Surface Science 120 (1982) 427–434
North-Holland Publishing Company

ION-ELECTRON EMISSION: THE EFFECT OF OXIDATION

J. FERRÓN *, E.V. ALONSO, R.A. BARAGIOLA and A. OLIVA-FLORIO †

*Centro Atómico Bariloche ** and Instituto Balseiro ***, 8400 Bariloche, Argentina*

Received 8 February 1982; accepted for publication 13 May 1982

We have studied electron emission from Al and Mo surfaces by 4–60 keV Ar^+ ions under ultrahigh-vacuum conditions and as a function of oxygen exposure. We found that the dependence of the electron yield γ on oxygen exposure, for a given metal, is similar to that of ϕ, the work function of the surface. Comparison of the results for Al and Mo shows, however, that the magnitude of the change in γ cannot be attributed solely to a change in ϕ. We propose that the effect of oxygen exposure on electron emission induced by ions, and by extension by photons and electrons, is related to a change in the escape probability of the electrons over the modified surface barrier, and to the emission of electrons from the oxide layer in the presence of the surface dipole field.

1. Introduction

It has been known for many decades that electron emission from surfaces, be it induced by photons [1], electrons [2] or ions [3–6], is strongly influenced by gas adsorption. Historically, this sensitivity was considered a nuisance in experimental work, and prompted the adoption of ultrahigh-vacuum techniques when they became available. Some early attempts were made to explain the effect of adsorption, but the topic was neglected for a long time until spectroscopic tools, based on measurements of energy distribution of electrons ejected from solids by different probes, became developed and applied to the study of gas adsorption. These spectroscopic tools, however, are concerned in most cases with the details of the shape of the energy distribution curves, but not with the absolute magnitude of the yields.

In the specific case of ion bombardment, which is the technique used in the present study, there exist few investigations devoted to systematic observations on the quantitative effect of adsorption on the electron yield, γ. Hagstrum [7] found that the potential emission of electrons from W, induced by slow He^+ and Ne^+ ions, decreases upon exposure to H_2, N_2 or CO. He explained this in

---

† Deceased.

* Present address: INTEC, Güemes 3450, 3000 Santa Fe, Argentina.

** Comisión Nacional de Energía Atómica.

*** Comisión Nacional de Energía Atómica and Universidad Nacional de Cuyo.

terms of changes in the work function and in the energy levels near the surface. In the impact energy range where kinetic electron emission dominates, Perdrix et al. [8] studied the effect of exposure to O_2, H_2, and K on the electron yield from Mo bombarded with He^+ and Ar^+ ions. These authors related changes in γ with changes in the escape probability of Auger electrons, produced by changes in the work function ϕ, following a model by Parilis and Kishinevskii [9]. In a previous paper [10], we have reported on the effect of ion-bombardment cleaning of oxide-covered surfaces of Inconel on its ion-electron emission properties. We proposed there that changes in γ are due to changes in the electron escape probability caused by changes in the total surface barrier induced by oxidation. Recently, Hasselkamp et al. [11] studied the effect of oxygen adsorption on electron emission from W bombarded with 500 keV Ne^+ ions, and found that changes in γ were proportional to changes in ϕ.

To investigate this matter further, we have studied the effect of oxygen adsorption on the yield and energy distribution of electrons ejected from aluminium and molybdenum surfaces by Ar^+ ions in the energy range 4–60 keV. The targets were chosen for their contrasting behaviour under exposure to oxygen: whereas for aluminium ϕ decreases with oxygen exposure by an amount which is small, and dependent on oxygen pressure; for molybdenum, and after a small initial fall, the change of ϕ with exposure is large, positive, and independent of pressure for the same total exposure.

2. Experimental

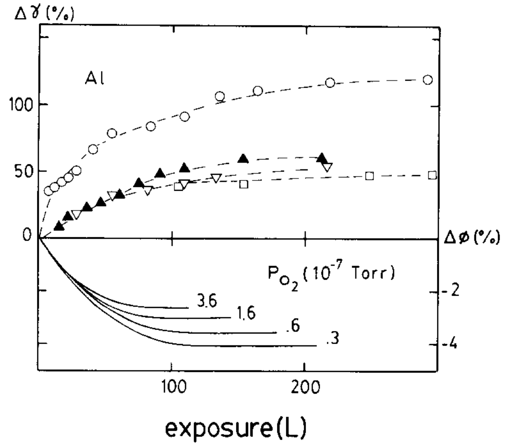
We have previously described in detail the equipment used to measure electron yields [12]. Its main parts are: an ion accelerator with a magnetic mass analyzer, a differential pumping stage (maintained at 10^{-8} Torr) between the accelerator and the target chamber, and an ultrahigh-vacuum (UHV) target chamber operated at a base pressure of 10^{-10} Torr. The electron yields were determined by measuring the currents to the target and collector. These electrodes, together with beam collimators and an electron suppressor, form an arrangement which was carefully studied to avoid spurious effects. The surfaces of the targets, which have a bulk purity better than 99.999%, were cleaned by sputtering with argon ions. In the case of Al, clean targets were also prepared by in situ evaporation under UHV conditions. The Mo target was textured 75% in the (100) direction and 25% in the (110) direction as determined by X-ray diffraction analysis. The oxygen used, of purity 99.9% was introduced to the target chamber through a servo-controlled leak valve and a trap at liquid nitrogen temperature; a residual gas analyzer installed in the system showed the absence of water vapour above the sensitivity limit of 10^{-11} Torr.

The measurements of electron energy distributions (EED) were performed in an UHV surface analysis system [13], routinely maintained at a base pressure of less than 3×10^{-11} Torr. The ion beams used in this study originated in a differentially pumped ion gun equipped with an electron bombardment ion source, and a Wien filter mass analyzer. The ion gun is pointed off the target, and we used electrostatic plates to steer the ions onto the target surface, at an angle of incidence of 45°. In this way, we avoided the contamination of the ion beam with energetic, non mass-analyzed neutrals formed by charge transfer from residual atoms issuing from the ion source region. To avoid problems resulting from residual spurious electric and magnetic fields, the electrons liberated from the target were accelerated with a 40 V potential. They were then energy analyzed with a hemispherical electrostatic energy analyzer aimed at 15° from the surface normal and operating at an energy resolution of 2% in the mode of constant retarding ratio (transmission proportional to the electron energy). For these measurements, the samples were cleaned by sputtering with 5 keV argon ions; the contamination remaining in their surface layers was determined to be less than the equivalent of 1% of a monolayer, by Auger electron spectroscopy.

We have previously described in detail the way the electron yields are determined, and the sources of errors [12]. These errors are $\pm(0.1\% + 30\ \text{eV})$ in the ion energy and $\pm 5\%$ in the electron yields; this last number includes systematic errors arising from the presence of neutral atoms in the beam and of sputtered and backscattered ions in the current reaching the electron collector. The oxygen pressures were determined with commercial ion gauges and are believed to be accurate to within 30%. We have taken particular care to use very low ion beam current densities ($< 5 \times 10^{-8}$ A/cm^2) for only the 5 s necessary for taking data, in order to cause negligible desorption by the ion beam. Similar precautions were taken during studies of EED, where measuring times were 10 times larger, but with smaller sputtering yields, and with 1/10th of the beam current density.

3. Results and discussion

Our experimental results are condensed in figs. 1 to 4. For Al, one can notice that the dependence of γ with exposure is essentially the same to that of the work function as measured by Agarwala and Fort [14]. Aluminium presents a particular behaviour under oxygen exposure which has attracted considerable interest [14–21]. One can observe in fig. 1 that both the slope of the work function versus exposure curve, and the final value of the work function, depend on oxygen pressure. The explanation that has been offered for this phenomenon is that oxygen can be either absorbed in a layer just below the surface, lowering ϕ, or be adsorbed outside thereby increasing ϕ, with the rate of incorporation, and therefore the relative amount in each state, depending on oxygen pressure. For Mo, we again observe a correlation



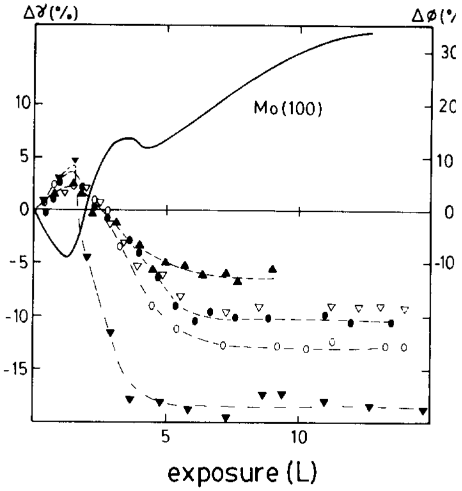


Fig. 1. Changes in electron yield for 30 keV Ar^+ on Al induced by oxygen exposure at: (○) 9×10^{-8} Torr; (▲) 1.5×10^{-7} Torr; (▽) 4.5×10^{-7} Torr; (□) 8×10^{-7} Torr. The full lines are the change in work function from ref. [14], at the indicated oxygen pressures.

Fig. 2. Changes in electron yield for Ar^+ on Mo, induced by oxygen exposure at 5×10^{-8} Torr. The impact energies are: (▼) 5 keV; (○) 30 keV; (●) 40 keV; (▽) 50 keV; (▲) 60 keV. The full line is the change in work function from ref. [22].

between changes in the electron yield and work function [22] with oxygen exposure; and no pressure dependence.

Changes in the yield can be decomposed into those due to potential and kinetic emission. Parker [23] has shown that potential emission yield γ_P for Ar^+ decreases by more than 75% upon oxygen adsorption. Therefore, and if one recalls that γ_P changes only slightly with ion energy in our energy range [24], one obtains for the maximum changes $\Delta\gamma/\gamma$ in kinetic emission from Mo, the values 7.5% (30 keV), 6% (40 keV), 5% (50 keV) and 4% (60 keV). These results are of the order of those obtained by Perdrix et al. [8] for Ar^+ on Mo at somewhat lower energies. For Al, where the measured changes $\Delta\gamma/\gamma$ are much larger, the influence of potential emission is negligible.

Kinetic electron emission can be described by the 3-step model [12] of electron excitation, transport and escape through the surface barrier, which leads to the phenomenological equation:

$$\gamma = PNL, \tag{1}$$

which contains the basic physics of the problem in terms of the average quantities: N, the mean number of excited (secondary) electrons per unit depth interval near the surface; L, the mean electron attenuation length, and P, the

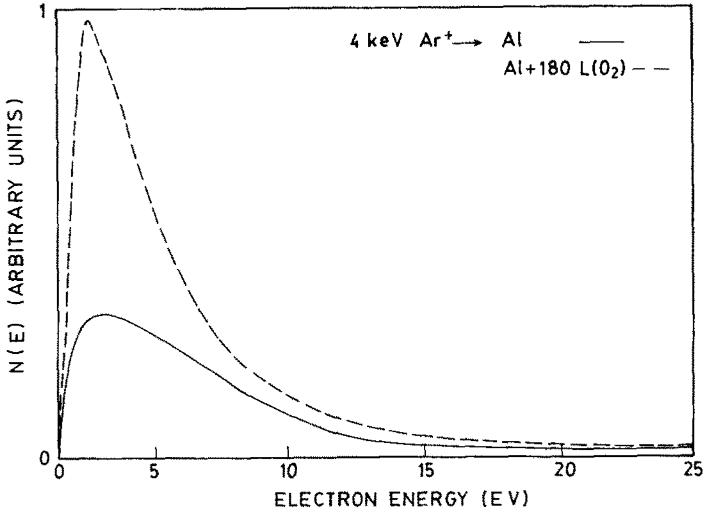


Fig. 3. Electron energy distributions for 4 keV Ar^+ bombardment of Al: (———) clean; (– – –) after exposure to 1.8×10^{-4} Torr s of oxygen. The data have not been corrected for the energy-dependent transmission function of the analysing system.

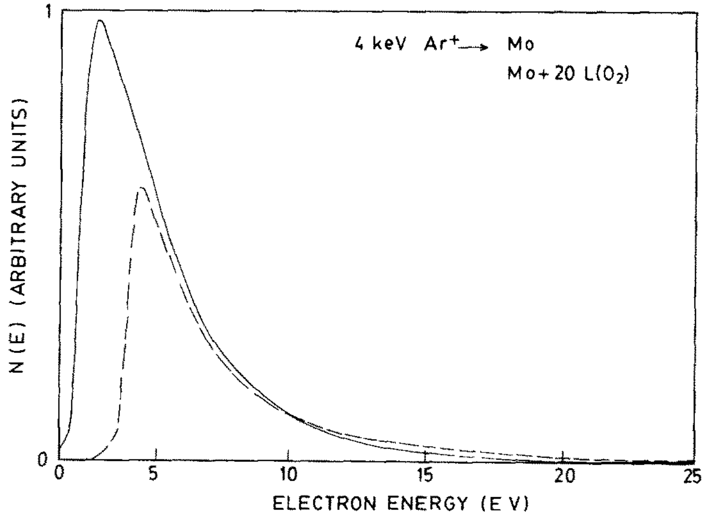


Fig. 4. Electron energy distributions for 4 keV Ar^+ bombardment of Mo: (———) clean; (– – –) after exposure to 2×10^{-5} Torr s of oxygen. The data have not been corrected for the energy-dependent transmission function of the analysing system.

mean probability of escape of the secondary electrons above the surface barrier, where the averages are taken over energy and angular variables. The 3-step model breaks down for the surface "oxide" * layer where excitation and escape cannot be treated as independent. Nevertheless, electron emission from the surface "oxide" and from the underlying metal can be separated. Since the valence electrons in the oxide are strongly bound compared with the metal, they are more difficultly excited by the low energy secondary electrons. We can then neglect the attenuation of these secondaries by energy loss within this layer. Within this approximation, electron emission from the "oxide", γ_o, and from the underlying metal, γ'_m, will be additive:

$$\gamma' = \gamma'_m + \gamma_o,$$

where γ'_m differs from γ of the pure metal because of the change in the surface barrier (inner potential I) caused by oxidation. This surface barrier acts on an internal isotropic distibution of excited electrons (which leads to the well known cosine distribution of emitted electrons) to give an escape probability [25]:

$$P = \tfrac{1}{2}\langle (E-I)/E \rangle, \tag{2}$$

where E is the electron energy inside the solid, and I is typically of the order of 12 eV, as derived from LEED studies [26–29]. Electrons excited deeper in the solid will feel, on first approximation, a barrier equal to that between the pure metal and vacuum, modified by the oxygen induced dipole. With these considerations, we obtain from (1) and (2):

$$\gamma'_m = \gamma P'/P = \gamma(1 - \Delta\phi\, \langle 1/E \rangle), \tag{3}$$

where P' is the escape probability over a barrier of height $I + \Delta\phi$; then:

$$\Delta\gamma/\gamma \sim \Delta\gamma_m/\gamma + \gamma_o/\gamma = -\Delta\phi \langle 1/E \rangle + \gamma_o/\gamma. \tag{4}$$

To estimate the contribution of the first term in (4) we notice that energy distribution curves (figs. 3, 4 and ref. [11]) show that $\langle 1/E \rangle$ is of the order of 0.05 eV^{-1} (leading to $P \sim 0.2$). Hence we obtain, for the larger oxygen exposure of figs. 1 and 2: $\Delta\gamma/\gamma(\text{Al}) < 0.01$ ($\Delta\phi < 0.2$ eV) and $\Delta\gamma_m/\gamma(\text{Mo}) \sim 0.1$ ($\Delta\phi = 1.8$ eV).

The value for Al is much smaller than the observed $\Delta\gamma/\gamma$ indicating that the change induced by adsorption is not due to the variation of the work function, but must be attributed instead to γ_o, i.e. to emission from the "oxide" layer. In contrast, γ_o is relatively small for oxygen on Mo, where $\Delta\gamma_m/\gamma$ is of the order of the observed $\Delta\gamma/\gamma$. The decrease in the yield in this case is then mainly caused by the increase in the barrier, and the observed variation of $\Delta\gamma/\gamma$ with ion energy is attributed to the accompanying decrease of $\langle 1/E \rangle$ [10,30], and to

---

* We loosely define here "oxide" as the region of the solid where valence electrons behave mainly as oxygen 2p electrons; it includes regions with chemisorbed and incorporated oxygen atoms.

the decreasing importance of potential emission [24].

At this stage we cannot provide a quantitative model for electron emission from the surface "oxide" layer, but it is reasonable to assume that γ_o is proportional to the concentration of oxygen in this layer, C_o, times an unknown function $f[\phi(C_o)]$ describing the effect of the dipole barrier and the interaction between oxygen atoms. Then, the difference in γ_o between the two metals can be attributed to the electric field in the dipole oxide layer. Considering that most of the electrons from this layer have small energies (fig. 3), this field will effectively suppress emission into vacuum from oxygen adsorbed on Mo and slightly favour it from oxygen incorporated into Al.

Acknowledgements

We thank Lic. J.L. Spino for performing the X-ray analysis. This work was partially supported by the Secretaría de Estado de Ciencia y Tecnología and by the International Atomic Energy Agency.

References

[1] G.H. Weissler, in: Handbuch der Physik, Vol. 21, Ed. S. Flügge (Springer, Berlin, 1956) p. 304.
[2] D.J. Gibbons, in: Handbook of Vacuum Physics, Ed. A.H. Beck, Vol. 2, Part 3 (Pergamon, Oxford, 1966).
[3] M. Kaminsky, Atomic and Ionic Impact Phenomena on Metal Surfaces (Springer, Berlin, 1965).
[4] D.B. Medved and Y.E. Strasser, Advan. Electron. Electron Phys. 21 (1965) 101.
[5] G. Carter and J.S. Colligon, Ion Bombardment of Solids (Heinemann, London, 1968).
[6] R.A. Baragiola, E.V. Alonso, J. Ferrón and A. Oliva-Florio, Surface Sci. 90 (1979) 240.
[7] H.D. Hagstrum, Phys. Rev. 104 (1956) 1516.
[8] M. Perdrix, J.C. Baboux, R. Goutte and C. Guillaud, J. Phys. D (Appl. Phys.) 3 (1970) 594.
[9] E.S. Parilis and L.M. Kishinevskii, Soviet Phys.-Solid State 3 (1960) 885.
[10] E.V. Alonso, R.A. Baragiola, J. Ferrón and A. Oliva-Florio, Radiation Effects 45 (1979) 119.
[11] B. Hasselkamp, A. Scharmann and N. Stiller, Nucl. Instr. Methods 168 (1980) 579.
[12] R.A. Baragiola, E.V. Alonso and A. Oliva-Florio, Phys. Rev. B19 (1979) 121.
[13] R.A. Baragiola, Springer Series Chem. Phys. 17 (1981) 39.
[14] V.K. Agarwala and T. Fort, Jr., Surface Sci. 45 (1974) 470.
[15] M.W. Roberts and B.R. Wells, Surface Sci. 15 (1969) 325.
[16] W.A. Krueger and S.R. Pollack, Surface Sci. 30 (1972) 263.
[17] G. Dorey, Surface Sci. 27 (1971) 311.
[18] R.L. Wells and T. Fort, Jr., Surface Sci. 33 (1972) 172.
[19] V.K. Agarwala and T. Fort Jr., Surface Sci. 54 (1976) 60.
[20] E.E. Huber, Jr. and C.T. Kirk, Jr., Surface Sci. 5 (1966) 447.
[21] P. Hofmann, W. Wyrobisch and A.M. Bradshaw, Surface Sci. 80 (1979) 344.
[22] R. Riwan, C. Guillot and J. Paigne, Surface Sci. 47 (1975) 183.
[23] J.H. Parker, Phys. Rev. 93 (1954) 1148.

[24] M. Perdix, S. Paletto, R. Goutte and C. Guillaud, Phys. Letters 28A (1969) 534.
[25] M.S. Chung and T.E. Everhart, J. Appl. Phys. 45 (1974) 707.
[26] J.S. Pendry, Low Energy Electron Diffraction (Academic Press, London, 1974).
[27] P.J. Jennings, Surface Sci. 88 (1979) L25.
[28] P.M. Marcus, F. Jona, S. Finch and H. Bay, Surface Sci. 103 (1981) 141.
[29] P.J. Jennings and S.M. Thurgate, Surface Sci. 104 (1981) L210.
[30] E.R. Cawthron, D.L. Cotterell and M. Oliphant, Proc. Roy. Soc. (London) A314 (1969) 39.