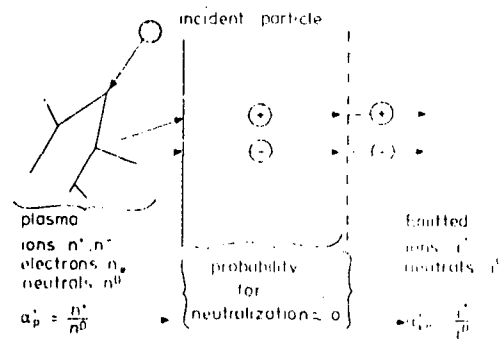


Figure 6. The local thermal equilibrium (LTE) model.

ization probability being practically zero, there is no loss of ions on leaving the target, and the degree of ionization α_{em}^+ of the emitted particles is the same as in the plasma (α_p^+) initiated in the target by the primary ion; i.e.

$$\alpha_{em}^+ = i^+/i^0 \sim \alpha_p^+ \sim n^+/n^0 \quad (2)$$

where i^+ = emitted positive ion current, i^0 = neutral particle 'current' sputtered from the target, n^+ , n^0 = concentration of positive ions or neutrals respectively in the plasma. If one measures the secondary ion current (see equation 1a) and if S^- and the transmission are known, only the value of α^+ remains unknown. Andersen assumes a local equilibrium in the target, and calculates the degree of ionisation in the plasma (α_p^+) -- and therefore due to relation (2) also α_{em}^+ -- from the complete Saha-Eggert equation:

$$\frac{n^+ n_e}{n^0} = \frac{u^+(T)}{u^0(T)} \cdot 2 \cdot \frac{(2\pi m k T)^{3/2}}{h^3} e^{-(E_r - \Delta E_p)/kT} \quad (3)$$

where n^+ , n^0 , n_e = concentration of ions, atoms, electrons in plasma; u^+ , u^0 , 2 = resp. partition functions; E_r = energy for transition from atom (grd. state) $\rightarrow$ ion (grd. state) = ionization energy; ΔE_p = depression of ionization potential in plasma; T = parameter ('temperature').

According to Andersen,³⁵ T is the absolute temperature. As we shall see later there is no thermodynamic equilibrium in the plasma.³⁶ We therefore prefer to call T a 'parameter' which describes the degree of ionisation in a plasma. The partition functions, the ionisation energy E_r and the depression of the ionisation potential in the plasma can be found from the literature.³⁷⁻³⁹ Therefore only two parameters remain unknown in the Saha-Eggert equation, viz. T and n_e . They can however be determined from measured ion currents of two elements with known concentration homogeneously distributed in a sample. Once T , n_e have been in principle calculated, the degree of ionisation of an arbitrary element can be calculated from equation (3), and then from equation 1(a) the concentration c_M of this element. Such a procedure, including moreover corrections for the influence of molecular and negative ions on the calculated concentration has been described by Andersen.³⁵

This model of Andersen has several aspects:

(1) It is a model which combines the aspect of ion generation in the plasma with the aspect of sputtering.

(2) It gives the possibility to calculate the concentration of the various elements by means of a relatively simple procedure. The same also holds for the model of Schroeer, which however is restricted to argon bombardment. Since oxygen is mainly

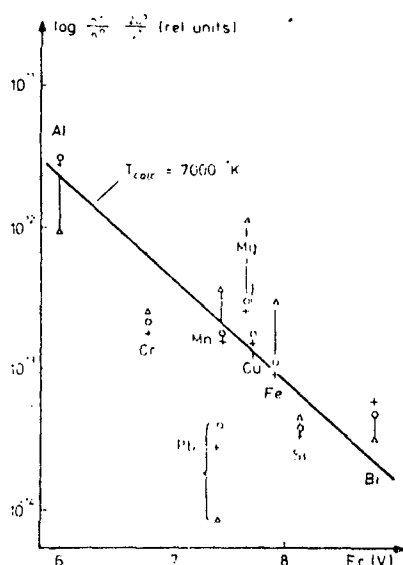


Figure 7. Check of the validity of the Saha-Eggert equation under ion bombardment. Sample: Al-standard (5B). Plot of $\log(n^+/n^0)/(2u^0/u^+)$ against ionisation energy E_r . The depression of ionisation energy (see equation 3) has been taken to be zero for all points. The 'temperatures' assumed for the calculation of the partition functions were 4000 K (+) and 7000 K (•). Points calculated assuming $2u^0/u^+ = 1$ (no partition function) are indicated by (Δ). Experimental conditions: $i_p(O_2^+)$ = 0.6 μ A, bombarded area A = 1.5 $\times$ 1.5 mm².

used in practice in order to achieve a high positive ion yield, our discussion will be restricted to Andersen's model.

(3) Andersen's model is unsatisfying with respect to the applicability of the Saha-Eggert equation. Especially one would like to investigate more in detail if the concept of temperature may be applied.

We have therefore³⁰ carried out the following studies:

(1) In order to check the applicability of the Saha-Eggert equation, as described by Andersen, we have analysed in our instrument (Cameca, SA; type IMS 300) an aluminium standard (Al5B). In Figure 7 we have plotted $\log(i^+/n^0)(2u^0/u^+)$ against the ionisation energy E_r , assuming that $\Delta E_r = 0$. We have further assumed, that $i^+ \sim n^+$ and have neglected contributions from molecular ions or negative ions.³⁵ The values for the partition functions have been obtained from tables³⁷⁻³⁹ assuming two 'temperature' values, viz. 4000 and 7000 K. One can see that the points, with the exception of Pb, fairly well lie on a straight line. The deviation for Pb might be due to inhomogeneity of the sample on a microscale. From the slope of the straight line a 'temperature' of $T_{calc} = 7000$ K is calculated, in good agreement with the assumption of an 'apparent temperature' of 7000 K. For comparison we have also given points, calculated without partition functions. The spread of these points, as can be seen from the figure, is much larger.

From these results one can conclude, that the Saha-Eggert equation can in first approximation be used to calculate an 'apparent temperature'. From the intersection of the straight line with the ordinate, one can (see equation 3) calculate the electron density n_e , provided that the ordinates are given in the appropriate units. The method of Andersen therefore seems to give the possibility of calculating the concentration of elements in metals from the measured SIMS spectra. Similar conclusions have been drawn by Rüdener,²⁰

(2) As regards the concept of temperature appearing in this connection, we have considered the following³⁶: let us assume that a hypothetic primary ion of mass number 30 and energy $E_p = 4$ keV, impinges on the target. The mean range of such an ion of approximately 100 Å is traversed in about 10^{-12} s, with a corresponding average velocity in the target of about 10^6 cm s⁻¹. We assume that a cylindrical shaped zone of 100 Å dia and depth is effected by the resulting collision cascades. From estimates of Brongersma⁴⁰ it follows that the heat dissipated by the primary ion is carried away from this volume in about 10^{-10} s or less.* If we compare this with the average rate of arrival of primary ions at the highest primary current density used³⁵ ($j_p = 1$ mA/cm²) corresponding to the arrival of about one ion in 10^{-4} s, on the zone with 100 Å dia we come to the following conclusion: The effect of a single ion penetrating into the target could only be a local temperature rise in a zone of about 100 Å within a time of 10^{-10} s, as the following ion, on the average, arrives only after a time which is large compared to the mean lifetime of one cascade. In other words the cascades which are generated by the individual ions are independent of each other. In this case the SIMS spectra should be independent of the primary beam current density in a large interval. Measurements to check this conclusion are being carried out at the moment.⁴¹ In conclusion we can say, that under the conditions described above no macroscopic temperature builds up in the target.

We have so far shown that the parameter T is not identical with the macroscopic temperature of the target. What then is the physical meaning of the parameter T ?

According to Boumans⁴² and Alkemade⁴³ the conditions for a (gaseous) plasma are characterised by *different* 'temperatures' co-existing at the same time, each of which describes a distinct aspect of the physical or chemical state of the system. For a plasma consisting of a mono-atomic gas we have according to Boumans⁴⁴ the following temperatures:

(1) Electron temperature, which is determined by the kinetic energy of the electrons.

(2) Gas temperature, which is determined by the kinetic energy of the heavy particles (atoms, ions).

(3) Excitation temperature, which describes the population of the various energy levels.

(4) Ionisation temperature, which governs ionisation equilibria.

For a plasma consisting of a molecular gas we have the following additional temperatures:

(5) Dissociation temperature, describing dissociation equilibria.

(6) Vibrational temperature, describing the population of the vibrational states.

(7) Rotational temperature, describing the population of the rotational states.

Only when all these temperatures have the *same* numerical value and Planck's law is fulfilled, a plasma may be said to be in complete thermodynamic (or thermal) equilibrium. If we transfer these conclusions to a plasma generated in the target by an ion bombardment we can conclude the following:

(1) The Saha-Eggert equation (3) has been derived from the mass action law for the reaction



assuming a local, partial equilibrium. We speak of *local* (equilibrium) because the perturbed region is restricted to about 100 Å diameter, of *partial*, because the Saha-Eggert equation in the above form exclusively deals with the ionisation temperature, and of *equilibrium*, if the reaction described in equation (4) is balanced, i.e. the reaction proceeds in both directions at equal, fast rates, such that the rate of exchange of (4) is faster than the energy dissipation from the perturbed zone. We are then dealing with a quasi-adiabatic process.

From the experimental values for the initial energy of the secondary ions and secondary electrons ($E_{\text{ion}} = 6 \text{ eV} = 6 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$, $E_{\text{el}} = 1 \text{ eV} = 6 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$) it follows, that this rate of exchange is of the same order of magnitude as the velocity of the phonons ($\approx 5 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$) which are responsible for heat dissipation from the perturbed zone. Considering Sigmund's work¹¹⁹ only the electrons have sufficient velocity to traverse the zone of 100 Å within the life time of the cascade.

In conclusion we can say that the quantity T in the Saha-Eggert equation is a parameter which describes exclusively the process given in equation (4). This parameter, however, has the *dimension* of a temperature, because for the case of thermodynamic equilibrium it is identical with the (thermodynamical) temperature. Moreover kT in the exponent of equation (3) has the dimension of an energy. It reflects, according to the interpretation of the Boltzmann-factor the average energy available for an atom in the cascade. According to Sigmund¹¹⁹ this energy should decrease with increasing primary ion energy.

4.3 The application of the Saha-Langmuir equation in a modified form has been used by Jurela⁶² for a calculation of positive and negative ion yield. Kelly *et al.*⁶ have shown that in some oxides of low binding energies thermal sputtering may be the dominant process.

5. Experimental approach to quantitative SIMS

5.1 Experimental work⁴⁵⁻⁵⁴ has shown the applicability of SIMS to quantitative work, assuming that the ion yield (see equation 1) is known.

Experimentally determined values for the absolute yield of positive ions^{45,51,55,56} and the relative yield for positive and negative ions^{26,55} show that the ion of a given element and of different elements may differ up to a factor of 100, depending on the matrix⁵⁵⁻⁵⁷ (metals, alloys, semiconductors).

These results were supported by other authors.⁵⁸⁻⁶⁸

Benninghoven⁵⁵ has determined the absolute yields from cleaned and oxidized metal surfaces under UHV conditions, as given in Table 1.

The increase in the ion yield from the clean metal to the fully oxidized state was found to amount to a factor 100, in good agreement with work of other authors.^{14,26,31,69} We have also calculated in Table 1 the degree of ionisation α^+ from Benninghoven's S^+ values assuming for convenience that the sputter rate of the metals is equal to the sputter rate of the oxidized metals (see also ref 6).

The influence of temperature and channeling^{70,71} and of residual gas⁷² has also been studied.

5.2 Instruments. For a review and evaluation of the different types of instruments, the reader is referred to a number of papers on this subject.^{3,73-77}

5.3 Quantities of importance to secondary ion mass spectrometry. Besides the ionic yield, described above, the following quantities are of importance for SIMS:

- (1) The lowest detectable concentration c_{min} of a particular element present in the sample.
- (2) Material consumption during an analysis.
- (3) Standard error due to statistical fluctuations in the ion current.
- (4) Waste of material.
- (5) Erosion rate in relation to background pressure.

5.3.1 The lowest detectable concentration (Table 2) can be derived from equation (1) as:

$$c_{\text{min}} = i_{s,\text{min}}/(\eta S^+ i_p) \quad (5)$$

where $i_{s,\text{min}}$ is the minimum detectable ion current. It can be kept low by using an electron multiplier;^{78,79} η = transmission of the instrument, can be optimized by suitable choice of the ion optics;^{80,81} S^+ = the ion yield; i_p = the primary ion current, cannot be chosen *ad libitum*, as the sputtered volume per s ($\dot{V}$) increases with i_p and consequently the volume $V = \dot{V} t_a$ consumed during an analysis (t_a = time for an analysis) also increases.

5.3.2 Relation between c_{min} and material consumption. It has been shown^{53,56} that $c_{\text{min}} \sim 1/\dot{V}(i_p) \approx 1/(\dot{z}A_b)$, . . . (4) where $\dot{z}$ is the erosion rate (cm s^{-1}) and A_b is the bombarded area. In order to obtain the lowest values for c_{min} one has to increase the primary ion current density and hence the material consumption is also increased (see Table 3). For a given value

Table 1. Absolute positive ion yields for clean metals and their respective oxides, using Ar^+ as primary ions (after Benninghoven⁵⁵). The degree of ionization $\alpha^+ = S^+/S$ has been calculated assuming that the sputter rate is the same for the metals and oxides. Increase in ion yield from clean to oxidized surfaces is shown in the last column.

Element	S^+_{clean}	α^+	S^+_{oxide}	α^+	$S^+_{\text{oxide}}/S^+_{\text{clean}}$
Mg	8.5×10^{-3}	4×10^{-3}	1.6×10^{-1}	8×10^{-2}	20
Al	2×10^{-2}	1×10^{-2}	2	1	100
V	1.3×10^{-3}	7×10^{-4}	1.2	6×10^{-1}	10^3
Cr	5×10^{-3}	3×10^{-3}	1.2	6×10^{-1}	200
Fe	1×10^{-3}	5×10^{-4}	3.8×10^{-1}	2×10^{-1}	380
Ni	3×10^{-3}	2×10^{-4}	2×10^{-2}	1×10^{-2}	7
Cu	1.3×10^{-4}	7×10^{-5}	4.5×10^{-3}	2×10^{-3}	30
Sr	2×10^{-4}	1×10^{-4}	1.3×10^{-1}	7×10^{-2}	700

Table 2. Calculated values²⁶ of the lowest detectable concentration $c_{\min}$ for some elements, assuming i_p (primary ion current) = 10^{-8} A, transmission $\eta = 10^{-2}$, and a minimum detectable ion current at the ion collector $i_{c,\min} = 2 \times 10^{-18}$ A. Values for S^+ (ion yield) have been taken from Table 1.

$c_{\min} (\text{ppma}) = \frac{i_{c,\min}}{\eta \cdot S^+ \cdot i_p} \times 10^6$		
Elements	S^+	$c_{\min}$ (ppma)
Cu	1.3×10^{-4}	150
Ni	3×10^{-3}	7
Al	2×10^{-2}	1
Oxides	S^+	$c_{\min}$ (ppma)
Cu	4.5×10^{-3}	5
Ni	2×10^{-2}	1
Al	2	0.01

of the bombarded area A_b however, increase of $\dot{V}$ means increase of the erosion rate $\dot{z}$, as $\dot{V} = \dot{z}A_b$.

Due to the slight 'thickness' of thin films, $\dot{z}$ can not be chosen too high especially when one wants to carry out an in-depth analysis. The two requirements of small values for $c_{\min}$ and small values of $\dot{z}$ are therefore conflicting.

5.3.3 Statistical fluctuations in the measured ion currents. The material consumption $\dot{V}$ (cm^3) may not be lowered beyond a certain minimum value $V_{\min}$, due to the corpuscular character of the ion current.⁸³ Morabito *et al.*⁶⁶ have shown the relation between this minimum volume $V_{\min}$ and the tolerated statistical fluctuation, expressed as standard error $\sigma_s(\%)$ in the detection current:

$$V_{\min}(\text{cm}^3) = \dot{V}t_a = \frac{1}{(\rho N)/M} \cdot \frac{10^6}{c_M \alpha^+ \eta} \cdot \frac{10^4}{\sigma_s^2 [\%]} \quad (6)$$

where ρ = density (g cm^{-3}), N = Avogadro's number, M = mass number and $\alpha^+ = S^+/S$ is the degree of ionisation.^{56,83} S is the sputter rate = number of sputtered particles per primary ion and c_M is the concentration in 'ppma'.

5.3.4 Efficient use of the sputtered material. When scanning through the mass spectrum and using only one collector for the ion currents, only one mass at a time is detected. The rest of the sputtered material is wasted. Simultaneous multi-element detection by photoplate^{84,85} or electrical multi-collector detection promises a more efficient use of the sputtered material. The decision whether to use photographic detection or electrical detection depends on how much material may be consumed, how many elements are to be analyzed and the required limit of detection, as can be seen from Table 4.

Single-collector electrical detection has in its favour the lower limit of detection as it only needs about 10 ions s^{-1} , but is limited to one element at a time. The photoplate, needing about 10^4 ions for a just detectable line, has a higher limit of detection but measures all ions of the spectrum at the same time.⁸⁶

Application of multi-collector electrical detection, e.g. oblong

Table 3. Relation between primary ion current, impinging on a given area, erosion rate $\dot{z}$, thickness of removed layer and minimum detectable concentration $c_{\min}$.

$$c_{\min} \sim 1/\dot{V} = 1/(\dot{z}A_b)$$

Primary ion i_p (A)	Erosion rate $\dot{z}$ ($\text{\AA s}^{-1}$)	Thickness of removed layer in $t_a = 200$ s	$c_{\min}$ (ppma)
10^{-8}	2	400 $\text{\AA}$	10
10^{-7}	20	4000 $\text{\AA}$	1
10^{-6}	200	4 μm	0.1

Bombarded area A_b : $100 \mu\text{m} \times 100 \mu\text{m}$ (10^{-4} cm^2)

Concl. simultaneous multi-element detection } $\rightarrow$ { Photoplate or multi-collector (electr. detection)
Statistical fluctuations $\sim (\text{sputtered volume})^{-1}$

channel plates with sufficiently small channel diameter may shift the decision in favour of the electrical detection.

5.3.5 Erosion rate $\dot{z}$ in relation to background pressure p_b . In order to reduce the contamination of the surface, due to adsorption of molecules from the residual gas, the erosion rate and hence the primary ion current density j_p must be much larger than the background pressure. A rule of thumb states⁸⁷ that this is the case for

$$j_p [\mu\text{A/cm}^2] / p_b [\text{torr}] \geq 10^8. \quad (7)$$

6. Improvement of SIMS measurements by means of experimental methods

6.1 Primary ions. The following parameters related to the primary ions must be chosen depending on the problem considered:

(1) Energy, angle of incidence, mass and ion current density of the primary ions, isotopic or mass separation of the primary ion.

(2.1) Noble gas ions (Ar^+ , Ne^+ , etc) or

(2.2) Reactive ions (oxygen, carbon, cesium).

(3) Charge of the primary particles.

(3.1) Positive ions: Ar^+ , O_2^+ , etc.

(3.2) Neutral particles: Ar^0 , which may be obtained by charge transfer from primary ions.

(3.3) Negative ions: O^- , Cl^- , C^- , etc.

(3.4) For the investigation of insulators, the choice of the charge of the primary particles is especially of importance. Figure 8 illustrates schematically the situation. The primary ion current i_p and the secondary current i_s (mainly consisting of secondary electrons) charge the surface of the insulator by the amount of ΔV with respect to its backside. If we denote by r the equivalent resistance of the insulator, the charging in a stationary state is given by

$$\Delta V = r(\pm i_p + i_s). \quad (8)$$

A positive or negative sign of the primary ion current i_p has to be chosen depending on charge of the primary ion. The equivalent resistance r depends on the specific resistivity ($\Omega \text{ cm}$) of

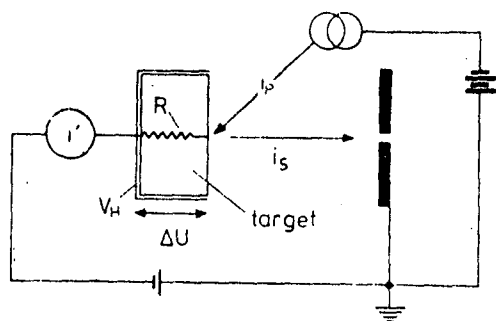


Figure 8. Equivalent electrical circuit to illustrate the charging of the insulator surface under ion bombardment: i_p = primary ion current, i_s = secondary current (secondary ions + secondary electrons); I = total current flowing through the insulator with equivalent resistance r ; ΔV = charging of the surface of the insulator with respect to the backside = target holder H . The target holder is at constant potential V_H .

the insulator material, on the dimension of the sample (lateral dimensions and thickness) and on the area which is hit by the primary ion current.⁹⁰

Remedies which are known at present for the reduction or compensation of charging are as follows:

- (1) Deposition of a conducting thin film or of a grid.
- (2) Use of Cs^+ as primary ions;³³ in this way a conducting layer is continuously built up by the primary ion bombardment.
- (3) Compensation of the charging by means of an extra electron beam.⁸⁸
- (4) Use of neutral beams:⁸⁹ the charging is reduced from the case of positive primary ions, see equation (8), to: $\Delta V_n = r i_s$ as the neutral beam does not bring any charge to the surface.
- (5) Application of special electrodes for draining excessive negative charge.⁹⁰
- (6) Shift of target holder potential V_H by ΔV in a direction opposite to the previous charging of the insulator.³²

6.2 Secondary ions (particles)

6.2.1 Secondary ion yield. As already discussed (Table 1) the positive secondary ion yield can be strongly increased by use of oxygen. In general the *absolute* yield of negative ions²⁶ is much smaller than that for the positive ions. However, when using Cs^+ as primary ions³¹ an increase by several orders of magnitude is achieved. Figure 9 shows the relative values according to Andersen³¹ for positive ion yield under optimum conditions, i.e. oxygen bombardment. Also shown are values for the negative ion yield obtained under optimum conditions, i.e. Cs^+ bombardment. For a better comparison we have taken the yields of positive and negative copper ions to be equal.

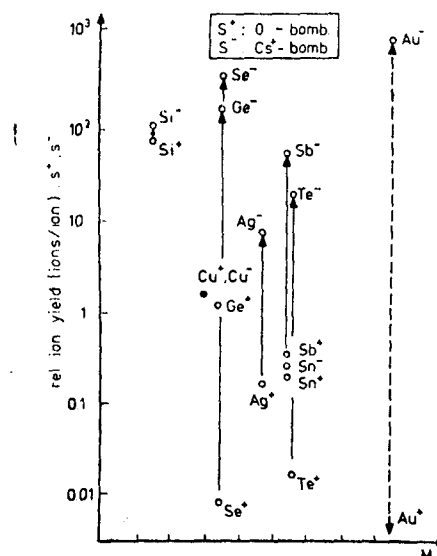


Figure 9. Relative yield for positive and negative secondary ions as a function of mass. For comparison the relative yield for Cu^+ and Cu^- are taken to be equal. The yield for positive ions was determined from measurements with primary O^- ions, the yield for negative ions was determined from measurements with primary Cs^+ ions. (After Andersen³¹.)

6.2.2 Species of secondary ions

- (1) Atomic ions: Fe^+ , Al^+ , Cu^+ .
- (2) Poly-atomic ions: among these we have molecular ions such as AlO^+ etc, generated due to the use of primary oxygen ions,⁵⁶ AlOH^+ , due to the presence of water in the system, heterogeneous cluster ions such as AlCu^+ , AlFe^+ etc.⁹¹ which appear especially when analysing alloys with high primary ion current density⁹¹ and isogeneous cluster ions such as Al_2^+ , Al_3^+ , Al_4^+ .²⁶

It has already been pointed out⁵⁶ that it is most advantageous for chemical analysis to work in a mode which preferably gives atomic ions. For studies of the chemical bonding, the poly-atomic ions, which constitute the fingerprint spectrum of a given compound^{92,93} can be used with advantage.

- (3) Discrimination between atomic ions and poly-atomic ions.

(3a) Discrimination due to difference in initial energy.

To illustrate this method Figure 10 shows the initial energy distribution of Al_3^+ and Al^+ .⁹¹ The energy spectrum of the Al^+ ions extends to much higher energy values than that of the Al_3^+ . By cutting out an energy band one can increase favourably the intensity of for instance the Al^+ ions with respect to the low energy Al_3^+ clusters.

To select an energy band, Poschenrieder and Herzog⁹¹ have used an electrostatic analyzer. A combination of ion mirror and

Table 4. Comparison of limits of detection with single-collector electric detection (multiplier) and photographic-plate detection for different amounts of material sputtered.

Volume V (cm^3) sputtered in $t_s \approx 1$ s	Number of particles in sputtered volume V	Number of ions coll./number of atoms sputtered	Limit of detection	
			Multiplier (1 line)	Photoplate (ca 100 lines)
2×10^{-12}	10^{11}	10^{-5}	10 ppm	10^4 ppm
2×10^{-9}	10^{14}	10^{-3}	10 ppb	10 ppm

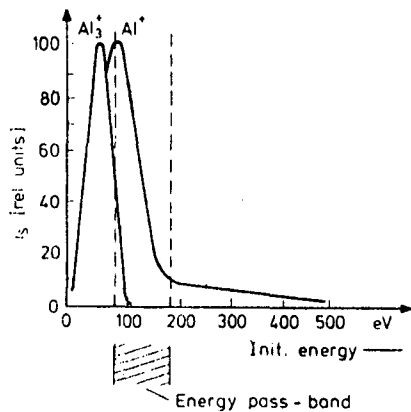


Figure 10. Energy distribution of secondary ions (after Poschenrieder and Herzog⁹¹) for atomic ions Al⁺ and isogenicous cluster ions Al₃⁺.

retarding potential-filter⁹⁴ as present in our instrument (Cameca; IMS 300) gives the same result.

A mass spectrum obtained by Poschenrieder when accepting low energy ions is given in Figure 11. One can see that a large number of poly-atomic ions populates the spectrum. However, when only ions with an initial energy above about 250 eV are accepted the mass spectrum reduces essentially to a few atomic ion peaks as shown in Figure 12. The poly-atomic ions have been reduced below the limit of detection. Only small peaks of molecular clusters (Al₂⁺ and Al₃⁺) are still present.

(3b) Discrimination due to the mass defect.

By using a mass spectrometer with high mass resolution (about 5000)^{82,95,96} the disturbing interferences between the atomic and poly-atomic ions can be separated. Results due to Evans⁹⁵ are given in Table 5.

6.2.3. Post-ionization of sputtered neutrals. It has already been mentioned that the ionic yield $S^+ = a^+S$, of different elements can differ up to a factor of 100. The large differences in the yield are mainly due to the differences in degree of ionization. The differences in sputter yield are much smaller and also less dependent on the matrix.^{5,7-9} It seems reasonable therefore to analyse the sputtered neutral particles by means of post-ionization and not to use, as described up to now, the ions which are directly emitted without any further ionization. Two approaches for such a post-ionization have been reported:

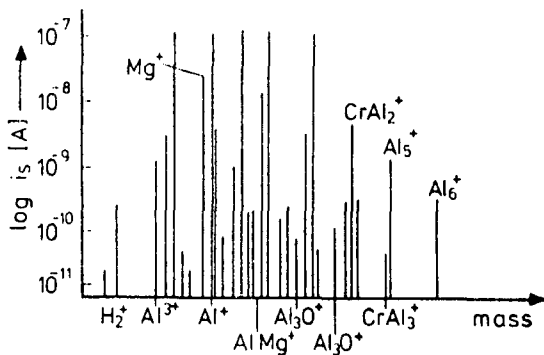


Figure 11. Mass spectrum of an Al-Mg alloy, bombarded with 12 keV Ar⁺ ions. Analyser was adjusted to accept low energy secondary ions of about 20 eV. (After Poschenrieder and Herzog⁹¹.)

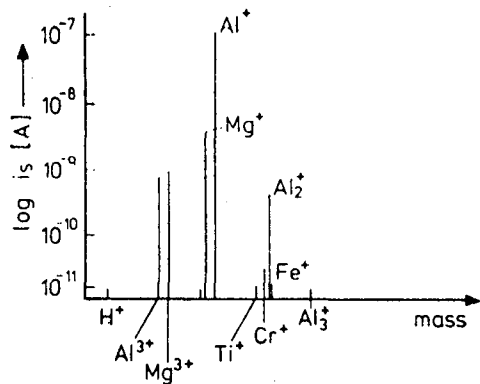


Figure 12. The same sample as in Figure 11⁹¹ with however strong suppression of poly-atomic ion species due to shifting the initial energy acceptance to 250 eV. (After Poschenrieder and Herzog⁹¹.)

(1) Oechsner⁹⁷ generates a plasma in a gas of 10⁻⁵ torr pressure. The electron temperature in this plasma is about 10⁵ K. Due to this relatively high temperature the energy of the electrons is high enough for ionization by electron impact. The ionization cross-section for different elements show small differences.⁹⁸

(2) Coburn and Kay⁹⁹ generate a plasma in a gas (Ar) of 10⁻² torr. The electron temperature is rather low (5000 K) and therefore the (thermal) electron energy is not sufficient to ionize by electron impact. Ionization of the gas molecules is obtained by means of the so-called Penning process via metastable argon atoms:



Here too, the ionization cross-section for different elements shows small differences.¹⁰⁰ It is expected that these methods of post-ionization will improve quantitative SIMS. When using these methods the following points have to be considered:

(1) Contamination of the target surface by the residual gas in front of the target. The system of Oechsner will give less contamination due to the smaller gas pressure.

Table 5. Required resolution to resolve analytical ions (atomic ions) from interfering poly-atomic ions (after Evans⁹⁵).

Interference type	Interfering ion	Analyt. ion	Required resolution
Multiply charged matrix ion	²⁸ Si ²⁺	¹⁴ N ⁺	950
	⁶² Ni ²⁺	³¹ P ⁺	3200
Matrix selfpolymers ions	¹⁶ O ₂ ⁺	³² S ⁺	1800
	²⁸ Si ₂ ⁺	⁵⁶ Fe ⁺	2950
Prim. ion-matrix molecular ions	Cu ₃ O ⁺	²⁰⁷ Pb ⁺	1050
	Si ₂ O ⁺	⁷⁵ As ⁺	3250
	AlO ₂ ⁺	⁵⁹ Co ⁺	1500
Hydride ions	³⁰ SiH ⁺	³¹ P ⁺	4000
	FeH ⁺	⁵⁵ Mn ⁺	3300
	SnH ⁺	¹²¹ Sb ⁺	19500
Hydrocarbon ions	C ₂ H ₃ ⁺	²⁷ Al ⁺	650
	C ₅ H ₃ ⁺	⁶³ Cu ⁺	650
	C ₂ H ₂	CN ⁺	2000

(2) Careful shielding is necessary to avoid contamination of the target surface by sputtered particles from the probe holder.

(3) The method at the moment, is limited to large area analysis.

Both approaches are very interesting also for fundamental research. The work of Oechsner enables to compare the yield for ionic molecular ions and neutral molecular ions¹⁰¹. From the measurements of Coburn and Kay one can get information on the lifetime of metastable atoms.

7. Application of SIMS

7.1 In thin film analyses, one is very often interested in the dependence of the oxygen content with depth. Figure 13 shows part of the spectrum obtained from a thin film of chromium oxide.⁹² Information about the oxygen profile could be obtained by means of the concept of fingerprint spectra in the following way: it has been pointed out^{92,102} that the fingerprint spectrum reflects the chemical bonding in a sample. From a data-bank of different chromium oxides we were able to conclude the existence of three different chromium oxides in this layer. From a linear superposition of the respective fingerprint spectra we were able to calculate the dependence of any mass line as a function of depth, and moreover to calculate also the concentration of these different chromium oxides. For more details see reference.⁹²

7.2 Depth-profiles. In order to obtain a depth-profile, one chooses a relatively large erosion rate. Typical values for the erosion rate are $z = 1 \text{ \AA s}^{-1}$ – $10 \text{ \mu m h}^{-1}$. When using small

erosion rates, e.g. for the analysis of thin layers, one must keep in mind however that the erosion rate must be larger than the adsorption rate (see equation 7). In principle a concentration profile is obtained²⁶ by measurement of the secondary ion current i_s as a function of bombardment time, provided that the erosion rate is constant:

$$i_s(t) = c[z(t)]. \quad (10)$$

A number of effects, however, disturbs the ideal relation as given by equation (10). These disturbing effects can be summarised as follows:

7.2.1 Primary ion beam inhomogeneity. Effect: curved crater bottom¹¹⁸ gives broadening of measured profile and loss in depth resolution. Remedy: Increase of effective beam diameter by defocussing^{26,74,96,103} or scanning^{31,104,105} of primary beam. Homogeneous inner part is cut out by suitable diaphragm¹⁰⁶ or electronic gating.³¹

7.2.2 Contribution from the crater rim. (1) Material from the crater rim is sputtered into the crater centre, resputtered and measured.^{109,118} This effect seems to depend on experimental conditions.¹⁰⁸ (2) Direct ion emission from the crater rim.

Remedy: (a) as sub 1, (b) preparation of a special sample with 'profile area' smaller than primary beam.¹¹⁰ Method (b) has limited applicability depending on the possibility of choosing the 'profile area' with suitably small dimensions.

7.2.3 Miscellaneous.

(1) Surface roughness present at beginning of sputtering is maintained if matrix is not polished or has porous structure.

(2) Preferential sputtering:^{111,118} polycrystalline material, or faceting (single crystal) leads to increase in surface roughness. Effect of (1) and (2): loss in depth resolution. Remedy: introduction of oxygen.¹¹²

(3) Inhomogeneous distribution across bombarded area of element under consideration.^{26,76} Wrong interpretation of result.

(4) Information depth:³ is a few monolayers or more (energy dependent).

(5) Charging of insulator surfaces due to ion bombardment.

(6) Recoiling: atoms are knocked deeper into the matrix. Effect is energy dependent^{110,113} but negligible below 5 keV primary ion energy.¹¹⁴

(7) Sputter rate not constant in time (depth), in particular when sandwiched layers are investigated.⁶⁹

(8) Possible change of concentration profile.¹²⁰

7.2.4 Quantitative aspects.

(1) Ion yield S^+ dependent on oxygen content. Remedy: flooding sample surface with oxygen^{32,67} use of fingerprint spectra for analysis of oxides.^{92,102}

(2) Possible interdependence of ionic yield for multi-element dopes; e.g. B-profile in Si, influenced by additional As diffusion.⁶⁹

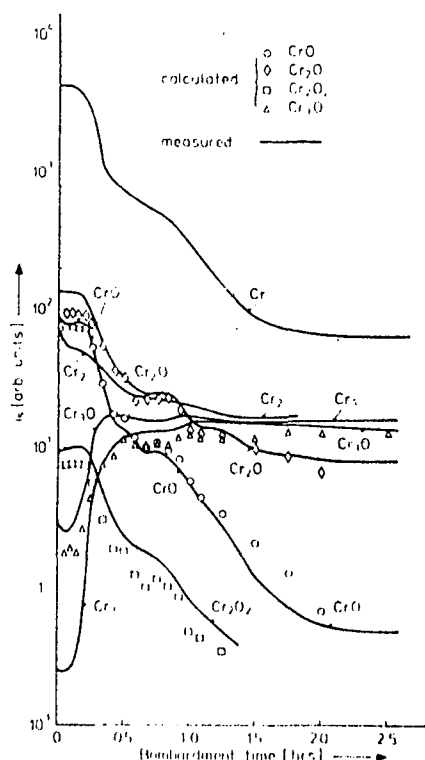


Figure 13. Dependence of different poly-atomic chromium ions as a function of depth. Experimental values: solid lines; calculated values are given by symbols. (After Werner *et al*⁹².)

Quality of SIMS profile measurement

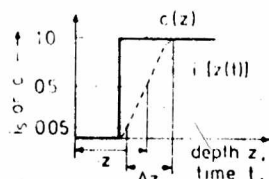
Step-function response delay $\Delta z = f(\text{instrument})$ Depth resolution: $R = \Delta z/z = \text{constant}$ Measured profiles: $\Delta z = f(\text{given profile} + \text{instrument})$ Reported values for R : 10–20%

Figure 14. Definition of the depth resolution: profile to be measured $c(z)$; ion current actually measured: $i_s(z)$ as a function of depth z (schematic).

7.2.5 Depth resolution of SIMS. For a definition of depth resolution let us assume that the profile to be measured follows an ideal step function as shown in Figure 14. The measured secondary ion current as a function of depth will in general be delayed by an amount of Δz . This delay Δz we measure arbitrarily as the difference in the z -values, for values of i_s between 5% and 100% of the maximum value of the secondary ion current. This step function response is only dependent on the instrument. It is easily seen, that the value of Δz reflects the depth difference between crater rim and the centre of the crater. If we denote a depth of the crater after a given time of bombardment t by z , then

$$z \sim j \cdot S \cdot t. \quad (11)$$

The difference Δz is then found to be

$$\Delta z \sim \Delta(jS) \cdot t \quad (12)$$

where j = primary ion current density; S = sputter yield.

From (11) and (12) it follows that the expression $\Delta z/z$ is constant, i.e. independent of the crater depth. This result we

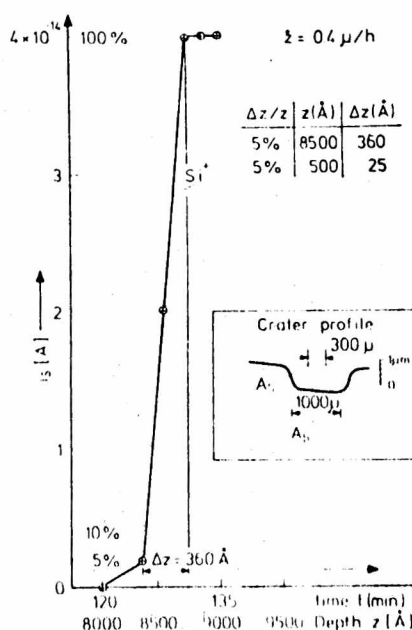


Figure 15. Actual profile of Si^+ measured in a thin film. Resolution in depth about 5%.

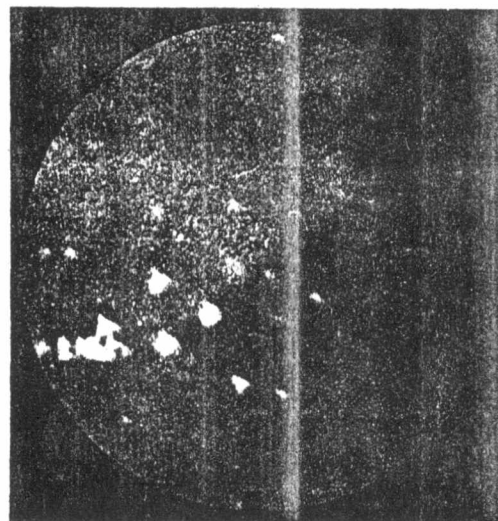


Figure 16. Ni^+ image of a polycrystalline Ni-sample taken after removal of about 3000 Å of a passivating Ni layer. Diameter of the whole area approximately 200 μm. To obtain this image a Ni layer of about 125 Å thickness was sputtered.

have verified experimentally by measurement of the crater profile after different times of bombardment. We have therefore chosen the expression

$$R = \Delta z/z = \Delta(jS)/jS = \text{const.} \quad (13)$$

as a measure of the depth resolution.

So far we have considered the response of a secondary ion mass spectrometer to an ideal step function distribution.

Profiles which are measured in practical samples in general will have larger delays Δz , depending on how the profile which is present in the sample deviates from the ideal step function. The delay Δz in this case reflects the contribution of the instrument and the profile.

Reported values of depth resolution according to the above definition are between 20% and about 5%.^{58,69,74,108} Due to the ease of availability of data, Figure 15 shows the results of our own measurement with a resolution in depth of about 5%.

After having discussed all the difficulties and remedies, the question may rise whether SIMS is useful in practice at all. A number of authors^{26,67,85,108,109,115} have compared this SIMS method with other well-established methods. The conclusion from their work is that within tolerable limits SIMS provides a reliable quantitative method for profile measurements in a given sample, provided that the necessary care in experimental set-up, as described above, has been taken.

7.3 Ion imaging of surfaces. Imaging of surfaces by means of secondary ions is obtained with one design^{104,105} in the same way as in the electron microprobe, viz. by scanning across the surface with a fine ion beam. In another design¹¹⁶ an image of the surface in the 'light' of secondary ions is obtained via the ion optics of the mass spectrometer.

Figure 16 shows the Ni^+ image of a polycrystalline nickel substrate, which was originally covered with a passivating nickel layer, after erosion of about 5000 Å. Several white spots are visible on this image which are remainders of a nickel compound¹¹⁷ from the passivating layer. Another feature of SIMS is reflected in the non-uniform intensity of this Ni^+ image.

Since the secondary ion yield is dependent on the crystallographic orientation, this clearly highlights the polycrystallinity of the nickel substrate.

8. Conclusion

In conclusion, one can say that SIMS, with a low limit of detection and relatively small material consumption has already found a wide range of applications in thin film and surface layer research. The quantitative aspect of SIMS is a weak point due to the dependence on standards. The existing theories allow us to hope, however, that this obstacle, too, will be removed in the not too distant future.

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*Note added in proof: From recent work of Sigmund¹¹⁹ a cascade lifetime—initiated by 4 keV O²⁺ or Ar⁺ ions, bombarding a Si or Fe target—of 10⁻¹⁴ sec is estimated.

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1. *Physikalisches Institut der Universität zu Köln*

Surface Oxidation Studies of Iron Using the Static Method of Secondary Ion Mass Spectrometry (SIMS)

By

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By the static method of secondary ion mass spectrometry (SIMS) the uppermost monolayer of a solid can be investigated for a long period, virtually without sputtering or destroying it. The iron-oxygen system was studied by this SIMS technique. The formation of an iron oxide film on a polycrystalline iron surface during oxygen exposure at room temperature was studied by observing the intensities of secondary ions typical for iron oxide. By observing the intensity variation of typical secondary ions during removal of these oxide films by ion bombardment further information could be obtained. An oxygen dose of some 100 L was found to be necessary to form a monomolecular oxide layer. Further admission of oxygen increased the thickness of the iron oxide film. A second oxide phase showing different secondary ion emission properties was formed simultaneously at the oxide-vacuum interface.

Mit der statischen Methode der Sekundär-Ionenmassenspektrometrie (SIMS) kann die oberste Monoschicht eines Festkörpers, nahezu ohne Zerstäubung oder Zerstörung, längere Zeit untersucht werden. Mit der SIMS-Technik wurde das Eisen-Sauerstoff-System untersucht. Die Bildung einer Eisenoxidschicht auf einer polykristallinen Eisenoberfläche während der Sauerstoffeinwirkung bei Zimmertemperatur wurde durch die Beobachtung der für Eisenoxyd typischen Intensitäten der Sekundärionen untersucht. Durch die Beobachtung der Intensitätsänderung der typischen Sekundärionen während der Beseitigung dieser Oxidschichten durch Ionenbombardement können weitere Informationen erhalten werden. Es wurde gefunden, daß eine Sauerstoffdosis von einigen 100 L notwendig ist, um eine monomolekulare Oxidschicht zu bilden. Weitere Zufuhr von Sauerstoff vergrößerte die Dicke der Eisenoxidschicht. Eine zweite Oxidphase mit unterschiedlichen Sekundärionenemissionseigenschaften wurde gleichzeitig an der Oxid-Vakuumgrenz-Fläche gebildet.

1. Introduction

In this paper the investigation of a chemical reaction at a solid-gas interface using secondary ion mass spectrometry as a tool for surface analysis is discussed. The technologically interesting system iron-oxygen was chosen as an example, as further studies of the corrosion of iron and its alloys will be undertaken. It is shown that it is possible to produce in a controlled manner oxide layers in the monolayer and submonolayer range. Thus details of the process of the surface reaction and the secondary ion emission process itself are obtained.

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2. Method

The processes occurring in the bulk and at the surface of a solid which is bombarded by ions are rather complicated and not yet completely understood [1]. Thus the secondary ion emission process can only be dealt with very briefly. The impact of a primary ion on the solid causes a collision cascade with two body collisions of the primary ion with target atoms, and also between target atoms. As a result particles can be emitted from the solid if an energy is transferred which is greater than the binding energy of the solid.

These secondary particles can be emitted in the form of neutral particles or ions (secondary ions). Primary ions in the low keV range generate secondary ions in the outermost atomic layers. Information about the chemical composition of the solid surface is obtained by analysing the secondary ions with a mass spectrometer.

Secondary ion formation can be attributed to several ionization processes [2]. Only those processes will be mentioned which occur as follows. Chemical ionization occurs if the emitted particle was chemically bound to other surface atoms before its emission [3, 4]. A very high ion production is observed from breaking ionic bonds [5]. With a clean metal surface secondary ion emission is due to the ionization process of kinetic emission [6, 7]. Ion yields obtained by this process are usually considerably smaller than those obtained from chemical ionization [8].

Using a simple model, the quantitative relation between the composition of a surface (e.g. a metal surface which is partially covered by a contamination layer) and its secondary particle emission is given by the formula

$$v_s = S\theta v_p$$

(v_s secondary particle flux of contamination atoms, S sputtering yield, θ relative coverage of contamination atoms, v_p primary ion flux). The secondary ion current density i_s for singly charged ions is

$$i_s = v_s \beta e_0 = S\theta \beta i_p$$

(β ionization coefficient of the secondary particles, i_p primary ion current density, e_0 elementary charge).

By using the method of secondary ion mass spectrometry the surface to be studied is in principle changed by the primary ion bombardment. This effect may consist of changes in the surface structure and of stimulation of chemical reactions. Additionally, alterations of the composition of the surface are brought about by primary ion implantation and sputtering of the surface, as in general the different components have different sputtering yields.

By sufficiently reducing the primary ion current density as is done in the "static method of secondary ion mass spectrometry" [9 to 12] used here, these difficulties can be made small enough to be neglected. Thus, a measuring time of about 800 s only causes the removal of 1% of a monolayer if a primary current density of $i_p = 10^{-9}$ A/cm² is used, which is typical for this work. This method therefore allows chemical surface reactions (e.g. solid-gas reactions) to be studied by observing the intensities of secondary ions during the formation of the emitting surface layer by the surface reaction. Thus this method of studying surface reactions is better than a dynamical method of secondary ion mass spectrometry (typical primary current density: $i_p = 10^{-5}$ A/cm²) [13 to 16]. Further informa-

tion about layers generated by solid-gas reactions (e.g. determination of depth profiles, only a single monolayer present) can be obtained by recording secondary ion intensities during sputtering (typical current density: $i_p = 10^{-7}$ A/cm²). Sputtering of monolayers and submonolayers is described by an exponential law [9, 10]:

$$O(q) = O(0) \exp(q/\hat{q}); \quad \hat{q} = e_0 \vartheta_0 / S, \quad q = e_0 v_p t$$

(q primary ion current density $\times$ time, ϑ_0 number of atoms per cm² in a monolayer, t bombarding time).

During these studies difficulties caused by increased ion bombardment cannot in principle be avoided [11].

3. Apparatus

For the investigations described here a UHV secondary ion mass spectrometer pumped by mercury diffusion pumps was used. While measuring, a residual gas pressure of less than 5×10^{-9} Torr was maintained at the target. During ion bombardment an additional argon gas pressure of 3×10^{-6} Torr maximum was superimposed. The main component of the residual gas was hydrogen. The partial pressure of oxygen was below 5×10^{-10} Torr. Oxygen could be admitted as a reactive gas by means of a variable leak valve (Fig. 1).

The target which was placed in the secondary ion source was bombarded by Ar⁺ ions generated in a gas discharge ion source (energy: 3 keV, angle of incidence with respect to the normal of the target: 70°). The target area hit by the primary ions was 0.11 cm².

Mass analysis was performed with a 60° magnetic sector field. Ions were detected by a secondary electron multiplier working in the counting mode.

4. Preparation of the Target

The polycrystalline target consisted of iron of 99.997% purity. Before putting it into the spectrometer it was mechanically polished and then rinsed with water, ethyl alcohol, and trichlorethylene. The remaining surface contamination was removed by sputtering in the spectrometer. The necessary ion dose was about 3×10^{-2} As/cm², which corresponds to the removal of some hundred monolayers. The degree of purity of the surface was controlled by secondary ion spectra.

After this cleaning procedure, the oxidation process was started by the admission of oxygen at a partial pressure which was generally about 10^{-6} to 10^{-8} Torr. The time required to generate a monomolecular oxide layer under these conditions was about 10 min. The oxidation process which proved to be

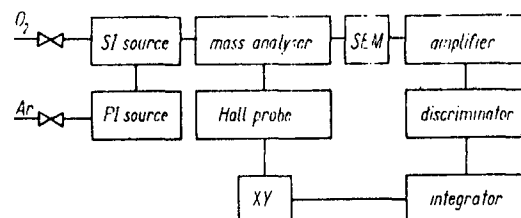


Fig. 1. Schematic of the secondary ion mass spectrometer

reproducible was repeated several times, the surface being cleaned by ion bombardment after each oxidation. During the whole investigation the target was held at room temperature.

5. Results and Discussion

The secondary ions characteristic of an iron oxide layer which are able to give information about the oxidation process were found from secondary ion spectra. The general composition of the secondary ions emitted by iron oxide is given by the formula Fe_mO_n ($m, n = 0, 1, 2, \dots$). The real characteristic ions are only those with the condition $m, n \geq 1$. Table I gives a summary of the secondary ion emission from a cleaned and oxidized iron surface. By observing the characteristic secondary ion intensities during oxidation and during defined removal of an oxide layer formed by oxygen exposure, details of the surface reaction of oxidation could be found. It was found that at least in the pressure range of 10^{-7} Torr which was investigated here the intensities of secondary ion emission were a function of O_2 dose (Fig. 2).

Table I
Intensities of secondary ions
(number of pulses per incident primary ion)

ion	positive ions		negative ions	
	cleaned surface	oxidized surface	cleaned surface	oxidized surface
O	1.3×10^{-10}	0.8×10^{-9}	1.0×10^{-8}	1.0×10^{-7}
O_2			1.5×10^{-9}	3.1×10^{-8}
Fe	1.4×10^{-8}	3.1×10^{-6}		
FeO	3.5×10^{-10}	1.3×10^{-7}	3.6×10^{-10}	6.2×10^{-9}
FeO_2			1.9×10^{-9}	7.8×10^{-8}
FeO_3			2.3×10^{-10}	3.3×10^{-8}
Fe_2	3.9×10^{-9}	0.7×10^{-8}		
Fe_2O	6.7×10^{-10}	3.3×10^{-8}		
Fe_3O_3	1.7×10^{-11}	2.5×10^{-9}		
Fe_3	2.0×10^{-10}	$< 10^{-9}$		
Fe_4	4.3×10^{-11}	$< 10^{-9}$		
Fe_5	1.4×10^{-11}	$< 10^{-9}$		

Fig. 3 shows the intensities of some secondary ions as a function of oxygen exposure. Initially an increase in intensity is found for all secondary ions. With the exception of the FeO^- ions whose intensity increases linearly a retarded

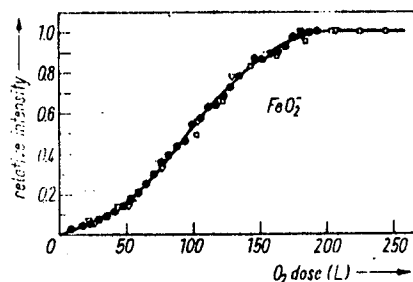


Fig. 2. Oxygen dose dependence of normalized FeO_2^- intensity recorded at different oxygen partial pressures:

● $p = 0.98 \times 10^{-7}$ Torr; □ 6.8×10^{-7} Torr;
▽ 3.7×10^{-7} Torr O_2

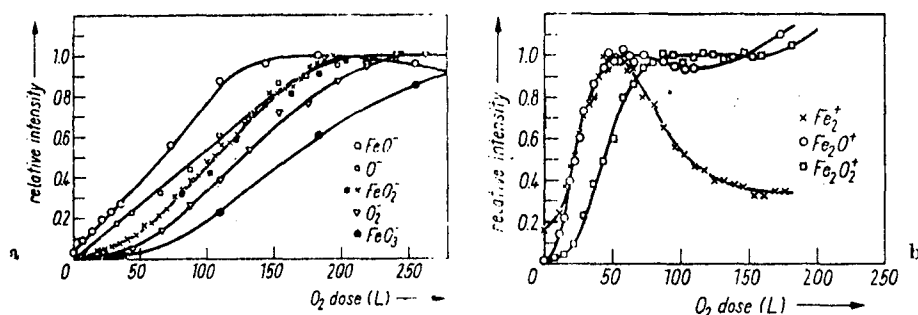


Fig. 3. Increase of normalized secondary ion intensities during oxygen exposure

intensity increase is observed for the negative oxide ions FeO_n^- (Fig. 3a). This retardation increases with n . The same behaviour is found for the positive secondary ions Fe_2O^+ and Fe_2O_2^+ (Fig. 3b). At an oxygen dose of approximately 100 to 200 L some secondary ion intensities have a maximum or an intermediate saturation, respectively (FeO^- , FeO_2^- , O^- , Fe_2O^+ , Fe_2O_2^+). Evidently, this behaviour is correlated to the formation of a complete oxide monolayer.

The retarded oxide formation is in accordance with some LEED studies [17, 18] giving reflexes only at oxygen doses of some hundred L which can be attributed to a FeO layer (whereas reflexes correlated to a 1/4 atomic oxygen contamination layer already appear at doses of some L).

That there is only a monomolecular oxide layer at the most after an oxygen admission of 200 L, can be concluded from removing such a layer by sputtering. As is shown in Fig. 4 an exponential decrease of intensity is obtained for the ions Fe^+ , FeO_2^- , and FeO_3^- . This behaviour is typical for a surface layer in the monolayer or submonolayer range.

The different oxygen dependence of the different ion intensities, especially the behaviour of the oxide ions (i.e. the different retardation and saturation behaviour), must be attributed to the gradual formation of the oxide monolayer [11, 19]. For the metallic ions Fe^+ and Fe_2^+ , the intensity increase is determined by the transition from kinetic emission to the more effective chemical emission. The pronounced maximum of the Fe_2^+ intensity (Fig. 3b) can be understood by assuming that for an optimum Fe_2^+ emission two conditions are necessary: (i) large ion yield (e.g. by chemical emission) and (ii) immediate neighbourhood of Fe atoms in pairs in the surface. For the clean metal, it is obvious that condi-

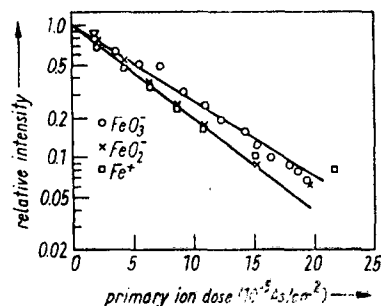


Fig. 4. Decrease of normalized secondary ion intensities during sputtering of an iron oxide layer (oxygen exposure: $D = 200 \text{ L}$)

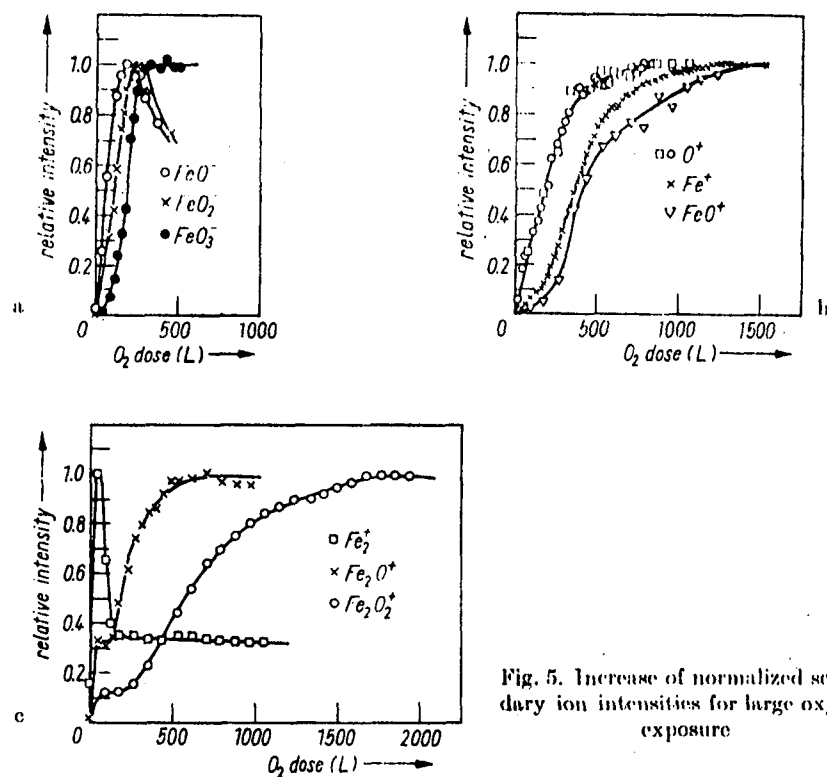


Fig. 5. Increase of normalized secondary ion intensities for large oxygen exposure

tion (ii) is fulfilled but not condition (i) (kinetic emission). For the oxide the conditions are reversed (FeO has the structure of NaCl). Evidently with a low oxide covering conditions (i) and (ii) are fulfilled at optimum when secondary ion emission takes place from the metal-oxide interface.

Further alterations of the secondary ion emission appear at oxygen doses > 200 L (Fig. 5). The FeO^- and FeO_2^- intensities decrease while the FeO_3^- , Fe^+ , and FeO^+ intensities continue to increase. The Fe_2O^+ and Fe_2O_2^+ intensities also increase after their intermediate saturation. A final saturation stage is only partially attained at an oxygen dose in the 10^3 L range. With oxygen doses of this magnitude, oxide layers consisting of several monolayers are formed as can be proved by controlled sputtering [20].

The intensity changes at high oxygen doses can be interpreted by assuming that a layer is formed which consists of a second oxide phase and is situated between the oxide phase formed at first and the gas phase. This new oxide phase shows a different secondary ion emission. The formation of this second oxide layer largely determines the secondary ion emission of the oxide layer for doses > 200 L as secondary ions are generated in the uppermost atomic layers of the target where the formation of this oxide phase takes place. The final saturation is reached when the surface is covered by a complete monolayer of the second oxide phase.

This assumption can be proved by observing several secondary ion intensities during sputtering of a thick oxide layer (oxygen exposure: $D = 1100$ L). At

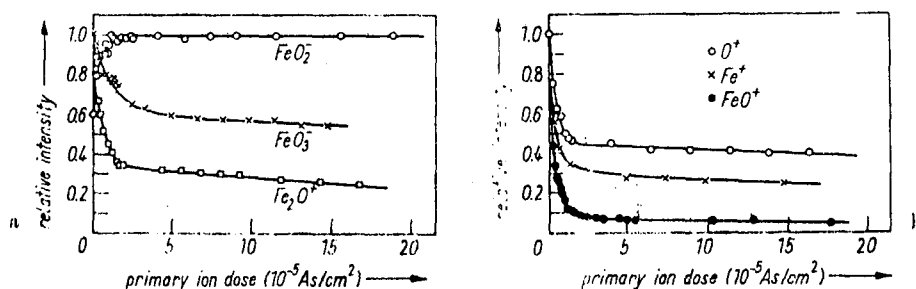


Fig. 6. Decrease of normalized secondary ion intensities during sputtering of a thick oxide layer (oxygen exposure: $D = 1100 \text{ L}$)

the beginning of ion bombardment a pronounced change in intensity is found for all secondary ions (except the Fe_2^+ ion). Thereafter the secondary ion emission is fairly constant for a relatively long period (Fig. 6).

A comparison shows that the oxide phase adjacent to the metal substrate (nearly constant ion emission) has the same properties of secondary ion emission as an oxide layer formed by an oxygen dose of 200 L . It consists of several monolayers as it is able to emit secondary ions with constant intensity during ion bombardment for ion doses in the 10^{-4} As/cm^2 range. In comparison, a single oxide monolayer shows an intensity decrease of about 90% after a bombardment by an ion dose of $1.5 \cdot 10^{-5} \text{ As/cm}^2$ (Fig. 4). The second oxide phase which is characterized by an increased FeO_3^+ and FeO^+ emission in relation to the first oxide phase (Fig. 5 and 6) is primarily removed by sputtering. It has a higher sputtering yield than the first phase and is thus removed relatively quickly. The decrease in intensity which is similar to an exponential decrease for several ions (FeO^+ , Fe_2O^+ , Fe^+ , O^+ , and FeO_3^+) indicates that with the oxygen doses used here this part of the oxide layer has the characteristics of a monolayer.

It can be suggested that the second oxide phase consists of an oxide richer in oxygen than FeO (e.g. Fe_3O_4 or Fe_2O_3). As at least a part of the Fe atoms is in the state of Fe^{+++} ions (instead of Fe^{++} ions as in FeO) in these oxides, it can be imagined that the different secondary ion emission properties of the two oxide phases are attributed to a change in the chemical valency of the iron atom.

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Ion Microprobe Analysis for Niobium Hydride in Hydrogen-Embrittled Niobium

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A hydrogen-embrittled niobium sample, fractured above the solvus temperature, has been examined using an ion microprobe. Ion images taken with Nb^+ , NbH^+ , H^+ , and NbO^+ ions reveal strong enhancement of the emission of the hydrogen-containing ion species from the walls of the main fracture and from a secondary crack. Comparison of the NbH^+/Nb^+ ion ratio from the crack walls with that observed from known niobium hydride precipitates demonstrates that the hydrogen-rich phase found on the fracture walls is niobium hydride. The results confirm a postulated mechanism of hydrogen embrittlement by stress-induced precipitation of niobium hydride.

The problem of hydrogen embrittlement in niobium has come under intensive study in recent years. Niobium is a refractory metal with nuclear properties which make it well suited for use as a first wall material in proposed fusion reactors. In such an environment, the metal must withstand exposure to isotopes of hydrogen in addition to intense radiation. It has been known for many years that the solution of hydrogen in niobium can lead to catastrophic embrittlement (1) even at concentrations as low as 0.1 at. % (2). The mechanism of the process has long been the subject of speculation. Although niobium can form a hydride, NbH , which is itself brittle, embrittlement can occur at hydrogen concentrations too low for hydride to be formed. Two of the most plausible mechanisms depend upon the extremely rapid diffusion rate of hydrogen in niobium. It can be shown thermodynamically that hydrogen will diffuse toward a region of tensile stress (3). In one proposed mechanism it is postulated that the increased concentration of hydrogen in solution in the high stress region reduces the lattice cohesion (4, 5). In the other mechanism, precipitation of niobium hydride is presumed to occur due to the reduction in the free energy of transformation by the stress field (6, 7); fracture then occurs in the brittle hydride. In either case, once a crack has begun, the region of high stress moves with the crack tip and the process of diffusion and fracture reoccurs, propagating the crack through the metal.

Extensive metallographic, scanning electron microscope (SEM), and electron diffraction studies at the University of Illinois (8) have produced strong support for the second mechanism. Chemical evidence of niobium hydride in the fracture region of an embrittled sample would provide final confirmation of the mechanism, since an increased solution concentration would rehomogenize when fracture relieved the stress. Since SEM evidence indicated that hydride-like layers occurred at fracture surfaces with dimensions of the order of microns, the ion microprobe analysis was necessary as this is the only technique capable of hydrogen analysis on this scale.

EXPERIMENTAL

An AEI IM20 ion microprobe was used in this study. Some features of this instrument and its performance have been described elsewhere (9, 10). The duoplasmatron primary ion source was operated with an oxygen gas feed. The primary ions generated under these conditions are O_2^+ , O^+ , and some NO^+ and NO_2^+ arising from nitrogen impurities in the gas feed. The primary ion impact energy at the sample was 15 keV, and the primary beam diameter at the sample was typically 5–10 μm . The secondary ion mass spectrometer is capable of a mass resolving power in excess of 5000. After a check of the spectral purity of the peaks of analytical interest at high resolving power, the instrument was operated routinely at a resolving power of 250.

Secondary ion images were obtained using the "Autoscan" attachment of the IM20 ion probe. This allows the primary beam to be rastered across a square region of the sample up to $256 \times 256 \mu\text{m}$ in size. A display oscilloscope is rastered synchronously with the primary beam. The ion signal due to any resolved secondary ion species is amplified using an ion-electron multiplier and electrometer amplifier. This signal is used to modulate the intensity of the display oscilloscope, thereby forming an image which qualitatively represents the distribution of the selected mass species on the specimen surface. The scan voltages are digitally generated staircase ramps, with the number of points per line selectable from 2^3 to 2^8 . Dwell time per point is continuously variable from 10 μs up to 1 s. All images shown in this article were obtained using a $128 \times 128 \mu\text{m}$ scan, 256 points/line and between 100 μs and 1 ms per point. Approximately 300 $\text{\AA}$ of the sample were sputtered for each image taken. The "line scan" feature of the "Autoscan" allowed the display of resolved secondary ion intensity vs. position along any selected line of the raster in the x or y direction.

Sample Preparation. Tensile specimens of the dimensions shown in Figure 1 were prepared from reactor grade rolled sheet, 0.040 in. thick (Wah Chang Albany Corp.). Purity was better than 99.9%. After machining, the samples were etched ($\frac{1}{2}\text{HNO}_3$, $\frac{1}{2}\text{HF}$, $\frac{1}{2}$ lactic acid), polished to about a 0.5- μm finish, re-etched, and UHV annealed at 2100 °C. Hydrogen (deuterium) charging was accomplished by equilibration with H_2 (D_2) gas in a UHV system, and bulk analysis of the charged samples was performed by a hot extraction technique (by Leco Corp.).

SECONDARY ION MICROGRAPHIC RESULTS

The ion microprobe was used to study a niobium-2 at. % hydrogen sample which had previously been fractured at 4 °C in an SEM study (8). At this composition, niobium hydride does not form on cooling to 4 °C, but it can be stress induced. Such hydride would be stable up to about 10 °C above room temperature because of a pronounced hysteresis associated with the transformation (9). The sample geometry is shown in Figure 1. It was part of a tensile sample which had fractured leaving a small secondary crack leading off at an angle to the main fracture. The fractured sample was imaged in the ion microprobe using Nb^+ and NbH^+ ions. Figure 2 shows three composite images of the small secondary crack in the sample. The SEM image was taken after the ion images and shows details of the crack and also the square ion-etched craters produced during ion imaging. It is evident from the ion images that the NbH^+ signal is

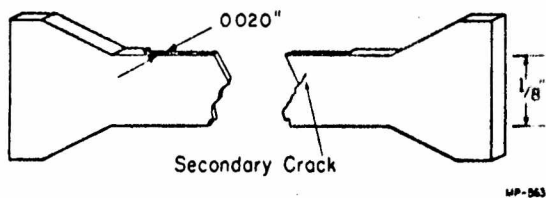


Figure 1. Sample geometry

enhanced (brighter) in the region of the crack. The Nb^+ image is similar to the SEM image, although of lower resolution, since the primary ion beam size was about $5\text{ }\mu\text{m}$.

In general, energetic ion bombardment of a surface generates ion species containing most of the possible combinations of the atoms present at the surface, so that the observation of NbH^+ secondary ions is indicative only of the presence of hydrogen in the outer surface layers and not necessarily of niobium hydride. Evidence will be presented in a later section in support of our conclusion that the enhanced NbH^+ signal arises from a niobium hydride phase. We will discuss here evidence from the images concerning the spatial extent of this NbH phase. A dark band to the left of the bright niobium hydride region in the upper half of the crack indicates that, at this point, the fracture occurred at the hydride-solid solution interface. Further evidence for such a fracture mode comes from images of the edge of the main fracture (Figure 3) which show patches of NbH rather than the continuous border that might be expected from fracture through the center of an NbH band. However, the image of the mouth of the crack provides evidence that NbH can exist on both sides of a crack. This re-

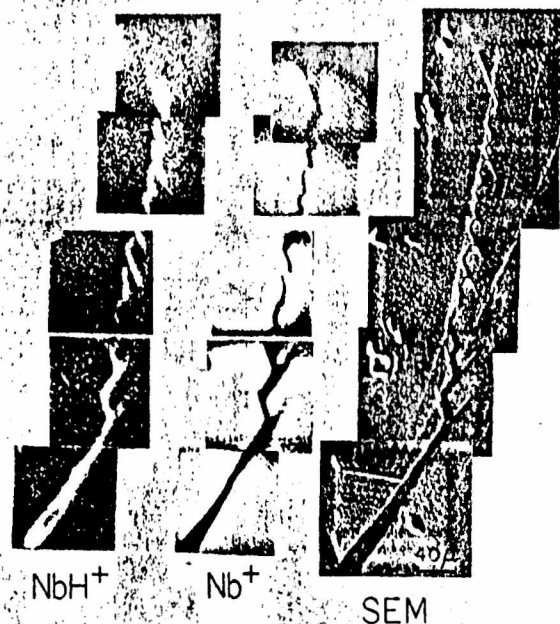


Figure 2. Composite ion and electron micrographs of secondary crack. All images are shown at same magnification

gion, shown enlarged in Figure 4, was studied in more detail. Since topographical effects can affect secondary ion intensities by impeding or enhancing ion extraction from the surface, the absolute NbH^+ and Nb^+ ion intensities are of less significance than the ratio, NbH^+/Nb^+ . This ratio is used here to characterize the samples.

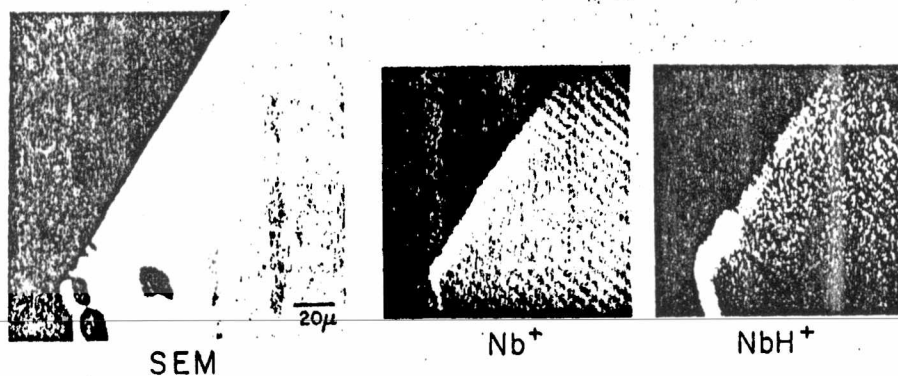


Figure 3. Main fracture edge. All images are shown at same magnification

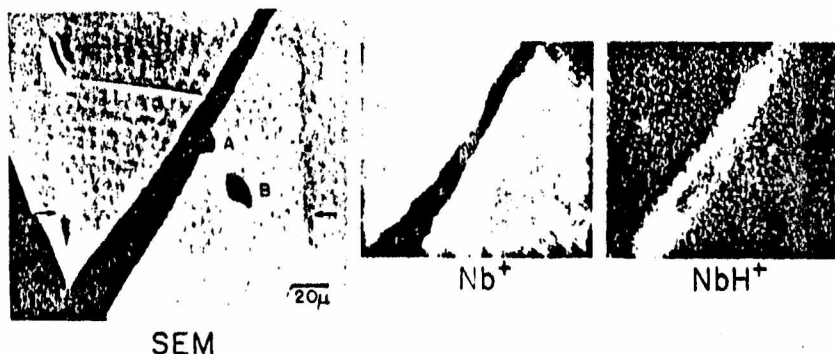


Figure 4. Mouth of secondary crack. Arrows indicate line scan position. Mass spectra obtained at points A and B. All images are shown at same magnification

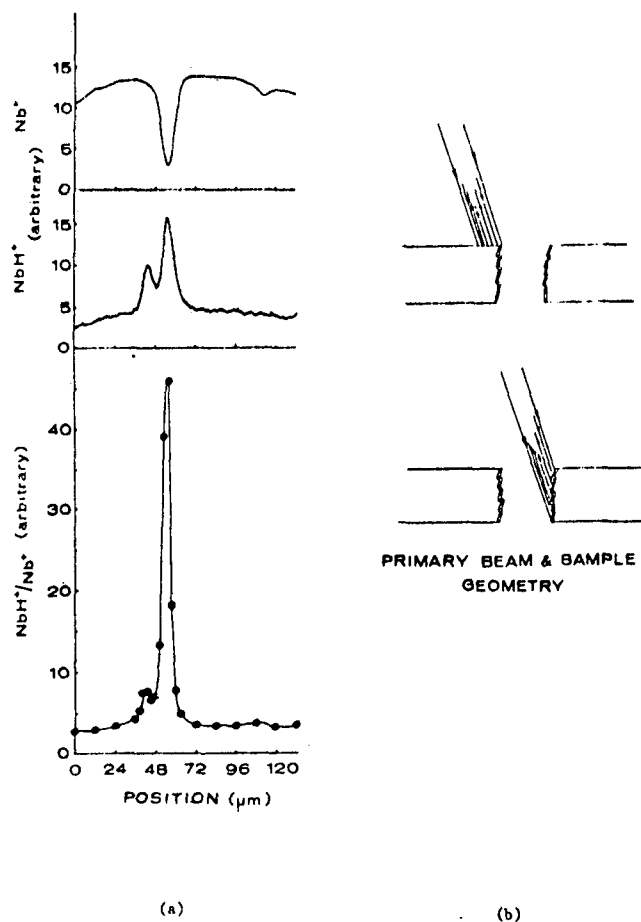


Figure 5. Line scans across mouth of secondary crack

To study the variation of the NbH^+/Nb^+ ratio in the fracture region of Figure 4, line scans were taken between the points marked by the arrows. The results are shown in Figure 5a. Scans of the Nb^+ and NbH^+ signals are shown, as recorded photographically from the display oscilloscope. The ratio NbH^+/Nb^+ was calculated from measurements on these two line scans and is plotted below them. The rather pronounced peak at $\sim 42 \mu\text{m}$ in the NbH^+ signal is seen to correspond to only a small enhancement of the ratio at this point, whereas a large increase in the NbH^+/Nb^+ ratio is seen at $\sim 60 \mu\text{m}$. The reason for this disparity involves the size of the primary beam and the angle at which it strikes the sample, as indicated in Figure 5b. The lateral extent of the hydride appears to be much less than the primary beam diameter. Thus, on the left-hand side of the crack, only a small fraction (10–15%) of the primary beam can sample the NbH layer. Since the beam impinges at an angle (17°), it can sample the fracture surface on the right of the crack, which should be almost all hydride. Secondary ions are not extracted efficiently from within the crack, so that both the NbH^+ and Nb^+ signals are reduced and only the ratio shows a strong enhancement. By orienting the sample so that the primary beam strikes the left-hand fracture surface, the ratio from the left side becomes dominant, confirming this topographical explanation. The thickness of the NbH layer thus appears to be about 10–15% of the primary beam diameter—i.e., about $1 \mu\text{m}$. This is in good agreement with the SEM observations (8).

The major secondary ion species produced by oxygen ion bombardment of hydrogen-containing niobium samples are Nb^+ , NbO^+ , NbH^+ , and H^+ . It was considered essential in this work to normalize all ion currents with respect to the Nb^+ current. The H^+ signal was not often used because, when the secondary ion magnetic analyzer was scanned

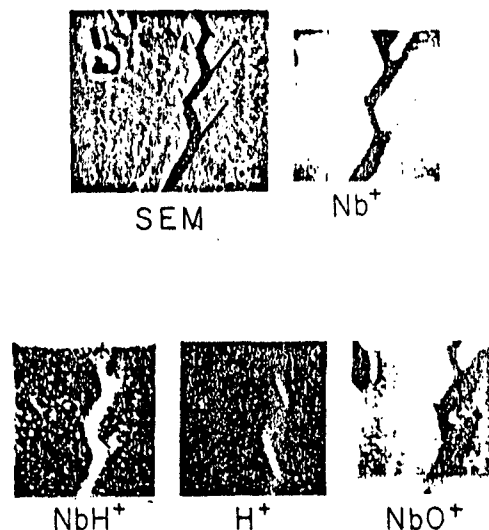


Figure 6. Portion of secondary crack imaged using the four major secondary ion species. All images are shown at same magnification

down to mass 1, changes in magnetic fringe fields along the primary ion path shifted the beam position at the sample by 20–30 μm . It was therefore impossible to obtain H^+ and Nb^+ ion intensities from exactly the same point. The H^+ signal was studied only to the extent necessary to confirm that it behaved similarly to the NbH^+ signal—that is, it was enhanced in the vicinity of the fracture. Figure 6 shows ion micrographs of a portion of the crack obtained with all four major ion species. The NbO^+ image shows surface topographical contrast more strongly than the Nb^+ image (e.g., slip lines are visible and contrast is dissimilar on the two sides of the crack). However, like the Nb^+ image and unlike NbH^+ and H^+ , the signal is diminished in the vicinity of the crack. The absence of such impurities as Zr and Mo, which could give a peak at mass 94, was confirmed by the absence of their other isotopes (and in any case they should not have been localized along the transgranular fracture surface).

Since the ion source vacuum system employed oil diffusion pumps and was not baked, hydrogen-containing species were present in the residual gas. The contribution of such species to the NbH^+ signal was evaluated by examining Nb–D solid solution samples. The residual hydrogen appeared to be associated with condensable gases such as water and hydrocarbons. With the ion source cold finger cooled with liquid nitrogen, the NbH^+ signal from the deuterated samples was small. Using the amplitude of this signal as a measure of the background gas contribution to the NbH^+ signal from the hydrogen-containing samples, we estimate that this contribution was no greater than about 20% of the lowest NbH^+ signal observed in this study. The possibility that preferential adsorption of background hydrogen was giving rise to an enhanced NbH^+ signal from the fracture surface is negated by the NbH^+ image of Figure 3 which shows discontinuous patches of high NbH^+ signal along the fracture surface.

We shall refer to the quotient

$$(\text{NbH}^+/\text{Nb}^+)_{\text{hydride}}/(\text{NbH}^+/\text{Nb}^+)_{\text{solid solution}}$$

as the *chemical contrast*. Good estimates of the NbH^+/Nb^+ ratios cannot be made from the line scans of Figure 5. To obtain more quantitative data, the primary beam was positioned at single spots—one inside the crack on the frac-

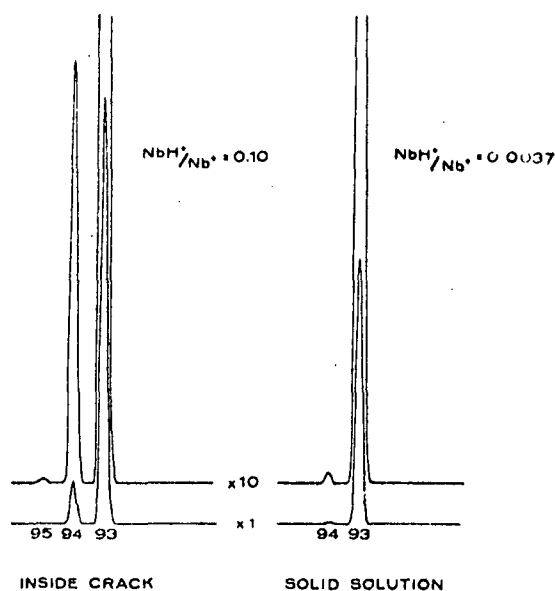


Figure 7. Mass spectra

ture surface, and the other well away from the crack in the solid solution region—and mass spectra were obtained at these two points. The spectra are shown in Figure 7. The NbH^+/Nb^+ ratio from the fracture surface is 0.10, and the chemical contrast between the fracture surface and solid solution is 27:1. Since the difference in hydrogen concentration between the fracture surface and the solid solution should be a factor of 25 if the fracture surface is hydride, the agreement between the chemical contrast and the concentration ratio is striking. The fracture surface is in fact so hydrogen-rich that some NbH_2^+ is seen at mass 95 in the fracture surface mass spectrum of Figure 7.

There exists no a priori relationship between secondary molecular ion intensities and surface composition and, in particular, there is no reason to expect that the NbH^+/Nb^+ signal ratio should be proportional to hydrogen concentration over the composition range from solid solution to bulk hydride. Thus, the agreement between the chemical contrast and the hydrogen concentration ratio in NbH and $\text{Nb-2 at. \% H}$ solid solution is not of itself proof that the fracture surface is NbH . To establish the identity of the hydrogen-rich phase at the fracture surface, it was necessary to examine the secondary ion behavior of standard samples. A niobium-5.5 at. $\% \text{ H}$ sample was examined, in which visible precipitates of NbH had formed on cooling to room temperature after hydrogen charging. The surface of the hydride precipitate did not give an enhanced NbH^+ signal but, as sputtering proceeded deep into the sample, evidence of hydride was found. Figure 8 shows the result of crude depth profiles on this sample (taken with poor depth resolution because of the need to erode deeply into the sample). The variation of the NbH^+/Nb^+ ratio with depth suggests that the niobium hydride had precipitated in layers. Layered precipitates have also been observed in transmission electron microscope (TEM) studies (11, 12). The spacing of the layers (3–4 μm) agrees quite well with the TEM observations (12). Also shown in Figure 8 is a depth profile through a region with no visible evidence of NbH precipitates which shows no enhancement in the NbH^+/Nb^+ ratio. The average of the peak NbH^+/Nb^+ ratios in Figure 8 is 0.095, in good agreement with the ratio of 0.10 obtained at the fracture surface. In addition, the chemical contrast between the NbH and solid solution regions is about 10:1 which again closely parallels the hydrogen concentration ratio between the two regions. The slow

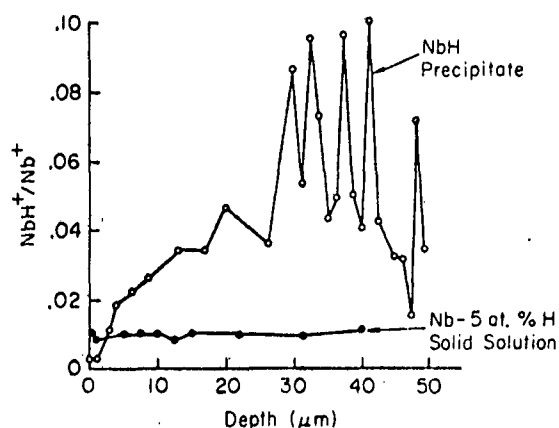


Figure 8. Depth profiles through precipitate and solid solution regions of $\text{Nb-5 at. \% H}$ sample

increase in the NbH^+/Nb^+ ratio in the hydride region is probably due to the sampling of layered precipitates not oriented perpendicularly to the sputtering front. When this occurs, the ion signal, which is an average value for the whole of the crater, represents the sampling of an arbitrary mixture of precipitate and solid solution.

Subsurface nucleation of hydride, as observed here, appears to be the rule in these samples. Examination of another $\text{Nb-5.5 at. \% H}$ sample, with sharply delineated precipitates apparently close to the surface, again showed no significant enhancement in the NbH^+/Nb^+ ratio within 5–10 μm of the surface. In an attempt to observe hydride precipitated at the surface, a sample containing 1 at. $\% \text{ H}$ was cooled in the ion probe to -100°C . Nucleation and growth of numerous small precipitates began at about -50°C . Once again the majority of precipitates showed no NbH^+/Nb^+ enhancement near the surface. Only in the small number of precipitates which had apparently nucleated at surface features—a scratch, a hardness test indentation—was hydride observed, and then only after eroding 10–20 μm into the precipitates. It is possible that surface nucleation may occur more readily on $\{111\}$ surfaces, since a cooled $\text{Nb-1 at. \% D}$ sample with $\{111\}$ surface orientation did produce precipitates detectable near the surface. The hydrogen-containing samples examined all had $\{110\}$ or $\{100\}$ surfaces. This point requires further study.

We conclude that, under the experimental conditions of this study, a NbH^+/Nb^+ secondary ion ratio of 0.10 ± 0.01 is characteristic of a niobium hydride precipitate in equilibrium with solid solution. It also appears that the NbH^+/Nb^+ ratio from hydrogen solid solutions can be proportional to the hydrogen concentration. However, the high diffusivity of dissolved hydrogen in niobium can give rise to variations in hydrogen concentration with such parameters as sample temperature, temperature gradients induced by primary beam heating, and sputtering rates; and these effects are being investigated. Such variations have been observed in work with deuterium solid solution samples, and the correspondence of the NbH^+/Nb^+ ratios with hydrogen concentration in solid solution is possibly coincidental. The NbH^+/Nb^+ ratios from hydride and deuteride samples appear insensitive to the parameters cited above. These ratios can thus be used with confidence to characterize niobium hydride or deuteride phases.

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Table III. Fixed-Time Reaction Rate Determinations of Phosphate

Digital readout ^a	Phosphorus concentration in ppm		Rel error, %	Rel std dev, %
	Taken	Found ^b		
6730	3	3.01	+0.33	1.48
11167	5	...	...	2.05
17800	8	7.97	-0.38	0.66
22249	10	10.01	+0.10	1.05

^a Average of 5 results.

^b Based on 5-ppm standard; integration time of 40 sec; pre-measurement time 40 sec.

Table III show considerably higher relative standard deviations than with synthetic slopes. This imprecision can be attributed to errors in sample introduction and preparation, and also to drifts in the spectrophotometric system and analog circuits. These drifts were made evident by rate measurements made on distilled water blanks containing no phosphate. The blanks gave an average readout of zero. However, the absolute value of the standard deviation of the blank was approximately equal to the standard deviations obtained when phosphate was present. Such drifts are small and normally

negligible when measurements are made over relatively large absorbance changes, but become highly significant when small concentration changes are measured. The effect of drifts in the spectrophotometer and analog circuits is presently under study.

Although the digital counting system described here contains no analog circuits, the reaction rate measurement system is limited by drifts and nonlinearities in the reaction monitor-signal modifier system and the V to F converter. At present, work is being done to replace these analog circuits with a photon counting system. This change involves replacing the current to voltage and V to F converters with a pulse amplifier and discriminator. Thus the photomultiplier tube will be directly interfaced to the fixed-time rate computer by photon counting circuits, and the entire rate measurement system will be completely digital in measurement and computation. This should lead to significant improvements in reaction rate measurements on chemical systems.

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Analysis of Thin Films by Ion Microprobe Mass Spectrometry

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The ion microprobe mass spectrometer was used to investigate isotopic and compositional gradients in thin films of both oxides and metals. Continuous recording of intensities, and sputter rates as low as 0.5 Å/sec enabled depth resolutions of the order of 20 Å. Oxygen isotope mixing in duplex Ta₂¹⁶O₅/Ta₂¹⁸O₅ films was shown to vary with the Ta₂¹⁸O₅ thickness added. Phosphorus gradients in Ta₂O₅ anodized in H₃PO₄ varied with film thickness and H₃PO₄ concentration. Homogeneities in thin films of Ag-Cu and Al-Ge-Nb depended on their modes of preparation. The ion microprobe is concluded to be a powerful tool for examining thin films.

THE CONCEPT of an ion microprobe mass spectrometer was first described by Herzog and Viehbock (1). A sample was bombarded with ions of energy in the KeV range causing surface atoms of the target to be sputtered, a small fraction of them being ionized. These secondary or sputtered ions were extracted into a mass spectrometer and analyzed.

A number of investigators have explored the application of this technique. Anderson (2) used positive and negative ions for bombarding the target, and Benninghoven (3) investigated the use of positive and negative secondary ions. Castaing and Slodzian (4) and Robinson, Liebl, and Andersen (5) demon-

strated that surface spatial resolution of the order of 1 μ can be obtained. Satkiewicz applied the technique to a variety of materials including metals, minerals (6), organic materials (7), and thin films (8). Relative ionization efficiencies were found to vary by several orders of magnitude from element to element (2, 3) so that detection limits vary widely. In favorable cases detectabilities in the ppm range are attainable. The removal rate of atoms from the sample is variable over a wide range—0.5 Å/sec for low ion current densities to 100 Å/sec for high current densities and high energy primary ions. Sputtering rates and ion yields are further influenced by parameters such as the nature of the bombarding ion, ion energy, sample and surface characteristics, and residual gas pressure, so that conditions must be optimized for a particular objective.

THIN FILMS

In addition to their great technological significance, thin films are of fundamental interest because they offer an opportunity to study an almost two-dimensional solid. Many analytical techniques have been used to study the physical,

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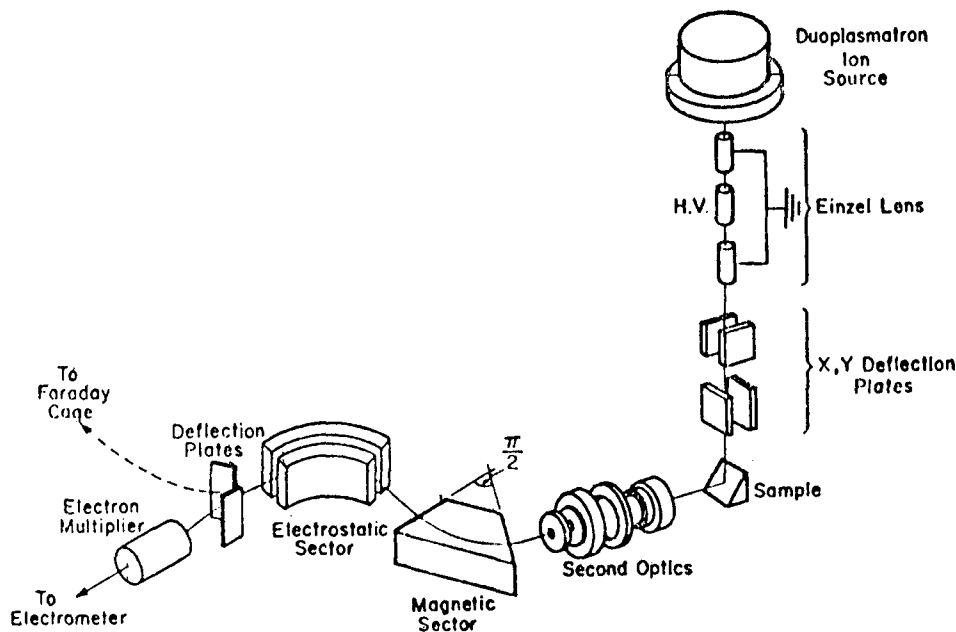


Figure 1. Schematic diagram of Ion Microprobe Mass Spectrometer

chemical, and structural properties of thin films (9). Chemical characterization requires a high degree of spatial resolution in the depth dimension. In a few specific cases, precision anodic stripping (10) can achieve depth resolutions of 100 Å. This technique, however, is not broadly applicable. Spark source mass spectroscopy is capable of good sensitivities for almost every element, but the depth resolution is only 1000 Å in the best of cases and more typically about 1 μ (11-13).

The ability to control penetration rates and the broad elemental coverage makes the ion microprobe particularly suitable to the study of thin films. Slow sputtering rates provide the best depth resolution. A corresponding signal decrease reduces detection limits, but this is generally tolerable as trace detection is not always necessary in thin film analysis. With these capabilities and limitations in mind, the ion microprobe mass spectrometer was evaluated as a technique for the chemical characterization of thin films.

EXPERIMENTAL

The GCA Ion Microprobe Analytical Mass Spectrometer (GCA Technology Division, Bedford, Mass.) was used for this study. A simplified representation of the instrument is shown in Figure 1. A duoplasmatron ion source provides the primary argon ions. These ions are then accelerated toward the sample with up to 15 KeV of kinetic energy. The ion beam diameter and position are determined by the Einzel lens and beam deflection electrodes. Sample bombardment by the primary ions causes sputtering of neutral atoms as well as positive and negative ions. In this study, the positive ions are extracted into a double-focusing mass

spectrometer for mass and energy resolution. A 20-stage Al dynode electron multiplier is used to detect the mass resolved secondary ions, and a vibrating reed electrometer and recorder provide a visual and permanent record of the ion intensity. Scanning the magnetic field during sputtering enables recording a mass spectrum of the secondary ions. A concentration *vs.* depth profile of a particular mass can be studied by setting the mass spectrometer to that peak and recording the intensity variations with time.

The following modifications and additions were made to the basic instrument.

Lif-O-Gen (Lif-O-Gen, Inc., Lumberton, N. J.) research grade argon and a two-stage regulator were used to supply argon to the duoplasmatron. This system is preferred over glass flasks in that it supplies a long-term constant pressure of primary gas, enabling more stable operation of the duoplasmatron. Also, the argon supply line is operated at a pressure above ambient, reducing contamination of the gas by inbound leakage.

All three Einzel lens electrodes in the primary optics were grounded, as suggested by Herzog and Satkiewicz (14), and the last aperture diameter was reduced to 3 mm. Aberrations due to the Einzel lenses were thereby eliminated.

A Faraday cage was inserted so that retraction of the sample holder allowed the primary ion beam to be monitored. The current was read on a digital panel meter.

The single coarse and fine controls provided for manual adjustment of the magnet current were replaced with a four position peak switcher. The shorting type, rotary switch, and coarse and fine precision potentiometers permitted selection of four preset magnet currents.

Samples were degreased, mounted on the sample holder, inserted into the target chamber, and the chamber evacuated to approximately 5×10^{-7} torr. At this time the primary ion source was started and adjusted to maintain 2.0 μ A of 14 keV Ar⁺ as measured by the Faraday cage. The primary ion current was monitored and the duoplasmatron adjusted until the ion current remained constant at 2.0 μ A for at least 15 minutes. Once the constant current condition was met, the sample was rapidly translated into the primary beam and the desired mass monitored *vs.* time.

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Table I. Comparison of Results of Pringle (16) and Ion Microprobe Study of $Ta_2^{18}O_5/Ta_2^{16}O_5$ Interface

Sample	$Ta_2^{18}O_5$, Å	$Ta_2^{16}O_5$, Å	Sputtering rate, Å/sec	1σ Distance, Å	
				Pringle (16)	This study
1	4141	298	0.67	62	110
2	3633	825	0.63	103	130
3	3144	965	0.73	111	150
4	2653	1261	0.67	127	170
5	2163	2180	0.66	167	215

RESULTS AND DISCUSSION

Optimization of spatial resolution and accurate calibration of penetration depth as a function of sputtering time requires an accurate knowledge of the magnitude and spatial homogeneity of the primary beam. If ions produced at any given time are to be interpreted as representative of the composition at a particular depth, then the primary ion beam must maintain a constant current density over its entire area. Any nonuniformities in the beam profile would result in some areas being sputtered at different rates than others. The ion sample at any time would then consist of ions from different depths.

The defocused mode of the primary ion optics was, therefore, studied by two techniques. (1) Thin films were vapor-deposited on glass slides and then sputtered. The uniformity of light transmission through the sputtered area was then examined with a microphotometer. (2) A series of Ta_2O_5 films were prepared by controlled anodization of Ta in suitable electrolytes. These films exhibit sharp interference colors, and color variations equivalent to thickness changes of as little as 30 Å can be visually detected. The Ta_2O_5 films were partially sputtered with the primary ion beam and the color uniformity of the craters was examined for depth inhomogeneities.

The instrument as received provided a nominally uniform beam with inhomogeneities greater than $\pm 10\%$. Excess cratering occurred primarily near the spot edges and, to a lesser extent, in the center of the sample. Experiments with the focusing apertures and lenses indicated that by grounding the Einzel lens electrodes and using the resulting divergent beam, craters were produced whose depth was homogeneous to within ± 50 Å at a total depth of 1000 Å, as determined by examination of the Ta_2O_5 interference colors. In addition to distortions caused by the primary optics, variations in the electrostatic field at the sample can be caused by sample holding clips. It was necessary to ensure that the sample holding device had no projections upward in the vicinity of the primary ion beam.

Accurate knowledge of penetration depths and sputtering rates is dependent on the constancy and reproducibility of the primary ion current. The as-received instrument had no provision for directly measuring the flux of bombarding ions. Even when duoplasmatron parameters were reset as carefully as possible, factors such as pressure dependence and filament aging resulted in irreproducible sputter conditions. Constancy of the target current was not sufficient to establish a reproducible sputter rate since the target current varies with primary ion current as well as secondary ion and electron emission effects, which in turn depend on surface condition, sample composition, and ion energy. To obtain a positive measure of the primary ion current, a Faraday cage was mounted below the sample holder on the primary beam axis. With the sample moved out of the ion path, the primary ion current was monitored with the Faraday cage and read on a digital panel meter. Primary beam currents can then be

monitored and adjusted. With a constant primary ion current, features and character of spatial distribution could be reproduced to about 3% of the actual depth.

An additional instrumental parameter plays a significant role in the development of this method for the study of thin films. Herzog *et al.* (15) showed that atomic and molecular ions sputtered from a sample have a different distribution with respect to initial kinetic energy. An examination of the secondary ion yield vs. secondary ion kinetic energy shows that the number of molecular ions drops rapidly with increasing kinetic energy, but the yield of atomic ions decreases only slowly at higher energy. Studies involving oxygen isotope tracers are subject to interference since both $^{18}O^+$ and $(^{18}O^{16}O)^+$ occur at mass 18. If the accelerating potential and the electrostatic analyzer voltage are preset to accept only those ions with high initial kinetic energy, then the interference of the molecular species $(^{18}O^{16}O)^+$ will be greatly reduced.

Isotope Gradients in Oxides. The anodic oxidation of tantalum has been studied extensively by various investigators and as such represents an ideal metal-oxide system with which to explore the capabilities of the ion microprobe. If Ta is anodized first in $H_2^{16}O$ and then in $H_2^{18}O$ (or $D_2^{18}O$), then a duplex film $Ta_2^{16}O_5$ and $Ta_2^{18}O_5$ will result. Pringle (16) used anodic stripping combined with activation analysis to study the ^{18}O - ^{16}O intermixing after the duplex anodization procedure. Oxygen isotope intermixing was found to vary as the square root of the added $Ta_2^{18}O_5$ thickness. The distance about the $Ta_2^{18}O_5/Ta_2^{16}O_5$ interface where the % ^{18}O varies by σ (i.e., 84–17% ^{18}O) is defined as d . Pringle's data were fit to the expression

$$d = 3.58 \sqrt{^{18}O \text{ thickness}} \quad (1)$$

Five samples of Ta anodized first in $H_2^{16}O$ and subsequently in $D_2^{18}O$ were obtained from AECL, Chalk River. The thickness/voltage relation during the anodization of Ta is well established (17) and precise values of the thickness of the $Ta_2^{16}O_5$ and $Ta_2^{18}O_5$ layers could readily be determined. These values are given in columns 2 and 3 of Table I. Samples were sputtered with the homogeneous ion beam and $^{18}O^+$ and $^{16}O^+$ intensities were recorded as functions of time. The depth at any time was determined by the sputter rate, which was calculated by measuring the time necessary for the $^{18}O/^{16}O$ ratio to reach 0.5 of its original value. This represented the time necessary to traverse the $Ta_2^{18}O_5$ thickness as determined by the anodization conditions. Calculated sputtering rates were substantially constant and are given in column 4 of Table I. Results for two of the samples are shown in

(15) R. F. K. Herzog, W. P. Poschenrieder, F. G. Ruedenauer, and F. G. Satkiewicz, Fifteenth Annual Conference on Mass Spectrometry and Allied Topics, Denver, 1967.

(16) J. P. S. Pringle, AECL Chalk River, private communication, 1970.

(17) L. Young, "Anodic Oxide Films," Academic Press, New York, 1961.

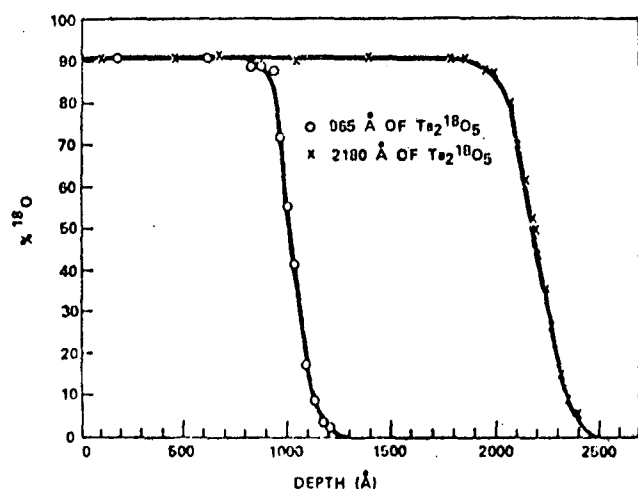


Figure 2. $\%^{18}\text{O}$ vs. depth for Ta_2O_5 anodized in $\text{H}_2^{18}\text{O}_2$ followed by $\text{D}_2^{18}\text{O}_2$

Figure 2. The spread at the $^{18}\text{O}/^{16}\text{O}$ interface increases with increasing $\text{Ta}_2^{18}\text{O}_5$ thickness in agreement with Pringle (16), and a comparison of observed σ values with those calculated from Equation 1 is given in column 5 and 6 of Table I. The Ion Microprobe results are somewhat larger than those of Pringle, but agreement between the two techniques is considered quite good. Some additional mixing of oxygen isotopes may have been caused by energy from the primary ion beam.

Impurity Gradients in Oxides. Tantalum films resulting from the anodic oxidation of tantalum are sensitive to the inclusion of impurity atoms from the electrolyte. Randall, Bernard, and Wilkinson (18) have shown that appreciable quantities of phosphorus are present in anodic films formed on tantalum in phosphoric acid solutions. Phosphorus gradients

(18) J. J. Randall, Jr., W. J. Bernard, and R. R. Wilkinson, *Electrochem. Acta*, **10**, 183 (1964).

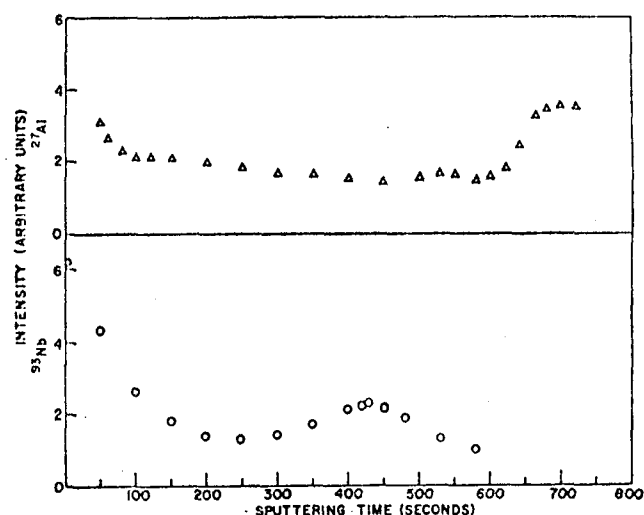
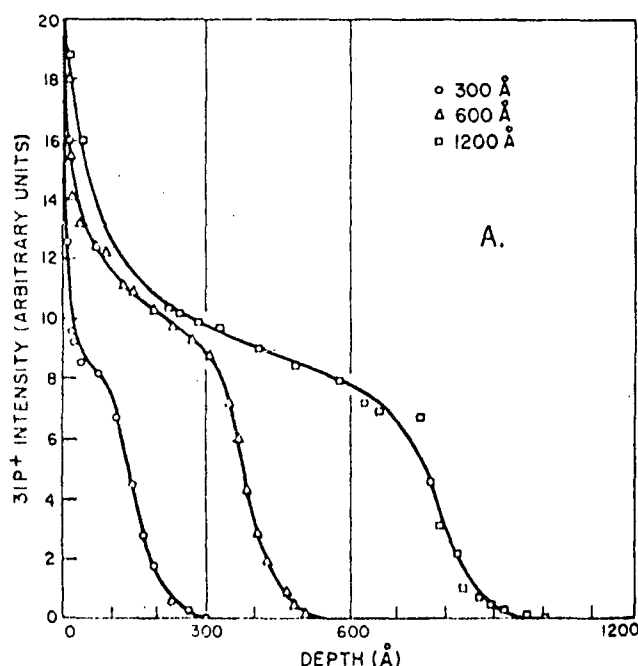


Figure 4. Intensity vs. sputtering time for $^{27}\text{Al}^+$ and $^{93}\text{Nb}^+$ for Al-Ge-Nb thin film

in these films were studied by radiotracer techniques and by electrical property measurements. Since the ion microprobe provides a continuous monitoring of concentration as a function of depth, it is well suited to examine impurity gradients in thin films.

Tantalum oxide films formed in phosphate electrolytes of different concentrations were examined and the phosphorus gradients are shown in Figure 3a and b. The $^{31}\text{P}^+$ intensity is much higher for films formed in concentrated $14\text{M H}_3\text{PO}_4$ than in those formed in $0.9\text{M H}_3\text{PO}_4$. In the $300\text{-}\text{\AA}$ films formed in $0.9\text{M H}_3\text{PO}_4$, the phosphorus signal drops rapidly from the oxide/solution interface and falls to zero at the oxide/metal interface. There is evidence of a small plateau in concentration in the $300\text{-}\text{\AA}$ film formed in concentrated H_3PO_4 . The thicker oxide films show definite evidence of phosphorus plateaus within the oxide films. Further details of these experiments will be reported in a separate communication.

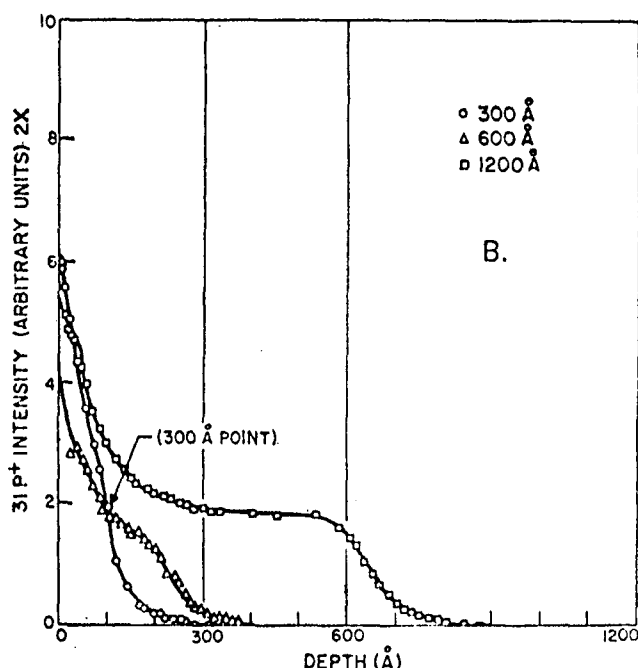


Figure 3. $^{31}\text{P}^+$ intensity vs. film depth for $300\text{ }\text{\AA}$, $600\text{ }\text{\AA}$, and $1200\text{ }\text{\AA}$ Ta_2O_5

(a). Anodized in $14\text{M H}_3\text{PO}_4$, (b). Anodized in $0.09\text{M H}_3\text{PO}_4$

Gradients in Metallic Films. The ion microprobe was used to study compositional variations in the metallic film Ag-Cu and the amorphous semimetallic alloy Al-Ge-Nb. Anderson (19) used a spectrophotometric method to monitor the vapor species produced by dc sputtering of the Ag-Cu eutectic alloy. He observed Ag/Cu ratios which varied with time and target temperature. At a target temperature of 80 °C, approximately 40 minutes of sputtering were required to obtain a constant Ag/Cu ratio. Longer presputter times were required at higher target temperatures.

Several films were prepared by sputtering an Ag-Cu eutectic onto a cooled target after long presputter times to achieve steady-state. These films were then examined with the ion microprobe for variations in the Ag/Cu ratio as a function of depth. No substantial variations were found in several samples prepared in this manner.

Thin film deposits of Al-Ge-Nb alloy were prepared by dc sputtering of an Al-Ge alloy button surrounded by an annulus of Nb. This configuration can be expected to lead to inhomogeneities in the ternary alloy film. The intensity versus sputtering time for $^{27}\text{Al}^+$ and $^{93}\text{Nb}^+$ in the Al-Ge-Nb

film is shown in Figure 4. Variations in concentration within the film are apparent.

CONCLUSIONS

The ion microprobe has been shown to be a powerful tool for exploring isotopic and composition gradients in thin films of both metals and insulators. Suitable modifications of the instrument have provided a uniform sputtering rate and crater profile, so that reliable analyses can be obtained as a function of depth into the sample. Continuous recording of intensities, and sputter rates as low as 0.5 Å/sec enable depth resolutions of the order of 20 Å.

ACKNOWLEDGMENT

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Application of Photoelectron Spectrometry to Pesticide Analysis

Photoelectron Spectra of Five-Membered Heterocycles and Related Molecules

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The photoelectron spectra of 15 five-membered aromatic heterocyclic and related compounds have been measured. It is shown that they are all sufficiently different to allow identification, and correlation diagrams have been prepared. The spectra are sensitive to changes in the substitution patterns of related compounds—e.g., 3-bromo- and 2-bromothiophene. The spectra are interpreted in terms of molecular orbital theory and it is shown that the electronegativity of the heterocyclic atom can be correlated with shifts of ionization potential.

WE ARE ENGAGED in examining the applicability of photoelectron spectrometry (PES) to the analysis of pesticides, herbicides, and other compounds of agricultural interest. This technique which measures the binding energies of electrons in molecules has considerable analytical potential (1) since the spectrum of a molecule reflects its molecular orbital energy diagram (2, 3). It has already been shown that the spectra of

relatively simple molecules, especially those containing atoms with nonbonding electrons, e.g., halogen, can be interpreted (1), and that the spectra of substituted benzene compounds can be correlated with the inductive or mesomeric effect of the substituent.

Most pesticides are too complex to have attracted theoretical chemists and pose technical difficulties to photoelectron spectroscopists. Nevertheless, rapid developments are taking place in theoretical chemistry and in photoelectron spectrometry so that we should be preparing for dealing with complex molecules by thoroughly investigating simpler pesticides, and examining closely related relatively complex molecules, which may serve as model compounds. This paper follows the last of these approaches by measuring and examining the photoelectron spectra of 15 five-membered aromatic heterocyclic and related molecules.

The question of whether the heterocyclic atom in the aromatic system can be identified is obviously of analytical interest as also are possibilities of identification of substituent groups and substitution patterns. There are theoretical treatments of some of these molecules which have helped to interpret spectra and to answer these questions. It has also proved possible to prepare correlation diagrams which show that qualitative identification *via* photoelectron spectrometry is possible and which may be of value in empirically interpreting the spectra of more complex molecules.

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² Professor R. E. Kirby is on sabbatical leave from Queens College of the City University of New York.

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Impurity Distributions in Anodic Films on Tantalum

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ABSTRACT

Anodization of tantalum in electrolytes containing phosphorus or fluorine ions resulted in the incorporation of a quantity of these elements into the anodic film. While phosphorus was concentrated in the outer portions of such films, fluorine was attracted to the oxide/metal interface. We employed an ion microprobe mass spectrometer to examine the concentration profiles of these elements in films formed by a variety of anodization procedures. These experiments demonstrated the usefulness of the IMMS as a tool for such work and, in addition, furnished information on the characteristics of both film growth and the distribution and movement of these impurities. The influence of fluorine-rich layers at the oxide/metal interface on the adherence of the anodic films was also shown.

During the anodization of tantalum (as well as several other valve metals), the inclusion in the product film of impurity atoms from the electrolyte is a common occurrence and impurity effects on both the characteristics of film formation and various film properties have been reported (1). In addition, it has been observed experimentally that the impurity distribution may not be uniform throughout the film and may, in fact, have an unusual variation with depth caused by the particular manner in which the anodization was accomplished. For example, the "two-layer" structure associated with films on tantalum anodized in sulfuric or phosphoric acid has been well documented (1-8). One can argue that important properties of these films

may be determined by both the amount and the distribution of the impurities within them.

Since the thickness of barrier-type anodic films on tantalum is generally limited to only a fraction of a micron, special techniques are required for their analysis. Most previous experiments concerning the direct determination of the impurity distribution within these films have involved radio-tracer methods combined with chemical sectioning. Chemical sectioning provides a surprisingly uniform removal of layers of the anodic oxide, although very careful experimental procedures are necessary to assure reproducible sectioning rates (1, 2, 4, 13).

We are examining the applicability of the Ion Microprobe Mass Spectrometer (GCA Technology Division, Bedford, Massachusetts) for the determination of impurity distributions in thin anodic oxide films. The details of the design and general operation of the IMMS have been described in detail previously (9). Basically, the instrument is a sputtering device in which the

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sputtered material is sampled by a mass spectrometer. Thus, for a constant sputtering rate, the output of the spectrometer furnishes a measure of the ion yield or concentration of a given material as a function of depth. Although, in principle, comparison of these ion intensities with appropriate standards would permit the determination of absolute concentrations, we have not yet attempted to use the IMMS as a tool for quantitative analysis. All of the profiles presented in this work are based on arbitrary ion intensity units, which may vary from experiment to experiment, and must be considered with this in mind.

In this paper we present results which test the sensitivity of the apparatus for various types of work with ultra-thin oxide films. These results concern the behavior of phosphorus and fluorine impurities incorporated during the anodization of tantalum and, in particular, the use of thin phosphorus-rich layers as "markers."

Experimental Procedure

Tantalum specimens¹ were prepared from $1 \times 2 \times 0.05$ cm coupons. These were annealed in vacuum (10^{-6} Torr) for 2 hr at 1600°C , mechanically polished through 0.3μ -alumina, and electropolished in a 90% H_2SO_4 -10% HF solution. A short length of tantalum wire was spot-welded to each specimen to facilitate handling and to serve as electrical contact during anodization. The polished specimens were then washed carefully and boiled in distilled water for 1 hr to remove or counteract the effect of the residual fluoride from the electropolishing bath.

The specimens were anodized at room temperature to a given voltage in a simple cell in which the initially high currents were limited to about 10 mA/cm^2 by a variable series resistor. The resistance was reduced to zero and the specimen held at full voltage for a "standard" time of 2 min in order to be able to apply previously determined thickness calibrations (10) to the films: 16.5 A/V in dilute Na_2SO_4 and KF; 13.2 A/V in concentrated (14.7M) H_3PO_4 . The "duplex" and "sandwich" type films dealt with in this paper were produced by sequential anodization in the various electrolytes. It was assumed that the increment of thickness produced by an additional anodization depended only upon the voltage increment and the particular electrolyte.

Results and Discussion

Anodization in 0.035M (0.5%) Na_2SO_4 .—The anodization of tantalum in dilute sulfate solutions produces amorphous, essentially stoichiometric tantalum pentoxide films which have uniform properties over a range of formation conditions. We utilized such films in the preliminary stages of this study to observe the effect of instrument variables, particularly those which controlled the size, intensity, stability, and uniformity of the argon ion-beam used for sectioning.

As reported previously (9), some modifications in the ion lenses and ion current measuring devices proved very useful in increasing the reliability of the instrument for our purposes. With these changes, the uniformity of the beam was improved, resulting in a sectioning (crater) geometry which produced a depth resolution useful for work with anodic films. The geometry of material removal was checked by observing intermittently the uniformity of the interference color of the remaining film at the bottom of the $3 \text{ mm} \times 4 \text{ mm}$ elliptical crater produced by the beam. At a depth of $1000 \text{ \AA}$, variations of the order of $\pm 50 \text{ \AA}$ across the crater were generally observed. Calibrations of the sputtering rates of these films as a function of the beam parameters were obtained by means of side-by-side color comparisons with a standard set of anodized specimens. Sputtering rates of $0.5\text{--}1 \text{ \AA/sec}$ used in this investigation could be reproduced from run-to-run to within $\pm 10\%$. By monitoring either the Ta or O ion intensities during sputtering of the films, the position

and effective "width" of the oxide/metal interface could be determined. Generally, a sigmoidal decrease of these intensities over a distance of about $200 \text{ \AA}$ was associated with the interface. This was viewed as a reasonable value, particularly since the surface of electropolished tantalum is not precisely planar on a fine scale (11).

Anodization in H_3PO_4 .—Anodic films formed on tantalum in H_3PO_4 solutions are known to contain significant quantities of phosphorus. Not unexpectedly, most of the properties of these films are significantly altered as a direct result of such incorporation. While a number of investigators have presented results which have been interpreted in terms of a nonuniform distribution of phosphorus, Randall *et al.* (4) were the first to include a quantitative description. These investigators found that all the phosphorus was concentrated in the outer half to two-thirds of the oxide, and that its concentration within this layer was uniform. Both the absolute concentration of phosphorus and the relative depth of the enriched layer depended upon the concentration of the electrolyte.

Typical phosphorus concentration profiles determined in the present investigation by the IMMS for films formed in concentrated (14.7M) H_3PO_4 are shown in Fig. 1. The phosphorus concentration drops off rapidly to a plateau which extends about two-thirds of the way through the film. The high apparent concentration at the electrolyte/film interface was also observed in earlier measurements (9) on films formed in both 14.7M and 0.9M H_3PO_4 . While the extent of the surface enrichment is reduced somewhat by ultrasonic cleaning of the specimens in detergent solution (used on the present specimens), its persistence suggests that more than simply a surface artifact or occlusion is involved. For the case of films formed in 0.9M H_3PO_4 , the phosphorus plateau extended about half way through the films; the high surface concentration was also observed. Thus, with the exception of our observation of phosphorus enrichment at the surface of the film, our profiles are in excellent agreement with those of Randall. Subject to the limitations discussed below, the phosphorus profile indicated that there is an apparent transport fraction for tantalum ions of about 0.65 for anodization in 14.7M H_3PO_4 .

"Sandwich" films and marker experiments.—The results that two distinct layers are formed when tantalum is anodized in H_3PO_4 solutions implies that both O and Ta ions are mobile. If additional oxide can only be formed at the electrolyte/oxide and oxide/metal interfaces and if the phosphorus itself is essentially immobile, it follows that sequential or multiple anodizations in concentrated and dilute electrolytes could establish zones rich in phosphorus entirely buried within

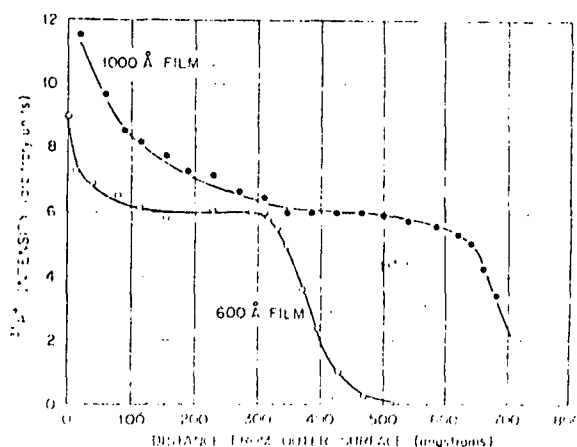


Fig. 1. Phosphorus concentration profiles in anodic films formed in concentrated (14.7M) H_3PO_4 to thickness of $600 \text{ \AA}$, (45.5V) and $1000 \text{ \AA}$, (75.8V).

¹ Not used in this study: Ta with Nb, Fe, W, and Si as major impurities.

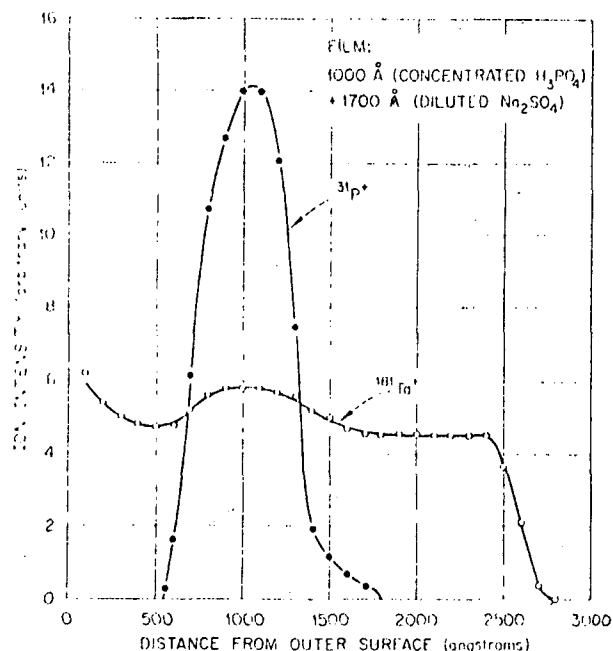


Fig. 2. Concentration profiles for tantalum and phosphorus across "sandwich" specimen formed by sequential anodization of tantalum in 14.7M H_3PO_4 (1000Å) and 0.035M Na_2SO_4 (1700Å), ● phosphorus profile; (—) tantalum profile.

the layer. The existence of such zones would present interesting implications regarding the properties of these films.

The results of a duplex anodization are illustrated in Fig. 2. In this experiment, a 1000Å film was formed in concentrated (14.7M) H_3PO_4 ; the specimen was carefully washed and then reanodized in 0.035M Na_2SO_4 to a total film thickness of 2700Å. The Ta and P ion profiles shown in the figure confirm the fact that the phosphorus existed in an isolated region within the film. The thickness of the phosphorus-rich zone is consistent with its thickness prior to the second anodization, except that it does not exhibit the expected asymmetric distribution favoring the side toward the electrolyte. The variations in the Ta ion intensities are thought to be primarily the result of drifts in the sputtering beam currents.

A test of the resolving power of the IMMS for locating and describing thin, embedded layers in oxide films is shown in Fig. 3. In this set of specimens, phosphorus-rich layers having thicknesses of about 17, 35, and 65Å were sandwiched between layers of plain oxide by a three-step anodization in 0.035M Na_2SO_4 , 14.7M H_3PO_4 , and again in 0.035M Na_2SO_4 . All three layers were easily resolved by the IMMS, resulting in the Gaussian-type curves for relative phosphorus concentration shown. The measured widths at half-maximum intensity were 85, 115, and 150Å, respectively, for the three phosphorus layers. Even if we ignore the possibility that the final anodization step caused a slight spreading of the phosphorus layer, these values indicate that the technique is capable of locating an internal interface of this sort to within about 40Å. (Note that an infinitesimally thin layer would exhibit an apparent thickness of 60–80Å.) It therefore appears that the resolution of the instrument is entirely satisfactory for defining impurity distributions on this fine scale.

This method was used to study the systematic movement and broadening of a thin phosphorus-rich layer during subsequent anodization in dilute electrolytes. If the phosphorus is indeed immobile, as suggested by Randall (4), it would serve as an ideal "marker" and

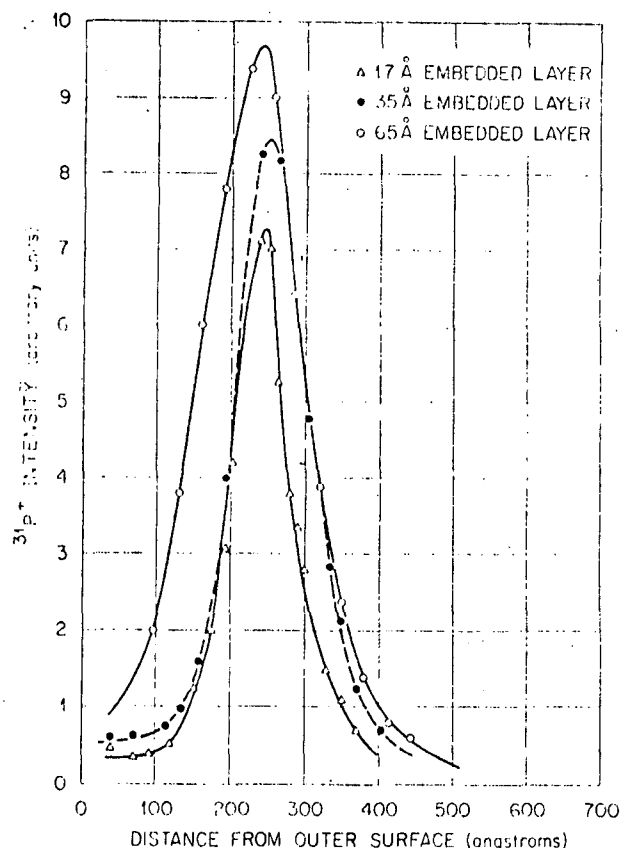


Fig. 3. Concentration profiles for thin phosphorus-rich layers embedded in anodic tantalum oxide film. The three specimens were prepared by (a) anodizing each to a film thickness of 500Å in 0.035M Na_2SO_4 , (b) reanodizing in 14.7M H_3PO_4 to add 25Å, 50Å, and 100Å of film, two thirds of which is phosphorus-rich, and finally, (c) anodizing again in 0.035M Na_2SO_4 to add 500Å more to the total film thickness.

25Å. If we neglect the effect of the pre-existing film and assume that the same phosphorus distribution exists here as in the thicker films of Fig. 1, the phosphorus-rich layer will be slightly less than 20Å thick, and its center will be located about 10Å from the outer surface. We then reanodized these specimens in 0.035M Na_2SO_4 to add increments of phosphorus-free oxide from 500–4000Å in thickness. The phosphorus profiles, determined by the IMMS and normalized to a constant peak intensity, are presented in Fig. 4. The final position of the marker layer is approximately in the center of the film for all specimens. Note also that the apparent thickness of the layer (defined as the width of

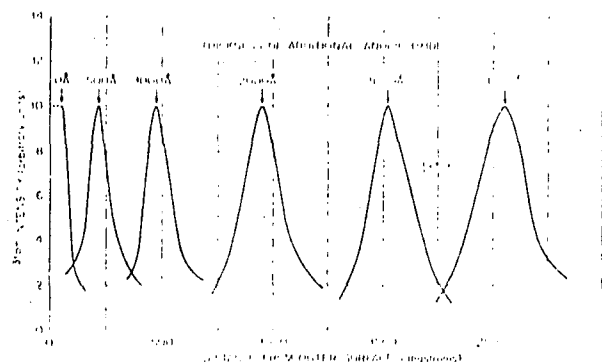


Fig. 4. "Marker" experiments with thin, phosphorus rich layers. Concentration profiles exhibited by 17Å marker layer (25Å film thickness) after subsequent anodizations in 0.035M Na_2SO_4 to add 500, 1000, 2000, 3000, and 4000Å of phosphorus-free oxide.

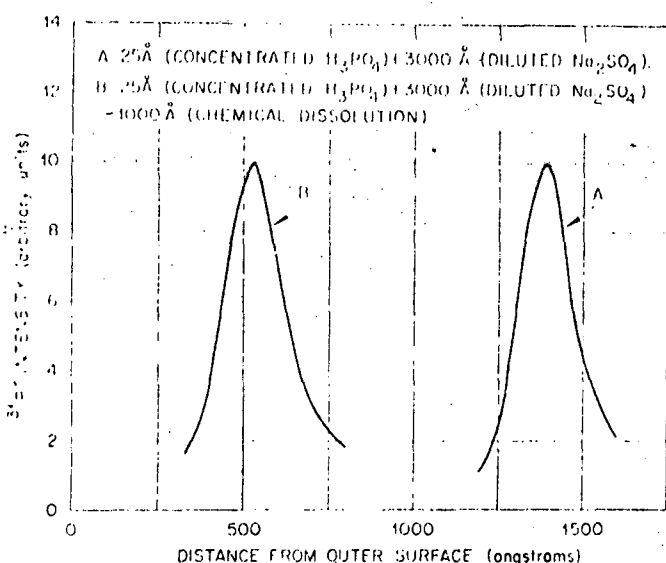


Fig. 5. Effect of marker layer depth on profile determination. Film 'A' contains a 17Å layer buried by subsequent anodization (3000Å) in 0.035M Na_2SO_4 . Film 'B' is identical, except that approximately 1000Å of the outer film has been removed by chemical dissolution in NH_4F -HF solution.

the profile at half-maximum intensity), increases with the thickness of added oxide.

The final position of the marker is determined by the relative transport fractions of the ions across the film and also by the extent of its movement induced by the electric field and/or the ion flux. If the degree of the latter type of migration is directly proportional to the amount of anodization after the marker is placed, the transport fractions obtained from the data of Fig. 4 and similar experiments will be in error by a constant factor which relates this movement to the total amount of new oxide formed. The extent of this error cannot be determined from these experiments. However, the apparent spreading of the marker as a function of continued anodization implies at least some small degree of interaction with the ion flux or that some oxide is forming internally.

An apparent spreading of the marker layer would also be observed if the crater formed by the IMMS beam changed in shape or became roughened in proportion to the depth eroded. In order to check this possibility, we repeated the 3000Å film experiment employing chemical means to remove a portion of the outer oxide. Approximately 1000Å of oxide was removed from this specimen by partially dissolving the film in a solution of 25g NH_4F in 100 cc HF. Figure 5 indicates that the marker profiles obtained "before and after" are virtually identical. Thus, unless the chemical removal of the oxide produces an identical roughening of the surface, it appears reasonable to conclude that

the marker spreading is a real, albeit a comparatively small effect.

The results of our experiments which bear directly upon the mechanism of anodic oxidation of tantalum in the manner previously described in dilute aqueous solutions are listed in Table I. If it is assumed that the phosphorus-rich layer serves as an inert, immobile marker (i.e. that its changes in position are solely a result of the motion of the Ta and O ions), then the fractional burying of the marker, $\Delta X/\Delta W$, is a measure of the tantalum ion transport fraction. In this expression, ΔX is the observed change in marker depth relative to the oxide/electrolyte interface during the period in which the total thickness of the film is changing by ΔW . The tantalum ion transport fractions are listed in the last column of the table and are sensibly constant with a value of 0.46 ± 0.05 . Their constancy points out that if the phosphorus marker is indeed mobile, contrary to our above assumption, it moves in virtually direct proportion to the extent of subsequent anodization.

In excellent agreement with the above results, perhaps because phosphorus was also used as a marker, Randall (4) obtained a value of 0.48 for the corresponding transport fraction. However, Davies *et al.* (12) utilizing injected Xe^{125} atoms as markers, and Whitton (14), using Kr^{85} , obtained values of about 0.3. In order to rationalize the two results on the basis of their face value, a difference in mobility of approximately 0.2 $\Delta X/\Delta W$ must exist for the phosphorus and the inert gas markers during anodization. It may be pertinent to note that the mass of the marker species (13), as well as the charge (14), will determine its relative mobility and final position in the film. Obviously, marker behavior is complex and the categorical interpretation of such results is dangerous.

Anodization in 0.09M (0.5%) KF.—It is well known that anodization of tantalum specimens prepared by polishing in reagents containing HF produces anodic films that are poorly adherent. It has also been shown (15) that anodization even in dilute fluorine-containing electrolytes permits large numbers of such films to be stripped in sequence from a single specimen. This is the basis of a sensitive microsectioning technique which is applicable to both tantalum and niobium, as well as their alloys. A reasonable explanation for this behavior is that a fluorine-containing film—perhaps an oxy-fluoride—is formed at the oxide/metal interface and serves as an efficient parting agent between the metal and the film. The fact that this parting layer remains in position at the interface during anodizing has been used as evidence to support the idea that cation migration is the primary mechanism of anodic film formation (1).

Our application of the IMMS to the examination of fluorine profiles in anodic films furnishes an explanation for the effect which is consistent with the fact that both tantalum and oxygen ions are mobile. A fluorine concentration profile for a 2000Å anodic film formed in

Table I. Movement of thin, phosphorus-rich layers during anodization

Configuration ^a	Phos. peak position with respect to E/O interface, Å	Final width of P-rich zone (at 1/2 max. int.), Å	Fractional burying $\Delta X/\Delta W$	Apparent Ta transport fraction, τ_{Ta}
500/100P/500	240	150	210/300	0.42
1000/100P/1000	490	200	460/1000	0.46
25P/1000	450	200 (?)	440/1000	0.44
500/25P/500	240	85	230/500	0.46
500/25P/500	250	90	240/500	0.48
500/50P/500	255	115	236/500	0.48
25P/500	220	95	210/500	0.42
25P/1000	475	130	465/1000	0.47
25P/2000	950	180	940/2000	0.47
25P/3000	1520	190	1510/3000	0.50
25P/4000	2060	230	2050/4000	0.51
25P/3000	1400	180	1380/3000	0.46

^a "P" indicates a phosphorus-rich layer. For example, 500/100P/1000 means the first anodization was carried out in dilute Na_2SO_4 to a thickness of 1000 Å, then the specimen was anodized in 0.035M Na_2SO_4 to a thickness of 1000 Å, and finally the specimen was anodized in 0.09M (0.5%) KF to a thickness of 500 Å.

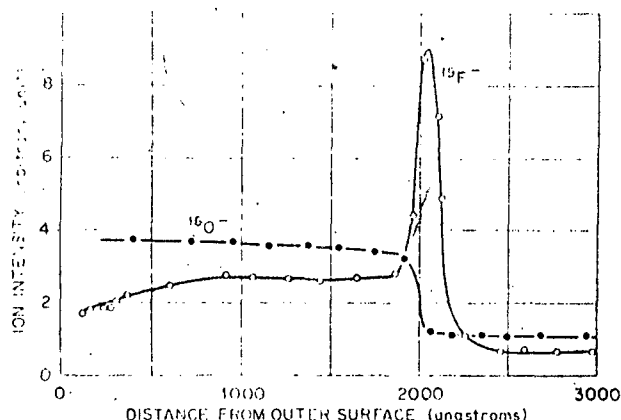


Fig. 6. Fluorine and oxygen concentration profiles in anodic film formed on tantalum in 0.09M (0.5%) KF. ○ Fluorine profile, ● oxygen profile.

a dilute KF solution is illustrated in Fig. 6. The concentration is essentially constant throughout the film, but rises abruptly at the oxide/metal interface. The oxygen profile, shown on a less sensitive scale, shows no such peak, but behaves in normal fashion through the interface. The presence of a fluorine-rich layer of some sort at the interface is evident. Furthermore, the width of the F peak at half-maximum intensity is only about 100 Å and, taking into account the resolution limits of the IMMS for such interfaces, we estimate the thickness of this layer to be less than 50 Å—perhaps much less.

In order to test the hypothesis that fluorine itself is mobile during anodization and may be driven through the film to the oxide/metal interface, we measured the fluorine profiles on a series of specimens which had been pre-anodized in a dilute sulfate solution to produce 500 Å adherent layers of fluorine-free oxide and then reanodized in 0.09M KF to produce increments of fluorine-containing oxide with thicknesses of 250, 500, and 1000 Å, respectively. If fluorine were immobile, none should be found within 500 Å of the oxide/metal interface. The results of these experiments are presented in Fig. 7. Reanodization to add 250 and 500 Å thickness to the oxide layer caused measurable amounts of fluorine to migrate into the formerly "plain" oxide layer as manifested by the considerable broadening of the F-distribution curves into this region. Reanodization to add 1000 Å of film, however, resulted in the

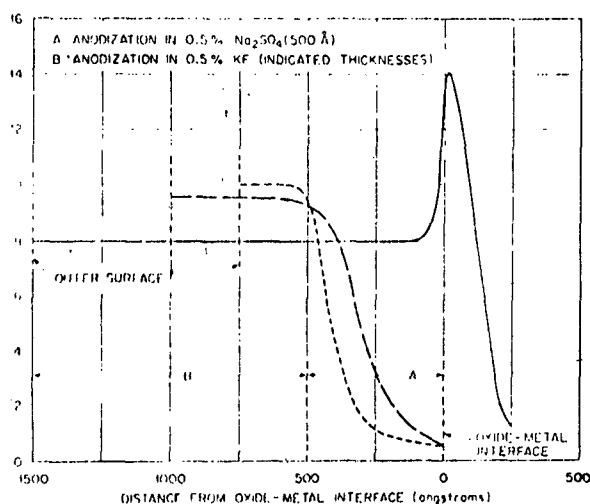


Fig. 7. Fluorine concentration profiles in anodic films formed stepwise on tantalum in dilute Na_2SO_4 and KF solutions. All three specimens were first anodized in 0.035M Na_2SO_4 to form 500 Å of fluorine-free oxide. They were then reanodized in 0.09M KF to the indicated total thicknesses.

fluorine finally reaching and apparently being concentrated at the oxide/metal interface. This behavior is similar to that for anodization wholly in KF, and the eventual formation of a discrete F-rich layer shows that the fluorine migrated toward the oxide/metal interface to an extent which depended upon the amount of anodization. Thus, if a fluoride-rich layer does not already exist at the interface, sufficient fluorine can migrate to cause its formation and perhaps continued growth.

It is pertinent to point out that the films which have the fluoride layer at the interface easily strip from the specimen; the others do not. These results are useful in understanding the action of fluorine in determining the relative adherence of anodic films on tantalum. Only very small amounts of fluorine at the interface are required to decrease markedly the adherence of the film. For example, we have found that the fluorine in a 50 Å film formed in dilute KF, when driven through an adherent anodic film to the interface, is sufficient to cause complete loss of adherence. Probably less than a monolayer of fluorine atoms is involved.

An estimate of the mobility of the fluorine was also obtained in these experiments. In order to drive fluorine from a "sandwich" through a given thickness of adherent film, it was necessary for additional oxide between two and three times this thickness to be formed. Holding the composite for extended periods of time under conditions where the electric field in the oxide was sufficient to maintain only very slow over-all growth rates did not cause appreciable fluorine movement. Apparently, gross ion movement, or the added field strength associated with it, was necessary to promote this effect.

Conclusions

The ion microprobe mass spectrometer has been shown to be a useful instrument for describing the distribution of impurities in thin anodic oxide films. The sputtering rates and crater shapes were controlled such that they varied very little with time and penetration depth (at least for several thousand angstroms). The effective resolution, in terms of the apparent thickness of a plane interface, was about 50 Å. The inclusion and movement of phosphorus and fluorine in anodic tantalum oxide films during a variety of anodization procedures were studied. The specific conclusion are:

(i) When films are formed in concentrated H_3PO_4 , the phosphorus concentrates in the outer two-thirds of the film implying, if the phosphorus is immobile, a value of the tantalum ion transport fraction of about 0.65. This is different from the value of 0.46 found for anodization in the dilute sulfate solution. It may be significant in this respect to point out that the high-temperature oxygen permeation rates through anodic films containing phosphorus have been observed to be much less than those through the plain anodic oxide (10).

(ii) Thin, phosphorus-rich layers of known thickness may be positioned in otherwise normal anodic films.

(iii) Phosphorus-rich layers spread only slightly during continued anodization.

(iv) If phosphorus is itself mobile during anodization, it moves in virtually direct proportion to the amount of anodization and, thus no direct values could be determined concerning the extent of this movement. Assuming the phosphorus marker layer to be immobile, the apparent tantalum ion transport fraction is about 0.46 for anodization in dilute sulfate solutions. The corresponding transport fraction determined by previous investigators using inert gas atoms as markers is about 0.3. Thus, if these markers are immobile, phosphorus is drawn to the oxide/metal interface by approximately 0.2 Å/Å during anodization.

(v) During anodization, fluorine-rich marker layers or fluorine ions from the electrolyte may be driven comparatively large distances through the film toward the oxide/metal interface. Thus, fluorine cannot be

A STUDY OF THE INTERACTION OF OXIDE-COATED ALUMINIUM WITH CHLORIDE SOLUTION USING SECONDARY ION MASS SPECTROMETRY*

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Abstract—A Cameca Ion Analyser has been used to examine aluminium surfaces, covered by barrier-type anodic films up to 720 Å thick, after natural immersion for 480–1500 min or a brief period of anodic polarization in near-neutral 1M potassium chloride solutions at 20°C. After natural immersion, there has apparently been slight film thinning and chloride is abundantly present on the film surface but there is no chloride measurable within the film material, nor is any residual chloride concentration in the tiny incipient pits, likely to be present at this stage, detectable. After anodic polarization, there is again evidence of a chloride peak on the film surface but no chloride within the film material itself. At the clearly detectable major pits, after passing through a surface chloride maximum, the chloride level is reduced until the inner oxide surface is reached, where a further chloride peak provides evidence for the pit undermining the anodic film. The results tend to support the pit initiation theory based on local attack at flaws in the preformed oxide film and provide no evidence for theories involving chloride ion entry into the film material *per se*.

INTRODUCTION

RECENT theories of the onset of localized corrosion usually involve either the concept of aggressive anion ingress into the lattice of the oxide film covering the metal or alloy surface, or alternatively preferential attack at flaws in this surface film. Thus, a.c. impedance measurements have been made on anodically oxidized aluminium surfaces during the "induction period", prior to the onset of gross corrosion in neutral chloride media.^{1–5} The results were originally interpreted in terms of penetration of the surface oxide film material by chloride ions via a field-independent anion exchange process.^{1–3} Recently,^{4,5} an alternative explanation of the observed impedance changes, involving preferential attack at flaws in, and subsequent undermining of, the surface oxide has been presented. In situations involving impressed polarization techniques, pit initiation processes have been invoked involving field-induced anion ingress into the surface oxide films.^{6,7}

Lately ion analysis has been used to study surface films, for example, phosphorus and fluorine profiles through anodic films on tantalum,⁸ metal concentration profiles through anodic films on various alloys⁹ and estimates of the degree of hydration of anodic alumina films.¹⁰ Fundamental aspects and the operation of one form of ion microprobe mass spectrometer have been detailed elsewhere.¹¹ Briefly, a beam of primary ions is employed to eject neutral atoms, positive and negative secondary ions

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from the specimen surface. A combination of ion emission microscopy and mass spectrometry is then used to define the location of component elements, usually in the form of ion images or in-depth profiles from a scanned area. At a constant sputtering rate, the spectrometer provides an approximate measure of the variation with depth of the concentration of a component element.

In the present work, anodically oxidized aluminium surfaces have been studied using ion analysis after short periods of immersion in, and after anodic polarization in, neutral chloride solutions. The objective was to obtain concentration profiles of chloride ions through various parts of the exposed films. As indicated later, the results must be regarded as semi-quantitative because of present difficulties in quantifying the results precisely in relation to appropriate standards, etc.

EXPERIMENTAL

Aluminium samples of 99.99% purity were electropolished in a perchloric acid/ethanol mixture prior to anodizing at 1 mA/cm² to 20 V, 30 V or more generally 60 V, in 3% ammonium tartrate solution, pH 7.0, at 20°C. Samples were then immersed for either 480 or 1500 min in 1M KCl solution, pH 6.0 or 7.0, at 20° ± 1°C, or polarized for 1 min in these electrolytes at -240 mV (SCE), using a Wenking potentiostat. Analar grade reagents and doubly distilled water were used throughout and adjustments in pH were made using very dilute solutions of hydrochloric acid or potassium hydroxide.

A Cameca IMS 300 ion analyser was employed, using a primary beam of positive oxygen ions, which gives a high secondary ion yield at a beam current of 200 nA. In order to achieve relatively uniform thinning of the area being analysed,^{8,9} a 250 µm square area was scanned, of which the central 100 µm square region was analysed. As a means of monitoring the film penetration and its general thinning, Al⁺ and AlO⁺ secondary ions were selected. Metal ions emitted from the oxide layer exhibit a greater intensity than from the pure metal, so in the present case there is a large decrease in the intensity of the Al⁺ ions in passing from the oxide to the substrate; Al⁺ ions produce a visible image for both the oxide layer and the metal, and the AlO⁺ ions define more adequately the oxide layer. A "flip-flop" circuit was used to record alternately the effective intensities of the two species during sputtering. Corresponding depth profiles of Cl⁻ ions were recorded directly through the films. A sputtering rate of ca. 100 Å/min was used throughout the work.

RESULTS AND INTERPRETATION

In-depth profiles of Al⁺ and AlO⁺ for 60 V films (ca. 720 Å) in the as-formed condition, and after a 480-min period of immersion in 1M KCl solution at pH 7.0, are depicted in Fig. 1. There is apparently evidence of slight film thinning, as a result of the immersion in chloride solution. The corresponding in-depth profile of Cl⁻ for the chloride-treated film is shown in Fig. 2, from which it is evident that a substantial amount of chloride ion was detected at the oxide-solution interface (too much to be a surface enhancement effect of the technique) but no chloride was detected through the bulk of the film material itself. The relative intensity of chloride within the film was recorded on the most sensitive scale of the ion probe, being essentially at background level, and probably below the few ppm level. Essentially similar results were obtained with the other film thicknesses and the pH 6.0 solution.

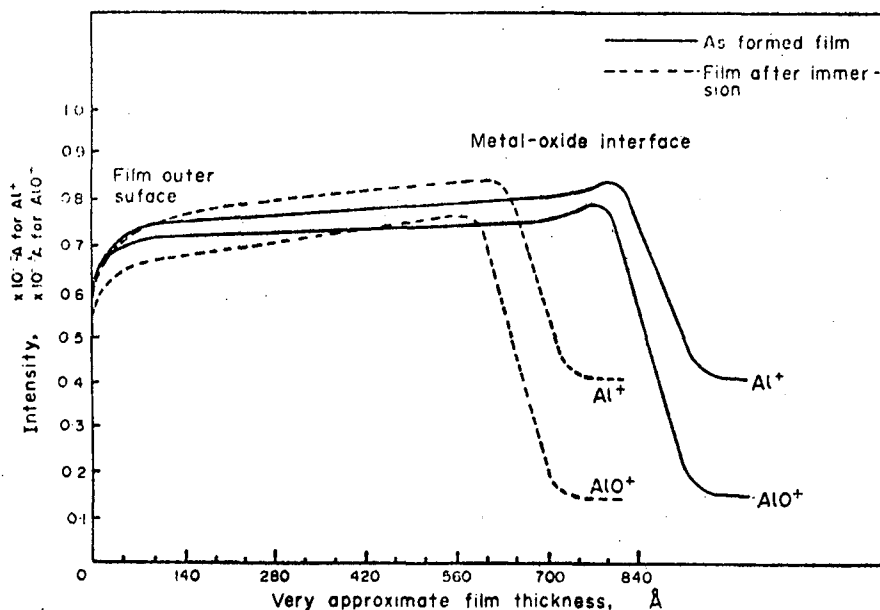


FIG. 1. Plots of apparent intensity of Al^+ and AlO^+ ions as a function of film thickness for 60 V (720 Å) anodic film, formed on aluminium in 3% ammonium tartrate solution, pH 7.0, at 20°C. (—) As-formed film. (---) After dipping in 1M KCl solution (pH 7.0) for 480 min at 20°C.

An in-depth profile of Cl^- for a pitted area of the sample covered by a 60 V anodic film and polarized in 1M KCl solution, pH 6.0, for 2 min at -240 mV (SCE), considerably above the so-called breakdown potential, is shown in Fig. 3. Since the area scanned was $250 \mu\text{m}$ square, with the area monitored being $100 \mu\text{m}$ square and including the pit, which was about $50 \mu\text{m}$ in size, the data refer to an average result referring to the pit and its immediate vicinity. The pit had, in fact, undermined the surface film, leaving a substantial quantity of the film intact over the pit mouth.^{4,6} The in-depth profile for Cl^- shows an initial peak, at the oxide-solution interface, followed by a reduction in intensity and subsequently a further peak. The corresponding ion images typical of the three regions on the profile (omitted in the interests of brevity and because they would not reproduce adequately in the journal) strongly suggested that the second peak of Cl^- intensity was associated with the pit surface beneath the original undermined film, which had possibly been thinned from within. The data in Fig. 3 and these images again indicate the presence of Cl^- on the oxide film surface, at local points of breakdown in the surface oxide film, and finally on the pit surfaces beneath undermined areas of oxide film, but no significant inclusion of Cl^- in the bulk oxide film itself.

Evidence of undermining of the surface oxide film was quite general on the polarized specimen surfaces. Figures 4 (a and b), for example, show Cl^- ion images of the same region of surface before and after complete sputtering of the surface oxide film. Although two points of breakdown penetration were evident from the very outset, a third point of chloride enrichment emerged quite suddenly at the oxide-metal interface, indicating attack at a tiny breakdown point in the surface film and subsequent

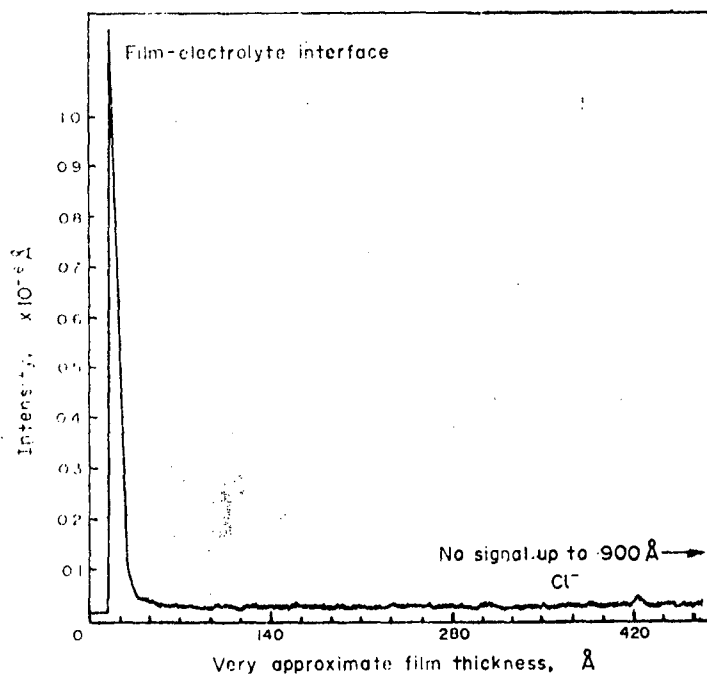


Fig. 2. Corresponding in-depth profile of Cl^- ion for the chloride-immersed specimen, characterized in Fig. 1.

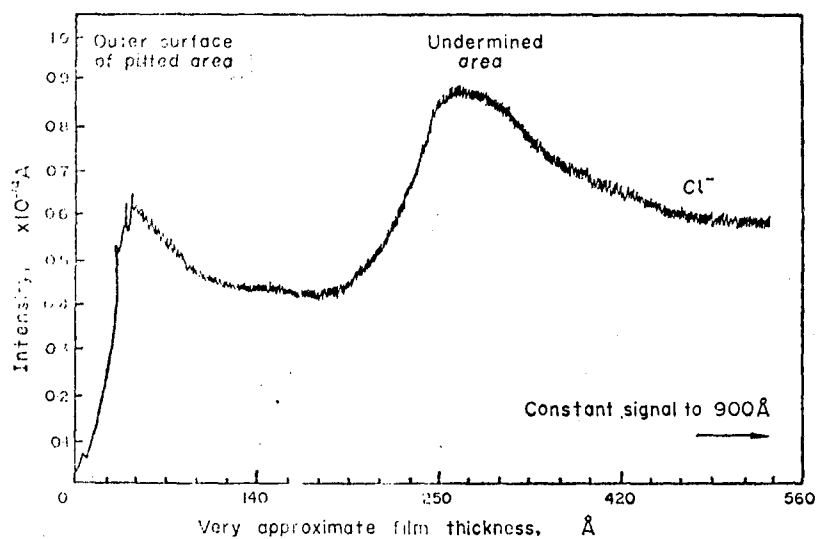


Fig. 3. In-depth profile for the Cl^- ion, relating to a 60 V (720 Å) film formed on aluminium in 3% ammonium tartrate solution, pH 7.0, and polarized in 1M KCl solution, pH 6.0, for 1 min at -240 mV (SCE). Area scanned 250 μm square, containing a pit. Area monitored, 100 μm square.

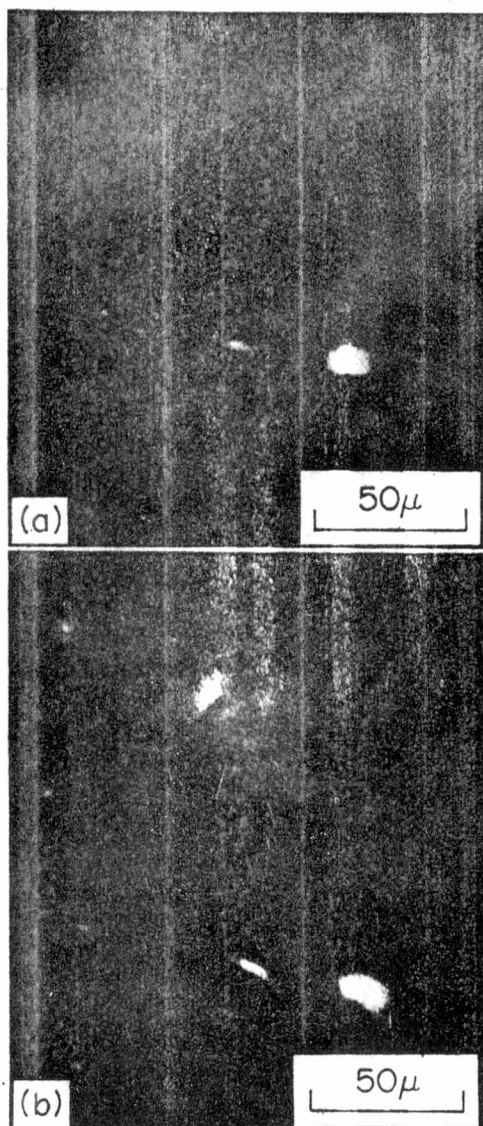


FIG. 4. Cl^- ion images for an area in the specimen described in Fig. 3. (a) Surface prior to sputtering showing two "open pits". (b) Surface after sputtering, indicating revelation of a third pit, which largely undermined the surface film and grew through a tiny flaw in the film.

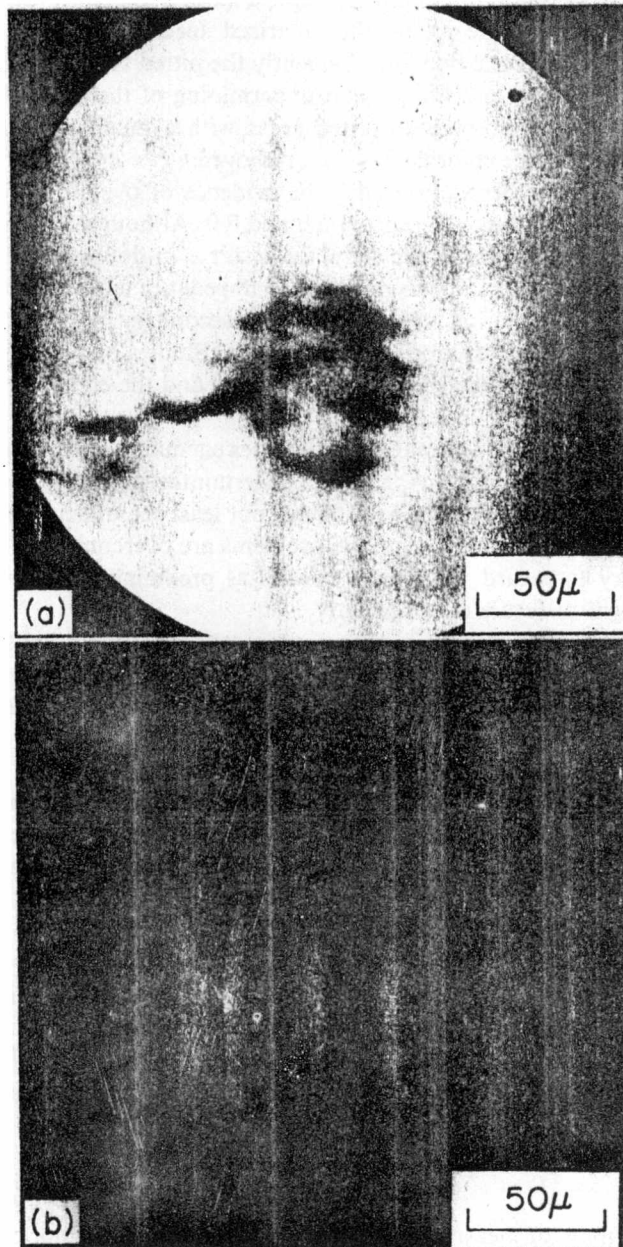


FIG. 5. Ion images for a further region of the specimen given in Fig. 3 after the film has been removed from the pitted area by sputtering. (a) O^- ion (b) Cl^- ion. Note oxygen still present in film on unpitted area but its relative absence in pitted area.

lateral undermining of the film. Likewise, Figs. 5 (a and b) show Cl^- and O^- ion images respectively of a single pit on the polarized specimen surface after partial sputtering of the total surface oxide film. Evidently the pitted surface is relatively rich in Cl^- , but deficient in O^- , indicating again undermining of the original surface film and its likely replacement on cleaned pitted areas with a much thinner air-formed type of film in regions where chloride has been removed.

As mentioned earlier, there appeared to be evidence of overall film thinning on immersion in chloride solution at both pH 6.0 and 7.0. Although the genuineness of this result cannot be discounted completely, the result is in doubt because it has not been reported by earlier workers¹⁻⁵ using sensitive impedance techniques. It should be borne in mind that the sputtering rate, as well as the secondary ion yield, may depend upon the ageing, degree of hydration, etc., of the film. Studies on hydration effects of thick anodic films on aluminium have been reported¹⁰ and the effect requires further examination.

This result highlights one of the current difficulties encountered with the potentially powerful technique of ion analysis. Apart from uncertainties about the uniformity and evenness of sputtering, there are other problems, not least the difficult of quantifying the analyses. It will be some time before the problems are overcome and in the meantime it is necessary to regard the present results as preliminary and subject to re-appraisal in the light of future developments.

It is interesting to enquire why chloride concentrating in the tiny pits, developing from flaws in the as-formed anodic film after immersion in chloride solution,^{4,5} is not readily detectable. It should be appreciated that the subject has not been fully explored and, in any case, apart from chloride adsorbed on the sides of the tiny flaw developing into a pit, it might be expected that the rest would be washed away during the minimal washing after the run, in the absence of extensive undermining at this stage. Assuming the maximum likely flaw population density¹² of $10^6/\text{cm}^2$, typically 500–2000 Å in diameter (averaging 1000 Å in diameter), a flaw area of about 10^{-4} of the total specimen area is obtained prior to immersion. Particularly if the rate of development of flaws into pits is slow, as in the natural immersion case, the incipient pits/flaws would not readily be resolved in ion images, with a maximum resolution of about 1 µm. The intensity profiles resulting from collecting secondary ions from an area 100×100 µm would be picking up chloride from a maximum of 100 incipient pit/flaws occupying a total of less than one square micron of the surface, neglecting any opening up or undermining. It is therefore perhaps not too surprising that no chloride is seen at the sputtering rates employed.

CONCLUSIONS

1. Within the limits of measurement, there is no inclusion of chloride ions in the bulk anodic alumina film, either as a result of natural immersion or by anodic polarization in near-neutral 1M potassium chloride solution.

2. Chloride ions were detected at the oxide-electrolyte interface for both naturally immersed and polarized specimens and in the latter case, where pitting had occurred, through the pit hole in the film and subsequently under the film at the metal-oxide interface.

3. Some film thinning apparently occurs, especially during natural immersion, but this result requires confirmation.

4. The results favour theories of attack at flaws in the film, with subsequent film undermining, rather than others involving halide ion entry into the film.

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A STUDY OF THE EFFECTS OF INHIBITIVE AND AGGRESSIVE IONS ON OXIDE-COATED ALUMINIUM USING SECONDARY ION MASS SPECTROMETRY*†

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Abstract—A Cameca ion analyser has been used to examine aluminium surfaces, supporting barrier-type anodic films *ca.* 720 Å thick, after natural immersion for 1–25 h in 1M chloride and chromate/dichromate solutions of varying pH, and neutral 1M phosphate solution. In chloride solutions, chloride is present on the film surface, but not within the film material *per se*, within the limits of measurement. The degree of film thinning is governed by pH, being more pronounced in alkaline than acid solutions. In chromate/dichromate solutions, chromium uptake occurs by two distinct mechanisms. The first is associated with relatively rapid chromate/dichromate reduction to Cr_2O_3 , probably hydrated, within flaws in the anodic film. The second is associated with a more gradual direct chromate/dichromate anion entry into the bulk material probably through the intercrystalline regions in the film, ultimately resulting in film thinning, even in neutral solutions. In phosphate solutions, phosphate anions penetrate and thin bulk anodic alumina in a similar manner to chromate/dichromate anions. The results are interpreted on the basis of the differing surface chemical properties of the various anions in relation to bulk alumina.

INTRODUCTION

A NUMBER of studies have been undertaken of the effects of aggressive and inhibiting anions on oxide-coated aluminium. The effects on anodic alumina of immersion in neutral chloride solutions have been studied using a.c. impedance measurements,^{1–3} autoradiography,⁴ and ion probe mass spectrometry.⁵ Rival theories favour either chloride ion penetration of the surface oxide film material via a field-independent anion exchange process,^{1,2} or preferential attack at flaws in, and subsequent undermining of, the surface oxide film.^{3–6}

The effects of chromate/dichromate solutions on aluminium surfaces supporting both air-formed and anodic films have been studied using a.c. impedance measurements^{3,7,8} and autoradiography.^{9,20} Chromate/dichromate solutions, even when neutral, induce thinning of anodic alumina films, and if anything, slight thickening of air-formed films.^{3,7,10} Although there is general agreement that chromate reduction plays an important role in the mechanism of passivation by chromate/dichromate solutions,¹¹ rival theories differ on the degree of localization of the process. On the one hand, it has been suggested that chromate adsorption at the oxide/electrolyte interface increases the field across a pre-existing air-formed oxide film. The increased

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field stimulates aluminium ion migration through the film, and oxidation of the ions at the oxide/electrolyte interface is supported by chromate reduction.⁸ Alternative theories favour the healing of flaws in pre-existing films, by chromate reduction to Cr_2O_3 at cathodic sites, and Al_2O_3 formation at anodic sites.^{3,8-10} Certain workers have suggested that, in addition to being reduced, chromate ions slowly adsorb at the oxide surface, preventing the conversion of Al_2O_3 to soluble, hydrated aluminium ions.^{9,10}

Recently, the development of the technique of ion microprobe mass spectrometry has greatly facilitated the investigation of anion interaction with surface oxide films. The fundamentals of the technique have been described in detail elsewhere.¹² Briefly, a beam of primary ions is employed to eject secondary atoms or ions from the specimen surface. The location of component elements can be defined in the form of ion images or in-depth profiles from a scanned area. At a constant sputtering rate, an approximate measure of the variation with depth of the concentration of a component element can be obtained.

In the present work, anodically oxidized aluminium surfaces have been studied using ion analysis after varying periods of immersion in chloride and chromate/dichromate solutions of varying pH, and neutral phosphate solutions. Primarily, the work was concerned with the detection and location of the anions within the film material, using in-depth profiles and ion images. At the present stage of development of the technique, the results must be regarded as semi-quantitative.

EXPERIMENTAL METHOD

Aluminium samples of 99.99% purity were electropolished in a perchloric acid/ethanol mixture prior to anodizing at 1 mA/cm^2 to 60 V (corresponding to a film thickness of ca. 720 Å) in 3% ammonium tartrate solution, pH 7.0, at 20°C. Analar grade reagents and doubly distilled water were used throughout, and adjustments in pH were made using solution of the appropriate acid or potassium hydroxide.

A Cameca IMS 300 Ion Analyser was employed, and details of the experimental technique have been given elsewhere.⁵ Samples were coated with gold prior to analysis, which facilitated the identification of previously analysed areas by the absence of interference colours. At the sputtering rates necessary to obtain clear ion images, it proved difficult to obtain a sequence of images showing the in-depth distribution of certain elements. This was especially true in the case of Cr^+ images. Alternatively, a technique was adopted involving partial sputtering of an area of film, and then alteration of the sputtering area so as to include the edge of the crater originally created. Sputtering the new area yielded information as to the in-depth distribution of an element on a single ion image. The technique is shown schematically in Fig. 7.

RESULTS AND INTERPRETATION

Chloride solutions

Previously, the effects of the immersion of oxide-coated aluminium in neutral 1M KCl solution for short periods of time have been reported,⁵ and the work has now been extended to include solutions of varying pH. Samples of oxide-coated aluminium were immersed in 1M KCl solutions at pH 2.5, 4, 8, and 10 respectively for periods of 24 h. In depth profiles of AlO^+ for the various immersed films, and for an as-formed film, are shown in Fig. 1. Previous work has suggested that Al^+ or AlO^+ profiles are approximate functions of film thickness and, at constant sputtering rate, should facilitate determination of the in-depth profiles of any other elements present in the film.⁵ The data in Fig. 1 suggest that film thinning occurred in all solutions,

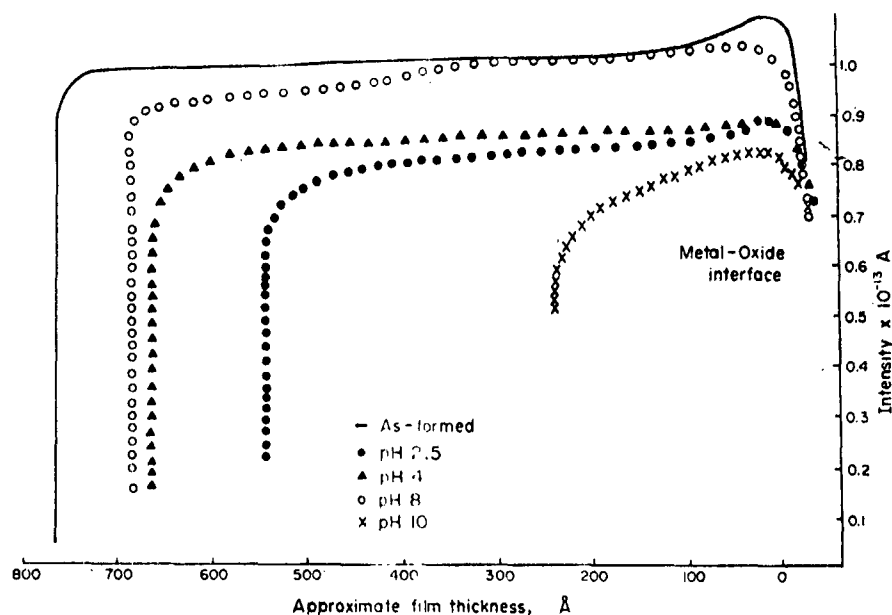


FIG. 1. AlO^+ profiles of films after 25 h periods of immersion in 1M chloride solution of varying pH.

but to a much greater extent in alkaline than acid solutions. The data must obviously be viewed with some caution, in view of the possible dependence of sputtering rate and secondary ion yield on ageing, degree of hydration, etc. However, at face value, the data suggest average thinning rates of *ca.* 3 Å/h at pH 4 and 8, 8 Å/h at pH 2.5, and 21 Å/h at pH 10. The profiles for any particular pH were reproducible to within 2%, which suggests very uniform thinning over the whole sample surface.

In-depth profiles of Cl^- for all samples were virtually identical to those reported previously⁶ for neutral 1M KCl solutions, i.e. a Cl^- peak was detected at the oxide/solution interface, but no Cl^- was detected through the bulk of the film material itself. Ion images of specimens immersed in solutions of pH 4 and 8 showed no evidence of Cl^- (apart from that at the oxide/electrolyte interface), as was the case for neutral 1M KCl solution.⁵ However, ion images of samples immersed in the pH 10 solution showed small, isolated Cl^- -rich areas, presumably associated with points of breakdown. Significantly, in only one area of the sample immersed in pH 4 solution was a detectable Cl^- ion image obtained, as shown in Fig. 2. As is evident, a number of isolated Cl^- -rich regions were detected after *ca.* 150 Å of the remaining film had been sputtered, apparently aligned along a scratch in the specimen surface.

Overall, the data obtained confirm the conclusions of the previous work in neutral solutions.⁵ Within the limits of measurement, there is no inclusion of Cl^- ions in the bulk anodic alumina film resulting from immersion in 1M KCl solutions over a wide range of pH. Film thinning is apparently related to pH, rather than the presence of Cl^- in solution, and is particularly severe in alkaline media. The Cl^- ion is detectable locally during sputtering, only when the corrosion rate is high enough to allow flaws

to develop into sizeable pits beneath the surface film during the relatively short immersion period, i.e. in relatively acidic or alkaline media.

Chromate/dichromate solutions

In-depth profiles of AlO^+ and Cr^+ for oxide-coated aluminium after various periods of immersion in 1M chromate/dichromate solutions at pH 7.3 and 2 are shown in Figs. 3 and 4 respectively. Film thinning has apparently occurred in both solutions. In the pH 7.3 solution, the films have thinned at an apparent rate of *ca.* 7 Å/h over a 25 h period, whereas in the pH 2 solution, the films have virtually disappeared in the same time period. Although the data in Figs. 3 and 4 suggest a non-uniform thinning rate (during the first hour, *ca.* 50 Å/h and 180 Å/h at pH 7.3 and 2 respectively), caution must be exercised in the absence of any detailed knowledge of the effects of ageing, hydration etc. on sputtering rates. The evidence from impedance measurements is that uniform film thinning occurs in chromate/dichromate solutions, albeit at rates greater than, for example, halide solutions of equivalent pH.^{1,3,7}

In-depth Cr^+ profiles in Figs. 3 and 4 show the same general trend for all films i.e. a relatively high Cr^+ yield in an outer layer of the film approximately 50–60 Å wide at pH 2, and 100–150 Å wide at pH 7.3. In fact, in all cases, Cr^+ was detected, albeit at relatively small levels, down to the metal/oxide interface, with the exception of the 25h, pH 2 specimen, where there was only a 50–60 Å thick, Cr^+ -rich film, remaining

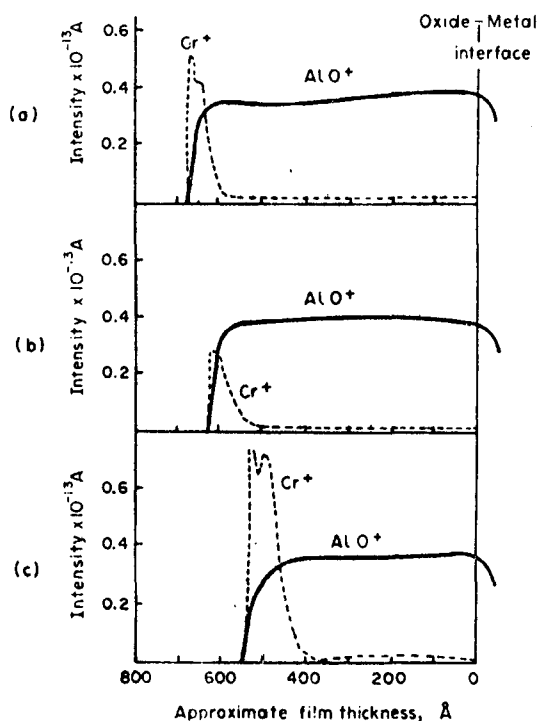


FIG. 3. AlO^+ and Cr^+ profiles of films after (a) 1 h, (b) 2 h, and (c) 25 h immersion in 1M chromate/dichromate solution pH 7.3.

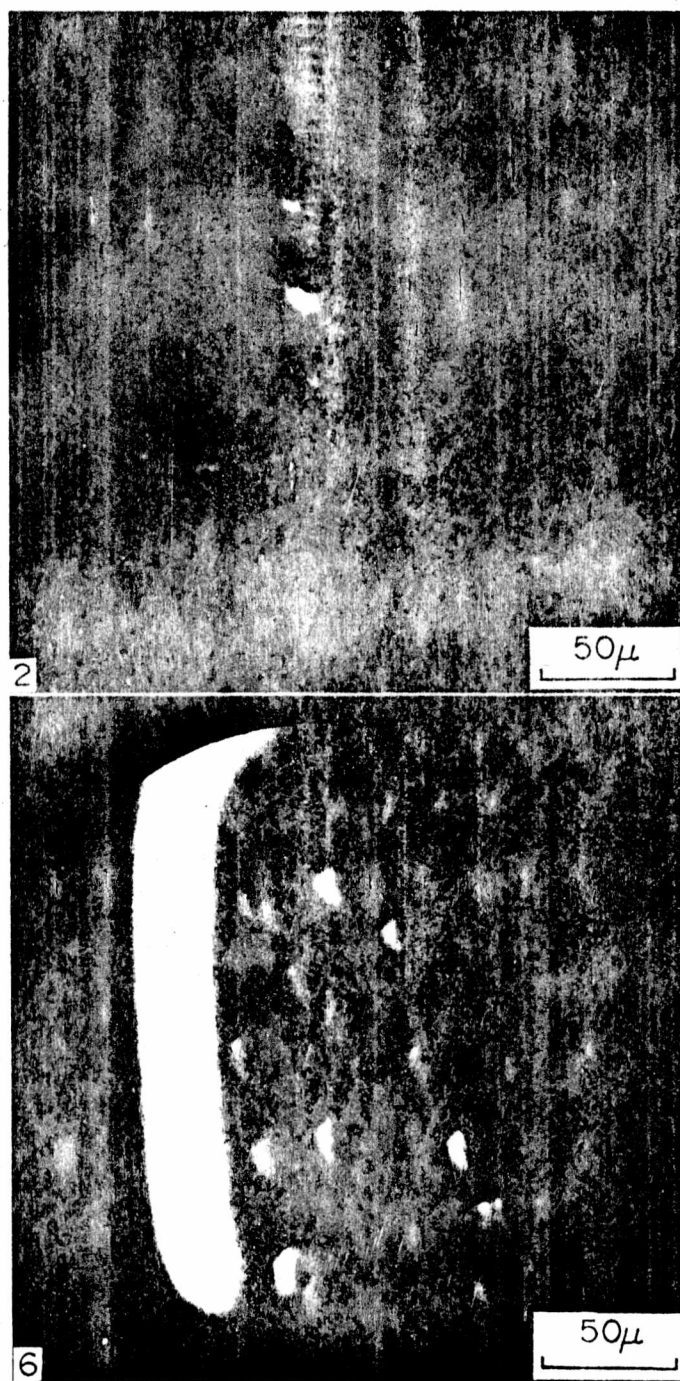


FIG. 2. Cl^- ion image after sputtering *ca.* 150 Å of film subjected to 25 h immersion in 1M chloride solution pH 4.

FIG. 6. Cr^+ ion image of film subjected to 25 h immersion in 1M chromate/dichromate solution pH 7.3.

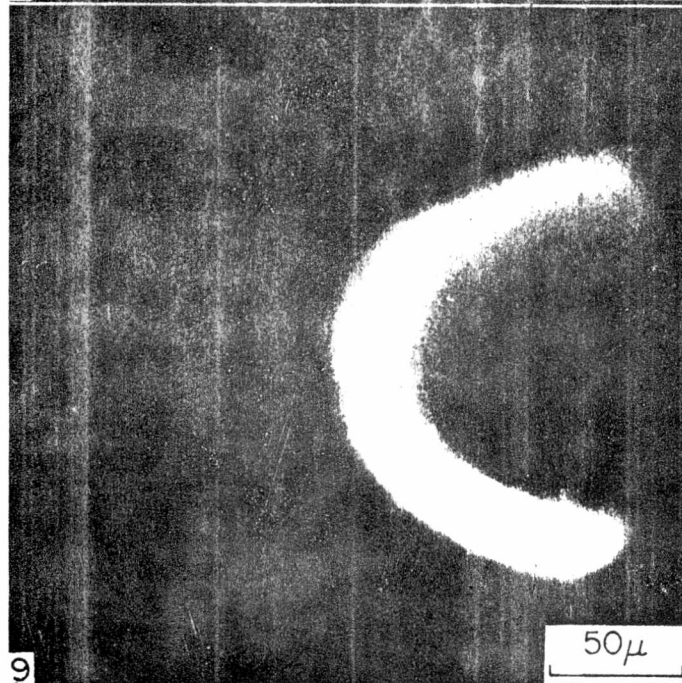
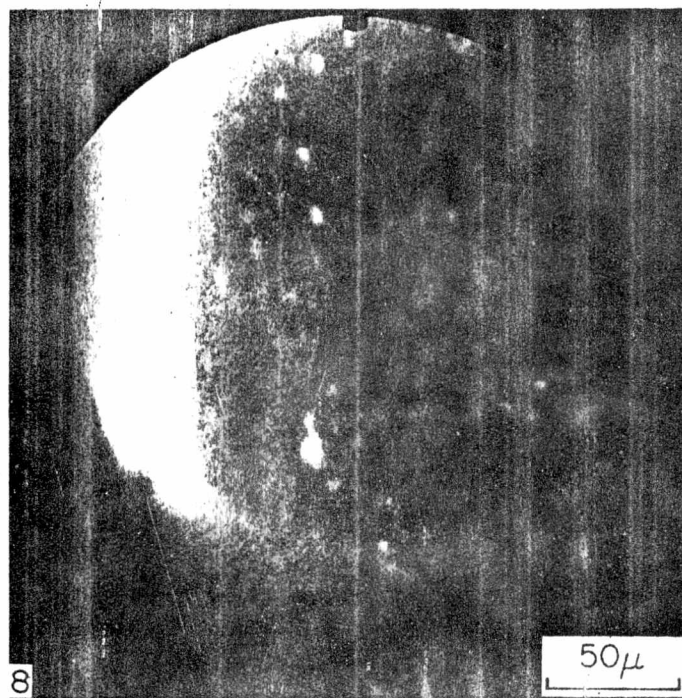


FIG. 8. Cr^+ ion image of film subjected to 1 h immersion in 1M chromate/dichromate solution pH 2.

FIG. 9. Cr^+ ion image of film subjected to 25 h immersion in 1M chromate/dichromate solution pH 2.

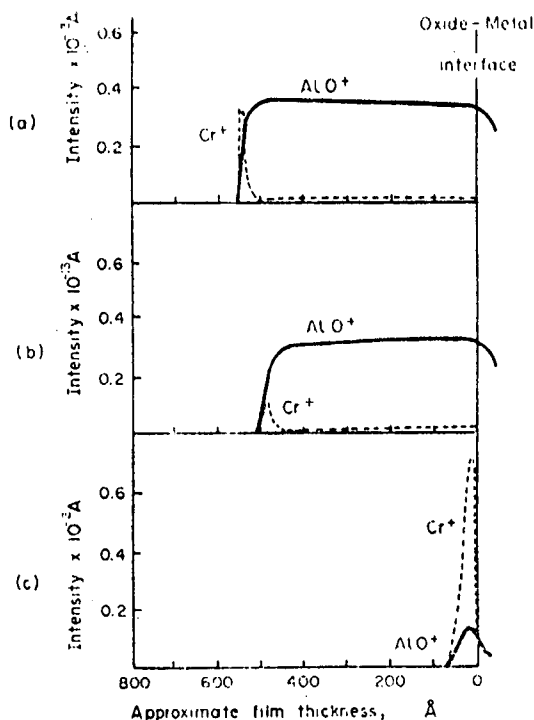


FIG. 4. AlO^+ and Cr^+ profiles of films after (a) 1 h, (b) 5 h and (c) 25 h immersion in 1M chromate/dichromate solution pH 2.

on the surface. This is in striking contrast to the effects of immersion in Cl^- -containing solutions, after which no Cl^- ion entry into the film material *per se* could be detected. Although it is recognized that the technique is, at best, semi-quantitative, it is interesting to look at the relationship between integrated Cr^+ yield and time for the two chromate/dichromate solutions, as shown in Fig. 5. The data at least suggest that chromium uptake is less at pH 2 than pH 7.3, consistent with the differing depths of penetration of the outer regions of remaining films. Interestingly, studies of the immersion of porous anodic alumina films in chromate/dichromate solutions have shown that chromium uptake decreases with increasing pH within the range 3.7–9.7.²⁷ Overall, this is consistent with autoradiographic studies of the chromate-induced passivation of mild steel, which suggested an optimum pH range for chromium uptake, for mild steel within the range 4–6, chromium uptake falling at higher or lower pH values. Furthermore, the data in Fig. 5 also suggest that chromium uptake on the anodic oxide-coated surfaces occurs relatively quickly during the initial stages of immersion, and thereafter more slowly, particularly in neutral solutions. This is again consistent with autoradiographic studies on both mild steel¹⁴ and aluminium surfaces initially supporting air-formed films.

A typical Cr^+ ion image, for a specimen subjected to 25 h immersion at pH 7.3, is shown in Fig. 6. The technique for obtaining such an image is described schematically in Fig. 7. The general distribution of Cr^+ within the film was the same for all immersion

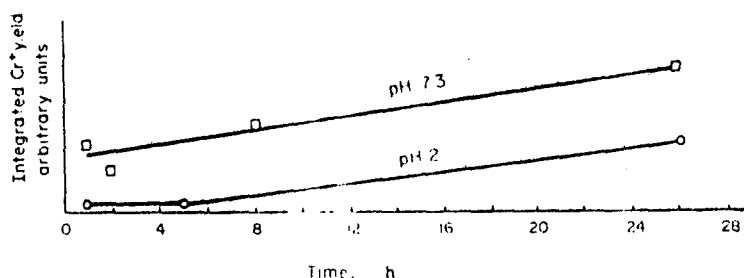


FIG. 5. Integrated Cr⁺ yields as a function of time for films immersed in 1M chromate/dichromate solutions of pH 2 and 7.3.

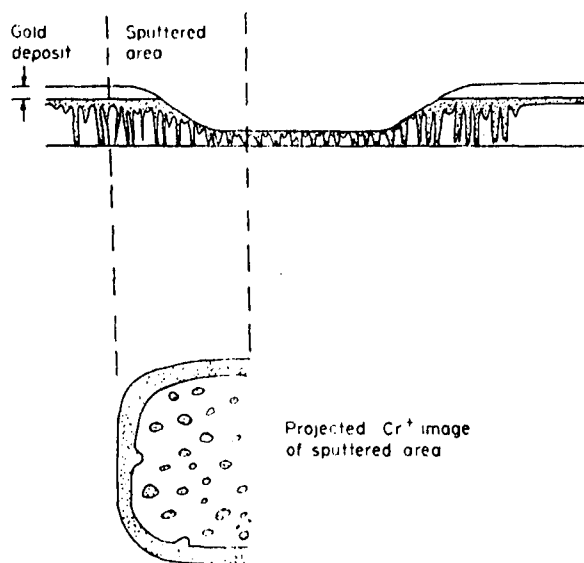


FIG. 7. Schematic basis for obtaining ion images shown in Figs. 6, 8 and 9.

conditions with the exception of the 24 h, pH 2 specimen i.e. an outer layer of uniformly distributed Cr⁺, beneath which Cr⁺ was heavily localized within the film, down to the metal/oxide interface. Such a distribution is consistent with the in-depth profiles shown in Figs. 3 and 4. The population densities of Cr⁺-rich spots were calculated for all immersion conditions, and were generally within the range $2.2\text{--}2.7 \times 10^5/\text{cm}^2$. The only notable exceptions to this figure were in the case of 1 h, pH 2 specimen, shown in Fig. 8, where the Cr⁺-rich spot population density was *ca.* $9.5 \times 10^5/\text{cm}^2$, and the 25 h, pH 2 specimen, shown in Fig. 9, where there was only a uniform layer of Cr⁺-rich oxide *ca.* 60 Å thick remaining on the specimen surface. In both solutions, there was a tendency for the population density of the Cr⁺-rich spots to reduce with immersion time, and significantly, in the pH 2 solution, the population density reduced from $9.5 \times 10^5/\text{cm}^2$ after 1 h immersion, to $2.5 \times 10^5/\text{cm}^2$ after 5 h immersion.

There is a striking similarity between the Cr^{3+} -rich spot population densities observed in the present work, and the population densities of so-called 'residual' flaws (10^4 – $10^6/\text{cm}^2$) observed using transmission electron microscopy in anodic films on aluminium of 99.99% purity.⁸ The origins of such flaws have been argued in detail elsewhere,^{6,8,15,16} but being associated with noble metal impurity segregation in the substrate, they are considered to act as preferred cathodic sites. It seems likely that chromate/dichromate reduction occurs at such sites, and that they thus become 'decorated' with probably hydrated Cr_2O_3 , revealing themselves at Cr^{3+} -rich spots in the ion images shown in Figs. 6 and 8. The uniformly distributed Cr^{3+} in the outer regions of films on immersed specimens is considered to be associated with a much slower penetration of the film by the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species themselves, the mechanism for which is argued in more detail below. Both processes are considered to contribute to the apparently large Cr^{3+} -rich spot population density observed after 1 h immersion in the pH 2 solution. Thus, some of the Cr^{3+} -rich areas evident in Fig. 8 are probably associated with the advance of the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species into the film material from the film solution interface, while others are associated with chromate/dichromate reduction of flaws in the film, proceeding from the metal/oxide interface.

Penetration of $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species into the oxide material can, of course, occur at the flaw walls, as well as at the film/solution interface. Indeed, this process probably accounts for the relatively large sizes of the Cr^{3+} -rich spots in Figs. 6 and 8, compared to the established maximum diameters (*ca.* 0.2 μm) of 'residual' flaws in anodic films.^{6,8,16,18} It is also recognized that some ionic distortion is possible during imaging, which might have some effect on apparent spot sizes etc.

Phosphate solution

Although made up by adjusting the pH of an orthophosphate solution with orthophosphoric acid, a neutral phosphate solution contains little, if any, PO_4^{3-} anion, being roughly equimolar in HPO_4^{2-} and H_2PO_4^- anions. In-depth profiles of Al^{3+} and P^{3+} for oxide-coated aluminium after 25 h immersion in such a solution are shown in Fig. 10. Evidently substantial film thinning has again occurred, equivalent to an average thinning rate of *ca.* 9 $\text{\AA}/\text{h}$ during the 25 h period. In the remaining film, P^{3+}

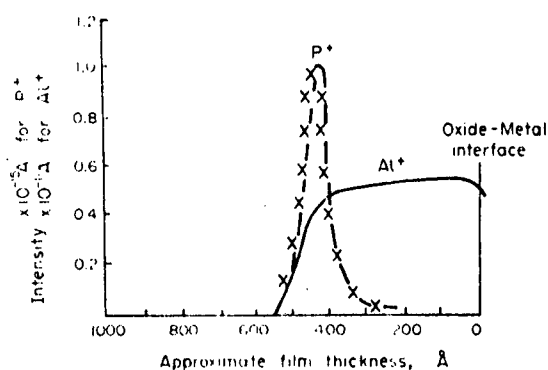


FIG. 10. Al^{3+} and P^{3+} profiles of film after 25 h immersion in 1M phosphate solution pH 7.

has apparently penetrated to a depth of *ca.* 150–200 Å, but no P^+ signal was detectable closer to the metal/oxide interface. Although the relatively weak P^+ signal made ion imaging difficult, it was apparent that the P^+ within the film was uniformly distributed, its concentration being at a maximum at the oxide/solution interface. The uniformly distributed P^+ in the outer regions of the film is considered to be associated with a gradual penetration of the film by the phosphate, in particular the HPO_4^{2-} species, as argued in more detail below.

It is worth commenting that there was no evidence in the present work of P^+ -rich spots in the film, possibly associated with the stiling of anodic sites by insoluble metal phosphate.^{13,21} Precipitation of phosphate obviously requires initial dissolution of the base metal, and this is minimal for aluminium in neutral solutions. Such spots are, in fact, associated with more acidic solutions, even in the case of iron.²² In addition observations of phosphate-rich areas have previously been restricted to air-formed films which are thought to have many more 'mechanical' flaws, and thus potential anodic sites, than anodic films.⁸

DISCUSSION

The data reported here confirm the somewhat paradoxical properties of inhibitive and aggressive anions in terms of their effect on anodic alumina. The Cl^- anion, renowned for its ability to promote pitting and stress corrosion cracking of aluminium and its alloys, apparently has little or no effect on the oxide film material *per se*. Indeed, the pH of the chloride solution examined was much more important than the presence of Cl^- itself in determining the degree of attack suffered by the surface oxide films. Alternatively, the chromate/dichromate and phosphate anions, renowned for their inhibiting properties towards aluminium and its alloys, are apparently relatively aggressive towards anodic alumina, having the ability to penetrate and disintegrate the film material *per se*. Accepting the reservations concerning the possible effects of ageing, hydration etc. on sputtering rates cited above, the data would suggest that neutral chromate/dichromate and phosphate solutions are more than twice as aggressive as neutral chloride solutions towards anodic alumina, and as aggressive as an equivalent chloride solution of pH 2.5. In the case of chromate/dichromate solutions, these effects are confirmed by impedance studies.^{1,3,7,8} In addition, both chromic and phosphoric acids are known to be aggressive towards porous films on aluminium. The chromate/dichromate and phosphate anions have the ability to penetrate, soften and ultimately dissolve the pore wall material at a rate greater than that attributable to acidity alone.¹⁷ Significantly, in the present study, the acid chromate/dichromate solution was much the most aggressive towards anodic alumina.

There is a strong correlation between the effects of the various anions on anodic alumina, and their established surface chemical properties in relation to bulk alumina.^{18–20} The principal zeta potential determining species are the H^+ and OH^- ions, although in neutral solutions (z.p.c. at pH 9.5), a reversal in sign of the zeta potential is observed associated with the chemisorption of species such as chromate/dichromate and the various phosphate anions. No such effects are observed with chloride, even in very strong solutions. The reduction in magnitude of the zeta potential in halide media can be interpreted as simple physical adsorption. It would thus appear that H^+ and OH^- ions are strongly chemisorbed on alumina surfaces,

and are only replaceable by anions having a stronger tendency to chemisorb on to the surfaces, given the limitations of relative bulk concentrations etc. Anions such as the chromate/dichromate and the various phosphates possess such a tendency, whereas the chloride anion does not.

Such differing properties are of great importance in relation to the effects of various anions on surfaces supporting amorphous Al_2O_3 films. Anodic alumina is generally supposed to consist of a relatively open array of amorphous, largely anhydrous crystallites $< 50\text{\AA}$ in diameter, permeated by molecular water, and with the crystallite surfaces carrying OH^- anions and possibly anions from the forming solution.^{25,26} The intercrystalline regions are thought to be accessible to water.²⁶ It is suggested that ions with a strong tendency to chemisorb on to alumina e.g. H^+ , OH^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, PO_4^{3-} , HPO_4^{2-} , etc. can penetrate the intercrystallite regions in the film, resulting in the gradual disintegration and dissolution of the film material. There is strong electron microscopic evidence for this in the case of porous films in chromic and phosphoric acids.¹⁷ In contrast, anions such as Cl^- cannot compete with H^+ or OH^- for the alumina crystallite surfaces, and are thus unable to penetrate the film material significantly. It is not surprising, therefore, that in the present study, neutral chromate/dichromate and phosphate solutions were observed to penetrate and ultimately to thin anodic alumina, whereas neutral chloride solutions appeared to exert little or no effect on the film material *per se*. However, the roles of the anions are reversed in relation to their effects on the substrate metal at the bases of flaws in the surface oxide film. The Cl^- anion can promote dissolution of the base metal, leading to pitting and subsequent undermining of the surface oxide film.⁵ However, where the CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions make contact with the base metal, they are not only reduced themselves to solid, probably hydrated Cr_2O_3 , with a subsequent stifling of cathode activity, but also promote precipitation of initially soluble aluminium dissolution products as solid hydrated Al_2O_3 , thus stifling anodic sites.⁸ Although the various phosphates cannot be reduced electrochemically, they do form highly insoluble salts with aluminium, and thus in corrosive media stifle anodic sites by the precipitation of initially soluble aluminium dissolution products.²¹

Finally it is appropriate to comment in more detail on the present work in relation to the work of others on chromate/dichromate induced inhibition and passivation. The present work provides strong evidence for a two-stage effect of chromate/dichromate solution on oxide-coated aluminium, as has been previously suggested:^{9,10,22}

1. An initial rapid uptake of chromium is associated with reduction of $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ at the bases of 'residual' flaws⁸ in the surface film, resulting in the stifling of such flaws with a mixture of hydrated Al_2O_3 and Cr_2O_3 . There is strong evidence for this in the ion images obtained in the present work, showing localized Cr^{+} -rich spots throughout the whole thickness of immersed surface films.
2. A more gradual uptake of chromium is associated with the penetration of the intercrystallite regions of the outer layers of the film by the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species. Although the driving force for this process is considered to be the pronounced tendency of the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ species to adsorb onto alumina surfaces, it is difficult to specify whether they do so as discrete anions, or as part of an aluminium-oxy-chromate complex. There is some evidence that complex formation could occur in the case of phosphate penetration of alumina films,^{23,24} but

certainly no direct evidence which could be used to explain chromate/dichromate entry.

In acid chromate solutions, a synergistic effect between H^+ and the $CrO_4^{2-}/Cr_2O_7^{2-}$ species might be expected. Film penetration and dissolution rates observed here and elsewhere^{17,27} reflect both H^+ and anion entry. Thus chromium uptake is observed to increase with decreasing pH within the range 3.7–9.7,¹⁷ within which range thinning rates are relatively small. At lower pH, the increased rates of H^+ and anion entry are reflected in markedly increased thinning rates, which can result in lower measured chromium uptakes and penetration on remaining films. For example, in the present study, although the measured chromium uptake and penetration after the immersion at pH 2 is less than at pH 6.3 (Fig. 5), the film in the pH 2 solution has thinned to a much greater extent than the film in the pH 7.3 solution. Relative to the as-formed film, the CrO_4^{2-} and $Cr_2O_7^{2-}$ species have, in fact, penetrated much further at pH 2 than at pH 7.3.

CONCLUSIONS

1. Within the limits of measurement, there is no inclusion of chloride ions in bulk anodic alumina film resulting from natural immersion in M KCl solutions over a pH range 2.5–10. The degree of film thinning appears to be governed by pH, being more pronounced in alkaline than acid solutions.
2. Chromium uptake into anodic alumina resulting from immersion in chromate/dichromate solutions occurs by two distinct mechanisms. The first is associated with relatively rapid chromate/dichromate reduction to hydrated Cr_2O_3 within flaws in the surface oxide film. The second is associated with a more gradual direct chromate/dichromate anion entry into the bulk film material through the intercrystallite regions in the film, ultimately resulting in film thinning, even in neutral solutions.
3. Phosphate anions can penetrate and thin bulk anodic alumina in a similar manner to chromate/dichromate anions.
4. The differing effects of the various anions bears a strong correlation to their surface chemical properties in relation to bulk alumina.

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A STUDY OF BARRIER FILM GROWTH ON ALUMINIUM IN SOLUTIONS OF FILM-PROMOTING AND AGGRESSIVE IONS USING SECONDARY ION MASS SPECTROMETRY*†

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Abstract—A Cameca Ion Analyser has been used to examine barrier-type anodic films grown on aluminium in neutral phosphate, chromate or phosphate/chromate solutions and in phosphate and chromate solutions containing relatively small amounts of chloride ion. Barrier layers grow at relatively high current efficiencies in phosphate solution, and are characterized by a rather wide phosphorus-containing layer adjacent to the oxide/solution interface. In chromate solutions, barrier layers grow at relatively low current efficiencies and contain little, if any, chromium resulting from the film growth process itself. Barrier layers grown in chromate-phosphate mixtures are generally typical of those grown in pure phosphate solutions, even at quite high chromate/phosphate concentration ratios. The presence of chloride ions in either phosphate or chromate solutions lowers the current efficiency of barrier film growth, and is associated with pitting of the aluminium substrate at the bases of flaws in the growing film, resulting in lateral undermining of the film. The results are explained in terms of a model for film development, involving growth partly by ionic migration and partly by a dissolution/precipitation process.

INTRODUCTION

THE UPTAKE of anions from the forming electrolyte during the growth of barrier oxide films on valve metals has been widely investigated. Studies have usually involved the use of radiotracer techniques, although, more recently, secondary ion mass spectrometry has been employed.^{1,2} Studies have included the growth of barrier layers on Ta in phosphate solutions,^{1,2} Zr in carbonate, sulphate and borate solutions³ and Al in phosphate,⁶⁻⁸ borate,⁹ carbonate and chromate¹⁰ solutions. Generally, evidence has been obtained that barrier oxide films are duplex in nature, electrolyte anions being restricted to an outer layer of oxide adjacent to the oxide/solution interface. The width of the anion-containing layer has been shown to depend on the metal, the anion and the forming conditions of the film. For example, in the case of alumina barrier films grown in phosphate solutions under a wide range of conditions, the phosphate-free region of oxide has been shown to be confined to the inner one third of the film.⁷

Investigations such as those referred to above have often been undertaken with the objective of establishing the degree of metal ion and O^{2-} or OH^- mobility during barrier film growth. As such, they have been criticized on the grounds that the electrolyte anions themselves might be mobile during film growth. For example, it has been suggested that the SO_4^{2-} ion is mobile during barrier layer growth on Zr³ and the F^- ion, and perhaps even the PO_4^{3-} ion, are mobile during barrier layer growth on Ta.² Alternative techniques for identifying mobile species during oxide film growth include the analysis of films containing inert gas marker species,¹¹ or growth in ^{18}O -containing solutions.¹²

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In the present work, barrier oxide films formed on Al in neutral phosphate and chromate solutions have been studied using ion probe mass spectrometry. The two solutions were chosen because of their widely differing behaviour in relation to the degree of anion inclusion in the anodic films which they grow. Both barrier^{4,8} and porous¹³ alumina films grown in phosphate-containing media are known to contain appreciable quantities of anion. Porous films grown in chromic acid solutions, on the other hand, are known to contain relatively little included anion.¹³ In addition, competition between different film-forming anions, and film-forming and aggressive anions, has been studied by analysing films formed in mixed phosphate chromate solutions, and phosphate and chromate solutions containing varying amounts of chloride anions.

EXPERIMENTAL METHOD

Aluminium samples of 99.99% purity were electropolished in a perchloric acid/ethanol mixture prior to anodizing at 1 mA/cm² and 20°C to 60 V in the various electrolytes used. An exception to this procedure was in the case of 1 M phosphate solution + 200 ppm KCl, where the anodizing voltage was allowed to proceed through a maximum of ca. 120 V before dropping again to 60 V. The basic anodizing solutions were chromate and phosphate solutions, the pH values of which were adjusted to 7 using the appropriate acid or potassium hydroxide. In one series of experiments, 1 M chromate and phosphate solutions were mixed in the appropriate proportions to provide a series of chromate/phosphate solutions of varying compositions. In another series, KCl was added to 1 M chromate and phosphate solutions at various levels up to a maximum of 200 ppm. Analar grade reagents and doubly distilled water were used throughout.

A Cameca XIMS 300 Ion Analyser was employed, and details of the experimental technique have been given elsewhere.^{14,15}

EXPERIMENTAL RESULTS AND INTERPRETATION

Phosphate solutions

In depth profiles of PO_2^- and AlO^- for a film formed in 1 M phosphate solution to 60 V (corresponding to a film thickness of ca. 720 Å) are shown in Fig. 1. Evidently the PO_2^- profile suggests that phosphate is incorporated within the outer two thirds of the film adjacent to the metal solution interface, in broad agreement with the work of others concerning barrier layer growth in phosphate solutions.⁶⁻⁸ The PO_2^- yield shows a maximum in the outer 100 Å of the film, and is thereafter relatively constant for a further 300 Å of film thickness, before declining to zero. No PO_2^- at all was

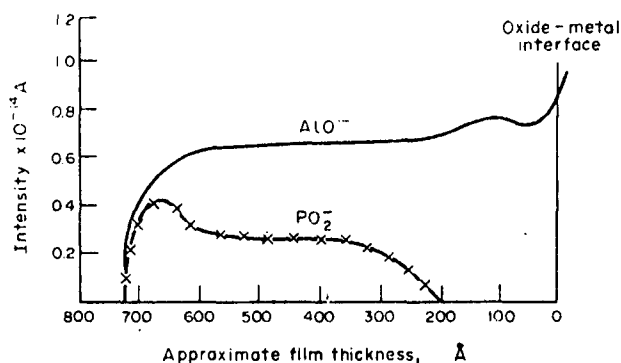


FIG. 1. AlO^- and PO_2^- profiles of 60 V film formed in neutral 1 M phosphate solution.

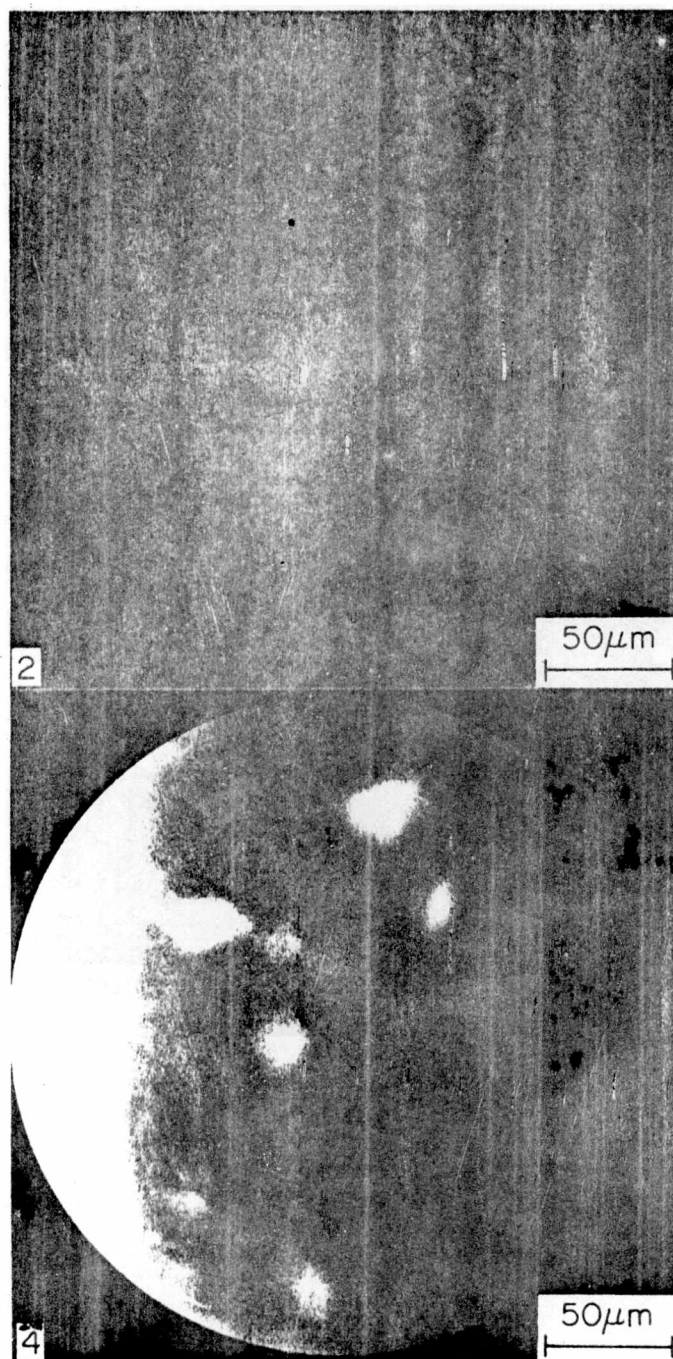


FIG. 2. PO_2 ion image of 60 V film formed in neutral 1 M phosphate solution.

FIG. 4. Cr^{3+} ion image of 60 V film formed in neutral 1 M chromate solution.

[facing p. 690]

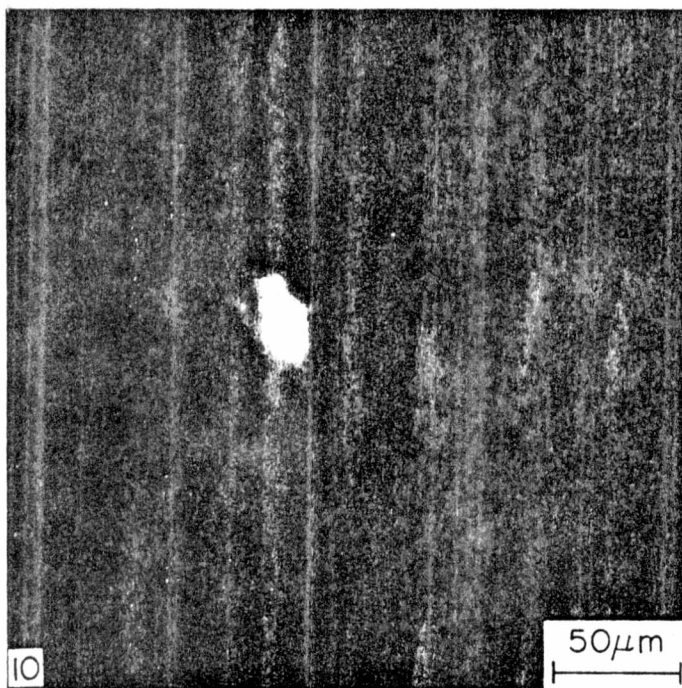


FIG. 10. Cl^- ion image close to oxide-metal interface of 60 V film formed in neutral 1 M phosphate solution containing 10 ppm KCl.

of the film, adjacent to the film/solution interface. Cr^{+} was, in fact, detected, albeit at relatively small levels, down to the metal/oxide interface. Ion images of Cr^{+} obtained at various stages during film sputtering suggest that Cr^{+} is uniformly distributed in an outer layer of film *ca.* 80 Å wide, but thereafter is distributed locally within the film, a typical Cr^{+} image being shown in Fig. 4. Data such as that shown in Figs. 3 and 4 were also obtained for films grown to 60 V in 0.01, 0.1, 0.25 and 0.75 M chromate solutions. In all cases, the Cr^{+} profiles and ion images obtained were virtually identical to those obtained in 1 M chromate solution, there being no evidence of a change in Cr^{+} yield in the outer regions of the films with chromate concentration in the forming solution.

The data shown in Figs. 3 and 4 are strikingly similar to those previously obtained for ammonium tartrate-formed films subjected to periods of immersion ≥ 1 h in chromate/dichromate solutions.¹⁶ In particular, the Cr^{+} -rich spot population density (*ca.* $1.8 \times 10^5/\text{cm}^2$) is very similar to that observed previously,¹⁶ and attributed to the decoration of 'residual' flaws in the film with hydrated chromium oxide. An attempt was made to distinguish between chromium inclusion in the film resulting from film growth, and chromium inclusion resulting from the short periods of exposure of the specimen to the solution before switching on the current, and after film formation but before removal for rinsing. A series of films grown to 60 V in ammonium tartrate solution were immersed in 1 M chromate solution at pH 7 for periods much shorter than those used previously,¹⁶ ranging from 1–10 min. In-depth profiles of Cr^{+} and AlO^{+} after 1 min immersion are shown in Fig. 5. The Cr^{+} profile is very similar to those observed previously for chromate immersion,¹⁶ i.e. a relatively high Cr^{+} yield adjacent to the oxide/solution interface, which ion images confirmed to be uniformly distributed, and a much smaller Cr^{+} yield down to the metal/oxide interface, which ion images confirmed to be locally distributed. The Cr^{+} yield was observed to increase

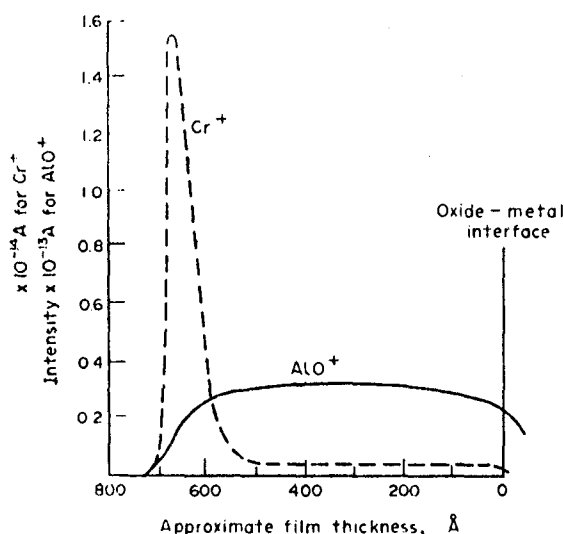


FIG. 5. AlO^{+} and Cr^{+} profiles of 60 V films formed in neutral ammonium tartrate solution, and immersed in neutral 1 M chromate solution for 1 min.

detected in the other one third of the film adjacent to the metal/oxide interface, the mass spectrum of which was typical of pure alumina.

In depth PO_2^- and AlO^- profiles were also obtained for a series of films grown to 60 V in 0.01, 0.1, 0.25 and 0.75 M phosphate solutions. In all cases, the profiles obtained were virtually identical to those obtained in 1 M phosphate solution, there being no evidence of a change in PO_2^- yield with phosphate concentration in the forming solution. Ion images of PO_2^- suggest a uniform distribution of included phosphate in the outer regions of the film. Although difficult to resolve, there was evidence in some images of discrete PO_2^- -deficient areas in the film, as shown in Fig. 2. Significantly, the population densities of such spots were generally *ca.* $1 \times 10^5/\text{cm}^2$, in close agreement with the Cr^+ -rich spot population densities observed during immersion of anodized surfaces in chromate/dichromate solutions, and attributed to flaws within the films.¹⁶ As in the previous work, the PO_2^- -deficient spots are much larger than would normally be expected for 'residual' flaws in surface films,¹⁶ but again, the picture is confused by ionic distortion during imaging.

The extent of phosphate uptake observed in the present study is substantially greater than that observed earlier for barrier layers previously anodized in ammonium tartrate solution, before a prolonged period of immersion in neutral 1 M phosphate solution.¹⁰ The data in Fig. 1 strongly suggest that both Al^{3+} and O^{2-} or OH^- are mobile during barrier layer growth in neutral phosphate solutions. Obviously, there are problems involved in calculating apparent transport numbers directly from data such as those shown in Fig. 1, arising principally from the possibilities of included phosphate mobility during growth, and of $< 100\%$ current efficiency during growth resulting from film dissolution at the film/solution interface. However, at face value, the data in Fig. 1 suggest an apparent metal ion transport number of *ca.* 0.72 which is in reasonable agreement with those previously observed for alumina film growth in phosphate solutions.⁷

Chromate solutions

In-depth profiles of Cr^+ and Al^+ for a film formed in 1 M chromate solution to 60 V are shown in Fig. 3. Evidently, the Cr^+ yield is relatively high in an outer layer

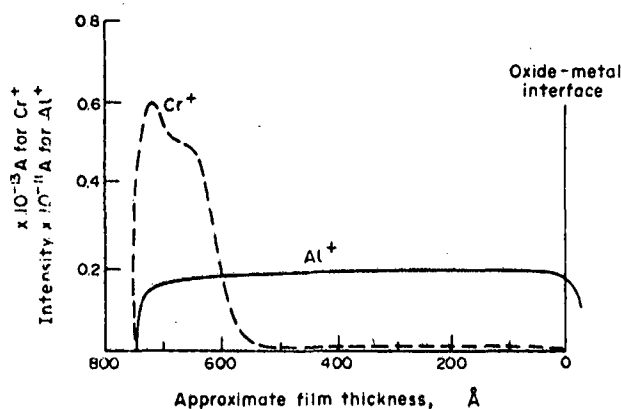


Fig. 3. Al^+ and Cr^+ profiles of 60 V film formed in neutral 1 M chromate solution.

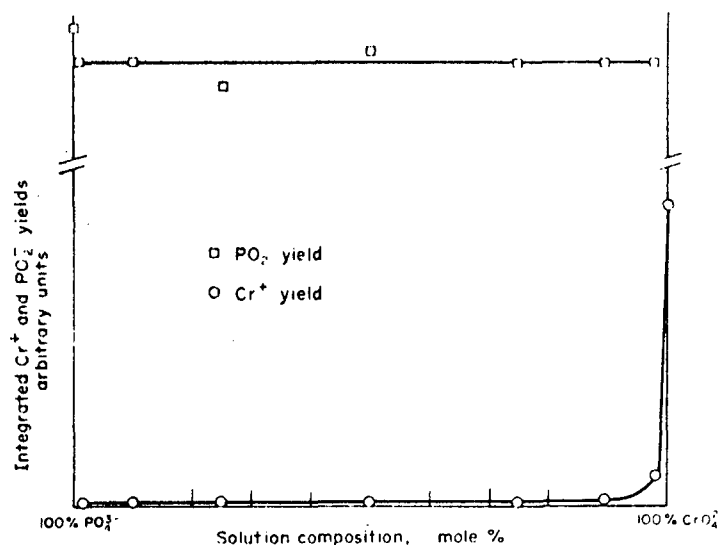


FIG. 6. Integrated Cr^{3+} and PO_4^{3-} yields for 60 V films formed in neutral chromate/phosphate solutions of varying composition.

order of magnitude lower and the Cr^{3+} -rich spot population density (*ca.* $0.4 \times 10^5/\text{cm}^2$) was much reduced relative to a film formed in 1 M chromate solution. Thus, the presence of even relatively small quantities of phosphate anion is sufficient, not merely to dominate the film growth process, but also to inhibit chromate reduction at the bases of 'residual' flaws in the surface oxide film.¹¹ It is possible that the latter effect is a result of competitive adsorption between the phosphate and chromate species, although this would seem unlikely at chromate : phosphate molar ratios as high as 99 : 1. It seems more likely that even small quantities of phosphate anion are sufficient to inhibit the small amount of anodic dissolution necessary to support the cathodic reduction of chromate.

The relative dominance of one anion in determining film properties is a common feature of alumina film formation in mixed solutions of film-promoting anions. Thus, relatively small additions of phosphoric acid to a chromic acid bath results in the formation of porous films typical of those grown in pure phosphoric acid baths.¹⁶ Similarly, small additions of sulphuric acid to a phosphoric acid bath result in the formation of films characteristic of the former acid.¹⁷

Chloride-containing solutions

In-depth profiles of Al^{3+} or AlO^- , Cr^{3+} or PO_4^{3-} and Cl^- are shown for films grown to 60 V in 1 M chromate + 20 ppm KCl, 1 M chromate + 200 ppm KCl and 1 M phosphate + 20 ppm KCl in Figs. 7, 8 and 9 respectively. The data shown are typical of a variety of experiments performed in chromate and phosphate solutions containing KCl at levels up to 200 ppm. In all cases, the presence of Cl^- had no effect on the sputtering characteristics of the films, or on the basic Cr^{3+} or PO_4^{3-} profiles of the films, which were identical to those obtained in Cl^- -free solutions. Also, the basic Cl^- profile was the same in all cases, i.e. a narrow peak at the oxide/solution interface,

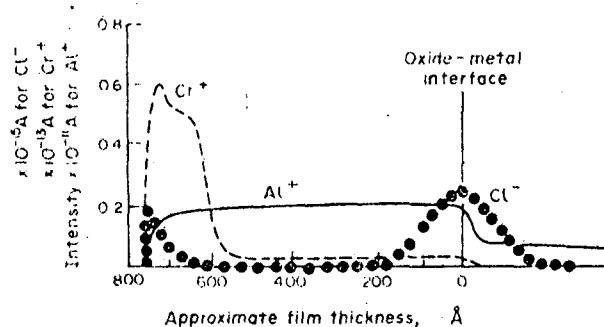


Fig. 7. Al^+ , Cr^+ and Cl^- profiles of 60 V film formed in neutral 1 M chromate solution containing 20 ppm KCl.

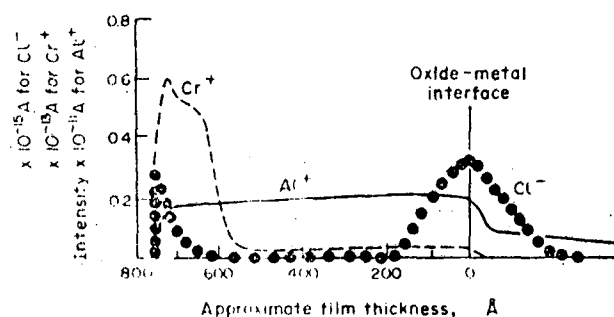
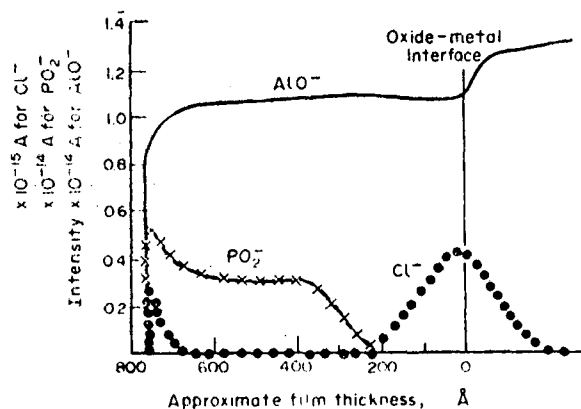


Fig. 8. Al^+ , Cr^+ and Cl^- profiles of 60 V film formed in neutral 1 M chromate solution containing 200 ppm KCl.



AlO^- , PO_2^- and Cl^- profiles of 60 V film formed in neutral 1 M phosphate solution containing 20 ppm KCl.

and a broader peak at the metal/oxide interface. In all cases, there was no evidence of Cl^- inclusion within the film material *per se*, relative to films grown in Cl^- -free solutions. The Cl^- yields at the oxide/solution and metal/oxide interfaces increased with Cl^- concentration in the forming solution (Figs. 7 and 8) and, at a given Cl^- concentration, were greater in phosphate than in chromate solution (Figs. 7 and 9). Ion images of Cl^- obtained at various stages during film sputtering confirm that the Cl^- yields at the metal/oxide interface are associated with pitting beneath, and lateral undermining of, the barrier film as it grows. A typical Cl^- ion image obtained close to the metal/oxide interface for a film grown in 1 M phosphate solution + 10 ppm KCl is shown in Fig. 10. The Cl^- rich spot in fact grew in size as the metal/oxide interface approached, and then reduced in size, ultimately vanishing, as sputtering of the metal itself proceeded.

In the case of one specimen in 1 M phosphate solution + 200 ppm KCl, film growth was allowed to proceed at 1 mA/cm^2 until a substantial degree of breakdown occurred. The voltage rose to a peak of ca. 120 V, and then fell as pitting beneath the growing film consumed an ever-increasing proportion of the charge being passed. The experiment was stopped when the voltage had fallen to 60 V, and the film was then analysed in the normal way. The in-depth Cl^- profile of the film is shown in Fig. 11. The film thickness (ca. 1400 Å) is consistent with the peak voltage of ca. 120 V attained. Evidently, the Cl^- distribution across the film is similar to those distributions obtained in Figs. 7-9, although the yields at all levels are much higher. The relatively high Cl^- yield obtained throughout the bulk of the film thickness was not due to Cl^- inclusion in the film material *per se*, but to the relatively large degree of localized breakdown which the film suffered. The profile is very similar to that obtained previously for low voltage breakdown in 1 M chloride solution.¹⁵

Overall, the data reported here are entirely consistent with that previously reported for barrier film breakdown under natural immersion and applied polarization in chloride solutions of varying pH.^{14,15} No evidence of any influence of the Cl^- ion on the oxide formation process itself could be detected, although at the relatively large

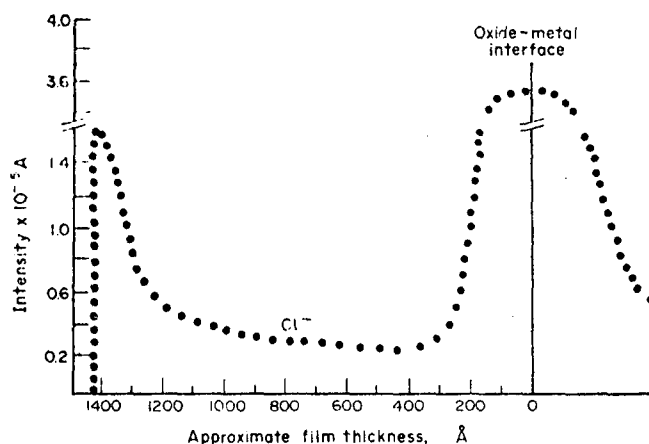


FIG. 11 Cl^- profile of ca. 120 V film formed in neutral 1 M phosphate solution containing 200 ppm KCl.

chromate/chloride and phosphate/chloride concentration ratios involved, none might be expected. However, there was again strong evidence of Cl^- ion access to the base metal through flaws in the surface oxide film. Even at the relatively low concentrations involved, the Cl^- ion apparently promotes dissolution of the metal, and undermining of the growing film, and thus progressively reduces the current efficiency of film growth.

DISCUSSION

The data reported here for barrier layer growth in neutral chromate and phosphate solutions fit into a general pattern of differing tendencies of solute anions to be incorporated into the films which they grow. The anion content of any particular film would seem to be a function of the depth of the anion-containing layer, as well as the absolute anion content of the film material *per se*. There is strong evidence in the case of the phosphate anion that the anion content increases with the current efficiency of growth.⁷

It is proposed that such data strongly support a model for oxide film growth involving two simultaneous processes:

- (a) Growth by ionic migration through an existing film occurs, i.e. both Al^{3+} and O^{2-} or OH^- are mobile and together form new oxide.
- (b) Growth by a dissolution/precipitation process occurs at the oxide solution interface, i.e. the metal ion transport number is always greater than that for O^{2-} or OH^- , and Al^{3+} ions not consumed in growth by ionic migration are initially ejected at the oxide/solution interface. As to whether such ions ultimately contribute to solid film growth depends on the efficiency of their precipitation at the oxide/solution interface.

In view of the importance of the latter process to the current efficiency of film growth, degree of incorporation of solute anions etc., it is appropriate to discuss further the possible fates of Al^{3+} species ejected initially at an oxide/solution interface. There would seem to be a number of possibilities:

- (a) Al^{3+} ions simply diffuse away into solution. Assuming that such ions were not involved in any other process at the oxide/solution interface, their interfacial concentrations would depend on the difference between their rate of ejection at the oxide/solution interface, and their rate of diffusion into bulk solution.
- (b) Al^{3+} ions are precipitated as the simple salt or as a complex of the solute anion. Many film-promoting anions form highly insoluble salts or oxy-anion complexes with aluminium, e.g. phosphate and sulphate. Certain anions are such efficient precipitants as to be established gravimetric analytical reagents for Al^{3+} , e.g. tartrate and malonate. The rate of precipitation will depend on, among other factors, the interfacial concentrations of Al^{3+} and the solute anion, temperature and interfacial pH.
- (c) Solute Al^{3+} ions hydrolyse, aggregate, and ultimately precipitate from initially colloidal alumina, with an associated tendency for the interfacial pH to fall. The rate of hydrolysis will depend on the interfacial concentration of Al^{3+} and temperature, and the rate of precipitation on pH. Many film-promoting anions are known to catalyse the rate of precipitation of colloidal alumina. In addition, many barrier film-promoting anions form weak acids, and will thus tend to neutralize any interfacial acidity resulting from hydrolysis.

Of course, the notion that Al^{3+} dissolution might be an integral part of the oxide film growth process on aluminium is by no means new. Thus, Siejká *et al.* have discussed models of porous film^{22,23} and to a lesser extent barrier film¹² growth involving the direct discharge of Al^{3+} cations into solution. However, the possible role of Al^{3+} precipitation has received relatively scant attention in the literature, and then largely in relation to porous rather than barrier film growth. Thus, Fukuda and Fukushima have discussed the formation of an aluminium hydroxide aggregate layer at the oxide/solution interface during porous film growth, resulting from the reaction of Al^{3+} cations with water.²⁴ It is proposed that Al^{3+} precipitation is an integral part of all film formation processes on aluminium, to an extent depending on the efficiency of the precipitation process. The composition of the precipitated outer layer of the film might be expected to vary with the anion in question. It seems likely that in all solutions the greater part of the material is solid alumina, resulting from the hydrolysis, aggregation and ultimate precipitation of initially ejected Al^{3+} species. The solute anions might be expected to be located in the intercrystallite regions of the ultimate film resulting from dissolution/precipitation process. The role of anions forming relatively soluble salts or complexes with Al would be restricted to catalysing colloidal alumina precipitation by adsorption. Such anions might be expected to show relatively low, if detectable, levels of incorporation, and promote inefficient film growth. On the other hand, anions forming particularly insoluble salts, e.g. tartrate, malonate and other organic anions, or perhaps oxy-anion complexes, e.g. phosphate,^{19,21} would be expected to show relatively high levels of incorporation, and promote current efficient film growth.

Bearing in mind the above considerations, a detailed explanation can be offered of the data obtained in the present study. Phosphate anions are efficient precipitants of Al^{3+} cations, and thus barrier films grow in neutral phosphate solutions at high current efficiencies, and contain relatively wide regions of anion incorporation (Figs. 1 and 2). The inner phosphate-free region in Fig. 1 has grown by Al^{3+} and O^{2-} or OH^- migration, and the outer phosphate-rich region by a dissolution-precipitation process. Time was not available for experiments aimed at elucidating detailed transport mechanism within a growing film. However, it is suggested that Al^{3+} and O^{2-} or OH^- migration occurs through intercrystallite regions in the outer, precipitated region of the film. Growth of the inner region of oxide can conceivably occur from the metal/oxide interface to the interface between the inner and outer regions of the film. In the latter event, some 'spreading' of the phosphate profile at the interface between the two oxide layers would be expected as the film thickness increases. It is interesting that there is some evidence of such spreading in Fig. 1, and a similar recent study on barrier film growth on Ta in phosphate solutions showed that the degree of spreading increased with film thickness.² Accepting that barrier layers on Al and Ta grow by similar mechanisms and that any included phosphate is immobile, this would suggest that some, at least, of the inner region of film grows at the interface between the two regions. The efficiency of precipitation of Al^{3+} and thus of total film growth, would not depend upon phosphate concentration in solution so long as sufficient phosphate were available for the solubility product of aluminium phosphate or oxy-phosphate to be rapidly exceeded at the film/solution interface. Not surprisingly, film growth and composition were found to be insensitive to bulk solution phosphate concentration in

the present study, suggesting that the precipitation process is rate controlled by the availability of Al^{3+} rather than phosphate at the film/solution interface.

In contrast to phosphate anions, chromate anions do not form highly insoluble aluminium salts or oxy-chromate complexes. The chromate species do, however, catalyse colloidal alumina precipitation by adsorption,¹⁴ and can thus indirectly promote precipitations of Al^{3+} as alumina at a growing film/solution interface. The latter process is, however, less efficient than direct precipitation, and as a result, barrier film growth in chromate solutions occurs at relatively low current efficiencies. A duplex film would still be expected, although for any particular film thickness, the inner region would be expected to be wider, and the outer region narrower, than an equivalent film grown at higher current efficiency in a solution of an efficient precipitant such as the phosphate anion. The level of included chromate in the outer region of the film would be expected to be much lower than in the case of phosphate solution, being the amount adsorbed onto colloidal alumina surfaces during film growth. In fact, no chromate at all was detected in the outer regions of films grown in the present study (Fig. 3), which could not be attributed to mere exposure of the film to the chromate containing solution. It seems likely, however, that a tiny, albeit undetectable, amount of chromate is in fact included in the outer, precipitated region of a barrier film grown in chromate solutions. It is interesting that film growth and composition were again virtually insensitive to bulk solution chromate concentration, suggesting that the catalytic effect of chromate on colloidal alumina precipitation is a relatively minor effect in terms of the film growth process as a whole.

Barrier layer growth in mixed phosphate/chromate solutions (Fig. 6), and indeed film growth in mixtures of film-promoting anions in general, is easily interpreted in terms of the above model. The anion whose precipitating powers are greater would be expected to dominate the overall film growth process, in terms of the current efficiency of growth, and the amount and extent of anion inclusion. Thus even relatively small concentrations of phosphate in a chromate solution are sufficient for the solubility product of aluminium phosphate or oxy-phosphate to be exceeded at a growing film/solution interface. As a result, the current efficiency of film growth increases, and the phosphate anion is included in the outer regions of the film.

The effects of the Cl^- ion on barrier film growth on Al in chromate and phosphate solutions highlight the need for a consideration of possible anion effects on the substrate metal itself, as well as on the film growth process. In the absence of any interaction with the substrate, the Cl^- ion might be expected to reduce the current efficiency of film growth, because of its poor efficiency as a precipitating agent for Al^{3+} . Thus AlCl_3 is relatively soluble, and although it hydrolyses rapidly, the Cl^- anion stabilizes locally produced acidity, and is known itself to inhibit colloidal alumina precipitation. However, the most significant influence of the Cl^- anion on the anodic behaviour of Al is its promotion of anodic dissolution of the base metal at the basis of flaws in the growing film, with associated undermining of the film. Thus, the very marked reduction in current efficiency of film growth in chloride solutions observed in the present work and elsewhere results from the effects of Cl^- anion at the metal/oxide, rather than the oxide/solution interface.

It is appropriate to comment on the relationship between barrier film growth on Al in neutral chromate and phosphate solutions, and the previously observed effects

of such solutions on ammonium tartrate-formed films under conditions of natural immersion.¹⁴ In the case of the chromate anion, a relatively consistent picture emerges, i.e. it is aggressive under natural immersion in the sense that it penetrates and thus thins anodic alumina, and aggressive under applied polarization in the sense that it promotes growth at low current efficiencies because of its relatively poor precipitating powers. However, the phosphate anion presents an interesting contrast, in that it can apparently penetrate and thin anodic alumina under conditions of natural immersion, and yet promote current efficient growth under applied polarization. This would suggest that the ability to penetrate intercrystalline regions in an as-formed film, associated with the adsorptive power of the anion¹⁴ is more important than the solubility of any dissolution products in determining the aggressivity of an anion towards anodic alumina under natural immersion.

It is worth commenting that a number of general features of barrier layer growth on valve metals are entirely consistent with the above model, in particular:

1. During barrier layer growth on Al in a variety of electrolytes, the anolyte becomes gradually turbid.²⁵
2. There is general agreement that barrier films on valve metals are duplex in nature, as evidenced, for example, by ellipsometric measurements on films grown on Ta in phosphate solutions,²⁶ thinning rate measurements on alumina films grown in phosphate solutions⁷ etc.
3. Films grow in non-aqueous solutions at higher current efficiencies than under equivalent conditions in corresponding aqueous solutions, as, for example, in the case of Al in borate solutions.²⁷ This is because the solubility products of salts are generally much lower in non-aqueous solvents which have lower dielectric constants than water. Thus, the efficiencies of precipitation, and thus of overall film growth, are higher in non-aqueous solutions.
4. Current efficiencies of film formation generally increase with current density of growth, as has been observed for Al in borate,^{11,27} citrate,^{11,27} carbonate, phosphate and tartrate solutions,²⁷ and Zr in sulphate, carbonate and borate solutions.³ This is because the increased rate of ejection of cations at the oxide/solution interface should increase their rates of direct precipitation and/or conversion by hydrolysis to alumina. In the absence of any attack on the substrate metal, a minimum current efficiency of growth might be expected, i.e. where the efficiency of precipitation of ejected cations is zero, film growth by ionic migration alone might still be expected. Significantly, Brock²⁷ observed in a study of alumina film growth in a wide range of electrolytes over a wide range of current densities of formation that there appeared to be a minimum current efficiency of formation of 25–30%, in the absence of any attack on the substrate metal.
5. Associated with the latter factor, the fraction of the film containing anion, and thus the total anion content, generally increases with increasing current density, and thus current efficiency, of formation. This has been observed, for example, in the case of Al and Ta in phosphate solutions^{7,8} and Zr in sulphate, carbonate, and borate solutions.³

Not surprisingly, bearing in mind the above considerations, studies of solution anion incorporation aimed at providing ionic transport numbers for growth have tended to give conflicting data. On the above model, apparent transport numbers will

vary with the efficiency of precipitation of ejected metal ions (where both Me^{2+} and OH^- or O^{2-} are mobile at the oxide/solution interface, and might merely reflect variations in current efficiency of growth, rather than genuine variations in ionic mobility. As to whether the solution anions themselves are mobile during film growth, once included in the film, the authors subscribe to the consensus view that incorporated ions are generally immobile. Certainly, spreading of the interface between the inner and outer regions of the film, i.e. the region over which the anion content varies from zero to its level in the outer region, is not considered to be evidence of anion mobility, but rather of growth of the inner region at the interface between the two regions. Where there is clear evidence of apparent anion mobility, i.e. a concentration peak at the metal/oxide interface, as in the case of film growth on Al in Cl^- -containing solutions in the present work, or on Ta in F^- -containing solutions,² it is suggested that this is not evidence of anion mobility within the film material *per se*, but rather attack on the metal at the bases of flaws in the growing film, resulting in pitting and film undermining as explained above.

Finally, it is appropriate to comment on the applicability of the model for barrier film growth developed above to porous film growth on Al in acid solutions. This will be the subject of a separate detailed publication; however, the essentials of the model are considered common to both types of film growth. The efficiency of precipitation of ejected Al^{3+} cations as alumina is markedly reduced at low pH, and the overall efficiency of precipitation, and thus film growth, is probably strongly related to the variation in solubility product of aluminium salts or oxy anion complexes with pH. For this reason, for any particular anion, the current efficiency of film growth generally decreases, but the anion content increases, as the pH is reduced. Once steady state conditions are achieved, the major film parameters (pore number, pore size, barrier layer thickness etc.) will be strongly related to the current efficiency of growth. It is considered that acidity has a special role to play in the pore nucleation process, which will be argued in detail elsewhere.

CONCLUSIONS

1. Barrier layers on Al grown in neutral phosphate solutions have a relatively wide phosphorus-containing layer adjacent to the oxide/solution interface. Their current efficiency of growth is relatively high.
2. Barrier layers on Al grown in neutral chromate solutions contain little, if any, chromium resulting from the growth process itself. The level and distribution of chromium which they contain is consistent with their short periods of immersion to the chromate solution prior to, and after, film growth. Their current efficiency of growth is relatively low.
3. Barrier layers on Al grown in neutral chromate/phosphate mixtures illustrate the dominance of the phosphate anion relative to the chromate anion in determining film characteristics. Films grown in solutions of molar chromate/phosphate ratios as high as 99 : 1 are typical of those grown in phosphate rather than chromate solutions.
4. Barrier layers on Al grown in neutral chromate or phosphate solutions containing small quantities of chloride anion are in general typical of those grown in pure chromate or phosphate solutions. Their lower current efficiencies of growth are

associated with chloride attack on the substrate at the bases of flaws in the growing film, resulting in pitting and lateral undermining of the film.

5. The results are explained in terms of a model for film growth, involving growth partly by ionic migration, and partly by a dissolution/precipitation process.

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SURFACE INVESTIGATION OF SOLIDS BY THE STATICAL METHOD OF SECONDARY ION MASS SPECTROSCOPY (SIMS)

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The physical and chemical properties of a solid surface are determined by its uppermost monolayers. Besides other methods like Auger electron spectroscopy (AES) and X-ray electron spectroscopy (ESCA) for example, the chemical composition of these uppermost monolayers can be investigated by the statical method of secondary ion mass spectroscopy (SIMS). In this method a relatively large target area (0.1 cm^2) is bombarded with a small primary ion current density ($10^{-9} \text{ A cm}^{-2}$). Thus a sputtering time of several hours is achieved for an individual monolayer. A mass analysis of the emitted positive and negative secondary ions gives information about the chemical composition of the uppermost monomolecular layer of the bombarded surface. Important features of SIMS are: detection of chemical compounds; isotope sensitivity; detection of hydrogen and its compounds; depth resolution in the range of a single monolayer; low detection limits ($\sim 10^{-6}$ monolayer or $\sim 10^{-11} \text{ g}$) for many elements and compounds.

The capacity of this method is demonstrated using as examples the initial surface oxidation of metals and semiconductors and adsorption phenomena on clean metal surfaces. In some special cases additional information on the chemical composition of the uppermost monolayer can be obtained by the electron induced ion emission from the surface.

1. Introduction

The topic of "The Second Symposium on Surface Physics" was the solid surface, that means the uppermost monolayers of a solid and processes taking place in these layers, as for example electron and ion emission, adsorption processes, chemical surface reactions, etc. Any research in surface science depends on an exact knowledge of the composition and structure of the uppermost monolayers, as these layers are responsible for the general behaviour of the surface of a solid. This apparently is the reason for the great number of contributions given at this conference dealing with the different methods of surface analysis. Most of these methods have been developed very recently, e.g. Auger electron spectroscopy and low energy ion reflection spectroscopy.

The intention of this contribution is to demonstrate that secondary ion mass spectroscopy, especially the statical method of secondary ion mass

spectroscopy¹⁻³), is capable of giving much information about the composition and structure of the surface. Some of this information is obtainable only with difficulties or not at all by other methods. Since the surface of a solid is sputtered during ion bombardment, secondary ion mass spectroscopy has until recently been regarded as a method completely unsuited for the analysis of an individual monolayer.

A perfect method of surface analysis should have the following properties:

- information depth in the monolayer range;
- detection of elements as well as chemical compounds;
- capability of isotope separation;
- high sensitivity;
- high resolution;
- applicable to all kinds of samples, e.g. to rough surfaces and to nonconducting samples;
- no discrimination against any component of the surface;
- no influence of the analysis process on surface composition and structure.

At the moment there exists no method satisfying all these requirements. So, for example, photo electron spectroscopy (ESCA) and Auger electron spectroscopy both are unable to distinguish different isotopes or to detect hydrogen. Low energy ion reflection on the other hand is not capable of identifying the binding state of a surface atom (that means it is not capable of detecting chemical compounds). At the moment there exists no method which does not change the composition and the structure of the uppermost monolayer during the analysis to a considerable degree. It will be pointed out in this paper to what extent the "Statical Method of Secondary Ion Mass Spectroscopy" (SIMS) is capable of investigating an individual monomolecular layer on a solid and how far this so called SIMS-method fulfills the conditions mentioned above. For this purpose it is necessary to examine the fundamental processes which take place during ion bombardment of a solid and the main features of the statical method. The second part of this paper deals with some typical examples of the application of SIMS to surface problems.

2. The secondary ion emission from a solid surface

2.1. THE EMISSION PROCESS

When a solid surface is bombarded with primary ions in the keV range for example, various processes take place in the surface region (fig. 1). Provided that it will not be reflected at the surface, the so-called primary ion (PI) will penetrate to a certain depth into the solid and will transfer its energy to the lattice atoms. Further impacts distribute this energy to an extended lattice zone. A fraction of this energy reaches the surface again where it can

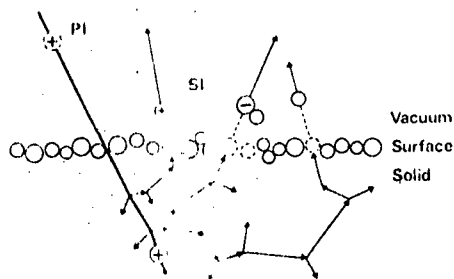


Fig. 1. Interaction of an ion with a solid surface.

induce the emission of a surface particle, which may be an atom or a cluster of atoms in a charged or uncharged state.

The processes taking place in the surface area can be divided into two groups:

- changes of the surface near the primary ion impact;
- emission processes.

The ion impact on the solid surface produces the following changes in a region around the point of impact:

- the primary ion will be integrated into the lattice;
- the energy transmitted to the lattice can give rise to lattice disorders and chemical reactions, especially at the surface, which is very often covered with an adsorption film;
- particles are removed from the surface (sputtering effect).

As a result of the various processes taking place in the vicinity of the primary ion impact the following emission products can be observed:

- secondary electrons;
- neutral atoms and clusters of atoms;
- positively and negatively charged atoms and clusters [so-called secondary ions (SI)];
- photons.

In secondary ion mass spectroscopy only the positive and negative secondary ion emission is used for the investigation of the surface composition.

The emission of secondary ions from a surface under ion bombardment was studied for the first time by Sloan and Press (1938), and Herzog and Viehbock (1949)¹⁻⁷. During the past decade secondary ion emission has been applied to the investigation of the chemical composition of bulk materials and thin films and, as a dynamical method, for the investigation of surface layers, too. I want to mention here works of Honig⁸), Herzog and coworkers^{7,9}), Castaing and coworkers^{10,11}), Werner¹¹⁻¹³), Fogel¹⁴⁻¹⁷), and Anderson¹⁸), e.g.

Until recently secondary ion mass spectroscopy has been regarded as not

being capable of the investigation of an individual monolayer on a solid. The reason was that the sputtering time for a single monolayer of the ion bombarded solid was in the order of a fraction of a second for the generally applied primary ion current densities.

The secondary ion emission from a solid is investigated with a secondary ion mass spectrometer. Fig. 2 shows such an instrument with the main units

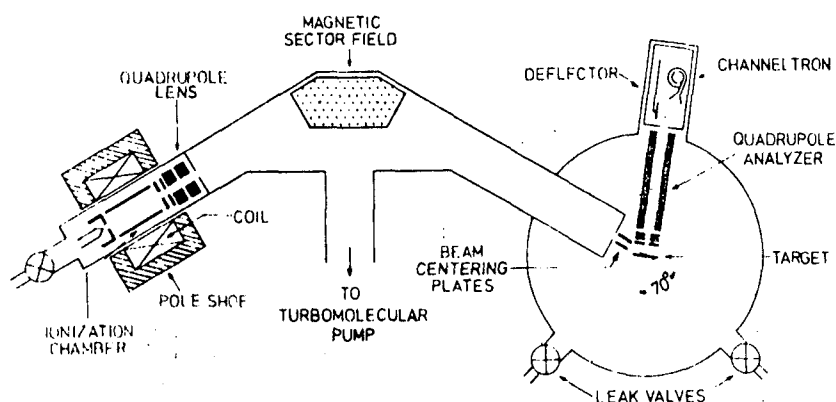


Fig. 2. Schematic of a secondary ion mass spectrometer with mass selected primary ion beam.

primary ion source, target chamber (secondary ion source), mass analyzer and ion detection unit¹⁹). In the primary ion source an ion beam of well defined composition (kind of ions, energy) is produced. This ion beam hits the target in the secondary ion source. The primary ion current density has to be uniform over the bombarded surface area. The SI emitted from the surface are analyzed in the mass analyzer which may be a magnetic sector field, a double focussing combination of magnetic and electric fields, a quadrupole mass filter or a time of flight mass spectrometer. In the detection unit the mass selected secondary ions are finally detected and registered. In order to get a maximum of sensitivity we use in all our experiments an open multiplier operating in the counting mode.

As an example fig. 3 shows the positive and negative secondary ion spectra of a contaminated molybdenum surface³). The surface was bombarded by 3 keV Ar^+ ions in a vacuum of 10^{-10} torr. The mass analyzer used here was a magnetic sector field. It is well known that such an untreated metal surface, even in ultra high vacuum, is covered with an oxide layer and a layer of contamination. Thus in the mass spectra the following surface compounds and their fragments are present:

H^+ and H_2^+ from hydrogen and hydrogen containing compounds, H_2O^+

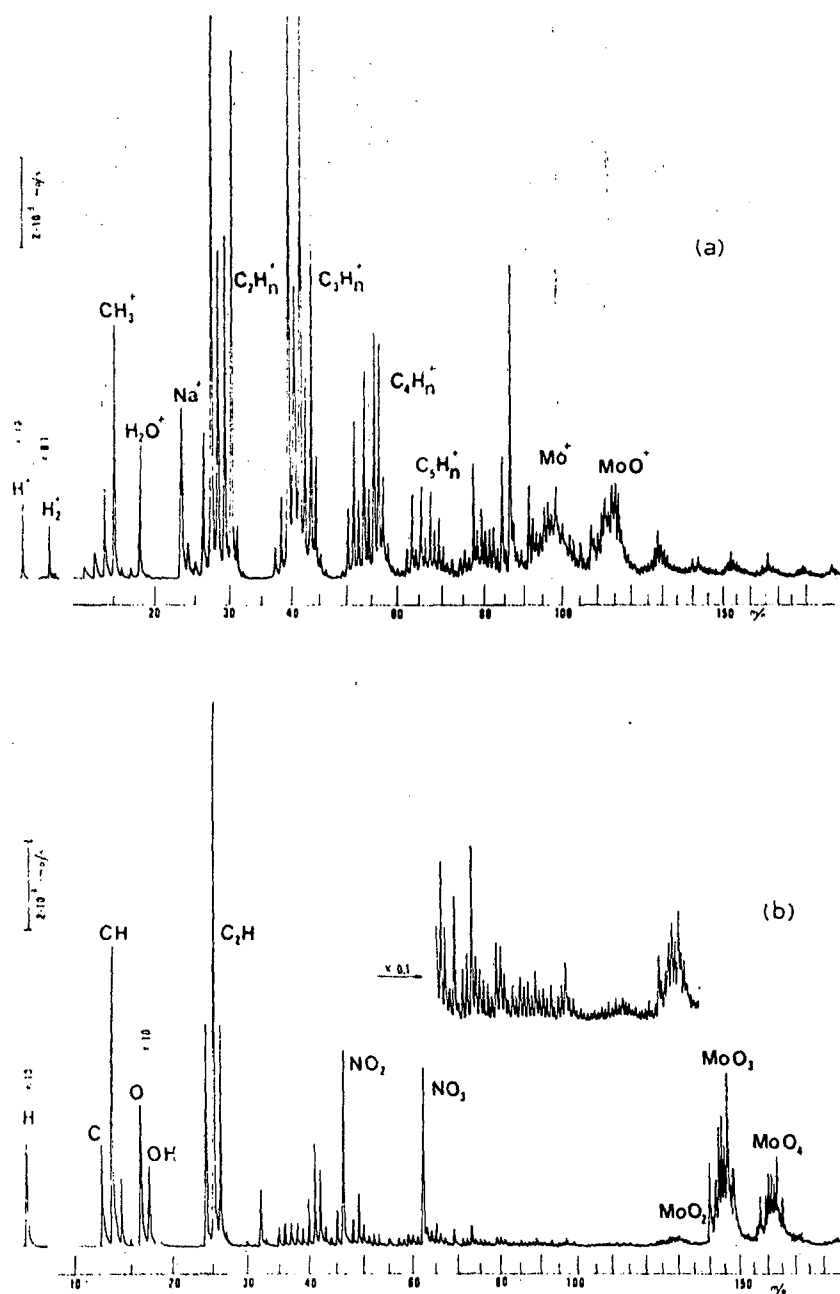


Fig. 3. Positive (a) and negative (b) secondary ion spectrum of a contaminated molybdenum surface. Primary ion current density: $10^{-9} \text{ A cm}^{-2}$. Residual gas pressure: 5×10^{-10} torr. Not more than 1% of the uppermost monolayer was removed during recording of a spectrum.

from water in the contamination layer, ions of the general composition $C_mH_n^+$ with up to 14 carbon atoms, ions of the general composition $Mo_mO_n^{\pm}$ from the oxide film on the molybdenum target, NO_3^- and NO_2^- of nitrate complexes, etc.

In the molybdenum and molybdenum oxide ion peaks the isotope separation is well evident. The poor resolution is due to the initial energy of the SI which is in the range of some eV.

Formally the process of ion emission can be treated as taking place in three steps²⁰⁾:

- energy transfer to a surface particle,
- ionization of the emitted surface particle during the separation from the surface,
- following electron exchange between the particle leaving the surface and the solid.

The energy transfer from the impinging PI to the emitted secondary particle has been described above. Fig. 4 shows a schematic drawing of the arrangement of two different kinds of atoms in the first few monolayers of a solid³⁾. In this example we consider metal atoms (Me) and oxygen atoms (O). The two types of atoms form a two-dimensional surface lattice on the metal surface. In principle secondary ions of the general composition $Me_mO_n^{\pm}$ can be knocked out of such a surface structure during ion bombardment.

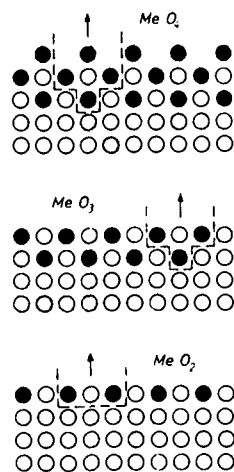


Fig. 4. Secondary particle formation out of different oxide layers on a metal surface.

In fig. 5 the negative secondary ion spectrum of such a surface structure is presented³⁾. The oxide structure on the molybdenum surface was produced by an oxygen exposure of 10^3 L of a surface cleaned by ion bombardment. In the spectrum some of the possible negative SI with different intensities are present.

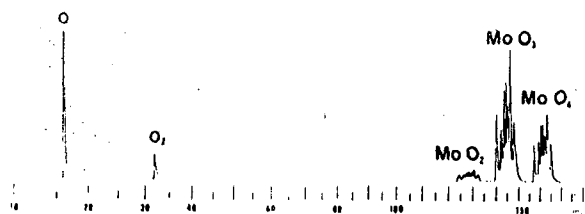


Fig. 5. Negative secondary ion spectrum of a molybdenum surface after oxydation with 100 L oxygen.

In fig. 6 the positive and negative secondary ion spectrum of another surface structure is presented: here the bombarded surface is a molybdenum surface covered with a monomolecular layer of butyl alcohol. Secondary ions typical of this surface structure are emitted, for example secondary ions of the general composition $C_mH_nO^+$ which are formed during the fragmentation of alcohol molecules on the surface. Besides the "fragment ions" also a kind of "parent ion" is emitted from this surface structure ($C_4H_9O^+$)²¹.

As a further example of the different secondary ion species emitted from a particular surface structure, figs. 7 and 8 give the NSI spectra of silver surfaces which had been treated with sulphuric acid and tartaric acid respectively²²). Also in these cases the complex surface structures yield ions characteristic of the chemical compounds or structure on the surface. In all cases besides fragment ions the "anion parent peak" is also present with a relatively high intensity. From these and other examples we can conclude that any special surface structure on a solid yields typical secondary ions, fragment ions as well as parent ions.

The electron exchange between the ion which leaves the surface and the solid may result in the neutralization of the ion. At the moment it is not possible to calculate the ionization and reneutralization probability for the different particles emitted from a particular surface structure. This calculation needs an exact knowledge of the electronic structure of the emission area during the particle emission²³⁻²⁶). At the moment it is only possible to deduce some more or less empirical rules from the experimental data. One of these is the fact that a high ionization probability exists for particles formed by the breaking of an ionic bond^{20,27}).

2.2. THE ABSOLUTE SECONDARY ION YIELD

In the preceding examples (figs. 4-8) we regarded the kind of secondary ions emitted from a specific surface structure. For an analytical application

of secondary ion mass spectroscopy it is very important to characterize a specific surface structure not only by the kind but also by the intensity of the emitted ions. For this reason we introduce the absolute secondary ion yield of a certain ion species during the bombardment of a solid surface which is completely covered by a certain surface structure. This secondary ion yield

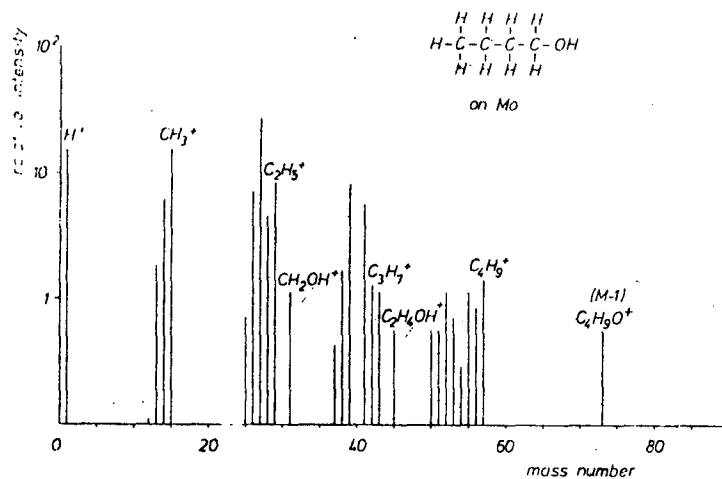


Fig. 6a.

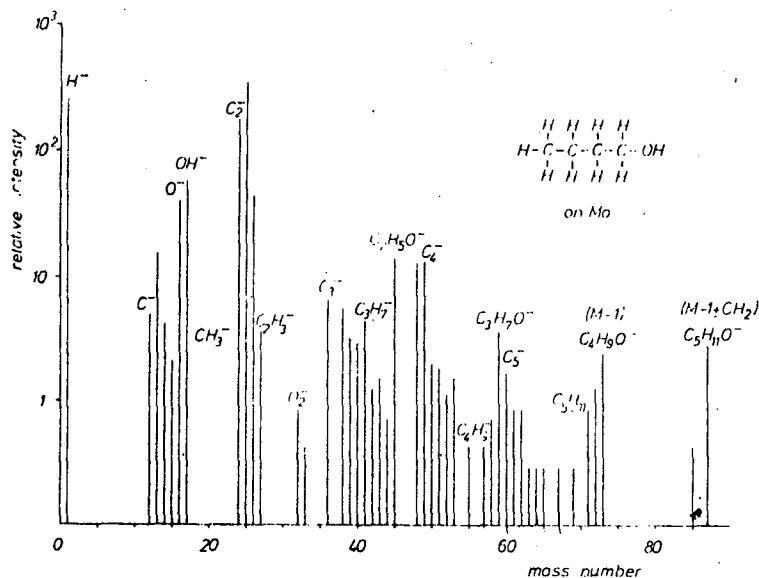


Fig. 6b.

Fig. 6. Positive (a) and negative (b) secondary ion spectrum of an adsorption layer of C₄H₉OH on a molybdenum surface.

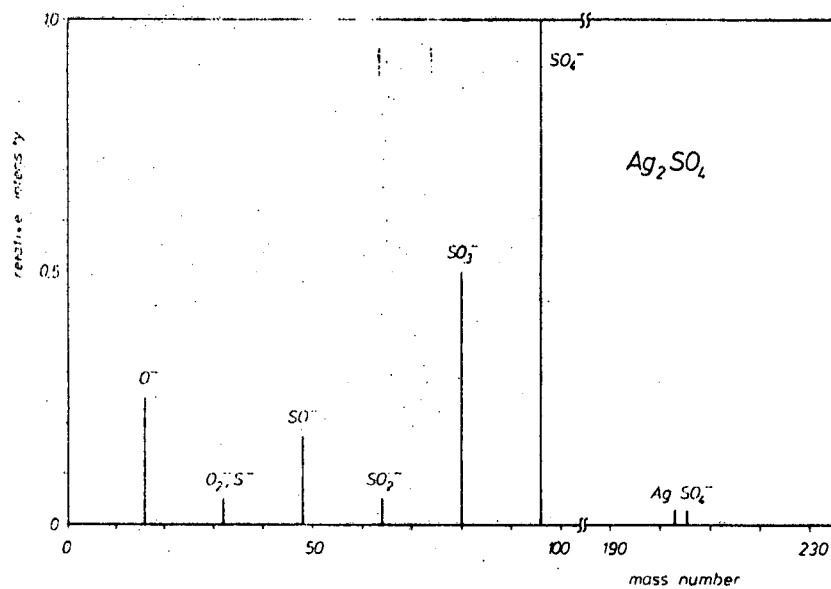


Fig. 7. Negative secondary ion spectrum of the uppermost monolayer of a silver surface treated with sulphuric acid.

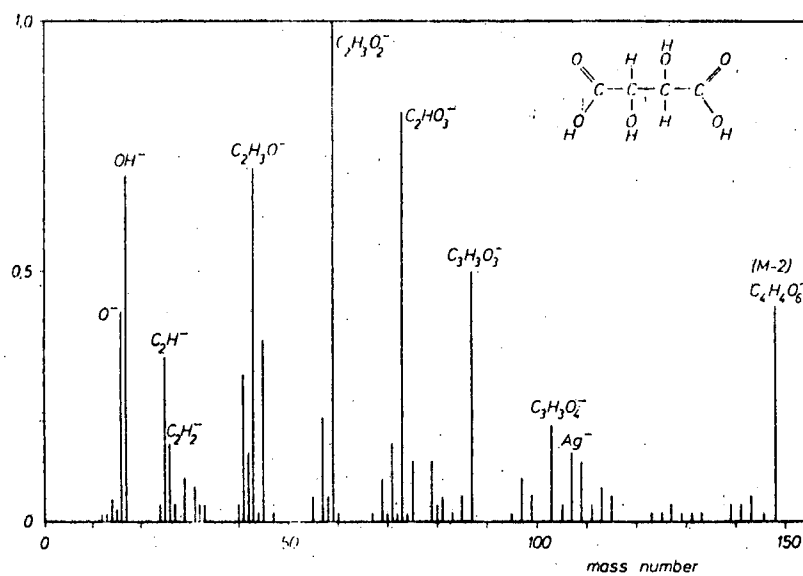


Fig. 8. Negative secondary ion spectrum of the uppermost monolayer of a silver surface treated with tartaric acid.

$S(A_n)$ depends on the surface structure and on the characteristics of the primary ions. Here the definition "surface structure" includes the elemental composition of the surface area, the geometrical arrangement of the atoms, their binding state, etc. The primary ions are characterized by their kind, their energy and their angle of incidence. For all surface investigations reported in this paper, we used 3 keV Ar^+ ions hitting the surface under an angle of 20° .

When a beam of well-defined primary ions hits a well-defined surface structure, various ions are ejected which can be noted as $A_1, A_2, \dots, A_n, \dots$. The absolute yield for one of these ions can be defined in the following manner:

$$S(A_n) = \frac{\text{Number of secondary ions } A_n \text{ emitted in a time } dt}{\text{Number of primary ions hitting the surface in } dt}$$

The experimental determination of $S(A_n)$ must be carried out with the surface totally covered by the specific surface structure (e.g. a completely oxidized surface of a metal or an adsorption layer with a relative coverage $\theta = 1$).

Table 1 gives some absolute secondary ion yields for metal ions Me^+ emitted from clean and oxidized metal surfaces²⁸). The values of $S(\text{Me}^+)$ are given for a metal surface which had been cleaned by ion bombardment (cleaned surface) and for a saturated oxide layer which had been formed on the cleaned surface by an oxygen dose of about 10^3 L at room temperature. It can be seen from the table that the values of $\gamma(\text{Me}^+)$ for a clean metal surface are in the range of 10^{-3} to 10^{-4} . For an oxidized surface these values rise by a factor of typically 1000 and $S(\text{Me}^+)$ reaches values of about 1 for a number of metals. These are unexpected high values.

In table 2 secondary ion yields are tabulated for some typical negative

TABLE I
Absolute secondary ion yields

Metal	$S(\text{Me}^+)$ Cleaned surface	$S(\text{Me}^+)$ Oxidized surface
Mg	0.0085	0.65
Al	0.02	2.0
V	0.0013	1.2
Cr	0.005	1.2
Fe	0.001	0.38
Ni	0.0003	0.02
Cu	0.00013	0.0045
Sr	0.0002	0.13

TABLE 2
Absolute secondary ion yields

Treatment	Secondary ion A	$S(A)$
HCl	Cl^-	1.3
HCN	CN^-	6.0
HNO_3	NO_3^-	5.0
	NO_2^-	0.7
H_2SO_4	SO_4^-	1.2
	HSO_4^-	1.0
	SO_3^-	1.0
	SO_2^-	0.1

secondary ions emitted from silver surfaces treated with various acids²⁸). In the first column the type of acid is listed, the next two columns give the ion species and their absolute yields. Also for the secondary particles which are created on the surface by breaking of an ionic bond, the absolute ion yields are in the order of 1. For silver surfaces treated with organic acids like acetic or tartaric acid we observed values in the same range.

Applying the definition of the absolute secondary ion yield $S(A_n)$ we can calculate the current of a specific secondary ion A_n registered by the ion detection unit (fig. 1). If a primary ion current

$$I_p^+ = j_p^+ A \quad (1)$$

hits a target area A which is covered with a specific surface structure giving rise to the secondary ion A_n with an absolute yield $S(A_n)$ then a secondary ion current

$$I'(A_n) = j_p^+ A S(A_n) \theta f \quad (2)$$

is registered by the detection unit, if f is the over-all transmission of the mass spectrometer and θ denotes the relative coverage of the bombarded surface with the surface structure of the given ion yield $S(A_n)$.

3. The statical method of secondary ion mass spectroscopy

During ion bombardment of a surface structure the uppermost monolayer of the solid will be removed. Because of this sputtering effect secondary ion mass spectroscopy was considered for a long time as a method well suitable for the elemental analysis of bulk material, depth profile analysis in thin films, etc., but as absolutely unsuited for the investigation of individual single monolayers on solids. To understand this prejudice we must regard the sputtering of a single monolayer on a solid in a more quantitative manner³):

We suppose the solid to be covered by a single monolayer of a surface structure which has an absolute secondary ion yield $S(A_n)$ for a secondary ion A_n . N is the particle area density, N_0 the particle density in a complete monolayer that means for a relative coverage $\theta=1$. Here, S is the total sputtering yield, that is the number of particles emitted from the surface by one incoming primary ion. j_p^+ is the primary ion current density. With

$$v = j_p^+ / e_0 \quad (3)$$

the change in the particle area density dN in dt is given by:

$$dN = vS \theta(t) dt. \quad (4)$$

Between the change in particle area density and the change in relative surface coverage $d\theta$ exists the following relationship:

$$d\theta = dN / N_0. \quad (5)$$

From this we find the following expression:

$$d\theta = \theta(t) \frac{vS}{N_0} dt. \quad (6)$$

The integration of this equation leads to the following time dependence of the relative coverage $\theta(t)$:

$$\theta(t) = \theta(0) \exp(-t/\hat{t}), \quad (7)$$

where $\hat{t}$, the average lifetime of the uppermost monolayer, is given by:

$$\hat{t} = N_0 / vS. \quad (8)$$

In eq. (2) we found for the secondary ion current registered by the ion detecting system:

$$I'(A_n, t) = j_p^+ A S(A_n) \theta f, \quad (9)$$

that means, $I'(A_n, t)$ is proportional to the relative coverage of the surface with the A_n -emitting surface structure. It results the following exponential time dependence of the secondary ion current $I'(A_n, t)$:

$$I'(A_n, t) \sim \exp(-t/\hat{t}). \quad (10)$$

That means: if a special secondary ion A_n is generated in a surface structure which is present only as a monomolecular layer on a solid with a total ion yield $S(A_n)$, if in addition the primary ion beam and the transmission of the instrument are constant and – that's very important – the yield $S(A_n)$ is independent of the relative coverage of the solid with the surface structure,

then we will observe the decrease of $I'(A_n, t)$ to be proportional to $\exp(-t/\bar{t})$.

If on the other hand we find an exponential time dependence of the secondary ion current $I'(A_n, t)$ we can conclude that the "parent surface structure" is present only in the original first monolayer on the surface and that $S(A_n)$ is independent of θ . We will make use of this conclusion later on.

With the expression for the time dependence of $\theta(t)$ for a primary ion current density in the range of 10^{-4} A/cm² we find an average lifetime $\bar{t}$ in the range of some tenths of a second, assuming a total sputtering rate of about 5. With such a high sputtering rate it is not possible to investigate the secondary ion emission of individual monolayers.

Therefore in our experiments we lowered the primary ion current density by more than 5 orders of magnitude compared with the above mentioned value. This way the average life time $\bar{t}$ of an individual uppermost monolayer could be raised into the range of some 10^4 sec, that means some hours. In some cases it is possible to lower the primary ion current density to 10^{-10} A/cm² thus reaching average life times of some days.

The lowering of the primary ion current density is accompanied by a corresponding decrease of the total number of emitted secondary ions. In order to overcome this difficulty we enlarged the bombarded target area to 0.1 cm² to compensate for the decrease in primary ion current density.

Summarizing the typical feature of this so-called "Static Method of Secondary Ion Mass Spectroscopy" (SIMS) is the bombardment of a relatively large target area with a relatively low primary ion current density – resulting in a very low sputtering speed for an individual monolayer, that means a long average lifetime in the range of some hours for an individual layer^{1, 2, 29, 30}. Two kinds of investigations are possible by SIMS:

(1) The chemical composition of an individual monolayer of a solid can be investigated with a high sensitivity which is in many cases in the order of 10^{-6} of a monolayer and even lower^{1, 2}).

(2) It is possible to investigate changes in the composition of an individual monolayer on a solid caused by diffusion processes, interaction with a gas phase, heating, etc. without a considerable change of the surface structure and composition^{2, 3}).

By some of the following examples it will be demonstrated that it is possible to investigate a surface reaction by SIMS, sputtering not more than 10^{-4} of the uppermost monolayer³¹).

4. Experimental

Fig. 2 gives the principle arrangement of a secondary ion mass spectro-

meter¹⁹). Here the primary ion beam is mass selected. The secondary ions are mass analyzed in a quadrupole mass filter and detected by a channeltron multiplier in a "not line-of-sight" arrangement. In the target chamber a basic pressure below 2×10^{-11} torr can be obtained. By leak valves gases can be admitted into the target chamber, thus allowing the investigation of surface reactions on the target. The mass spectrometer is evacuated by a turbomolecular pump connected to the magnetic field area of the primary ion source and by a combination of a titanium sublimation pump and an ion getter pump in the target chamber.

Besides the primary ion generating system and the vacuum system we have found the arrangement for measuring the primary ion current to be of extreme importance for quantitative measurements with SIMS²⁸).

During the observation of a surface reaction e.g., the composition of the surface changes over a wide range and also the yield of secondary electrons and positive and negative secondary ions. We found that the best way to obtain an exact measurement of the real primary ion current is to use a Faraday cage arrangement.

5. Typical examples of surface investigations by SIMS

The capacities of SIMS for monolayer investigations will be demonstrated in the following by some typical examples:

An example of the investigation of a realistic (or practical) surface was a particular piece of a silver catalyst which had been used over a long period for the oxydation of ethylene. We studied the chemical composition of the uppermost monolayers as well as changes in its composition induced by ion bombardment, by heating and by surface diffusion processes^{3,32}).

An example of the investigation of chemical reactions of metals with gases is the first step of surface oxidation of an atomically clean metal surface in the monolayer and submonolayer range^{1,3,27,33,34}).

An example of the investigation of a chemical reaction on a semiconductor surface is the oxidation of silicon³⁵).

An example of the investigation of a well defined adsorption layer is the interaction of H_2 and O_2 with the (100) face of tungsten²⁹).

5.1. THE ORIGINAL UPPERMOST MONOLAYER OF A SILVER CATALYST

The majority of activation and contamination processes in a catalyst takes place in the uppermost monomolecular layer. Fig. 9 shows the negative secondary ion spectrum of the original first monolayer of a silver catalyst³). The various mass lines can be associated with certain types of secondary ions, partially by means of known isotope ratios (like for Cl^-), partially by

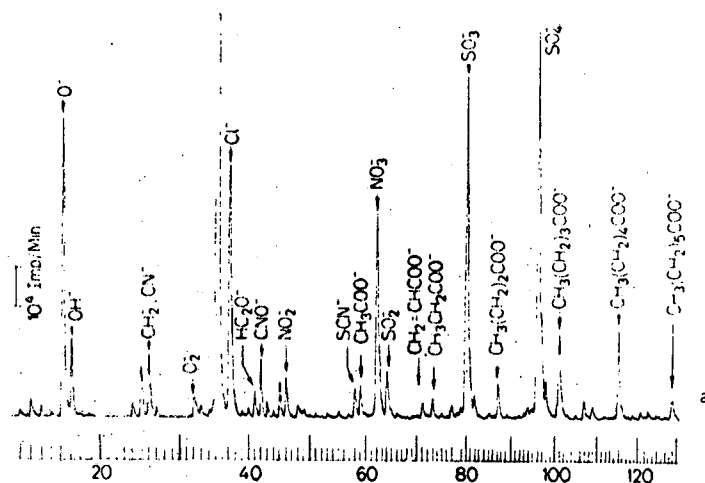


Fig. 9a.

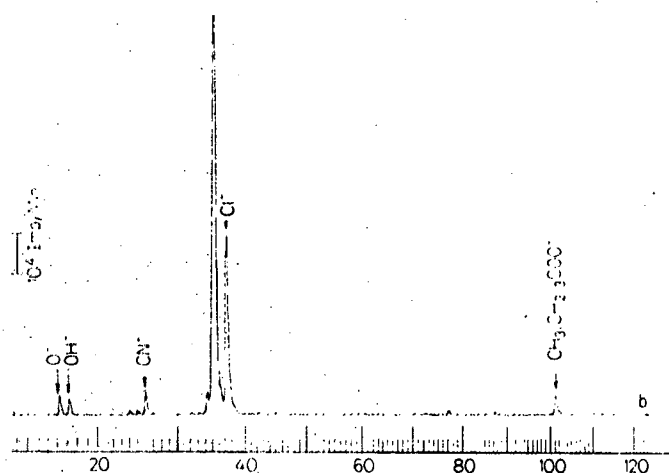


Fig. 9b.

Fig. 9. Negative secondary ion spectrum of a silver catalyst. Original first monolayer (upper spectrum) and after the removal of about 20 monolayers (lower spectrum).

Primary ion current density: 10^{-9} A cm $^{-2}$.

means of secondary ion spectra of known compounds. Hence the masses 96, 80 and 64 can be associated with the ions SO_4^- , SO_3^- and SO_2^- which are produced during the removal of the uppermost monolayer. Further, hydroxide, cyanide, chloride, rhodanide, nitrate, and many fatty acids can be detected in the uppermost monolayer.

By comparing the absolute intensities of the individual mass lines with the

results of measurements we carried out with suitable anion complex saturated silver surfaces, the absolute coverage of the surface can be assessed. The sensitivity of SIMS for anion complexes on a silver surface is about 10^{-6} of a monolayer or 10^{-14} g.

The lower spectrum in fig. 9 indicates that the majority of the components identified on the surface are only present in a "near surface" zone of the catalyst. After the removal of approximately 20 monolayers only the Cl^- ions are present in undiminished strength in the spectrum. The recording time for the spectra in fig. 9 was in each case 400 s. Since, at a primary ion current density of $10^{-10} \text{ A cm}^{-2}$, assuming a sputtering rate of 5, the life of a monomolecular layer is approximately 4×10^4 s, about 1% of a monolayer was removed during the recording time.

Accurate detection of the depth distribution of the various surface components enables observation of the time dependence of the intensity of the various mass lines, when relatively high primary ion current densities are used. The results of the measurements (fig. 10) indicate that many of the secondary

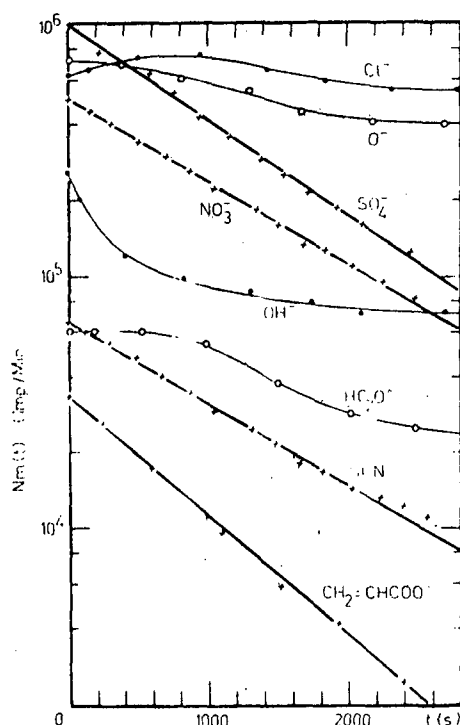


Fig. 10. Time dependence of some of the negative secondary ions emitted from the original uppermost monolayer of a silver catalyst (fig. 9). Primary ion current density: $2 \times 10^{-10} \text{ A cm}^{-2}$.

ions shown in the spectrum follow an exponential time dependence. According to this the corresponding parent compounds or components were only present on the catalyst in the first monomolecular layer. The somewhat varying value of the total sputtering rate S for the different complexes is expressed in the varying rise of the individual lines. In agreement with the spectrum in fig. 9, Cl^- and O^- are also present in the deeper-lying layers.

As only less than 1% of a monolayer is removed during the recording time, it is possible to observe changes in the chemical composition of the original uppermost monolayer of the catalyst, resulting from chemical reactions with a surrounding gas phase, from thermal decomposition of compounds, from diffusion processes etc. If the silver catalyst investigated is heated in the target chamber, among other findings a strong reduction will be noticed in the mass lines 62 (NO_3^-) and 46 (NO_2^-) at a temperature of 250°C (fig. 11): Thermal decomposition of the nitrate in the uppermost monolayer takes place. The secondary ions corresponding to the sulfate complex change their intensity very little up to a temperature of 400°C. The mass number 101 produced by the carboxylic acid complex $\text{CH}_3(\text{CH}_2)_3\text{COO}^-$ increases sharply when the catalyst is heated.

Mass number 101 and a number of other carboxylic complexes reappear in the uppermost monolayer, if the catalyst is heated again after sputtering removal of all surface components (fig. 12). These secondary ions apparently come from compounds, which reach the surface from the interior of the catalyst during heating (along grain boundaries or capillaries)³².

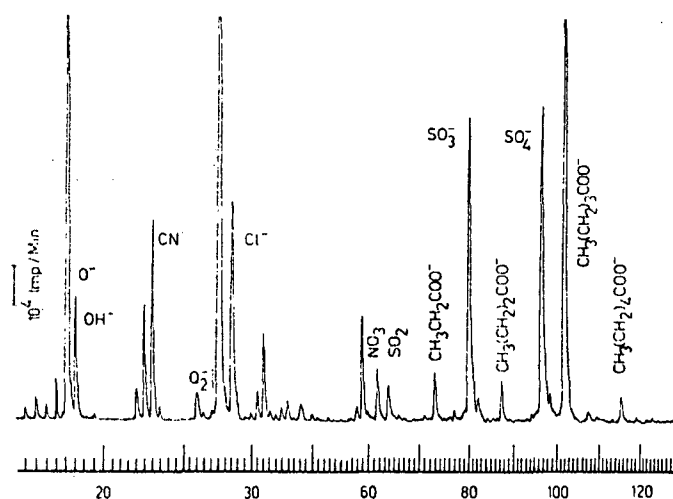


Fig. 11. Negative secondary ion spectrum of the uppermost monolayer of a silver catalyst after heating to 250°C. Primary ion current density: $10^{-9} \text{ A cm}^{-2}$.

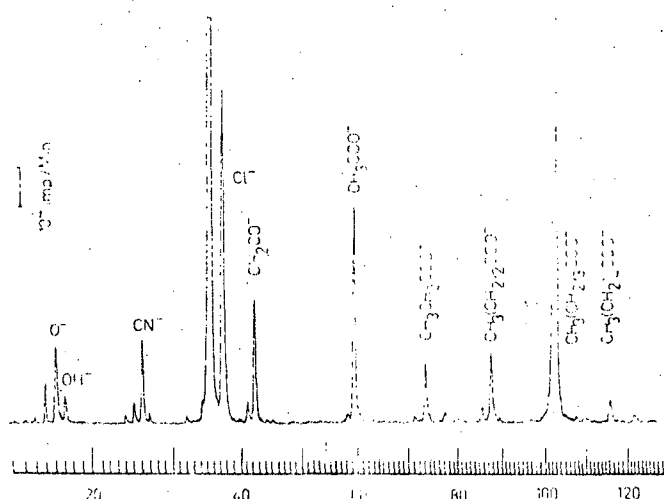


Fig. 12. Negative secondary ion spectrum of the uppermost monolayer of a silver catalyst after removal of 20 monolayers and heating to 250 °C. Primary ion current density: 10^{-3} A cm $^{-2}$.

5.2. OXIDATION OF METAL SURFACES

The oxidation of clean metal surfaces by oxygen was studied in our laboratory in a series of experiments by SIMS. In all these investigations the experimental procedure was the following³⁾: The polycrystalline metal target was mounted in the target chamber (secondary ion source) and cleaned by high current density ion bombardment. After removal of at least some thousand monolayers the secondary ion spectrum was recorded. Besides ions of contaminations especially secondary ions of the general composition Me_m^+ appeared in these spectra.

After the cleaning procedure oxygen was admitted into the target chamber (5×10^{-8} – 5×10^{-7} torr). During oxygen exposure the intensity of secondary ions typical of the oxide layer on the surface was measured. An information concerning the thickness of an oxide layer could be obtained by removing the oxide layer during high current density ion bombardment and simultaneous registering secondary ion intensities. All these experiments were carried out at a basic pressure in the target chamber of at least some 10^{-10} torr.

5.2.1. Oxidation of aluminium

As an example of a relatively simple oxidation process some results of the investigation of surface oxidation of polycrystalline aluminium are given in figs. 13 and 14³²⁾. In the negative secondary ion spectrum of an oxidized

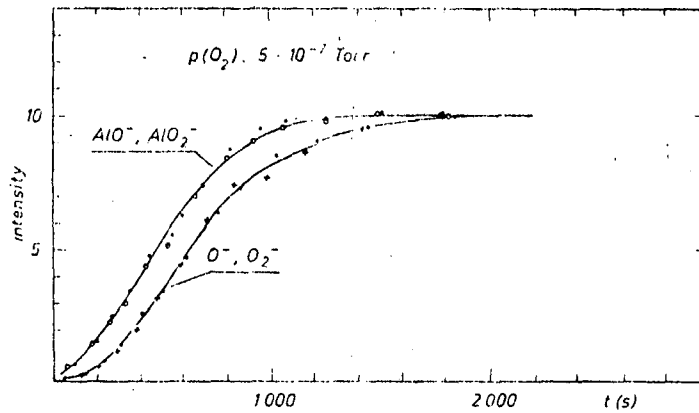


Fig. 13. Increase of negative secondary ion intensities during oxygen exposure of a clean aluminium surface.

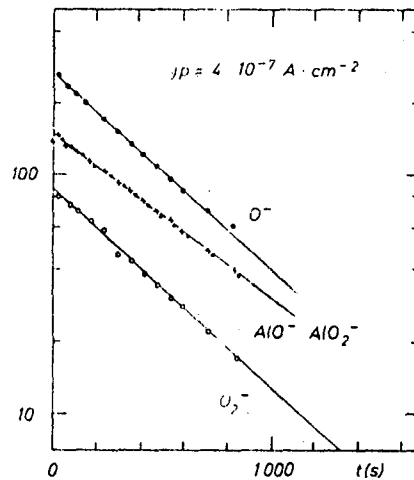


Fig. 14. Decrease of negative secondary ion intensities during sputtering of a monomolecular oxide layer on aluminium. The oxide layer was formed by an oxygen dose of 1000 L on an aluminium surface which had been cleaned by ion bombardment.

aluminium surface the secondary ions O^- , O_2^- , AlO^- and AlO_2^- are found with relatively high intensities.

Fig. 13 gives the intensity increase of these secondary ions during oxygen exposure. After about 1000s, corresponding with an oxygen dose of about 500L, a saturation behaviour can be observed. That means, the surface now is apparently covered with a closed oxide layer which does not undergo further changes. It is not possible to learn anything about the increase in thickness of this layer during a further oxygen admission from fig. 13. This,

however, can be done by observing the decrease of typical secondary ion intensities during removal of the oxide layer by high current density ion bombardment (fig. 14). For one order of magnitude the secondary ions O

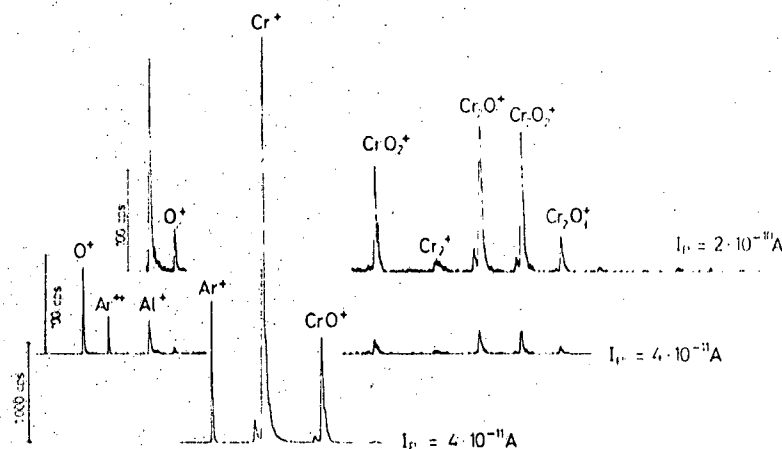


Fig. 15a.

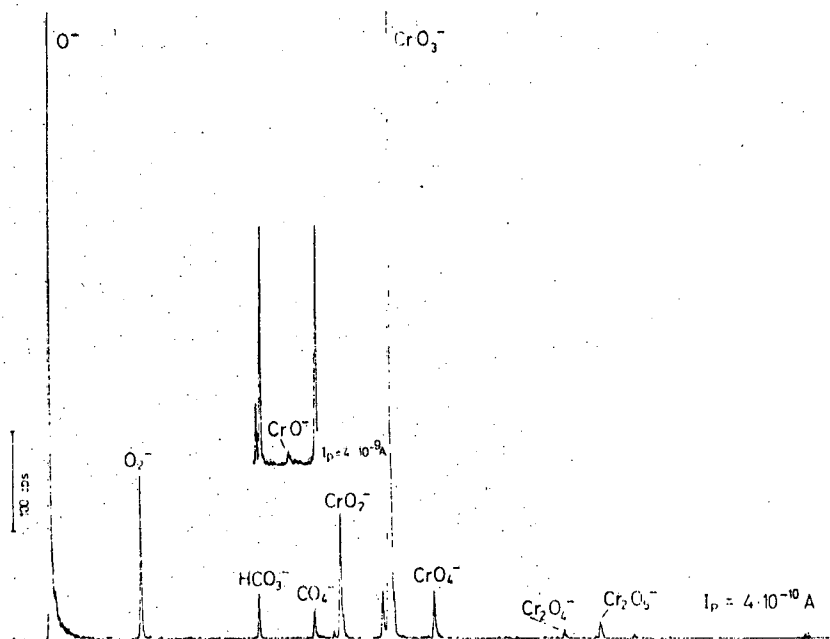


Fig. 15b.

Fig. 15. Positive and negative secondary ion spectrum of an oxide covered chromium surface. The oxide layer was formed by an oxygen dose of 1200 L on a chromium surface cleaned by ion bombardment.

O_2^- , Al^-O and AlO_2^- follow exactly an exponential time dependence [eq. (10)] thus indicating that the corresponding parent structure has a thickness of no more than one monolayer. Further experiments have revealed that the thickness of this oxide layer does not increase when the oxygen dose raises to some 10^4 L.³⁶⁾ The fact that the secondary ions AlO^- and AlO_2^- have the same time dependence in fig. 13 as well as in fig. 14 indicates that the same surface compound is responsible for these two kinds of ions.

5.2.2. Oxidation of chromium

A polycrystalline Cr surface³⁴⁾ shows a more complicate oxidation behaviour. Fig. 15 gives the secondary ion spectra of an oxidized polycrystalline Cr surface. A number of secondary ions of the general composition $Cr_mO_n^\pm$ appear in the spectra. In figs. 16 and 17 the increase of some of these lines during oxidation of the clean metal surface at room temperature is given as a function of the total oxygen dose. The different secondary ions show very different oxygen dependences which can be explained by the formation of different oxide structures on the surface. At an oxygen dose of about 600 L all secondary ions show a saturation behaviour.

For the observation of the different steps of oxidation the ions CrO_2^- , CrO_3^- and CrO^+ , typical of different oxide structures in the uppermost monolayer, are important (fig. 17). These different SI appear successively and reach their saturation in the same succession.

The oxygen dose dependence of the different SI can be explained by the

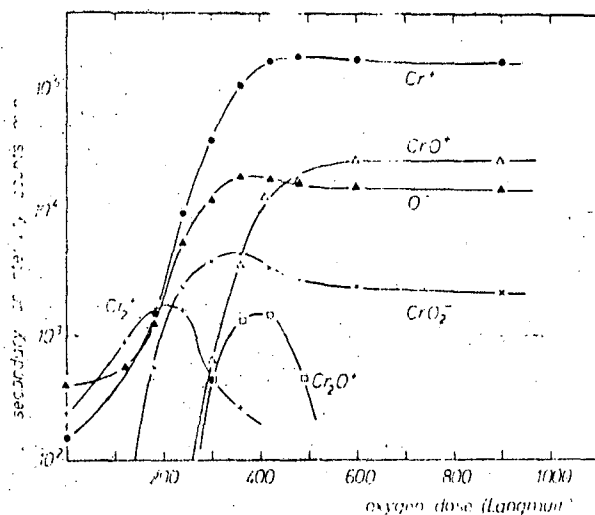


Fig. 16. Increase of secondary ion intensities during oxygen exposure of a clean chromium surface.

following model of surface oxidation: during the first step of oxidation (oxide phase I) in the beginning CrO_2^+ and with increasing thickness of this oxide phase also CrO_3^+ ions are emitted (fig. 18). At the end of the oxidation process a higher oxide is formed on the top of the oxide phase I, resulting in the emission of CrO^+ ions.

These models can be proved by observing the behaviour of different secondary ions during sputtering of an oxide layer. Fig. 19 gives the results for an oxide layer which had been formed by an oxygen dose of 1200 L. This oxygen dose is much higher than the saturation dose of 600 L (fig. 17). At the beginning of the sputtering process we observe a sharp decrease of CrO^+ . That means the parent structure of CrO^+ (oxide phase II) is sputtered with high sputtering rate. During the decrease of CrO^+ the oxide phase I becomes the uppermost layer of the bombarded surface. Thus we observe a simultaneous increase in CrO_2^+ . The CrO_2^+ emission is constant during a relatively long period. That means, the oxide phase I has a thickness of more than one mo-

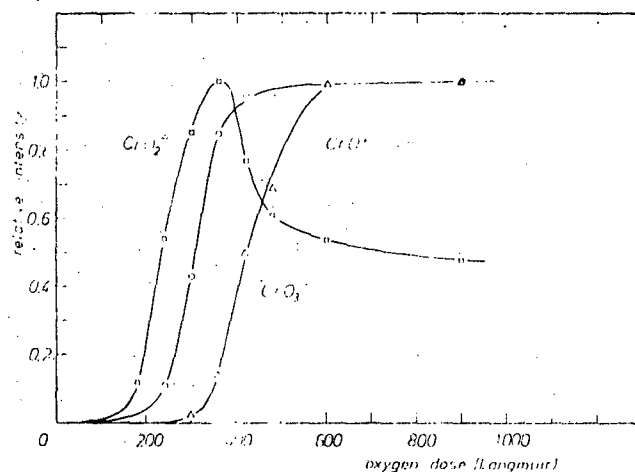


Fig. 17. Increase of secondary ion intensities during oxygen exposure of a clean chromium surface.

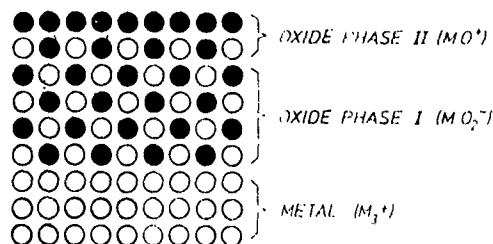


Fig. 18. Model of an oxide layer on a metal surface.

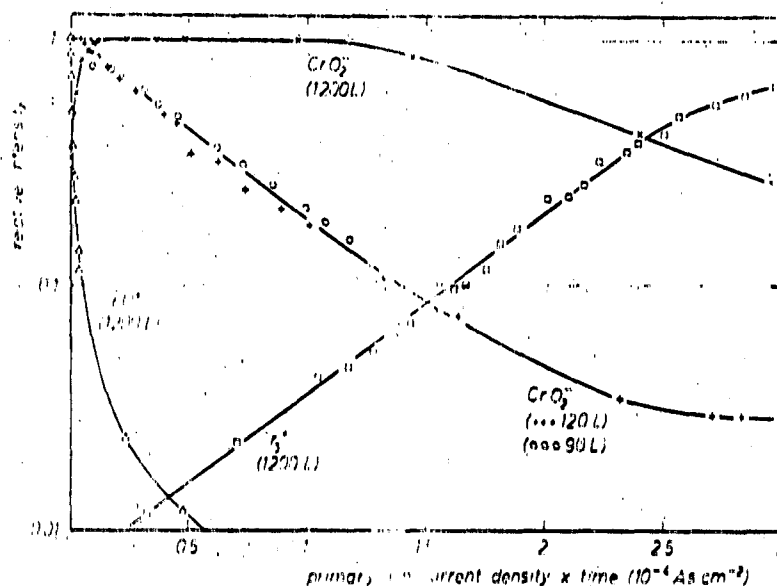


Fig. 19. Change of secondary ion intensities during sputtering of different oxide layers on chromium. The oxide layers were formed by oxygen doses of 1200, 120 and 90 L.

monolayer. At a primary ion dose density of $10^{-4} \text{ A s cm}^{-2}$ the CrO_2^+ intensity decreases. The oxide phase I now vanishes and the pure metal surface appears at the surface. This results in a corresponding increase in Cr_3^+ , typical of the clean metal surface.

If a cleaned Cr surface is oxidized by an oxygen dose of only 100 L the oxide phase I is formed on the surface with a thickness below 1 monolayer. This can be proved by the decrease of CrO_2^+ during sputtering of such a layer. In fig. 19 the intensity of CrO^+ (90 L, 120 L) follows an exponential time dependence indicating that the oxide phase I now is free of a covering structure (no increase in CrO^+ at the beginning of the sputtering process) and has not more than monolayer thickness.

5.2.3. General oxidation behaviour of metals

Figs. 20 and 21 give some general results for different metals⁽²⁴⁾. It is seen from the diagrams that different metals show typical behaviour during oxygen exposure. The general oxidation behaviour of metals cleaned by argon ion bombardment can be summarized as follows:

- Oxide formation on a clean metal surface occurs at relatively high oxygen doses.
- The oxide formation is terminated only at an oxygen dose of some 100 L.
- Two steps of oxide formation can be observed: the first step is character-

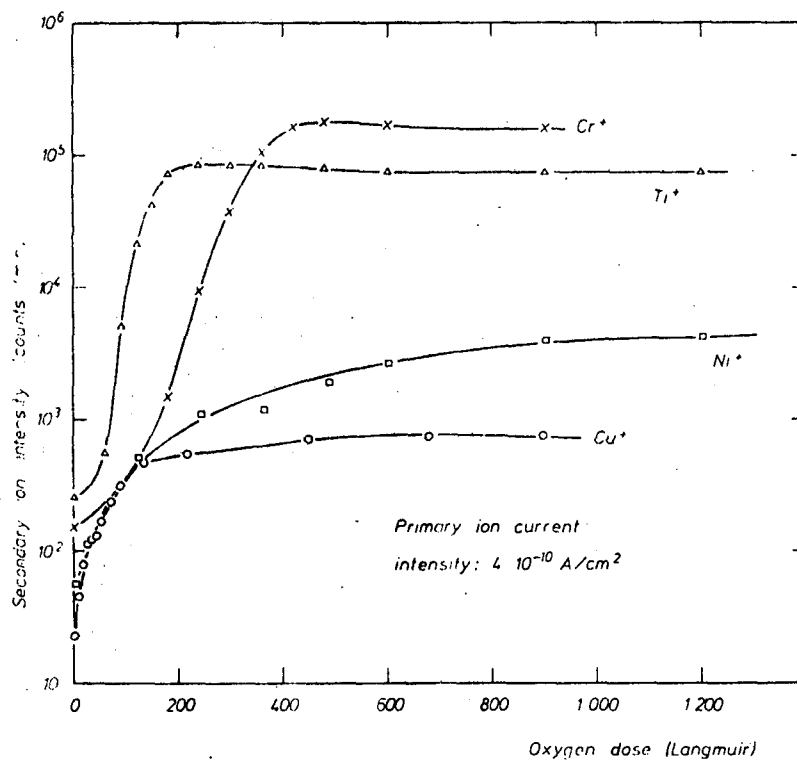


Fig. 20 Increase in Me^+ emission during oxygen exposure of different clean metal surfaces.

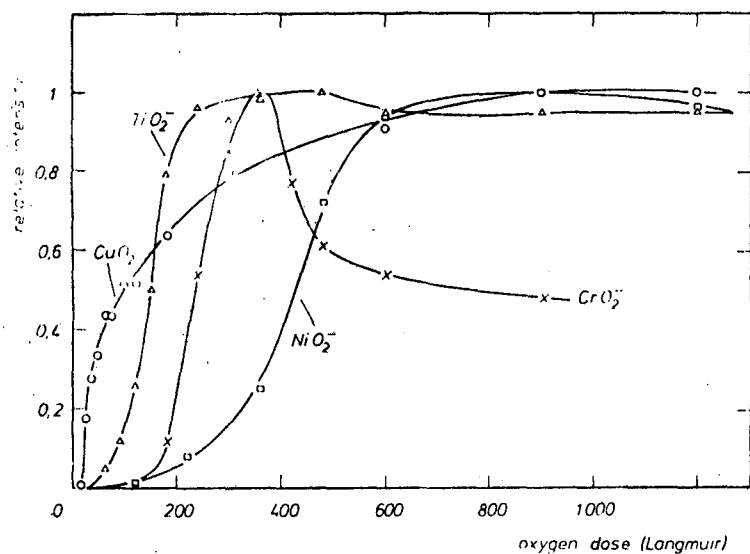


Fig. 21. Change in MeO_2^+ emission during oxygen exposure of different clean metal surfaces.

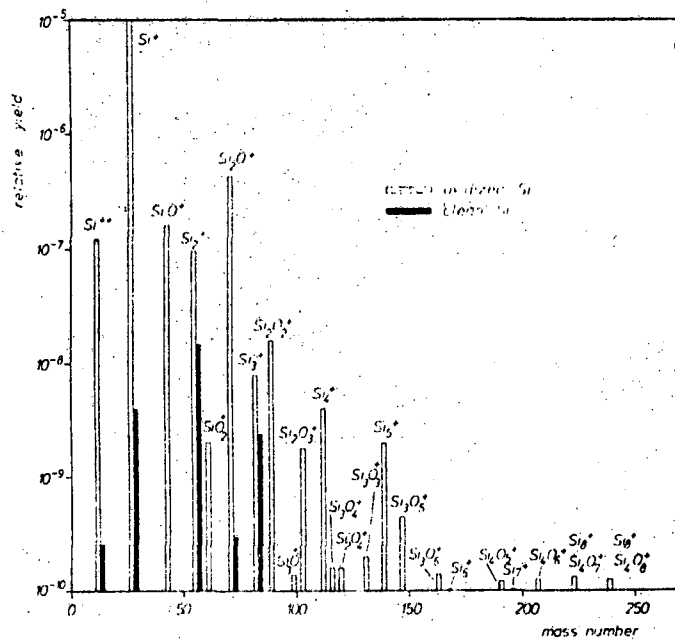


Fig. 22a.

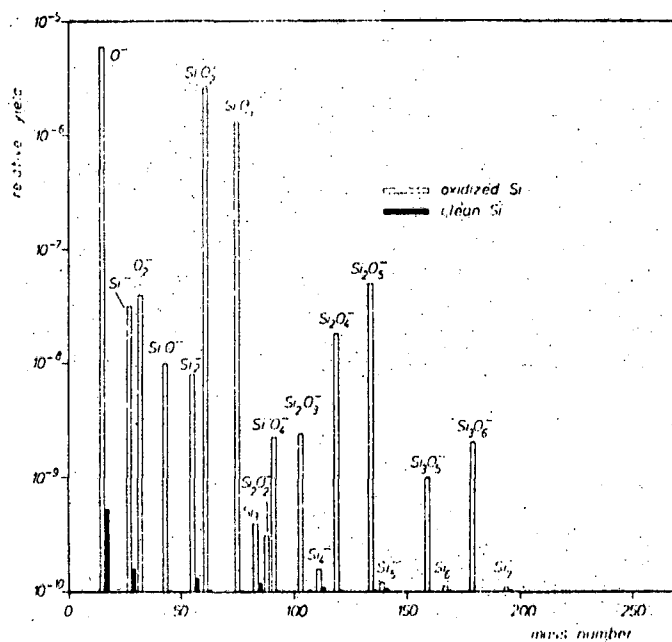


Fig. 22b.

Fig. 22. Positive and negative secondary ion spectra for a clean and an oxidized silicon surface.

ized by the appearance of MeO_2^- and MeO_3^- ions at a relatively low oxygen dose (oxide phase I). The second step is characterized by the appearance of the ions MeO^+ at high oxygen doses (oxide phase II).

- During the first step of oxidation MeO_n^- ions with increasing n are emitted with increasing oxygen dose.
- The sputtering rate of the MeO^+ parent structure is about ten times the sputtering rate of the MeO_2^- parent structure.

5.3. OXIDATION OF SILICON

As an example of the investigation of surface reactions on a semiconductor surface some results concerning the oxidation behaviour of silicon are given in figs. 22–25³⁵). The positive and negative secondary ion spectra of a clean and an oxide covered silicon surface are shown in fig. 22. SiO_2^- is the most intense secondary ion typical of an oxidized surface. Therefore we used this secondary ion for the study of the oxidation behaviour of a clean silicon surface.

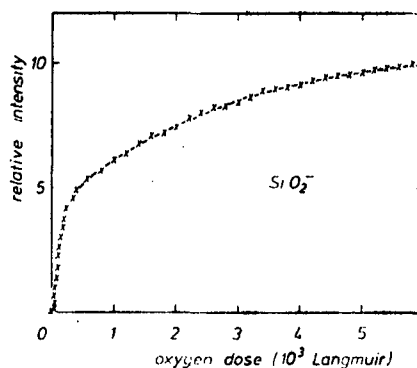


Fig. 23. Increase of SiO_2^- intensity during oxidation of a clean silicon surface.

Fig. 23 shows the increase in SiO_2^- during oxygen exposure of a silicon surface cleaned by argon ion bombardment. A sharp rise of SiO_2^- at low oxygen doses is followed by a slower increase up to more than 6000 L. The sharp rise at the beginning of the oxidation process corresponds with a sticking probability of oxygen on the clean surface of some 10^{-3} , in good agreement with the results obtained by other methods. The thickness of an oxide layer formed by an oxygen dose of about 6000 L is not more than one monolayer. That is evident from fig. 24. The increase in SiO_2^- follows an exponential ion dose dependence for 2 orders of magnitude.

The oxidation of a clean silicon surface is very sensitive to H_2O contaminations in the surrounding gas phase. This can be seen in the two spectra of fig. 25. The upper spectrum corresponds to an oxide layer which had been formed by a total oxygen dose of 10^3 L. The fraction of water vapour in the gas phase during the oxidation was below 10^{-4} . Only the secondary ions O^- , SiO_2^- and SiO_3^- are present in the mass spectrum. If on the other hand during the oxidation of the clean Si surface the fraction of H_2O in the gas phase exceeds some 10^{-3} , the resulting SI spectrum is completely different. Now the secondary ions OH^- , SiO_2H^- and SiO_3H^- appear besides the secondary ions typical of a clean oxide layer (lower spectrum in fig. 25).

5.4. ADSORPTION OF H_2 AND O_2 ON W(100)

As an example of the investigation of a well defined surface structure by SIMS some results for the interaction of a clean W(100) surface with hydrogen and oxygen are given in figs. 26 and 27²⁹⁾.

In these investigations the surface consisted of (100) faces of tungsten crystals. The surface here was cleaned only by heating. Not only the ion induced secondary ion emission had been used for the observation of changes in the surface structure but also the emission of electron induced secondary ions. It is well evident from figs. 26 and 27 that important additional information can be obtained by simultaneous application of SIMS and EID (electron induced desorption).

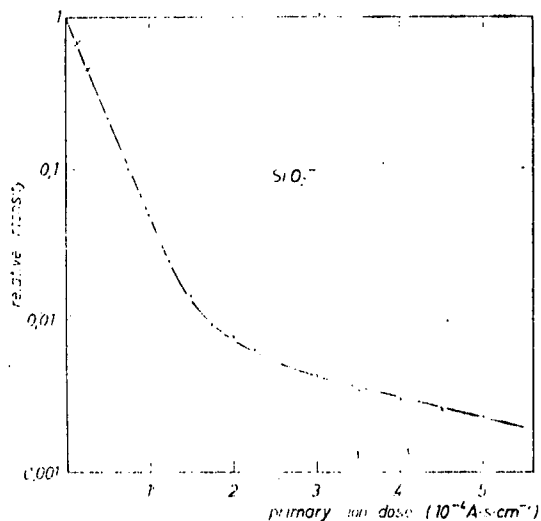


Fig. 24. Decrease of SiO_2^- intensity during sputtering of a monomolecular oxide layer on silicon. The oxide layer was formed by an oxygen dose of 6000 L on a silicon surface which had been cleaned by argon ion bombardment.

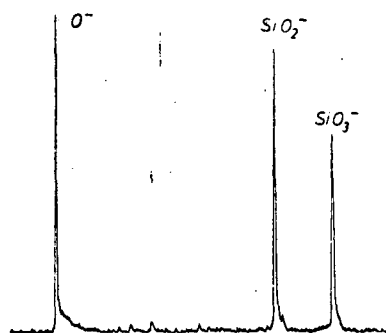


Fig. 25a.

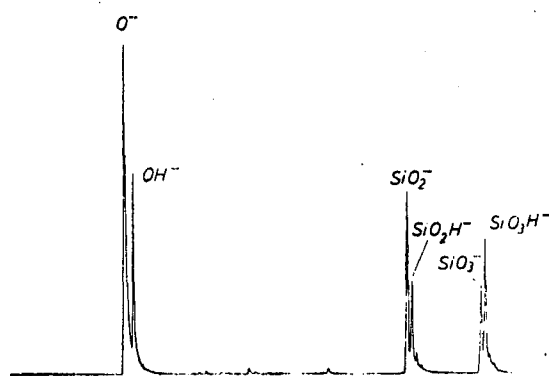


Fig. 25b.

Fig. 25. Negative secondary ion spectra of oxide layers on silicon formed in a pure oxygen atmosphere (fraction of water vapour less than 10^{-4} , upper spectrum) and in a water vapour contaminated oxygen atmosphere (fraction of water vapour some 10^{-3} , lower spectrum). The total oxygen dose was 1000 L in both cases.

Fig. 26 presents the increase in H_i^+ and H_e^+ as a function of the hydrogen exposure for a clean tungsten surface. The index i stands for ion induced emission, the index e for electron induced emission. A continuous increase in H_i^+ can be observed. A sticking probability near 1 for H_2 on W(100) can be derived in good agreement with other measurements. On the other hand the emission of electron induced secondary ions H_e^+ shows a maximum and a following decrease. That means the different binding states of hydrogen on the tungsten surface which does not influence the emission of H_i^+ can be identified by the observation of the electron induced emission of H_e^+ .

Fig. 27 gives some results of a study of the interaction between oxygen and tungsten. In this case additional information can be obtained from the observation of O_e^+ .

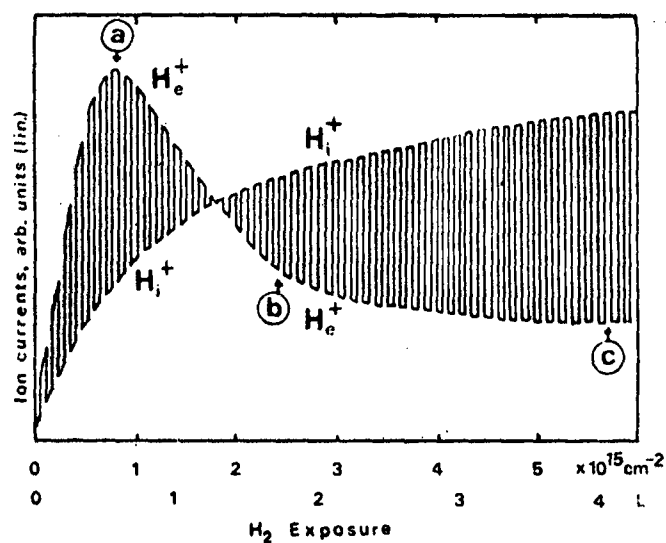


Fig. 26. Simultaneous recording of electron (He^+) and ion (H_i^+) induced H^+ ion emission during hydrogen adsorption on tungsten.

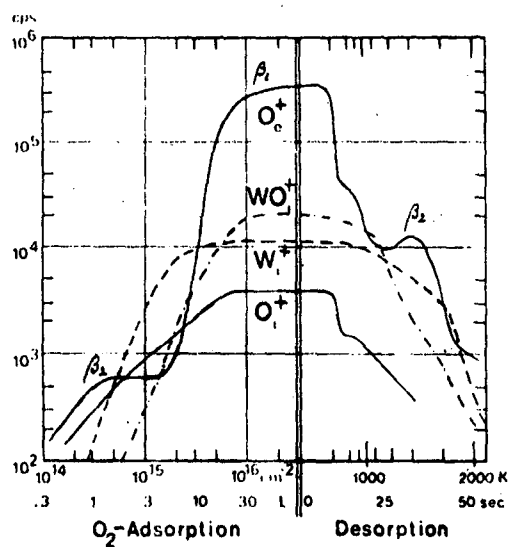


Fig. 27. Emission of electron and ion induced secondary ions during oxygen adsorption on a clean tungsten surface and during heating of an oxide layer.

6. Conclusion

It was the intention to demonstrate that the statical method of secondary ion mass spectroscopy is a powerful tool for the study of individual monolayers on surfaces by treating the fundamentals of secondary ion emission and presenting some typical examples of surface investigations with SIMS. In the past mainly two facts hindered the application of secondary ion mass spectroscopy to monolayer investigations:

- The destruction and removal of the uppermost monolayer of a solid during ion bombardment.
- The fact, that it is not possible to predict exactly the composition and intensity of secondary ions emitted by a given surface structure.

It was shown, that the first difficulty - the destruction and removal of the uppermost monolayer - could be reduced to a negligible amount by applying a statical method, the main feature of which is the bombardment of a relatively large target area with an extremely low primary ion current density.

Concerning the second problem - the sort and intensity of the emitted secondary ions - two important facts could be shown:

- Any specific surface structure - e.g. an oxide layer on a metal or an adsorption layer - gives rise to a specific secondary ion spectrum.
- For a large number of monomolecular or submonomolecular layers it is evident, that the intensity of a characteristic kind of secondary ion is proportional to the degree of coverage of the surface with the corresponding surface structure. This was demonstrated by the exponential time dependence of characteristic ion intensities during sputtering of these layers.

The main features of SIMS as a method for monolayer investigation are:

- information depth in the monolayer range;
- isotope separation;
- detection of chemical compounds;
- detection of hydrogen and its compounds;
- detection limits $<10^{-6}$ of a monolayer or $<10^{-14}$ g for many elements and compounds;
- capacity of quantitative analysis;
- very small disturbance of the surface during the analysis;
- detection of changes in the concentration within the first monolayers;
- differences in sensitivity for different surface structures (elements, compounds): more than 3 orders of magnitude.

Compared with other methods of surface analysis such as AES, ESCA, or ion reflection, especially three features should be mentioned: Detection of hydrogen and its compounds, direct detection of surface compounds by their fragment ions, isotope separation with high mass resolution,

and very high surface sensitivity for many elements and compounds.

The main problem in applying SFMS to surface analysis is the fact that the sensitivity changes in a wide range for different surface structures (e.g. a factor of more than 1000 for metals) and that it is necessary to make calibration measurements for quantitative analysis.

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INVESTIGATION OF SURFACE REACTIONS
BY THE STATIC METHOD OF
SECONDARY ION MASS SPECTROMETRY

II. THE OXIDATION OF CHROMIUM IN THE MONOLAYER RANGE

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By means of the static method of secondary ion mass spectrometry the oxidation of a polycrystalline chromium surface cleaned by ion bombardment was investigated at room temperature in the oxygen dose range up to 1600 L. Two different oxide phases are formed on the surface, one covering the other. The secondary ion yield for the Cr^+ ions from an oxidized surface amounts to 1.1.

I. Introduction

When a clean chromium surface is exposed to oxygen from the gas phase, oxygen is incorporated into the lattice, i.e. an oxidation takes place after initial formation of an adsorption layer. There are only a few investigations of the interaction of chromium surfaces with oxygen. Haque and Farnsworth¹⁾ found an initial sticking probability of 0.3 for clean surfaces by LEED. After an oxygen exposure of some 100 L (1 L = 10^{-6} torr sec) they discovered alterations in the LEED patterns which they ascribed to changes in the surface structure or a surface oxidation. Houston and Park²⁾ investigated clean and oxidized chromium surfaces by soft X-ray appearance potential spectroscopy. They found characteristic changes in the spectrum during the interaction of chromium with oxygen at 600 °C. Coad and Rivière³⁾ investigated the low energy Auger spectrum of partially oxidized chromium. They explained the structure of the spectrum by analogy with the spectra of clean and oxidized vanadium. Kennett and Lee⁴⁾ investigated the initial stages in the oxidation of (100) and (110) chromium surfaces under high vacuum conditions.

On the (100) surface an ordered oxygen structure was observed, and on the (110) surface a layer with a different symmetry from the substrate was found. By heating the crystal other oxide types could be found. Several other in-

vestigations (e.g. refs. 5 and 6) are concerned with the development of thick oxide layers (in the μm range) at high oxygen pressure and high temperature. Investigations of the mechanism of oxide formation on a chromium surface in the monolayer range are not known to us.

In this work the oxidation of a polycrystalline chromium surface cleaned by ion bombardment was investigated in the oxygen exposure range up to 1600 L at room temperature by means of the static method of secondary ion mass spectrometry (SIMS) ⁷).

When the surface is bombarded with primary ions, secondary ions are emitted. These ions are mass-separated and detected. Their number and kind are characteristic of the structure and chemical composition of the surface. By using a low primary ion current density (10^{-9} A/cm²) the average lifetime of a monolayer is increased to several hours so that only a negligible part of this monolayer (1% or less) will be removed during the measurements. Moreover, ion implantation, chemical reactions, and lattice defects caused by primary ions can be neglected. Changes of the surface due to the residual gas can be prevented by a sufficiently low pressure in the vacuum system. By using a large target area (0.1 cm²) and a single-ion counting technique for the detection of the secondary ions the detection limit was about 10^{-4} of a monolayer.

A detection limit of 10^{-6} of a monolayer or even less can be achieved for some elements by using higher primary ion current densities, which, on the other hand, lead to a shorter lifetime of the layer under investigation ⁷).

Additional information on the properties of thin layers can be obtained by observing the secondary ion emission during the removal of this layer by a higher primary ion current.

The adsorption of oxygen taking place at oxygen exposures of less than 50 L was not investigated in this work. The study of this process with SIMS is complicated by the fact that the secondary ions $\text{O}^{\pm}$ and $\text{O}_2^{\pm}$, which are typical for the adsorption layer, are also emitted by oxides with high yields. Thus traces of oxides on the surface can hinder the detection of adsorbed oxygen. However, the adsorption process can be easily studied by electron induced desorption (EID) ^{8,9}).

2.1. THE SPECTROMETER

The investigations were carried out with a bakeable secondary ion mass spectrometer made of stainless steel with gold and copper gaskets. The vacuum was generated by two mercury diffusion pumps in series and a liquid nitrogen cool trap.

After bakeout the residual pressure, measured by a Bayard-Alpert ionization gauge, was in the 10^{-10} torr range. Oxygen could be admitted into the

reaction chamber by a variable leak valve. By preliminary experiments it was ensured that during oxygen admission the oxygen partial pressure checked with the total pressure. Another variable leak valve was used for the admission of argon into the primary ion source, which was constructed according to Finkelstein¹⁰.

The primary ions (Ar^+ , 3 keV) hit the target surface at a grazing angle of 20° . The ion beam was defocussed and apertured to achieve a sufficiently homogeneous primary ion current density across the beam. By using a system of electrostatic lenses, the secondary ions emitted by the target were focussed on the entrance slit of a single focussing magnetic sector field analyzer with the radius $r = 10$ cm and the geometrical resolution $m/\Delta m = 250$.

The secondary ions were detected in a multiplier by a single-ion counting technique. The secondary ion spectra could be recorded by a X - Y recorder. The X axis was driven by a Hall probe in the magnetic field of the analyzer, the Y axis by the secondary ion intensity.

2.2. THE PRIMARY ION CURRENT MEASUREMENT

For all quantitative secondary ion investigations exact measurements of the primary ion current I_p^+ are necessary. During the primary ion bombardment currents of reflected primary ions I_r^+ , positive secondary ions I_s^+ , negative secondary ions I_s^- , and secondary electrons I_e^- may leave the target, if not suppressed by electric potentials. Thus the current I registered on the target is

$$I = I_p^+ - |I_r^+| - |I_s^-| + |I_s^+| + |I_e^-|.$$

The species and number of the secondary particles depend on the structure and the chemical composition of the bombarded surface. During chemical reactions on the surface the currents I_s^+ , I_s^- , and I_e^- can change by several orders of magnitude.

The oxidation of a metal surface is representative of this behaviour, as the surface is entirely different before and after the oxidation process.

The exact measurements of the primary ion current was carried out with a Faraday cup formed by connecting the target with the surrounding electrodes. Only a negligible fraction of particles emitted from the target could leave this cup¹¹.

The electrodes having convenient negative potentials, the total positive yield

$$S^+ = (|I_s^+| + |I_r^+|)/I_p$$

for the surface under investigation could be determined. By comparison of S^+ with the sum of all positive secondary ions detected in the multiplier the over-all transmission of the apparatus was found to be 1×10^{-5} .

3. The secondary ion emission of clean and oxidized chromium surfaces

During primary ion bombardment an oxidized chromium surface will emit secondary ions of the composition $\text{Cr}_m\text{O}_n^{\pm}$ ($m=0, 1, 2, \dots$ and $n=0, 1, 2, \dots$). Multiply charged ions may appear, too. A clean chromium surface only emits secondary ions of the species Cr^+ , Cr_2^+ , Cr_3^+ , ...

Figs. 1 and 2 show the positive and negative secondary ion spectrum of the

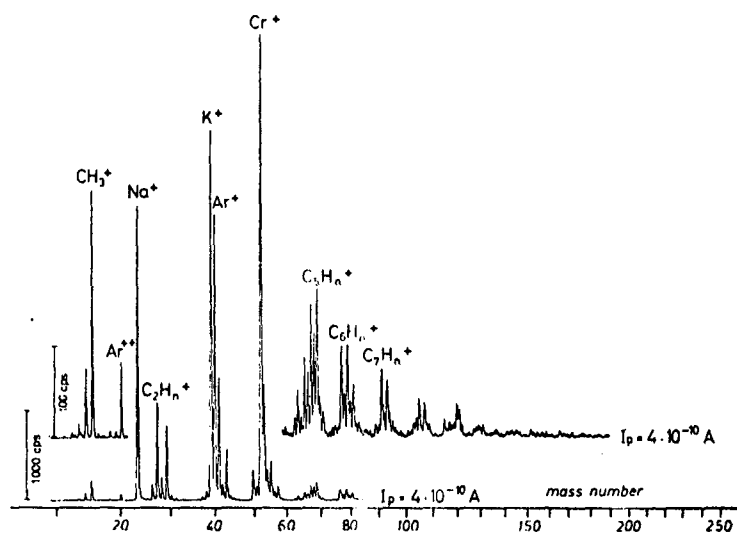


Fig. 1. Positive secondary ion spectrum of the original first monolayer.

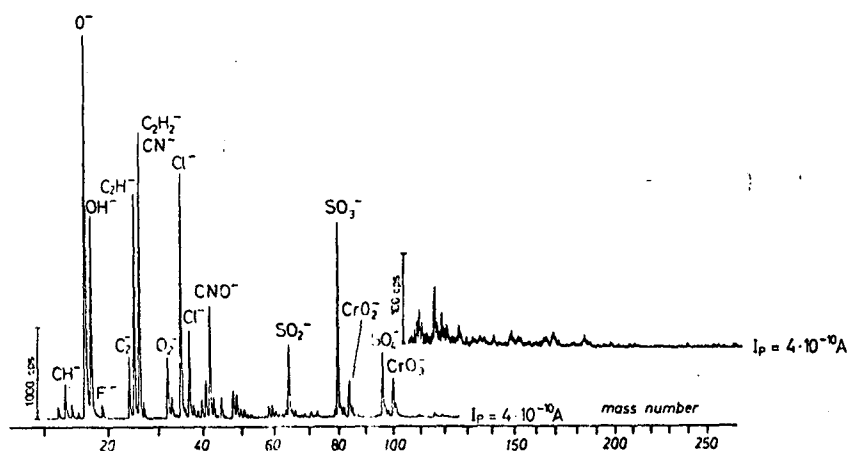


Fig. 2. Negative secondary ion spectrum of the original first monolayer.

original first monolayer. Evidently, the surface was covered with a contamination layer consisting of hydrocarbons, oxides, hydroxides, different anions, and other contaminants, represented by their typical secondary ions.

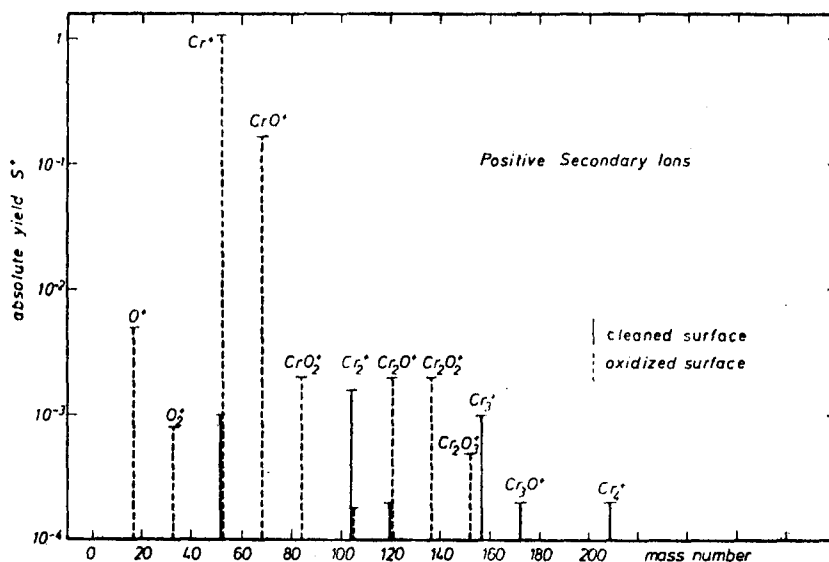


Fig. 3. Absolute yields for the positive ions emitted from a cleaned and an oxidized surface.

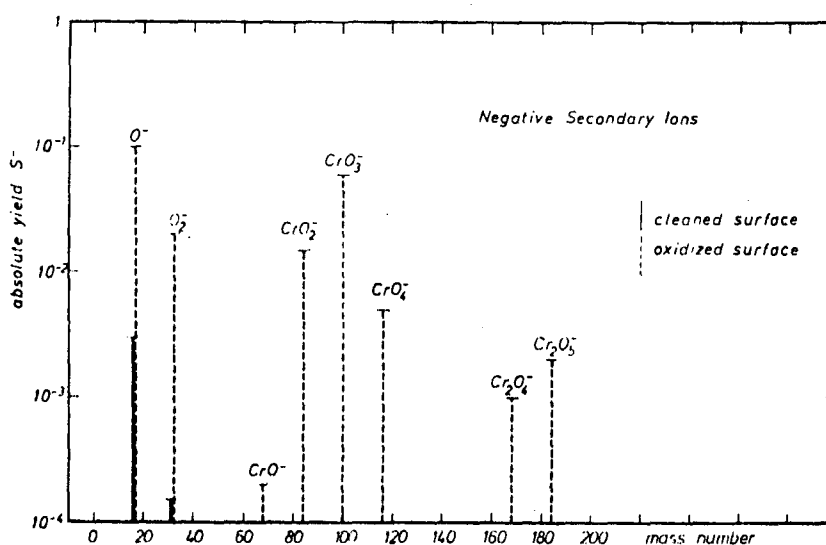


Fig. 4. Absolute yields for the negative ions emitted from a cleaned and an oxidized surface.

Figs. 3 and 4 show the absolute yields $S^\pm$ (number of emitted secondary ions per incident primary ion) for some secondary ions emitted from a chromium surface cleaned by a primary ion current exposure density of 0.1 A sec/cm^2 and from a surface oxidized after cleaning by an oxygen dose of 1600 L^{12}). The detection limit for $S^\pm$ was 10^{-4} .

The traces of oxides and oxygen of the cleaned surface were caused by bulk impurities. They could not be reduced by further ion bombardment.

In the positive spectrum of the cleaned surface only Cr^+ , Cr_2^+ , and Cr_3^+ could be found with higher intensities. After the oxidation, the additional ions O^+ , O_2^+ , CrO^+ , CrO_2^+ , Cr_2O^+ , Cr_2O_2^+ , and Cr_2O_3^+ appeared. The Cr^+ peak increased, whereas the Cr_2^+ peak decreased and the Cr_3^+ peak disappeared.

The negative spectrum of the cleaned surface shows only O^- and O_2^- from bulk impurities. After the oxidation, these two peaks increased by more than one order of magnitude, and additional peaks of CrO^- , CrO_2^- , CrO_3^- , CrO_4^- , Cr_2O_4^- , and Cr_2O_5^- could be found with yields greater than 10^{-4} .

4. Changes of the secondary ion emission during the formation of an oxide layer

In fig. 5 the yields $S^\pm$ of some interesting secondary ions are plotted against

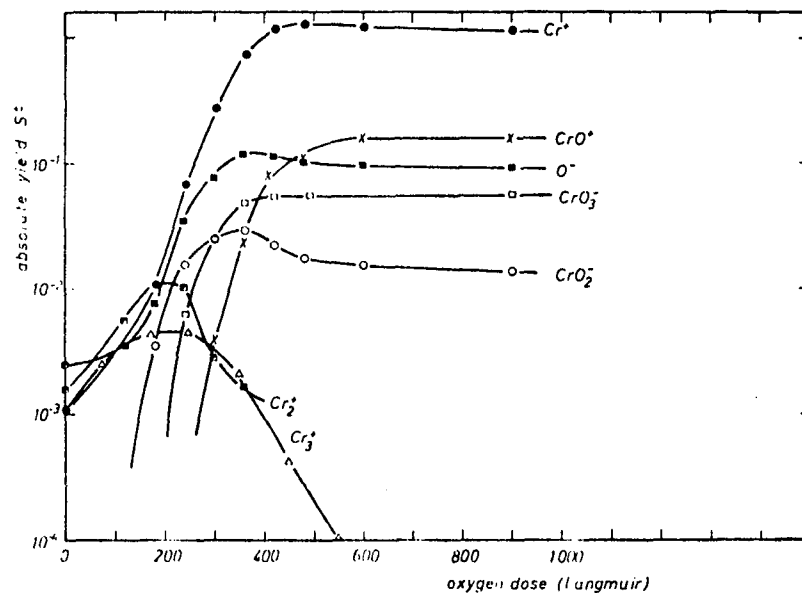


Fig. 5. Absolute yields of some secondary ions as a function of the oxygen dose.

the oxygen dose. Fig. 6 shows the relative intensities for Cr_3^+ , CrO_2^+ , CrO_3^+ , CrO^+ , fig. 7 for Cr^+ , CrO^+ , CrO_3^+ , and S^+ . At a sufficiently high oxygen dose all yields reach a saturation, some of them after passing through a maximum.

By several measurements it was ensured that the course of these curves depended only on the oxygen dose (pressure $\times$ time)^{7, 13}.

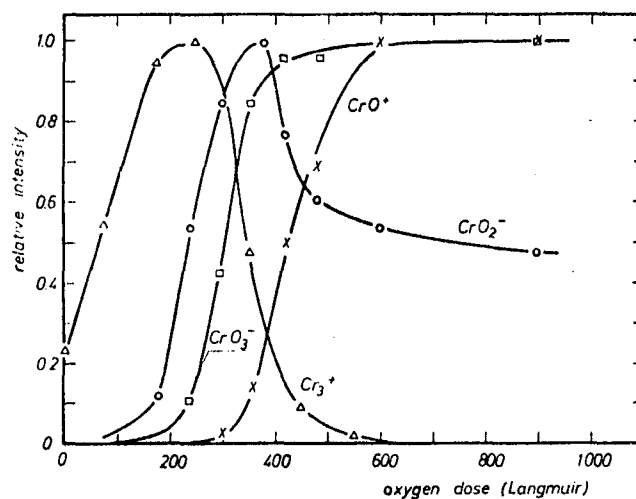


Fig. 6. Relative intensities of some secondary ions as a function of the oxygen dose.

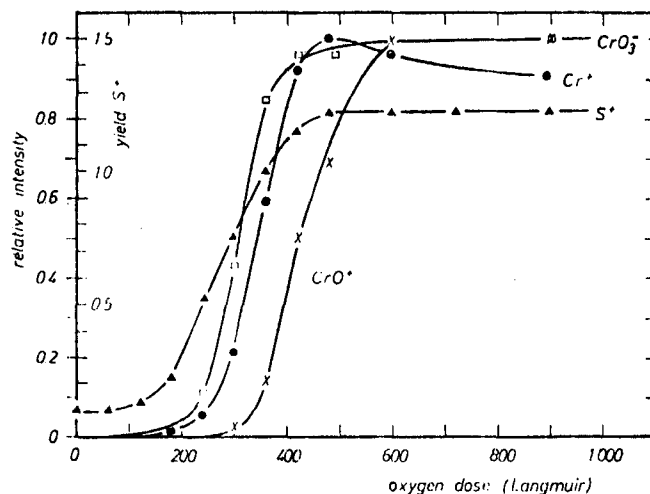


Fig. 7. Relative intensities of some secondary ions and total positive yield as a function of the oxygen dose.

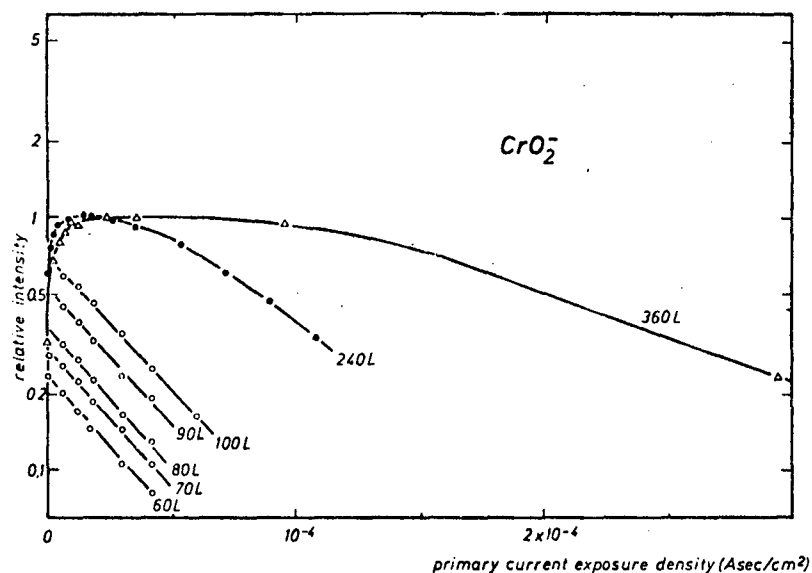


Fig. 8. Relative intensity of the CrO_2^- ions as a function of the primary ion current exposure density for some oxide layers formed during different oxygen exposures.

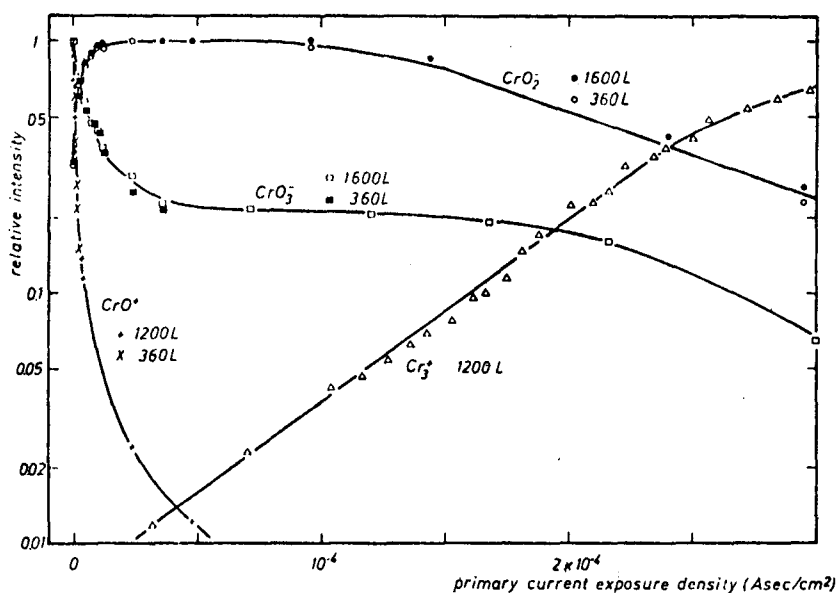


Fig. 9. Relative intensities of some secondary ions as a function of the primary ion current exposure density for different oxide layers.

5. Changes of the secondary ion emission during the removal of the oxide layer

The oxide removal investigations were carried out as follows: The surface was cleaned by ion bombardment. Then oxygen was admitted up to a certain degree of oxidation. The oxide layer was gradually removed by ion bombardment, and the secondary ion intensities were observed.

In fig. 8 the CrO_2^- intensity is plotted against the primary ion current exposure density for some oxide layers formed during different oxygen exposures.

The curves of 60, 70, 80, 90, and 100 L indicate an exponential decrease; the curves of higher oxygen exposures show a fast initial increase followed by a range of constant emission and a subsequent slow decrease. Fig. 9 shows the course of the CrO_2^- , CrO_3^- , CrO^+ , and Cr_3^+ intensities during the removal of an oxide layer formed by 360, 1600 or 1200 L oxygen.

6. Discussion

The following simplified statements can be made about the secondary particle emission from metals and metal oxides:

- (1) The atoms of an emitted secondary cluster (particle consisting of several atoms) must have come from adjacent sites on the surface*.
- (2) An emitted cluster tends to preserve the sign of charge given by the sum of the charge of its constituent atoms in the lattice before the emission.
- (3) The yield of a certain secondary particle species is proportional to the surface coverage with the parent compound emitting these particles, as long as the coverage does not exceed one monolayer.

These statements are corroborated by the results presented in this work and the results for the oxidation of several other metals which will be published in subsequent papers.

The oxidation process can be described by a simple model: During oxygen admission to the clean surface, an adsorption layer is formed at first. Only after an oxygen dose of about 50 L the formation of an oxide layer begins. Thus an excess dose of oxygen is necessary to start the oxidation process, if an initial sticking probability of about 0.3 is assumed¹).

In the 50-100 L range an oxide layer emitting CrO_2^- ions is formed on the surface (fig. 6). The chromium atoms have a low positive valence state. So the negative charge of the oxygen atoms is dominating.

The CrO_2^- intensity during the removal of an oxide layer formed by an

* If a secondary ion Me_mO_n^+ appears, however, it can not be concluded that the target has the composition Me_mO_n .

oxygen dose of 60–100 L (fig. 8) follows an exponential law:

$$\theta(t) = \theta(0) \exp(-t/\bar{t}) \quad \text{with} \quad \bar{t} = \vartheta_0/Sv,$$

where $\theta(t)$ is the relative coverage at time t , $\theta(0)$ the relative coverage at the beginning of the ion bombardment, $\bar{t}$ the average lifetime of a monolayer, ϑ_0 the particle area density of a complete monolayer, S the sputtering rate (number of emitted particles per incident particle) for a complete monolayer, and v the primary particle flux.

According to Benninghoven⁷⁾, this leads to the conclusion that the oxide layer formed by 60–100 L oxygen does not exceed one monolayer, and that the yield of CrO_2^- is proportional to the coverage of the surface with the oxide structure.

The emission of Cr_2^+ and Cr_3^+ ions in the same low oxygen dose range (figs. 5 and 6) indicates that two or three chromium atoms can still be found on adjacent surface sites. The initial increase of the emission can be explained by an increasing ionization probability for an emitted Cr_2 and Cr_3 particle during the oxidation process⁷⁾. On the other hand, the probability of finding chromium atoms on two or three adjacent sites is decreasing during further oxidation. At high oxygen doses the Cr_2^+ and Cr_3^+ emission should decline. As the experiments show, this effect is more pronounced for Cr_3^+ than for Cr_2^+ .

At higher oxygen exposures the emission of CrO^+ ions begins. The probability for the emission of positive secondary ions of this composition increases with an increasing positive valence state of the chromium atoms. According to the work of Siegbahn et al.¹⁴⁾ on ESCA the increase of the valence state should lead to shifts in the energies of Auger electrons. These shifts were observed on tantalum by Haas and Grant¹⁵⁾ and on vanadium by Szalkowski and Somorjai¹⁶⁾.

When the oxide layer grows thicker than one monolayer, the emission of CrO_3^- and CrO^+ ions begins, whereas the emission of CrO_2^- ions decreases after passing through a maximum. This leads to the conclusion that a second oxide phase emitting CrO^+ ions is formed on the surface. This conclusion is confirmed by the results presented in figs. 8 and 9: When a thick oxide layer is removed, the CrO_2^- emission shows a fast initial rise, remains constant for a long time and finally decreases. By comparing the CrO^+ and CrO_2^- removal curves it becomes evident that the main decrease range of CrO^+ coincides with the initial increase of CrO_2^- . Obviously the upper phase (phase II) characterized by CrO^+ emission must be removed at first. This phase contains more oxygen atoms per chromium atom than the deeper layers. The chromium atoms occupy a higher valence state, and many CrO secondary particles are positively charged.

These considerations are in good agreement with the results of Werner et al.¹⁷⁾ who investigated thick oxide layers by means of secondary ion mass spectrometry and discovered that the CrO^+ emission from the oxide layer increases with increasing oxygen percentage.

When the phase II has vanished, the lower phase I reappears. The CrO_2^- emission is significant for this phase I, whose thickness, according to the CrO_2^- removal curve of fig. 9, amounts to more than one monolayer. As the CrO_3^- curves indicate, these ions are emitted from both phases. The results for 360, 1200 and 1600 L oxygen exposure demonstrate that in this exposure range the oxide layer does not change.

During ion bombardment, the Cr_3^+ emission is steadily increasing. As the oxide layer is removed, the probability for the existence of three chromium atoms on adjacent sites increases.

As fig. 7 shows, a high total positive yield S^+ (mainly Cr^+ ions) is reached only when the phase II is formed.

By means of the monolayer removing law mentioned above and the results shown in figs. 8 and 9 with $\vartheta_0 = 5 \times 10^{14} \text{ cm}^{-2}$ a sputtering rate $S_I \approx 2$ for the phase I and $S_{II} \approx 20$ for the phase II was found.

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DEVELOPMENTS IN SECONDARY ION MASS SPECTROSCOPY AND APPLICATIONS TO SURFACE STUDIES

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In secondary ion mass spectroscopy (SIMS) positively and negatively charged atomic and molecular particles, emitted from a surface during ion bombardment, are mass analyzed. These secondary ions give important information about the chemical composition and structure of the solid surface. Today SIMS is a widely employed technique for bulk, thin film and surface analysis. The process of secondary ion emission from a solid may be divided into energy and momentum-transfer, fragment formation (e.g. formation of a positively or negatively charged or neutral particle), and the subsequent electronic transitions which take place during the removal of the particle from the surface. At present there exist some models which deal with energy transfer, fragmentation process and the electronic transitions which give a qualitative idea of the type of the emitted particles and their charge. There exists a quantitative theory concerning the emission of positively charged atoms under well-defined surface conditions, as well as an empirical semiquantitative model for molecular ion emission from a solid (crystal lattice) with ionic bonds. For the analytical application of SIMS the following different perturbation processes on the surface during the ion bombardment have to be considered: The removal of surface atoms (sputtering, knock-on-implantation, selective sputtering), changes in crystal structure and amorphisation, generation and destruction of surface compounds, implantations, and ion bombardment induced adsorption of particles from the gas phase. In all these perturbations one has to distinguish "first order" and "second order" effects. First order effects are changes in the surrounding surface region due to the impact of one single bombarding particle. In principle they are inevitable. It is an important problem, how far these first order effects limit the SIMS information concerning the composition and structure of the surface. Second order effects become important if the surface is bombarded with a high primary ion dose. Under these conditions the impinging particles hit surface regions, which have already been changed during the preceding bombardment process. These second order effects can be avoided if the surface is bombarded with only a small primary ion dose (static mode of SIMS). Secondary ion mass spectroscopy is a powerful analytical tool in surface science. With the "static mode of SIMS", monolayer analysis can be effected. Gas-surface interactions can be studied without any important change of the surface. By use of higher primary ion beam intensities profiling of surface layers in the monolayer range can be effected. When applying this profiling technique second order effects are inevitable and this creates problems in the evaluation of profiling spectra. The main advantages of SIMS over other techniques in the field of monolayer analysis of solids are the ability to detect hydrogen, organic compounds and isotopes, high mass resolution, structure and compound sensitivity and high absolute sensitivities. At the present time the main problem in application and understanding of secondary ion emission is the quantitative interpretation of molecular spectra from different surface structures. In the future, experimental developments are to be expected in the construction of high transmission and high resolution instruments, especially for simultaneous multi-mass registration.

1. Introduction

If a solid surface is bombarded by ions in the keV range complex processes of energy transfer and electronic interaction happen in the surface zone of the solid. As a result of these different processes, atomic and molecular particles, electrons, and photons, are emitted. In addition, various changes in the surface zone of the target take place.

The emission of positively and negatively charged atomic or molecular particles (secondary ions), had been studied firstly by Arnot et al. [1]. The first analytical application had been carried out by Herzog and Viehböck [2]. Today secondary ion emission is a widely employed technique for chemical analysis of solids [3-5]. The present applications may be divided into bulk analysis, profiling of thin layers, imaging, and monolayer analysis [6]. In bulk analysis one takes advantage of the high sensitivity of secondary ion mass spectroscopy, in the profiling technique of the depth resolution in the range of some Å, in the imaging technique of the possibility of scanning the target area by a small spot primary ion beam, and in monolayer analysis one uses the high sensitivity of secondary ion mass spectroscopy in an appropriate way.

In this paper one of these four fields will be emphasized: The monolayer analysis and its application to surface reaction studies. Like in all different modes of secondary ion mass spectroscopy also in monolayer analysis one makes use of the fact, that the emitted secondary ions reflect the composition of the bombarded surface. Only those types of atoms will be emitted which are present in the near surface zone. The only atoms which are emitted as a cluster ion are those which occupied adjacent sites on the surface (fig. 2) [7].

Nowaday bulk and thin film analysis by secondary ion mass spectroscopy (SIMS) are well established techniques [3-5]. Monolayer analysis is a more recent field of application. With regard to the sputtering effect of the probing ion beam secondary ion emission has been believed to be completely inadequate for the analysis of an individual single monolayer for a long time. It was by the static method of secondary ion mass spectroscopy [6,8,9], that this field of application became feasible: by lowering the primary ion current density by some orders of magnitude the life time of one single monolayer during ion bombardment increases in the range of hours.

There are two main problems in applying SIMS as an analytical tool. (a) What is the exact relation between the types and intensities of the emitted ion species on one hand and the surface composition on the other? (b) What are the changes in the surface zone during the sputtering process?

It is the intention of this work to point out the analytical possibilities of SIMS in monolayer analysis and surface reaction studies. In order to demonstrate the capacities and problems of this application, the following topics will be treated:

- ~ The ion solid surface interaction with emphasis on secondary ion emission and ion induced changes in the surface zone.

Secondary ion spectra of well defined surface structures.

The present status of theoretical understanding of secondary ion emission.

- The application to surface reaction studies demonstrated by some significant examples.

2. The ion surface interaction

2.1. General considerations

In the following the interaction of a single ion with a well defined surface structure will be treated in more detail. During the interaction of an ion with a solid surface, various elementary processes will occur. A rough calculation of relaxation times for these processes like ion penetration, lattice perturbation by impact cascades, etc., shows, that all these processes will happen in a time which is below 10^{-12} sec. For primary ion beam densities $< 10^{-6} \text{ A cm}^{-2}$ no interference of processes caused by different primary ions will occur - assuming a total cross section below $1000 \text{ \AA}^2$ for all interaction processes between the impinging primary ion and the surface. For that reason, in most cases the interaction of an ion with a solid surface may be treated as the collision between one single primary ion and the solid surface.

In fig. 1 some processes resulting in the emission of a heavy particle (atom or molecule) are presented. A primary particle may penetrate a certain distance into

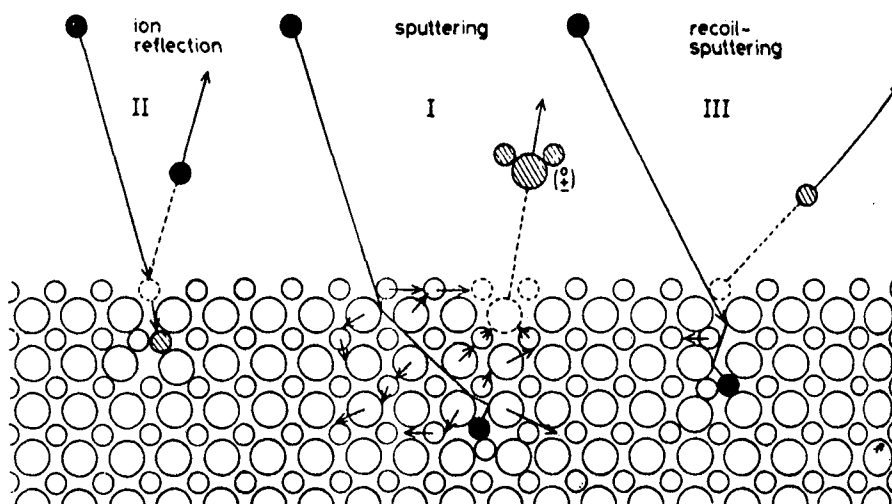


Fig. 1. Interaction processes of an ion with a solid surface resulting in the emission of heavy particles.

the surface zone, and will be trapped (ion implantation). During the penetration into the lattice, the energy of the particle is dissipated in the surrounding lattice zone. A small fraction of this energy can reach the surface with a momentum direction pointing out of the surface. This can result in the emission of a secondary particle, maybe atomic or molecular in a charged or uncharged state (I, sputtering). The interaction of a primary ion with a surface atom can also result in the reflection of the primary ion (II) [10,11]. A direct energy transfer process from the incoming primary ion to a surface atom in a single collision can also result in the emission of a surface particle with relatively high energy (III, recoil sputtering). The average energy of sputtered particles (I) is in the range of some eV for primary ion energies of some keV [12,13].

The results of ion impact on the target are to be divided into two groups (table 1): emission processes, and changes in the surface zone of the solid.

2. Emission processes

As a result of ion impact, atomic and molecular particles, electrons, and photons are emitted from the surface (table 1, fig. 1). The emitted atomic and molecular particles may be in a neutral or charged (secondary ions) state. They can be in the ground state or in an excited state. The atomic and molecular particles originate from an emission zone of some atomic layers. That is true especially for molecular ions, which cannot at all cover any distance in the lattice. Atomic ions or neutrals, especially those with high kinetic energy, may also come out of deeper layers.

Table 1
Effect of ion impact on a solid surface: emission processes and changes in the surface zone

Emission processes	Changes in the surface zone of the target
Atomic and molecular particles	Loss of surface particles
Neutrals	Sputtering
Positive ions	Recoil implantation
Negative ions	
Excited particles	Implantation
Electrons	Primary ions
Surface processes (Auger de-excitation, c.g.)	Surface atoms (recoil)
Bulk processes (ionization, c.g.)	Lattice destruction
Photons	Imperfections
Gas phase processes	Amorphization
Surface processes	Chemical effects
Bulk processes	Breaking of bonds
	Bond formation

The ion induced secondary electrons result from various surface processes like Auger de-excitation or Auger neutralization of impinging primary ions or emitted secondary particles. They also result from bulk processes like ionization and Auger transitions. The energy distribution of secondary electrons gives some important

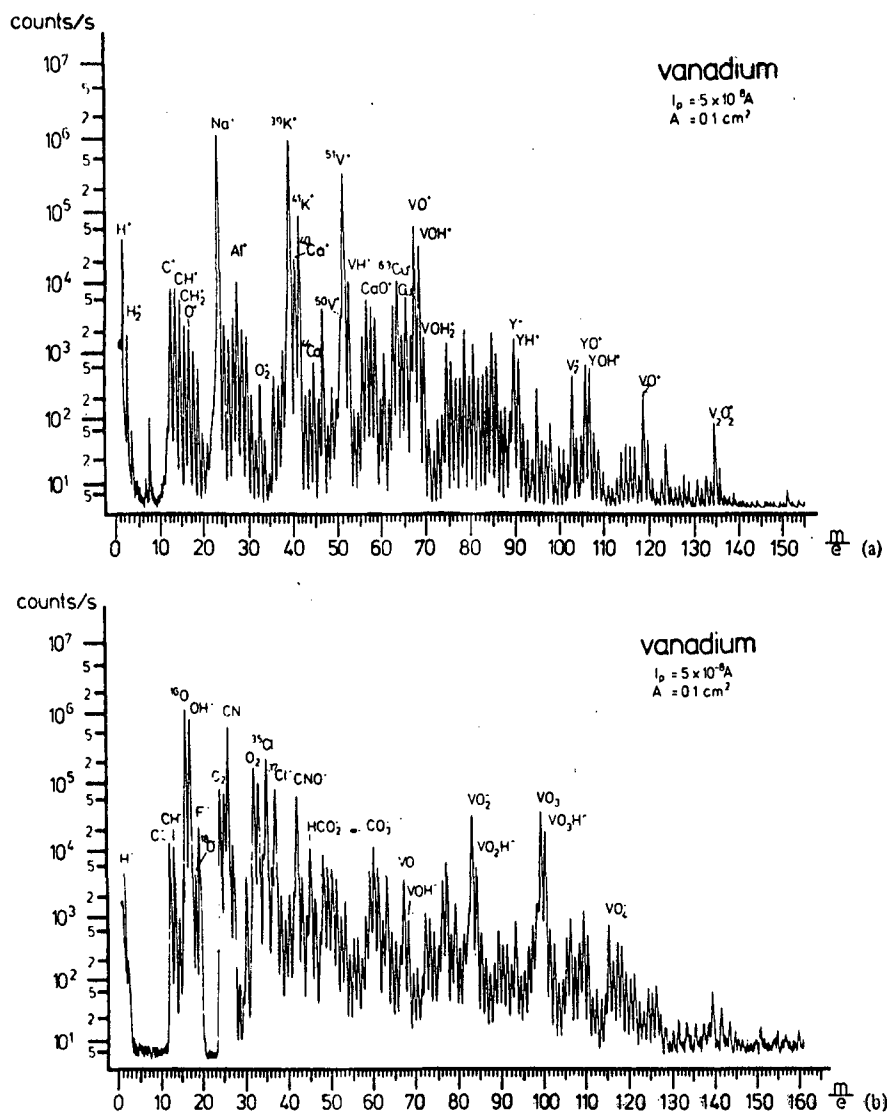


Fig. 2. Positive and negative secondary ion spectrum of a contaminated vanadium surface, logarithmic intensity scale. Bulk concentration of yttrium: $< 5 \times 10^{-4}$.

information on the elementary processes occurring during the ion bombardment of a surface and the emission of secondary ions [14].

The emitted photons are generated in front of the surface, in the surface area and in the bulk of the target [15,16]. Different processes as de-excitation and neutralization are responsible for the appearance of this emission. Ion induced photon emission carries important information concerning the emitting surface atoms, that means, the chemical composition of the surface.

2.3. Changes in the target

In SIMS the mass analysis of the emitted secondary ions gives the desired information on the chemical surface composition. But not only emission processes take place during ion bombardment (fig. 2). As a result of the energy transfer to the lattice near the surface, a certain region surrounding the point of impact of the primary ion, remains in a changed state (fig. 3). We can distinguish four different groups of surface changes:

- (a) Loss of surface atoms out of the emission zone as a consequence of the emission of atomic and molecular particles and recoil implantation.
- (b) Implantation of primary ions and recoil surface atoms.
- (c) Changes of the lattice structure as for example creation of imperfections, amorphisation, etc.
- (d) Chemical effects as breaking of bonds and bonds formation.

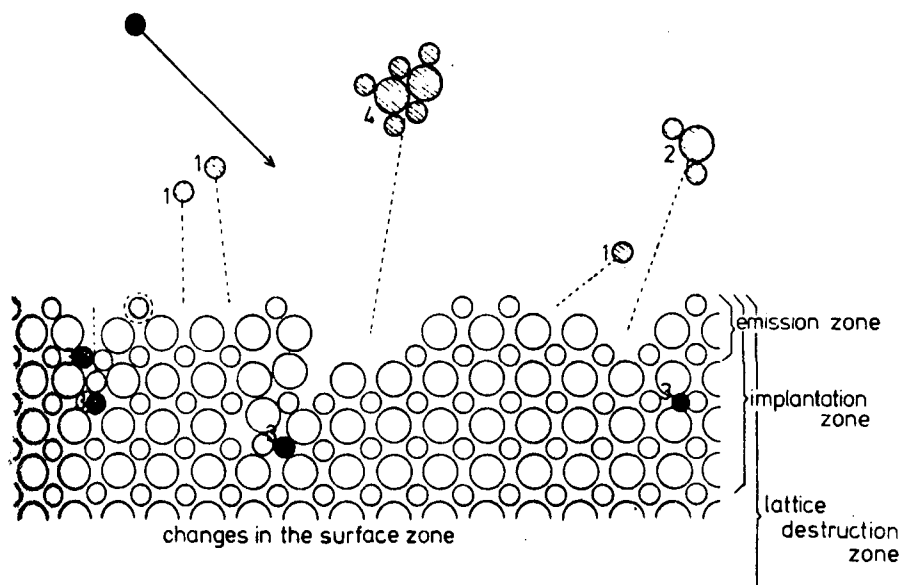


Fig. 3. Ion bombardment induced changes in the surface zone of a solid.

The chemical effects (d) are closely related to the lattice destruction (c).

In SIMS only one group of emission processes is used for the chemical analysis: the emission of positively and negatively charged atomic and molecular species. All other emission processes, as well as changes of the target are of no primary interest in SIMS but they must be considered very carefully because they give rise to many instrumental problems (especially the emission processes), and have a large influence on the secondary ion emission. That is true especially for the ion induced changes of the target in the case of high total primary ion dose density bombardment.

3. The secondary ion emission

3.1. General considerations

For the application of secondary ion emission as a surface analytical tool, we must know the relationship between the atomic and molecular composition of the probed surface on one hand (the so-called surface structure), and the emitted secondary ion species and their intensities on the other. The answer to this question may be given in two steps: Firstly we must get an idea of the ion species which are emitted from a given surface structure, secondly we must establish a quantitative relationship between the surface composition and the ion intensities.

3.2. Emitted ion species

In order to answer the question, what types of ions will be emitted from a given surface structure let us consider a simple two-component lattice (e.g. metal-oxygen, fig. 4). During the sputtering process, particles of this lattice will be emitted from the surface, single atoms as well as clusters. We suppose, that one condition for the formation of a cluster is that the cluster atoms are located on adjacent sites of the lattice before the emission [7]. That means, in the case of a metal oxygen lattice we can expect particles of the general composition: M_mO_n , or more general for a multi-component structure, secondary particles of the composition $A_mB_nO_o$ ($m, n, o = 0, 1, 2, \dots$). In this way we can establish a matrix of possible clusters. The formation probability of a special cluster is a complex function of many parameters as local arrangement, bond strengths and masses of the participating atoms, momentum transfer etc. Theoretical considerations result in a decreasing formation probability for clusters with many atoms. This is confirmed by experimental results [17].

What will be the charge state of an emitted cluster? In principle each possible cluster can be ejected as positively or negatively charged or neutral particle. But especially in the case of metal oxygen surface structures and anion complexes we have learned from the experimental results that for emitted particles a tendency

FRAGMENT FORMATION IN A TWO COMPONENT LATTICE

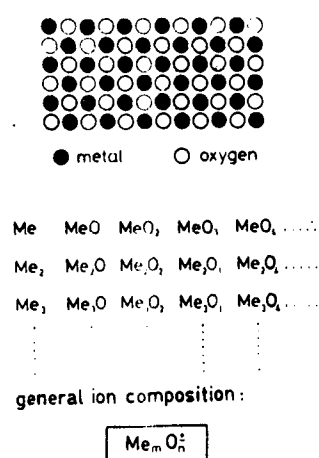


Fig. 4. Fragment in a two-component lattice.

exists for charge conservation related to the charge state in the lattice [7]. That means, for example, preferential emission of positive metal atoms Me^+ and negative oxygen atoms O^- from a metal oxygen structure, and an increasing tendency for MeO and MeO_2 to be emitted as positively charged particle with increasing oxygen concentration [7] which is equivalent to an increasing valence state of the metal atoms.

Figs. 5–7 present some typical SIMS spectra emitted from well defined surface structures composed of one kind of atoms (Si(111) at room temperature and 1275 K [19,20], fig. 5) two different kinds of atoms (silicon–oxygen surface structure [21], fig. 6) and three different kinds of atoms (mixed oxide: $\text{V}_2\text{O}_5 + \text{Fe}_2\text{O}_3$ [23], fig. 7).

Figs. 8 and 9 present spectra of more complicated surface structures: acetate complexes on copper [24] and 1- and 2-butanol adsorbed on molybdenum [25] respectively. Recently we succeeded in detecting high yield parent peak emission ($M+1$ and $M-1$) from arginine on silver.

3.3. Quantitative description of secondary ion emission

If one applies SIMS to quantitative surface analysis, secondary ion emission has to be treated quantitatively. We consider a surface partially covered by a certain surface structure, which gives rise to the ejection of secondary ions X_n ($n = 1, 2, 3, \dots$). The relative coverage of the surface with the parent structure corresponding to the ions X_n may be θ . We come to the following expression for the detected ion

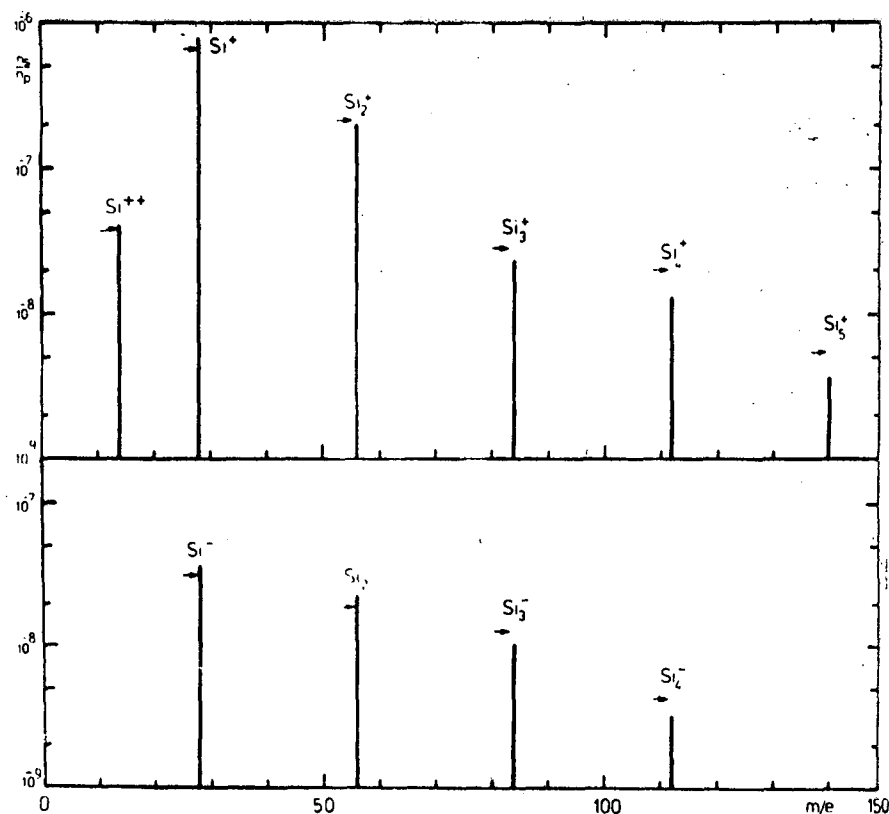


Fig. 5. Secondary ion spectrum of a surface structure composed of one atomic species: Si(111) at room temperature and 1275 K (arrows), $\text{Si}_{nm}^{\pm}$ emission [20].

current $I(X_n)$:

$$I(X_n) = A j_p \theta S(X_n) f, \quad (1)$$

where A is bombarded target area, j_p is primary ion current density, θ is relative coverage of the surface with the parent structure corresponding to X_n ($n = 1, 2, 3, \dots$), $S(X_n)$ is absolute secondary ion yield of X_n , which means:

$$S(X_n) = \frac{\text{number of emitted particles } X_n}{\text{number of impinging primary ions}}$$

for a surface completely covered with a parent structure corresponding to X_n ($n = 1, 2, 3, \dots$), and f is overall transmission of the secondary ion mass spectrometer,

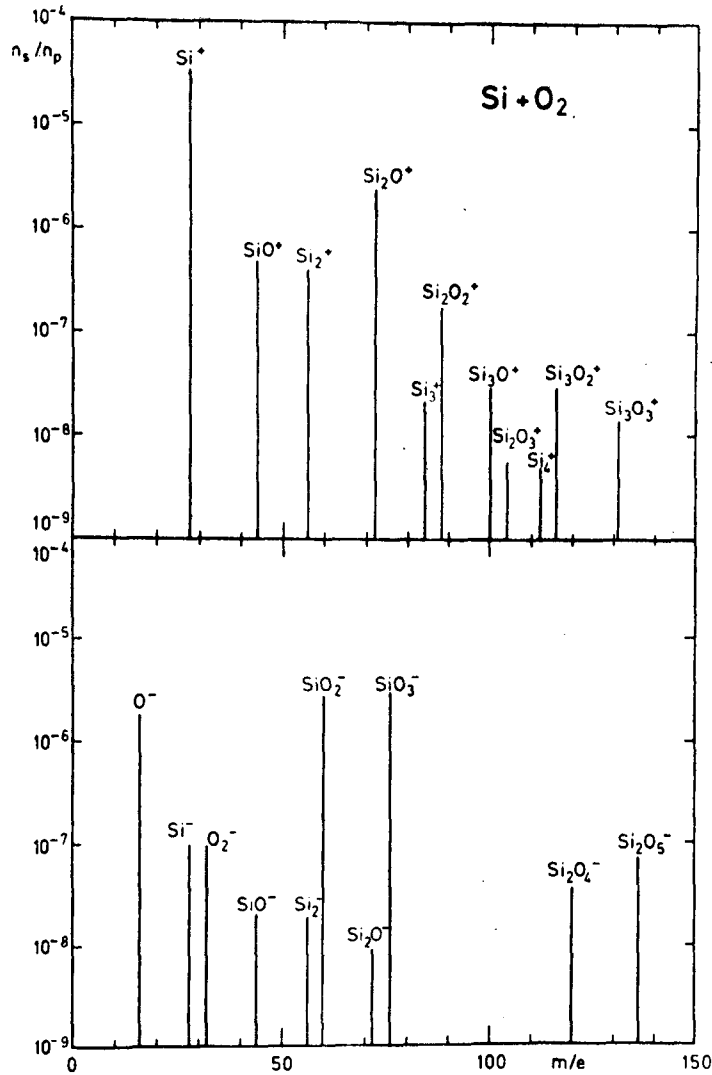


Fig. 6. Secondary ion spectrum of a surface structure composed of two atomic species: Si(111) + 10 L O₂, Si_mO_n[±] emission [21].

which means:

$$f = \frac{\text{number of detected particles } X_n}{\text{number of ejected particles } X_n \text{ from A}}$$

In order to get some feeling for the numerical values, the V⁺ emission from oxygen

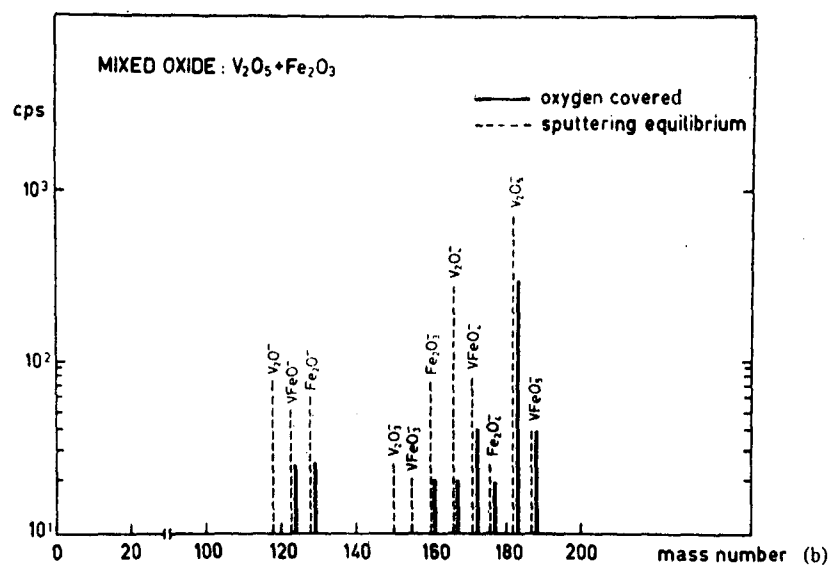
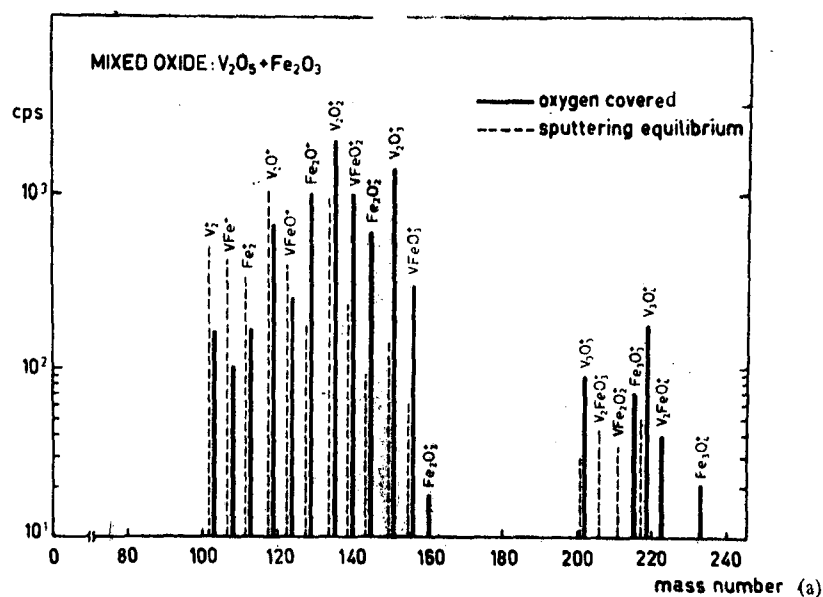


Fig. 7. Sections of the secondary ion spectrum of a surface structure composed of three atomic species: mixed oxide $V_2O_5 + Fe_2O_3$, $V_mFe_nO_m^+$ emission [23]. Full lines: sputtering equilibrium after prebombardment with 1.6×10^{16} ions/cm². Dashed lines: after subsequent 6×10^3 L. O_2 exposure, $i_p = 4 \times 10^{-8}$ A cm⁻².

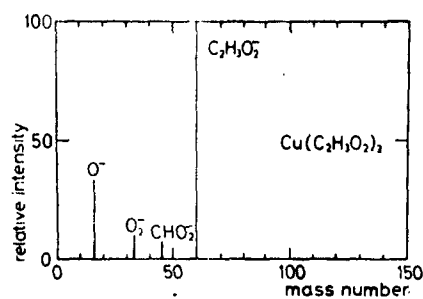


Fig. 8. Secondary ion spectrum of a surface radical: acetate complex on a copper surface [24].

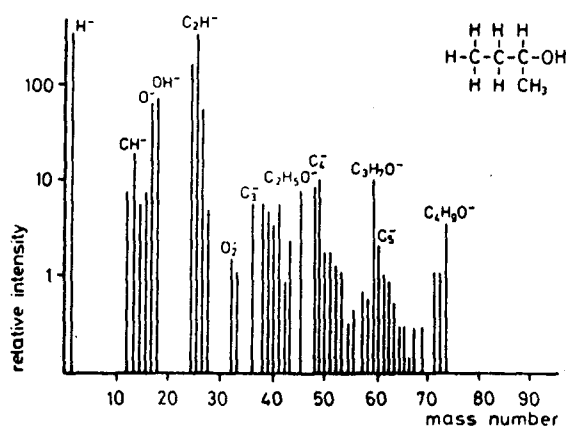
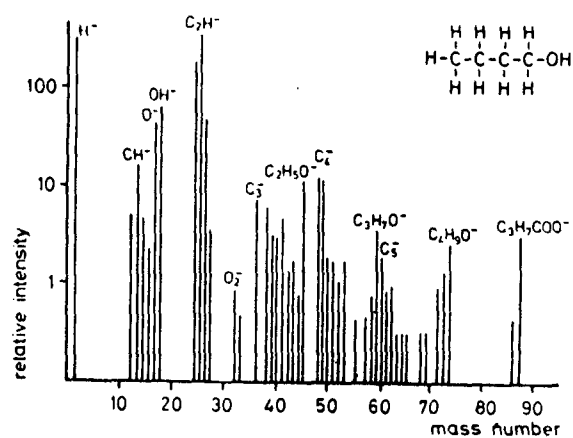


Fig. 9. Secondary ion spectrum of adsorbed molecules: 1- and 2-butanol on molybdenum. Surface oxidation to the corresponding acid is possible only for the secondary alcohol ($C_3H_7COO^-$ emission, upper spectrum) [25].

covered vanadium [26] may be considered. For a primary ion current density $j_p = 10^{-9} \text{ A cm}^{-2}$ on a target area $A = 0.1 \text{ cm}^2$ (under these bombardment conditions the average life time of a single monolayer is in the range of many hours) a detected secondary ion current $I(V^+) = 1.5 \times 10^{-15} \text{ A}$ results, if an overall transmission $f = 5 \times 10^{-5}$ for the spectrometer (which is a reasonable average value) and a secondary ion yield $S(V^+) = 0.3$ for an oxygen covered vanadium surface, bombarded with 2.5 keV Ar^+ ions is assumed. This detected ion current corresponds to a counting rate of about 10^4 cps.

Once the overall transmission of the secondary ion mass spectrometer is known, the absolute ion yield $S(X_n)$ can be calculated from the primary ion intensity $I_p = j_p A$ and the detected secondary ion intensities $I(X_n)$. In table 2 the absolute ion yields $S(\text{Me}^+)$ for 17 cleaned (by ion bombardment) and oxygen covered elements are listed. $S(\text{Me}^+)$ is in the range of 10^{-4} for clean surface and rises by about 3 orders of magnitude, if we pass to the oxygen covered element. Besides Me^+ and O^- also other ions of the general composition $\text{Me}_m \text{O}_n^+$ are emitted from an oxygen metal surface structure. Some of the appropriate yields are tabulated in table 3.

Table 2
Absolute secondary ion yields $S(\text{Me}^+)$ for clean and oxygen covered surfaces

Metal	$S(\text{Me}^+)$ Clean surface	$S(\text{Me}^+)$ oxygen covered surface
Mg	0.01	0.9
Al	0.007	0.7
Ti	0.0013	0.4
V	0.001	0.3
Cr	0.0012	1.2
Mn	0.0006	0.3
Fe	0.0015	0.35
Ni	0.0006	0.045
Cu	0.0003	0.007
Sr	0.0002	0.16
Nb	0.0006	0.05
Mo	0.00065	0.4
Ba	0.0002	0.03
Ta	0.00007	0.02
W	0.00009	0.035
Si	0.0084	0.58
Ge	0.0044	0.02

Table 3
Yields of oxide-specific secondary ions MeO_n^+ for 17 oxidized elements

Metal	Me^+	MeO^+	MeO_2^+	MeO^-	MeO_2^-	MeO_3^-	MeO_4^-
Mg	0.9	0.0015	—	0.01	0.0025	—	—
Al	0.7	0.0006	—	0.02	0.02	—	—
Ti	0.4	0.5	0.007	—	0.008	0.018	—
V	0.3	0.6	0.01	0.0001	0.002	0.01	0.0001
Cr	1.2	0.2	0.0025	0.00025	0.018	0.07	0.006
Mn	0.3	0.007	—	0.004	0.03	0.004	—
Fe	0.35	0.014	—	0.0007	0.0085	0.0035	—
Ni	0.045	—	—	0.007	0.06	—	—
Cu	0.007	—	—	0.0015	0.015	—	—
Sr	0.16	0.035	—	0.013	0.006	—	—
Nb	0.05	0.3	0.06	—	0.0008	0.02	—
Mo	0.4	0.3	0.017	—	0.0014	0.085	0.014
Ba	0.03	0.017	—	0.0009	0.007	—	—
La	0.002	0.02	0.005	—	0.001	0.008	0.0002
W	0.035	0.15	0.012	—	0.0012	0.13	0.01
Si	0.58	0.011	—	0.00038	0.058	0.058	—
Ce	0.02	0.0012	—	0.00081	0.045	0.0081	—

3.4. State of the theoretical treatment of secondary ion emission

For a more quantitative application of SIMS to surface and bulk analysis one should be able to calculate the yields $S(X_n)$ of the different ion species X_n emitted from a well defined surface structure. At the moment there exist some more or less empirical formulas for the calculation of ion yields $S(X_n)$ or ionization coefficients $\beta^+(X_n)$, especially for positively charged metal ions ($X_n = \text{Me}^+$). But in no case it is possible to make the calculation without fitting parameters.

One can disentangle the extremely complex process of secondary ion emission into three steps between four different states of the emitting surface area (fig. 10): the energy transfer to a surface region of the bombarded solid, the formation of an "excited" cluster (or single atom) "in" the solid surface, and the separation of this cluster (or atom) from the surface. During the separation of the excited particle electron exchanges between the particle and the solid resulting in ionization or neutralization can happen. For this 3-step process we have to distinguish four different states of the surface:

- (a) Initial state: the undisturbed arrangement of the surface atoms.
- (b) Virtual state: the impact cascade energy had been transferred to a number of

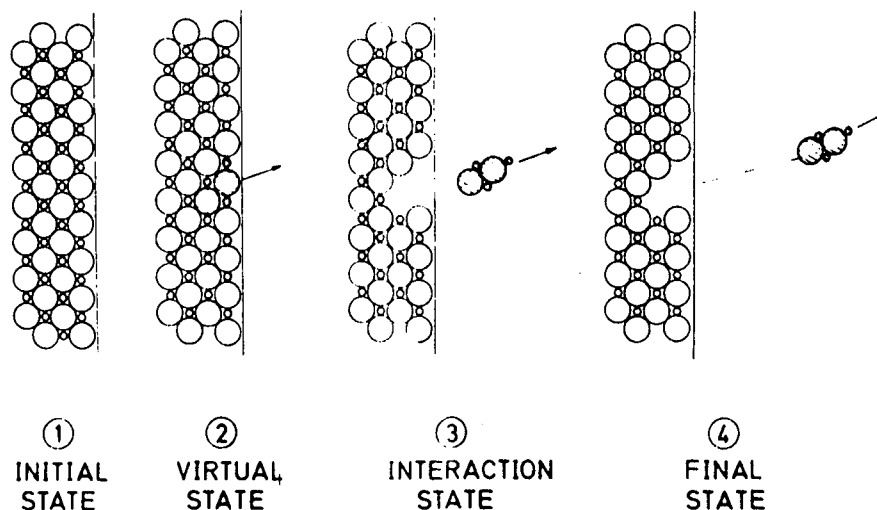


Fig. 10. Formation and emission of a cluster ion in a 3-step process, different states of the emission area.

surface atoms. These atoms constitute a virtual cluster, still incorporated in the lattice. The cluster has a charge equal to the sum of charges of the incorporated atoms.

(c) Interaction state: the emitted particle is separated a small distance ($\text{\AA}$ -range) from the surface. The charge state of the particle is not yet fixed. There exists a strong electronic interaction between the solid and the secondary particle, which may result in changes of the charge state of the particle being emitted.

(d) Final state: the emitted particle is a long distance from the emitting surface. No further interaction between the ion, for example, and the surface is possible. The emission area remains damaged.

Although we have no satisfying theoretical treatment of this ion emission process at the moment, there exist some descriptions of the ionization probability β which show - at least in one case [27] - an astonishing high agreement with experimental data. All these treatments are based on more or less reasonable assumptions, but in all cases fitting parameters have to be introduced.

Andersen [27] postulates a plasma in the bombarded area and an equilibrium between the neutral and charged atomic particles on the one hand and the electrons on the other. Starting with the Saha-Eggert equation he derived the following expression for the ionization coefficient $\beta(\text{Me}^+)$, e.g.:

$$\beta(\text{Me}^+) = \frac{(2\pi m_e kT)^{3/2}}{n_e} \frac{2B^+(T)}{B^0(T)} \exp\left(-\frac{I + \Delta E(n_e, T)}{kT}\right) \quad (2)$$

where $\beta(\text{Me}^+)$ is ionization probability for Me^+ ,

$$\beta(\text{Me}^+) = \frac{\text{number of emitted Me}^+}{\text{number of all emitted Me}^0}$$

m_e is electron mass, n_e is electron concentration in the plasma, T is plasma temperature, $B^{0,+}$ are partition functions for neutral Me^0 atoms and Me^+ ions respectively, I is ionization energy for the atom Me^0 , and ΔE is reduction in the ionization energy I due to the plasma.

Here fitting parameters are n_e and the electron temperature T . The fitted values of T vary between 5000 and 15000 K. The model is highly successful in calculating the elemental composition of solids from the corresponding positive atomic ion emission.

Schroeer [28] assumes in his quantum mechanical model that the sputtered atoms leave the surface in a neutral, unexcited state and are subsequently ionized by a quantum-mechanical transition of the atoms' valence electrons to the top of the conduction band of the metal. The ionization probability is calculated using the adiabatic approximation, giving

$$\beta(\text{Me}^+) = [A/(I - \phi)]^2 [\hbar v/a(I - \phi)]^n, \quad (3)$$

where A is surface binding energy of the sputtered atom, ϕ is work function, v is velocity of the sputtered atom, and n (~ 2.5) and a (~ 1.5 Å) are fitting parameters. This model has been tested with reasonable success by bombarding pure metals with 12 keV Ar^+ ions.

The emission models of Andersen and Schroeer as well as some further models [29–31], not treated here in more detail, mainly describe the emission of metal ions Me^+ . It is apparent from table 3, however, that also many oxygen containing ion species Me_mO_n^+ are emitted with high intensities from a metal oxygen lattice. Starting with the experimental results listed in table 3 we have established the following empirical formula for the description of secondary ion yields $S(\text{Me}_1\text{O}_n^+)$ [18]:

$$S = S(K, q, m) = S_0 M(m, q) \exp\{- (G^0 - K - \alpha q)^2 / 2\gamma^2\}. \quad (4)$$

Independent variables are: K , fragment valence; $q = \pm 1$, fragment charge; and m , mass number of the metal ions.

Mass functions are: $M(m, +1) = (m/m_0)^{-n}$, and $M(m, -1) = 1$.

Material constants are: G^0 , lattice valence, and α , displacement parameter (see fig. 11).

Universal constants are: $S_0 = 2.4 \times 10^{-2}$, $\gamma = 0.98$, $m_0 = 235$, $n = 2.4$.

Most important quantities in this formula are the fragment valence K , which is the formal valence of the metal atom in an emitted secondary ion, assuming that the oxygen atom carries always two negative charges, and the lattice valence G^0 ,

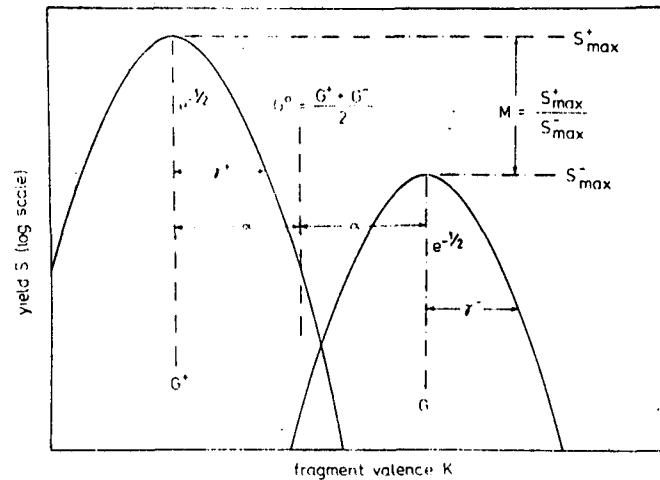


Fig. 11. Representation of parameters [18].

equal to the average valence of the metal atoms in the metal oxygen structure of the lattice. Fig. 12 presents the application of this formula to the emission of CrO_n^+ species from a chromium surface exposed to 100 L O_2 . The experimental values fit very well with the description by the formula represented by two Gaussian distributions (parabolas in the logarithmic scale).

3.5. Static method of SIMS [8,9]

Applying SIMS to the investigation of individual monolayers and surface reactions, we have to consider in more detail the sputtering of a single monolayer. If we start at $t = 0$ with a relative surface coverage of $\theta(0)$ by the interesting surface component, giving rise to the emission of secondary ions X_n , we come to the following expression for the coverage $\theta(t)$ at time t :

$$\theta(t) = \theta(0) \exp(-t/\tau), \quad \tau = \vartheta_0 / \gamma S, \quad (5)$$

where ϑ_0 is number of particles per cm^2 in a closed monolayer, γ is primary ion flux density (number of impinging primary ions on 1 cm^2 in 1 sec), S is total sputtering yield for the surface layer, and τ is average life time of one monolayer.

From this and eq. (1) we come to the expression for the detected secondary ion intensity $I(X_n, t)$ during sputtering of a single monolayer:

$$I(X_n, t) = A j_p S(X_n) f \theta(0) \exp(-t/\tau). \quad (6)$$

This time dependence was found in numerous experimental monolayer investigations [6,8,9]. A similar, but more complicated relationship describes the situation in the case of multilayer sputtering.

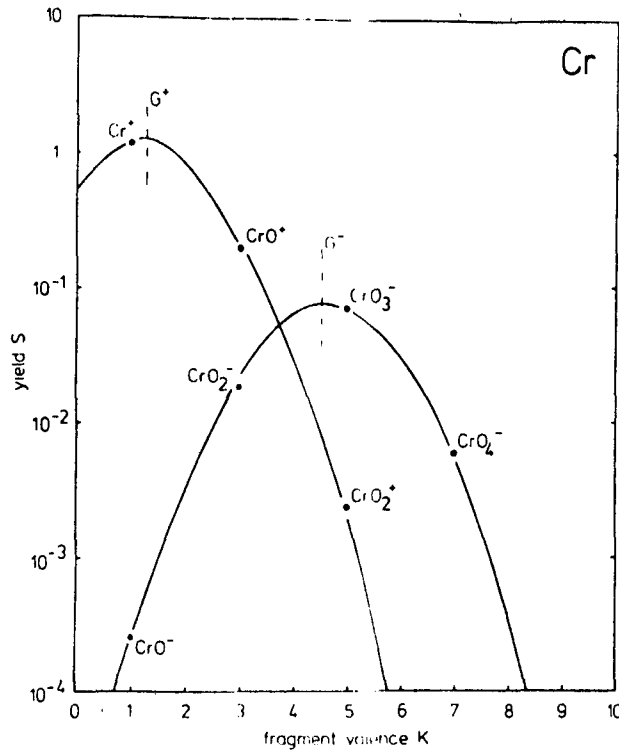


Fig. 12. Valence model: application to $\text{CrO}_n^\pm$ emission [7,18].

If we want to investigate, for example, a surface reaction on a solid without any disturbance of the reaction itself by the ion bombardment, we must choose a monolayer life time τ which is long compared with the time of ion bombardment during the investigation. That means we have to lower the primary ion current density to an extremely low value, and in order to compensate this effect, we have to bombard a large target area A . We call this technique, in which the average life time of a single monolayer is in the order of many hours (sometimes in the order of days) the static method of secondary ion mass spectroscopy.

For the detection limit of a given component in a single monolayer we find values between 10 and 0.01 ppm of one monolayer, corresponding to characteristic secondary ion yields between 1 and 10^{-3} .

3.6. Changes in the surface composition and structure by impinging ions

The condition of static SIMS is characterized as follows. The sputtering cross section σ_s describes the average sputtering effect due to one primary ion. It is re-

lated to the total sputtering yield S and the number of particles in 1 cm^2 of a closed monolayer ϑ_0 by $\sigma_s = S/\vartheta_0$. The sputtering areas σ_s are distributed statistically over the surface. Their average distance has to guarantee a sufficient low probability of overlapping each other during one experiment.

But it is not only the sputtering loss of particles which changes the surface during ion bombardment. A larger area can be perturbed by changes in the geometrical arrangement of surface atoms by bombardment induced chemical reactions or desorption and adsorption processes (see fig. 23 e.g.) etc. The surface area perturbed by all these effects (including particle loss by sputtering and recoil implantation) may be described by σ_p (in general $\sigma_s < \sigma_p$). We come to the more precise condition for static SIMS:

$$v\sigma_p \ll 1. \quad (7)$$

Regarding the effects of ion bombardment of a solid surface it is useful to distinguish "first order effects" and "second order effects" (fig. 13).

First order effects are due to changes of the surface area near the point of impact of each impinging primary ion. In principle these first order effects are inevitable. For a straightforward interpretation of secondary ion emission in static SIMS an important question arises: to what degree are the structure and composition of the emission area changed by the impinging ion, before the secondary ion, generated by this same primary ion, is ejected? No definitive answer can yet be given to this question. Some help may come from computer simulation of low energy impact cascades in solids [32].

Second order effects occur if a secondary ion is ejected from a surface area already changed by the preceding ion bombardment. They are the result of the previous ion bombardment induced changes of the surface. They can be avoided applying static SIMS: during the same experiment the perturbed zone will not be probed by another primary ion. In static SIMS virtually only first order effects are

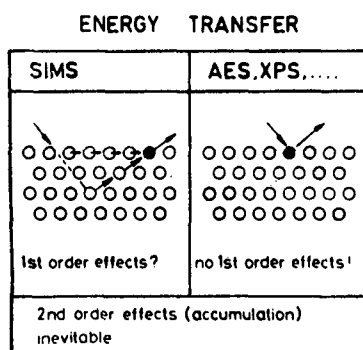


Fig. 13. First and second order effects in static SIMS and AES.

to be expected. In dynamic SIMS (high primary ion current densities, removal of numerous monolayers), however, second order effects are inevitable. It is an astonishing experimental result that in dynamic SIMS many complex molecular secondary ions are also emitted with high yields, (e.g., parent peaks of alcohols and amino acids).

First order effects are typical of SIMS and the flash filament technique, e.g. They do not exist for most of the other techniques of surface analysis, as for instance AES or ESCA. These two groups of surface analysis techniques are different with regard to the energy transfer from the exciting particle to the emitted particle which carries the information concerning the emitting surface zone. In AES, for example, the time between energy transfer to the excited atom and the ejection of the Auger electron is so short that no change in the geometrical arrangement of surface atoms, in their binding state etc., can take place.

In SIMS the energy of a single impinging ion is spread over a region surrounding the point of impact. Only a small fraction of this energy is responsible for the emission of the secondary particle. In principle, the arrival of a side-cascade at the particle to be emitted before the main cascade responsible for the emission cannot be excluded (fig. 13).

Second order effects are to be expected for all methods of surface analysis without any exception.

4. Application in surface reaction investigations

Today secondary ion emission is widely employed in bulk analysis, profiling and in imaging techniques [3–6]. A very promising, more recent application is the investigation of surface reactions by the static method [6]. Compared with other surface analysis techniques as AES or ESCA, e.g., static SIMS has some unique capacities as,

- detection of all elements including hydrogen (important for the detection of hydrocarbons),
- detection of chemical compounds,
 - extremely high sensitivity for many elements and compounds,
- isotope sensitivity,
- "lateral resolution" in the range of atomic distances, due to the emission of cluster ions.

These capacities will be demonstrated by some significant results of surface reaction studies recently obtained in our laboratory.

In surface reaction studies, the change in chemical composition of a surface has to be determined with a negligible influence of the analytical technique on the reaction itself. The changes in the surface zone may result from gas exposure, heating, ion, electron or photon bombardment etc. There exist different ways to get information on these surface processes by SIMS:

- The static secondary ion spectra gives information on the surface composition and the short range order of surface atoms (by cluster ions) at any stage of the reaction.
- The thickness and composition of surface layers resulting from the surface reaction, can be determined by controlled sputtering.
- Different surface binding states of the same component (hydrogen or oxygen atoms, e.g.) and exchanges between these states can be studied by isotope technique.

4.1. Surface reactions of vanadium

In our laboratory we have carefully studied the secondary ion emission of V_2O_5 [23] and the interaction of O_2 [26] and $(H_2 + O_2)$ [33] with a clean polycrystalline vanadium surface at room temperature. The secondary ion yields $S(V_m O_n^+)$ of an oxygen saturated surface (oxygen dose $D > 100$ L) are very similar to that of the compact V_2O_5 , thus indicating the formation of an oxide layer on vanadium at room temperature. In addition two electron sensitive oxygen states, called β_1 and β_2 according to the succession of their thermal desorption (O_e^+ in fig. 14), could be detected. Their desorption cross section was found to be 10^{-16} and $< 10^{-19}$ cm² respectively, for 250 eV electrons. The β_1 -state is closely correlated with the emission of VO_3^- , VO^+ and VO_2^+ , whereas no direct correlation exists between the emission of VO^- and VO_2^- and the β_2 -state. This β_2 -state seems to correspond to single oxygen atoms bound to single vanadium atoms.

The relative changes of the most intense secondary ions VO_n^+ during O_2 exposure are presented in fig. 15 [26]. The complex behaviour of the O_2 dose dependences for different ions can be described in a qualitative manner by the valence model, assuming an increase of G^0 during oxygen enrichment of the surface. This increase in G^0 results in corresponding shifts of the two Gauss curves describing the changes in positive and negative secondary ion emission (fig. 16). This model describes also

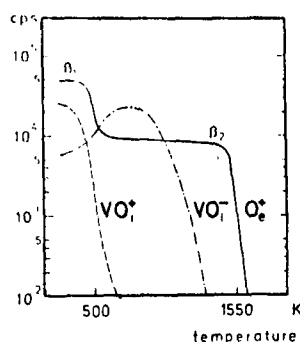


Fig. 14. Change of electron (O_e^+) and ion (VO_1^- , VO_1^+) induced ion emission from an oxygen covered (100 L O_2 exposure) vanadium surface. Temperature increase: 15 K s^{-1} [26].

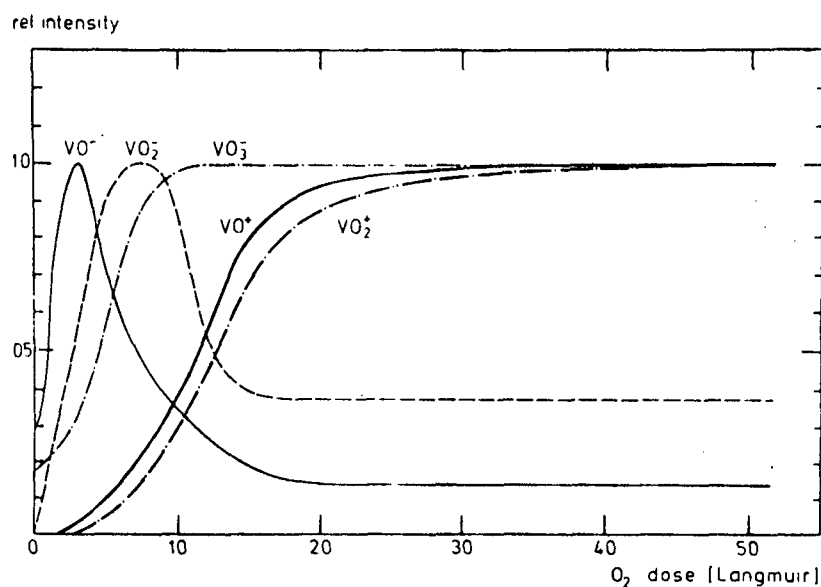


Fig. 15. Change of secondary ion emission during O_2 exposure of a clean vanadium surface [26].

the changes in secondary ion emission during a controlled oxygen removal by selective sputtering (fig. 17) [26].

Applying an isotope technique, it is possible to get additional information on the mechanism of surface reactions. This can also be demonstrated by the vanadium oxygen interaction.

For an O_2 exposure exceeding 100 L no further change in secondary ion emission takes place (fig. 15) [26]. Apparently the oxygen concentration in the uppermost monolayer remains constant. If we now change from $^{18}O_2$ to $^{16}O_2$ (fig. 18) the emission of $V^{18}O^-$, e.g., decreases whereas the emission of $V^{16}O^-$ increases in

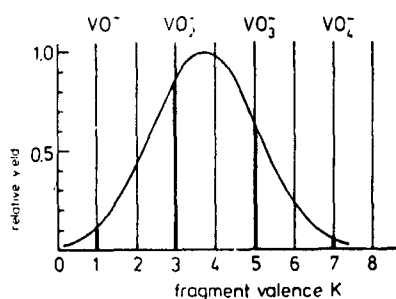


Fig. 16. Valence model: change of secondary ion yields during change of O^- (oxygen surface concentration) [26].

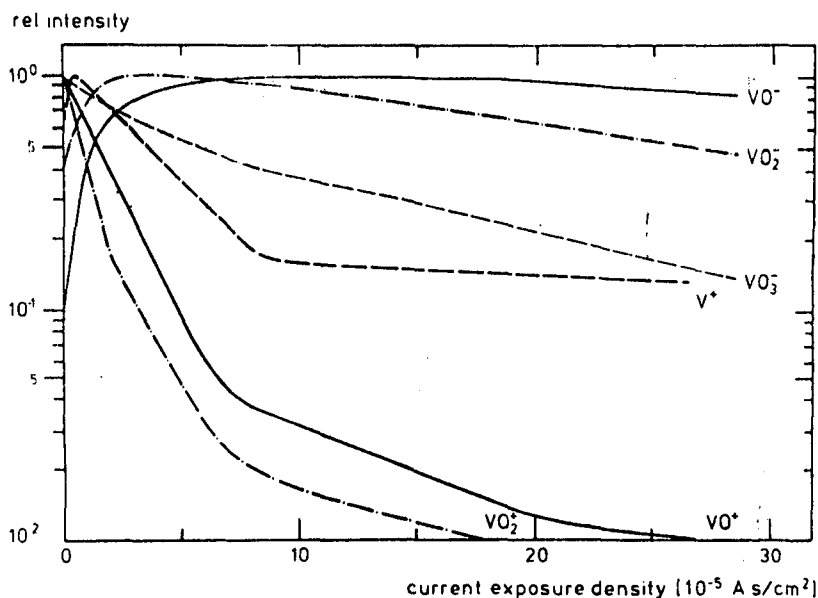


Fig. 17. Change of secondary ion emission during sputtering of an "oxide layer" on vanadium generated by 100 L O_2 exposure of a clean vanadium surface [26].

such a manner, that the sum of the VO^- intensities remains constant. Obviously a further oxygen incorporation into the "saturated" surface occurs. The replaced surface oxygen may desorb or penetrate deeper into the lattice. A more detailed evaluation of the experimental results of figs. 17–19 makes evident, that at least a fraction penetrates into the lattice, resulting in an increase of oxide layer thickness [26].

Figs. 20 and 21 give some results of the investigation of a 3-component reaction between a vanadium surface, oxygen and hydrogen [33]. If an oxygen covered vanadium surface is exposed to H_2 , secondary ions typical of an oxidized surface will be emitted (fig. 20). In addition hydrogen containing cluster ions are emitted, indicating the presence of H_2O (H_2O^+ , $O_2H_2^+$, VOH_2^+ , etc.) and OH groups (OH^- , VOH^+ , etc.) on the surface. If the succession of gas exposure is changed (fig. 21), a completely different spectrum will appear. Obviously the concentration of H_2O on the surface is decreased drastically. By a more detailed evaluation of the experimental results, it is possible to distinguish OH groups, adsorbed H_2O and V–H bonds.

4.2. Surface reactions of Si(111) [34,35]

Some results of surface reaction studies for a single crystal surface are presented in figs. 22–24 [35]. During O_2 exposure of a Si(111) surface at room temperature

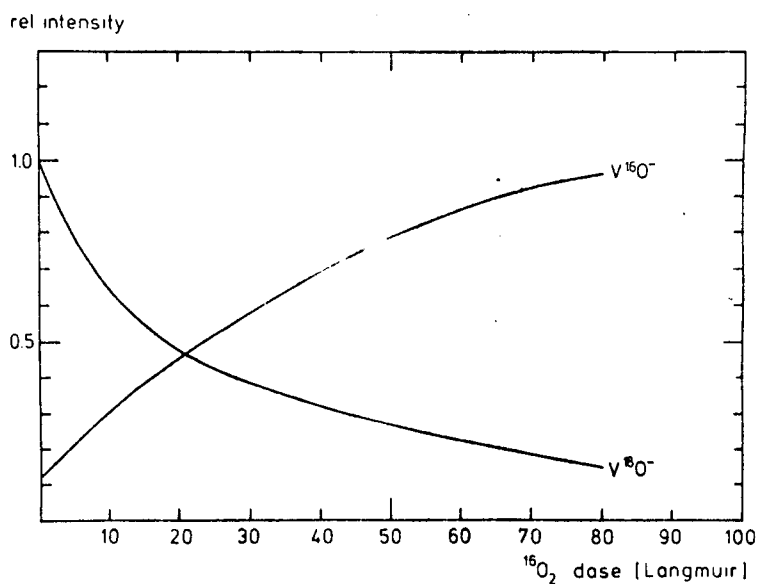


Fig. 18. Investigation of surface reactions by SIMS isotope technique: changes of VO^+ emission from a vanadium surface exposed to 100 L $^{18}\text{O}_2$ as a function of subsequent $^{16}\text{O}_2$ exposure [26].

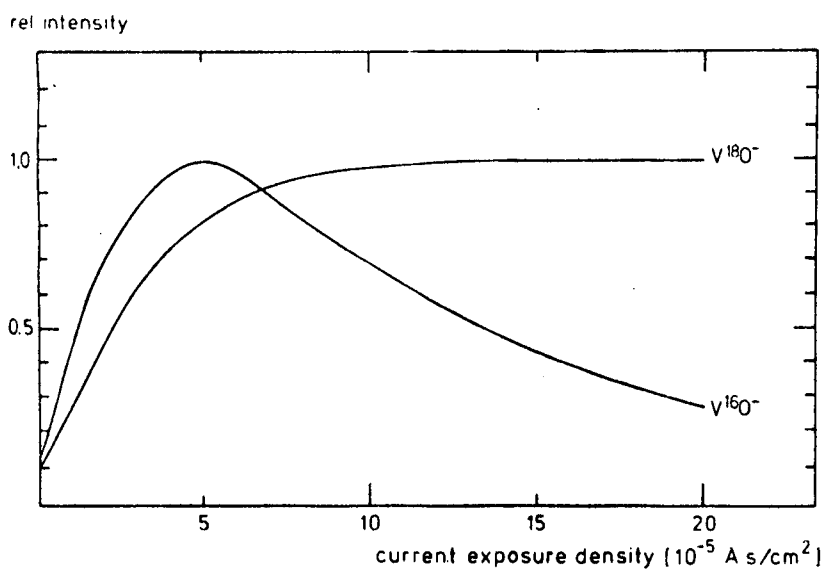


Fig. 19. Investigation of surface reactions by SIMS isotope technique: Changes of VO^+ emission during sputtering of an oxide layer formed by successive exposure of 100 L $^{18}\text{O}_2$ and 100 L $^{16}\text{O}_2$ to a clean vanadium surface [26].

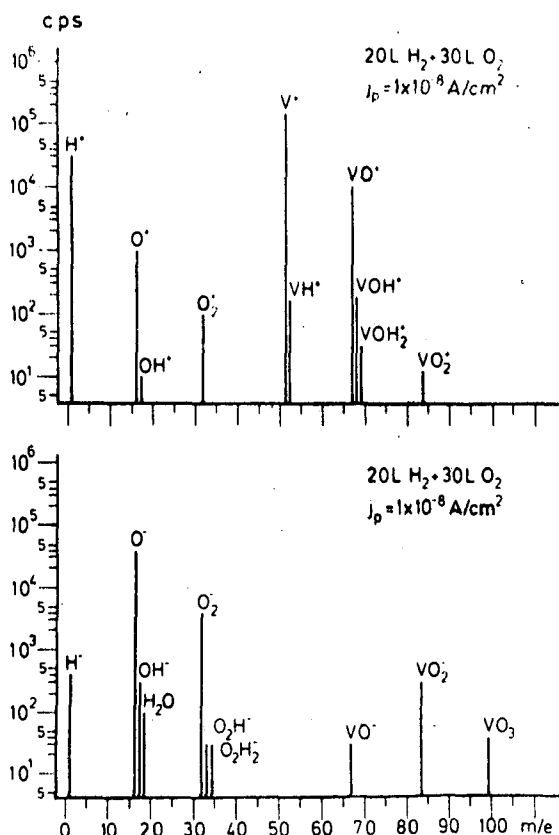


Fig. 20. 3-component surface reaction: secondary ion emission from a vanadium surface after 20 L H₂ exposure, followed by 30 L O₂ exposure. Surface oxidation of vanadium is indicated by VO_n⁺ emission [33].

one observes a rapid increase of SiO₂⁻ emission, accompanied by a slower increase in Si₂O₄₍₅₎⁻ (fig. 22). This and other experimental results can be explained assuming an initial formation of small oxide islands (responsible for the early SiO₂⁻ emission) which grow together to large oxide islands and finally to a closed monolayer (responsible for the delayed Si₂O₄₍₅₎⁻ emission) during further oxygen incorporation; This model is confirmed by the results of fig. 23. During heating up to 500°C of the Si(111) surface preexposed to different O₂ doses, the intensity of SiO₂⁻ decreases whereas the intensity of Si₂O₄₍₅₎⁻ increases without any additional O₂ exposure. Obviously a conglomeration of small islands to large islands takes place during heating.

Fig. 24 [36] finally represents the secondary ion spectra of a Si(111) surface

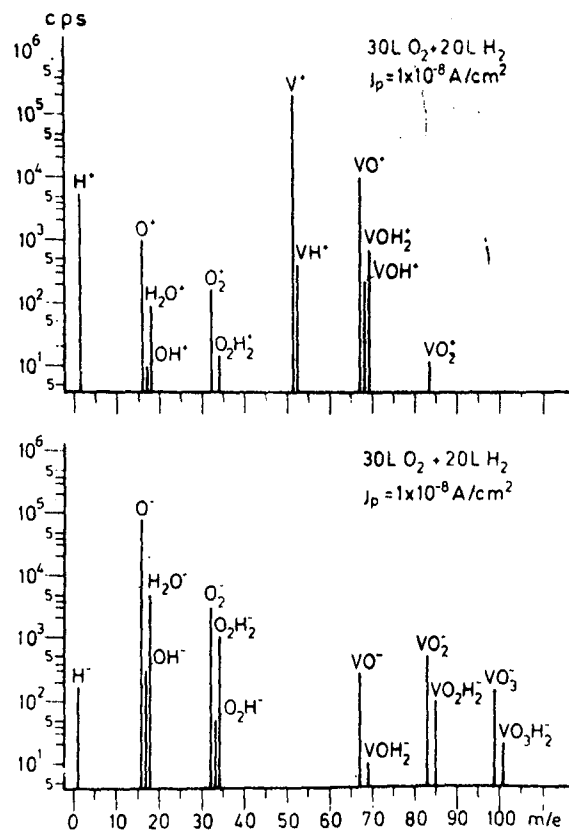


Fig. 21. Three-component surface reaction: secondary ion emission from a vanadium surface after 30 L O₂ exposure followed by 20 L H₂ exposure. In addition to an oxide formation H₂O formation on the surface is indicated [33].

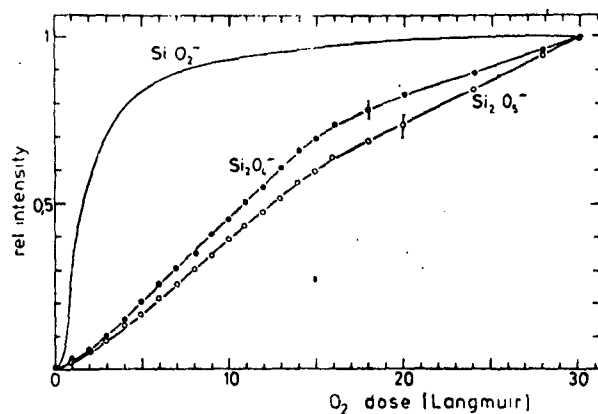


Fig. 22. Increase of SiO₂⁻ and Si₂O₅(4)⁻ intensities during O₂ exposure of a clean annealed Si(111) surface [19].

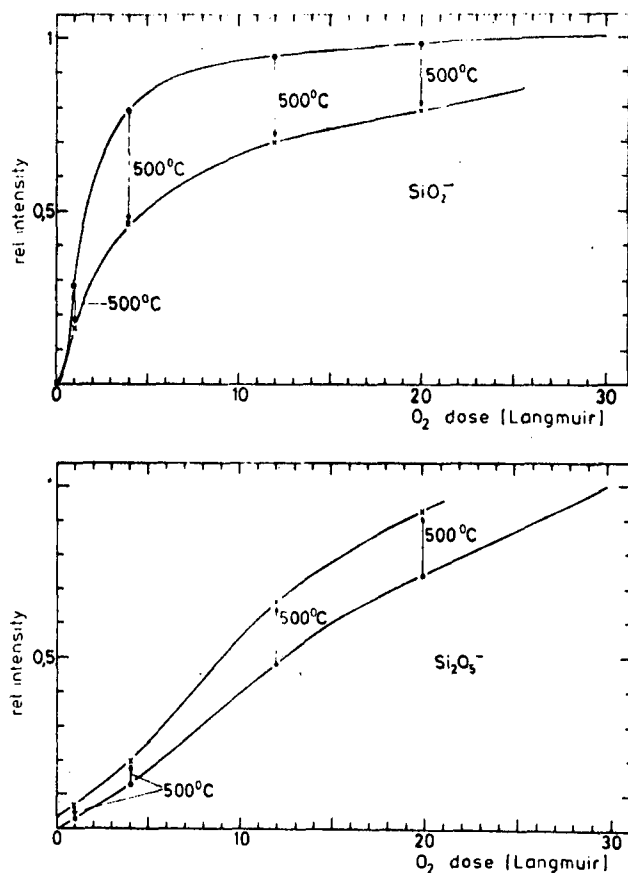


Fig. 23. Change of surface oxide structure during heating of an oxygen covered Si(111) surface. As the O₂ exposed surface is heated to 500 K the intensity of SiO₂⁻ decreases, the Si₂O₅⁻ yield increases simultaneously as indicated by the arrows [19].

after H₂O exposure of 100 L. This interaction apparently does not result in a considerable oxidation of the surface. This becomes evident by the weak Si⁺ emission. A surface structure is generated which gives rise to the emission of secondary ions of the general composition Si_mO_nH_o[±]. A more detailed examination of the Si(111)-O₂ reaction indicates a strong dependence of ion bombardment during the H₂O exposure. All secondary ion intensities increase considerably if during water exposure the surface is ion bombarded. This may be regarded as an impressive example for ion bombardment induced surface reactions. It reveals the importance of extremely weak primary ion current densities for the investigation of surface reactions.

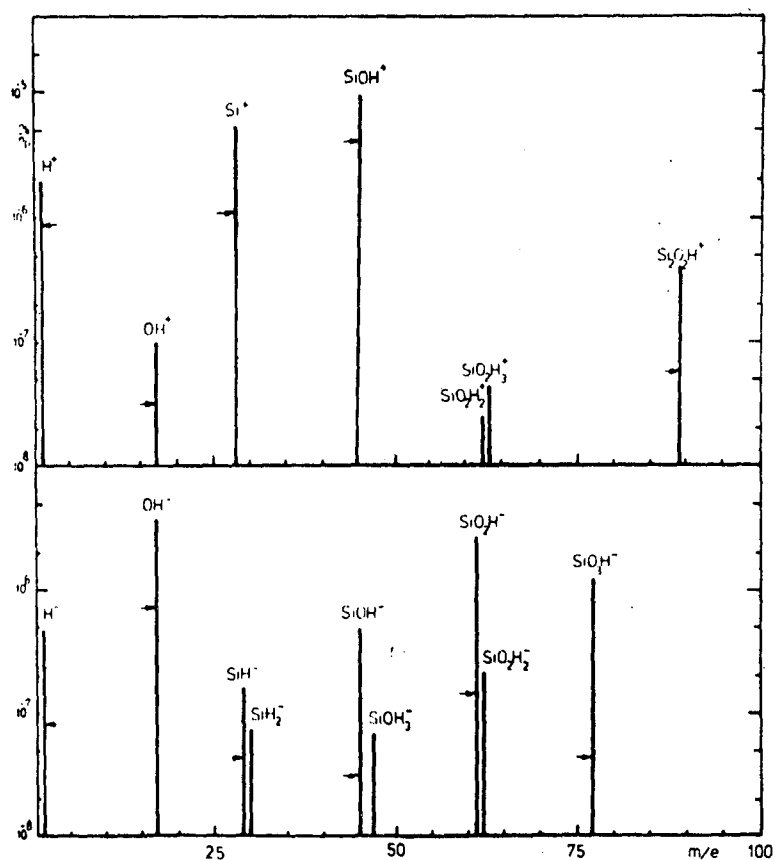


Fig. 24. Ion bombardment induced surface effects: secondary ion spectrum of Si(111) after 100 L H_2O exposure during simultaneous ion bombardment (total lines) and without simultaneous ion bombardment (arrows) [20].

5. Further developments

Whereas to-day secondary ion mass spectroscopy is a well established technique for bulk analysis, thin film analysis, and surface imaging, its application to monolayer analysis and surface reaction investigations however is at a very early stage. Due to some unique features as hydrogen sensitivity, compound detection, isotope separation, and a high absolute sensitivity static SIMS is expected to get an increasing importance in this new field of application.

Central topics of future developments are:

- (a) Evaluation of more detailed models for the surface near ion-lattice interaction in the low energy range, including lattice perturbations, cluster formations, chemical effects and ion emission processes.

Table 4

Main features of static SIMS as a technique for surface reaction studies and monolayer analysis

Positive:	- Information depth in the "monolayer range" - Detection of all elements including hydrogen - Detection of chemical compounds - "Lateral resolution" in the range of atomic distances - Isotope separation - Extremely high sensitivity for many elements and compounds ($<10^{-6}$ monolayers) - Quantitative analysis after calibration - Negligible destruction of the surface
Negative:	- Large differences in sensitivity for different "surface structures" (factor 1000) - Problems in quantitative interpretation of molecular spectra - Ion induced surface reactions

- (b) Further development of simple emission models especially for molecular ions, with regard to practical application.
- (c) Systematic determination of static secondary ion spectra of further well defined surface structures, in order to prove models and theoretical considerations.
- (d) Development of high transmission instruments ($f > 10^{-4}$) capable of detecting all masses simultaneously, in order to lower the minimum primary ion dose densities in static SIMS experiments.
- (e) Application of high resolution instruments in organic hydrocarbide surface studies.
- (f) Development of easy to operate combined instruments. The electron spectroscopical methods of surface analysis on one hand and secondary ion mass spectroscopy on the other show, to a certain extent, complementary features. Therefore the application of appropriate combined instruments seems very promising.

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