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Effect of ^{60}Co γ Rays on High-Resistivity p-Type Si

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Defects created by γ rays in high-resistivity (1000 to 10 000 $\Omega\cdot$cm) boron-doped silicon have been studied by Hall effect and resistivity measurements. Only one energy level is observed at 0.268 eV above the valence band by irradiation at 300°K. Its statistical weight is equal to $\frac{1}{2}$. The defect annealing between 100° and 200°C occurs by the agency of another defect. In some special cases, a more complex association with a third defect can be observed, which introduces another level at 0.21 eV above the valence band. All the results obtained are compatible with the divacancy assuption. Furthermore, we observe, by irradiation at 77°K, the formation of unstable defects, which disappear at 170°K.

I. INTRODUCTION

THE authors have studied the characteristics of an energy level located at 270 meV above the valence band and resulting from defects produced by gamma irradiation of p-type silicon with a ^{60}Co source. This energy level has been observed by several other authors under various experimental conditions (bombardment by electrons, fast neutrons, and gamma rays of various energies) using specimens of widely different resistivities (1 to 500 $\Omega\cdot$cm).

Yet its exact nature is not known. Its energy in the forbidden gap and the statistical weight that may be attributed to it vary according to each author. We have attempted to produce a finer definition of these data. We have further studied the reduction of the defect-introduction rate with temperature, have observed the low-temperature formation of a defect that is unstable above 180°K, and have attempted to determine whether the two occurrences are correlated. Finally, we have determined the high-temperature annealing characteristics of the site concerned.

Our experiments have been conducted on high-resistivity silicon. The total number of defects introduced in all cases was low, generally about 2×10^{12} defects/cm^3, so as to avoid interactions between adjacent defects as much as possible.

II. EXPERIMENTAL CONDITIONS

The silicon used was a high-resistivity (1000 to 10 000 $\Omega\cdot$cm) boron-doped silicon purified by the float-

ing zone process, produced by Monsanto or Siemens. Its oxygen concentration, estimated by infrared absorption, was lower than 10^{16} atoms/cm^3.

We used standard equipment to measure resistivity and Hall effect on a 1-mm-thick specimen; the samples were irradiated in a 10 000-Ci source of ^{60}Co producing a flux of 900 000 R/h. The irradiation temperatures could be varied between 80° and 350°K, and measurements could be performed both in the presence and in the absence of gamma flux.

III. IRRADIATION AT ROOM TEMPERATURE

A. Determination of Position in Energy Band and Statistical Weight

(a) After irradiation at room temperature, the study of the variation of the Hall coefficient with temperature revealed the formation of an energy level which is stable at room temperature. This is a well-known occurrence.

Figure 1 shows the variation of the number of carriers with the position of the Fermi level in the case of a specimen of 7000-Ω·cm resistivity irradiated in a flux of 6.8×10^{15} photons/cm^2.

The number of carriers p is deduced from the Hall coefficient by the equation

$$p=r/R_He,$$

where R_H is the Hall coefficient, r is the numerical factor $[0.84(T/300)^{-0.21}]$ (see Ref. 1), and r is the electronic charge.

The Fermi level is determined by the equation

$$E_F-E_V=kT\log(p/N_v),$$

where E_F is the Fermi level, E_V is the valence band level, and N_v is the number of equivalent states of the valence band, where $N_v=2(2m_pkT/h^2)^{\frac{3}{2}}$ and $m_p=0.59m_0$. (See Ref. 2.)

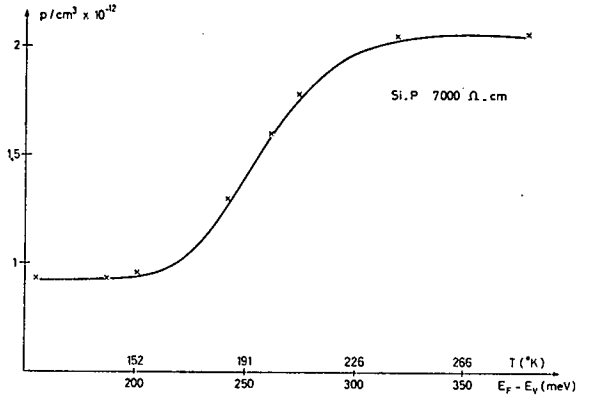

FIG. 1. Variation of the number of carriers with the position of the Fermi level, after γ irradiation. × experimental points, —— theoretical curve.

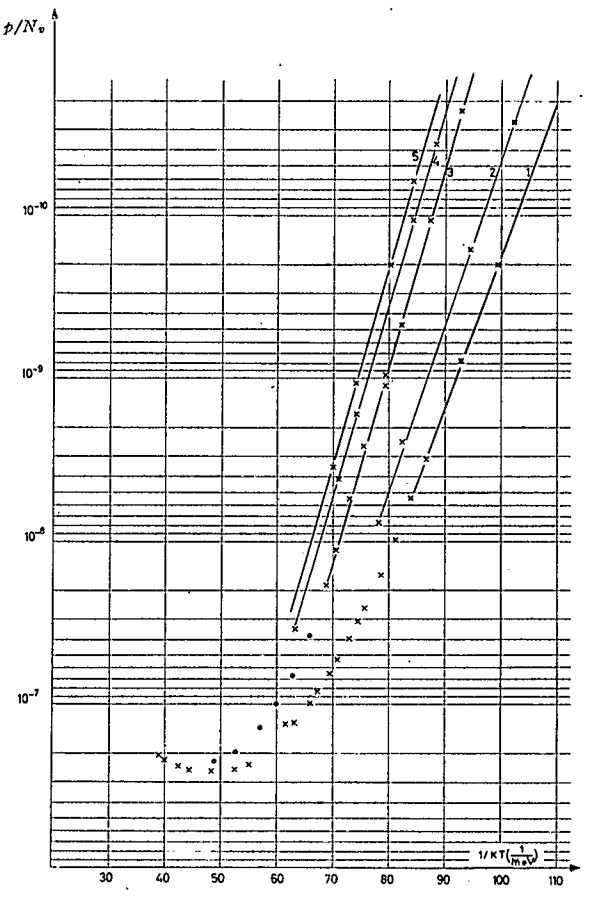

FIG. 2. Logp/N_v variation vs $1/kT$ for various irradiation doses. 1: 2.4×10^{16} photon·cm^{-2}, $E_{D_0}-E_V=210$ meV. 2: 3.4×10^{16} photon·cm^{-2}, $E_{D_0}-E_V=227$ meV. 3: 5.86×10^{16} photon·cm^{-2}, $E_{D_0}-E_V=268$ meV. 4: 1.13×10^{17} photon·cm^{-2}, $E_{D_0}-E_V=268$ meV. 5: 1.68×10^{17} photon·cm^{-2}, $E_{D_0}-E_V=268$ meV.

Figure 1 also shows the theoretical curve $p=f(E_F)$ calculated on the assumption of only one energy level, with a degree of occupancy defined by

$$f_0=\{1+\gamma_D\exp[(E_{D_0}-E_F)/kT]\}^{-1},$$

where E_{D_0} is the position of the defects in the energy band, and γ_D is the statistical weight of the level.

Good agreement is obtained between the experimental curve and the theoretical curve for the pair of values

$$E_{D_0}=256\text{ meV},$$
$$\gamma_D=1.$$

With respect to a series of 12 specimens obtained from different silicon rods (with resistivities ranging from 1000 to 10 000 Ω·cm) the spread of results on E_D is less than ±5 meV.

But it is in fact possible to find other pairs of values E_{D_0} and γ_D producing good agreement between these

[1] J. Messier and J. G. Merlo-Flores, J. Phys. Chem. Solids 24, 1539 (1963).
[2] B. Lax and J. G. Mavroides, Phys. Rev. 100, 1950 (1955).

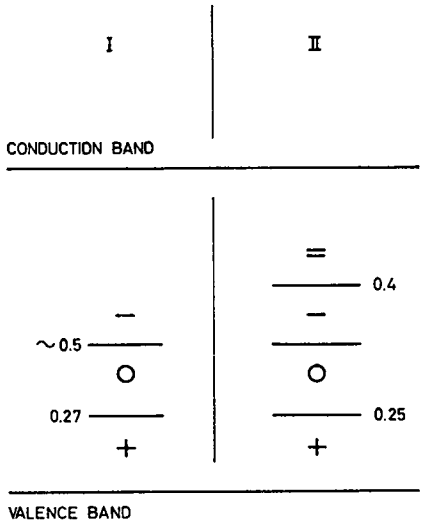

FIG. 3. Charge condition of the defects studied as a function of the Fermi level position. I: Present authors. II: G. D. Watkins and J. W. Corbett.

curves. For example, curves $p=f(E_F)$ related to:

$$E_{D_0}-E_V=256 \text{ meV} \quad \gamma_D=1,$$
$$E_{D_0}-E_V=268 \text{ meV} \quad \gamma_D=\tfrac{1}{2},$$
$$E_{D_0}-E_V=244 \text{ meV} \quad \gamma_D=2,$$

lead to very similar possible solutions. The deviations between the values of p in the three cases considered, for a given Fermi level position (or a given temperature) are always less than 0.5%, which is less than the experimental error. Thus, such curves merely determine a relationship between E_{D_0} and γ_D.

(b) If the number of defects created is much larger than the initial number of holes present in the crystal, the curve $\log(p/N_v)$ becomes a linear function of $(E_{D_0}-E_F)/kT$ at low temperature.

The variation of $\log(p/N_v)$ as a function of $1/kT$ is shown in Fig. 2 for various irradiation doses. It will be observed that for a sufficient number of introduced defects, the slope of the linear portion of the curve is independent of p. It corresponds to a value of $E_{D_0}=268$ meV.

Consideration of the results in paragraphs (a) and (b) thus results in the following values:

$$E_{D_0}=268 \text{ meV}, \quad \gamma_D=\tfrac{1}{2}.$$

As Klein[3] and Wertheim[4] observe, if the energy position of the level is linearly dependent on temperature ($E_D=E_{D_0}+\alpha T$), $E_{D_0}=268$ meV is the energy position of the level for $T=0°$K, and $\gamma_D=\gamma_0 e^{\alpha/K}$, where γ_0 is the true statistical weight of the level.

TABLE I. Summary of the results obtained by several authors.

Reference	Resistivity (Ω·cm)	Radiation	E_D-E_v (eV)	γ_D
Wertheim (Ref. 4)	1 to 10	1 MeV electrons	$0.268+5.10^{-5}T$ or	1
			$0.268+10^{-4}T$ or	½
			0.268	2
Vitovskii *et al.* (Ref. 5)	50 to 500	$\gamma(^{60}Co)$	0.230	1
Malovetskaya *et al.* (Ref. 6)		1 MeV electrons	0.210	1
Hill (Ref. 7)	5	0.7 MeV and 4.5 MeV electrons	0.3	1
Sonder and Templeton (Ref. 8)	5 to 50	$\gamma(^{60}Co)$	0.28	1
Present Authors	5.000	$\gamma(^{60}Co)$	0.268	½

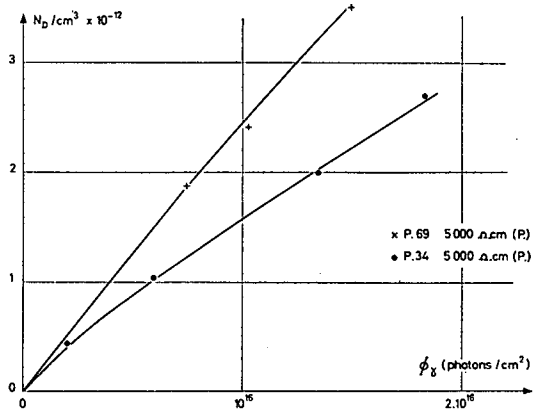

FIG. 4. Number N_D of D defects vs the γ-ray doses ϕ_γ.

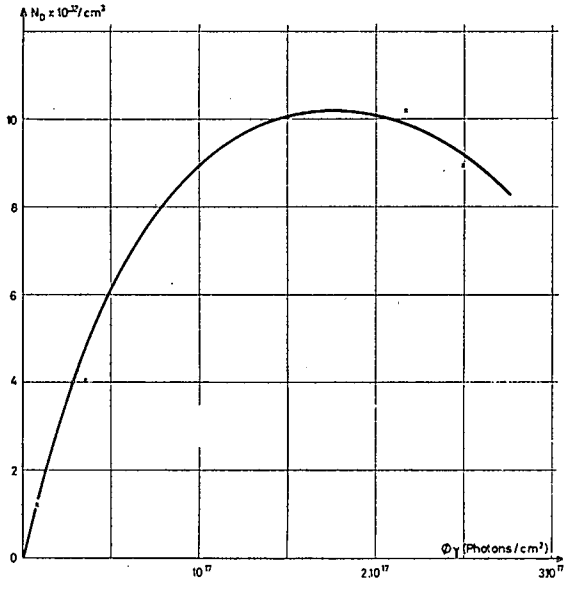

FIG. 5. Number N_D of D defects vs the doses ϕ_γ, for high dose. —— calculated curve.

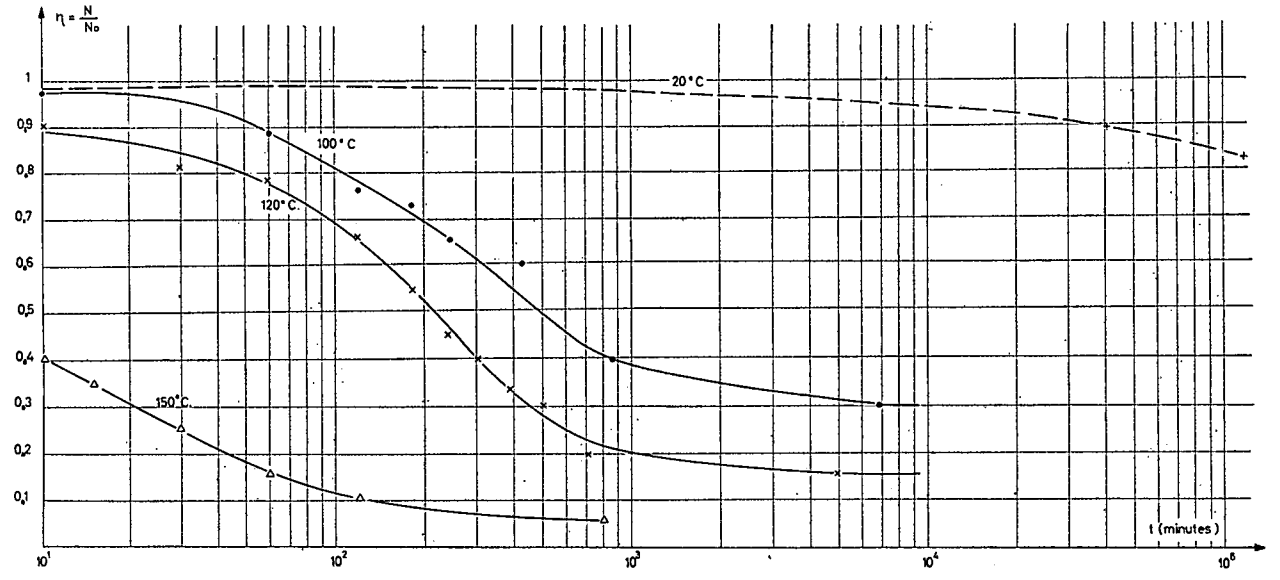

FIG. 6. Proportion $\eta = N/N_0$ of remaining defects after annealing for a time t at various temperature T.

(c) *Discussion of results.* Table I summarizes the results obtained by several authors.[4–8]

Quite substantial spread appears in the values of E_{D_0}. In fact, if we calculate the various experimental curves on the assumption that $\gamma_D = \frac{1}{2}$, according to Vitovskii[5] we obtain $E_{D_0} = 258$ meV, whereas $E_{D_0} = 268$ meV according to Vavilov.[6] The results obtained by Wertheim[4] also lead to $E_{D_0} = 268$ meV, but for $\gamma_D = 2$.

Thus, we see that some of the differences are due to the value of γ_D adopted.

Further, we shall show in Sec. IIIBb (High-temperature annealing) that a variation of the level position in the energy band may occur under certain experimental conditions. In our view, this explains the remaining differences noted.

In conclusion, our experiments show that immediately after irradiation at low doses, the formation of a single energy level is observed ($E_{D_0} = 268$ meV, $\gamma = \frac{1}{2}$), which is probably associated with a definite defect structure.

(d) *Interpretation of results.* Figure 3 represents the charge condition of the defect studied as a function of the Fermi level position, considering the existence of a second energy level due to this defect, and situated at the center of the forbidden band, as already demonstrated by Messier[9] in the same material.

It will be observed that the level scheme in Fig. 3 is in good agreement with that of the divacancy deduced by Watkins and Corbett,[10–15] and by Bemski *et al.*[12] from electronic resonance experiments, at least for the two lower levels.

For the sake of simplicity, the letter D^- is used in the following to designate the defect studied.

According to the level configuration suggested by Watkins,[13] the statistical weight γ_D of the level should be of the order of 2, and not $\frac{1}{2}$, as determined by us. Such a difference may however be explained by the fact that γ_D, derived from thermal activation measurements, is not necessarily the real statistical weight of the level.

B. Number of Defects Created as a Function of Dose and Their Stability at Room Temperature

(a) The number of D defects produced as a function of the dose is shown in Fig. 4 for two specimens of the same resistivity (5000 Ω·cm), purified by the floating zone method. Both were irradiated at 308°K, but were obtained from different rods.

We observe that the initial defect-introduction rate at a given temperature is the same for all specimens (to within the experimental accuracy of flux determination, which is of the order of ±20%).

[8] C. A. Klein, J. Appl. Phys. **30**, 1222 (1958).
[4] G. K. Wertheim, Phys. Rev. **110**, 1272 (1958).
[5] N. A. Vitovskii, T. V. Mashovets, and S. M. Ryvkin, Fiz. Tverd. Tela **4**, 2845 (1962) [English transl.: Soviet Phys.—Solid State 4, 2085 (1963)].
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[7] D. E. Hill, Phys. Rev. **114**, 1414 (1959).
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[10] G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. 31, 86 (1961).
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[12] G. Bemski, B. Szymanski, and K. Wright, J. Phys. Chem. Solids **24**, 1 (1963).
[13] G. D. Watkins, *Proceedings of the Symposium on Radiation Damage in Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1965).
[14] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).
[15] J. W. Corbett and G. D. Watkins, Phys. Rev. **138**, A555 (1965).

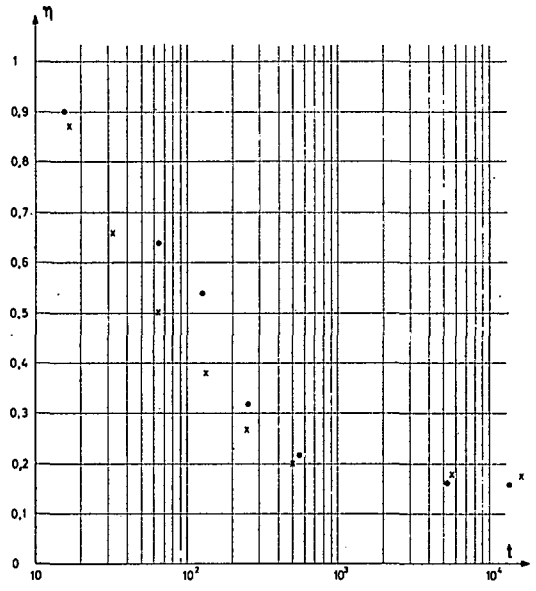

FIG. 7. Variation of as a function of annealing time at $T=120°C$ in the case of two specimens obtained from nearby location on the same crystal. Doses: ● 6.75×10^{15} photon·cm^{-2}, × 1.35×10^{16} photon·cm^{-2}.

On the other hand, the curves show that substantial differences of N_D appear at a relatively high γ number, according to the origin of the crystal. In certain cases (Fig. 5) we even observe a reduction in the number of defects introduced, when the integrated flux is increased.

(b) *High-temperature annealing.* Figure 6 shows the proportion of remaining defects after annealing as a function of time at various temperatures T, all specimens having been submitted to the same initial irradiation.

Figure 7 shows the variation of η as a function of annealing time at 120°C, in the case of two specimens obtained from nearby locations of a crystal, but variously irradiated (4.5 MR and 9 MR).

In Fig. 8, we compare the part of η which anneals with temperature $[\eta'=(\eta-\eta_F)/(1-\eta_F)]$ with the theoretical curves for bimolecular annealing $(\eta'=(1+t/\tau)^{-1}$, in which $\tau=A/N_0$, $N_0=$number of defects before annealing, $A=a$ constant).

It may be observed that the annealing law is approximately bimolecular. But Fig. 7 shows that it differs substantially from this latter in that a terminal plateau η_F appears, indicating limit annealing.

The fraction η_F is strongly dependent on temperature, but not on the initial dose received by the specimen.

For this reason we consider that the annealing of D defects occurs by the agency of another defect (I) produced by the radiation, the limit annealing being probably due to the disappearance of the I defects.

(c) *Modification of the nature of D by prolonged annealing.* No variation of the level E_{D_0} was observed subsequent to annealing as defined in Fig. 8.

However, after prolonged annealing (about fifteen days at 120°C) a gradual transformation of the D sites and a new variety D' of defects are observed, introducing energy levels at about 210 meV above the valence band, although the total number of defects present in the crystal no longer varies.

The same occurrence is observed in the case of a highly irradiated (100 MR) specimen of 5000 Ω-cm), after two years annealing at room temperature.

In fact, we observe that the transformation is much more rapid if the crystal has been bombarded with thermal neutrons, that is to say, if defects have been formed in small clusters, instead of uniformly throughout the crystal as in the case of gamma irradiation.[16] For example, it has been found that with a neutron bombardment, no more than three days at 120°C are required to produce the transformation of D into D'.

C. Variation of the Defect Introduction Rate with Irradiation Temperature

(a) If the specimen is irradiated at a temperature T between 77° and 300°K and then raised to room temperature within about 10 min, it is found that defects identical to the D defects are formed. The energy position of the level does not vary with irradiation temperature, but the rate of introduction decreases with temperature (Fig. 9). Also we have tried to determine whether the defects studied were related to the unstable defects produced at low temperature. Our experiment is described in the following paragraph.

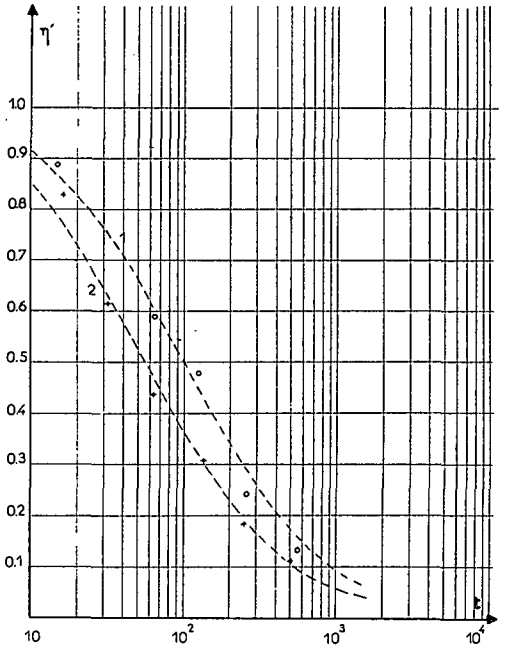

FIG. 8. Calculated curve assuming a bimolecular annealing of the from $1/(1+t/\tau)$. Curve 1: $\tau=100$, curve 2: $\tau=56$.

[16] M. V. Chukichev and V. S. Vavilov, Fiz. Tverd. Tela 3, 1522 (1961) [English Transl.: Soviet Phys.—Solid State 3, 1103 (1961)].

(b) *Formation of unstable defects by irradiation at 77°K.* (1) With low-temperature irradiation, a reduction of the number of holes (Δp) proportional to the integrated flux is noted. We observe that Δp is not dependent on the initial hole density (10^{11} to 10^{13} holes/cm^3). An average of 14×10^{-5} holes are removed per incident photon, per cm^3 (Fig. 10).

If the specimen is kept at 77°K for several days after irradiation, no variation of conductivity is observed. Figure 11 shows, on the contrary, the gradual disappearance of conductivity variation measured at 77°K, after annealings of 10 min at gradually increasing temperatures. The annealing temperature is given in abscisca vs the quantity,

$$f=(\sigma_T-\sigma_0)/(\sigma_{77}-\sigma_0),$$

where, σ_0 = conductivity before irradiation, measured at 77°K, σ_{77} = conductivity after irradiation, measured at 77°K, σ_T = conductivity after 10 min annealing at temperature T, measured at 77°K.

(2) Measurement of the number of carriers during the annealing periods leads to the assumption that these unstable defects introduce energy levels about 150 meV above the valence band.

(3) The rate of stable D defect introduction is about $1.5\times10^{-5}D$ photon^{-1} cm^{-1}. If irradiation at 77°K is continued for a lengthy period, the unstable defects introduced are electrically neutral. Under these conditions, the rate of introduction of stable D defects falls to zero.

IV. INTERPRETATION AND DISCUSSION OF RESULTS

It is always difficult to determine the physical nature of a defect with certainty by means of the Hall effect. However, a considerable amount of data concerning the nature of defects in silicon has been obtained, thanks in particular to research employing electronic resonance methods, so that it is now possible, by comparison, to advance certain assumptions.

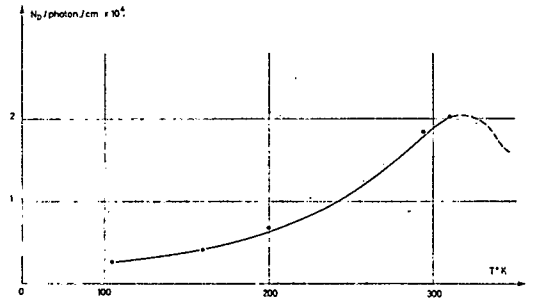

FIG. 9. Variation of the introduction rate of D defects vs the irradiation temperature.

A most probably correct assumption is that the D sites are divacancies, owing to the facts that:

(a) The positions of the energy levels introduced into the forbidden band by the D sites correspond to those of divacancies, at least insofar as the two lower levels are concerned;

(b) According to Watkins[10,14] the energy of motion of the divacancy is $E_A=1.3$ eV which account for the stability of the D sites at room temperature. This value also explains why, at annealings between 100° and 200°C in the case of gamma irradiation, no change in the energy positions of the levels is noted. The elementary movements of D are then too few and for them to become associated with other defects or impurities;

(c) The high temperature (100° to 200°C) annealing is by the agency of another defect (I), which is mobile at the annealing temperature. It should be noted that Wertheim[4] observed no annealing up to 450°C in samples with high impurity contents, and that annealing is observed at lower temperature in samples purified by the floating zone process, and finally that Vavilov[6] observed substantial annealing even at room tempera-

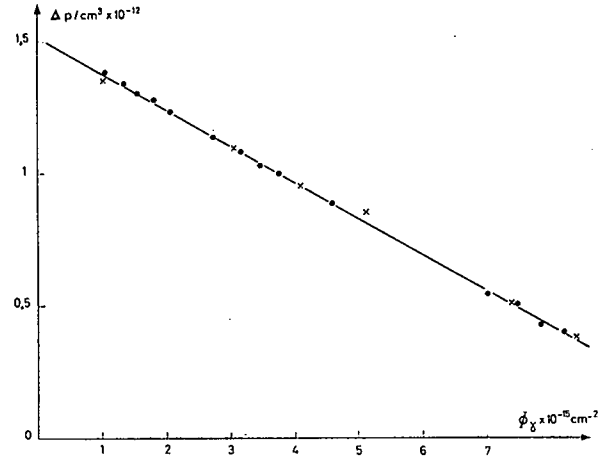

FIG. 10. Variation of the number of carriers Δp as a function of the irradiation dose. ● 7700 Ω·cm, × 5600 Ω·cm.

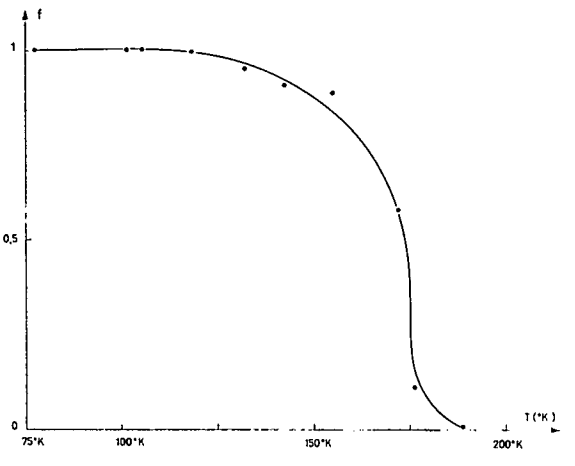

FIG. 11. Nonannealing part of defects after isochronal annealings (15 mn) vs annealing temperature.

ture in samples containing little oxygen (5×10^{15} atoms/cm^3).

It is for these reasons that we put forward the assumptions that the rate of annealing is governed by the density of sites capable of trapping the I defects and slowing them down. I defects could be interstitial silicon atoms trapped in the vicinity of oxygen atoms or other impurities, or possibly other interstitial atoms resulting from reactions such as[13]

$$Si_{int}+Al_{subs} \rightleftarrows Al_{int}+Si_{subs}.$$

(d) The variation in the rate of D site introduction according to radiation dose at room temperature may also be explained by annealing in an irradiation field of the D defects with interstitial atoms although at this temperature, annealing rates after irradiation are slow: Interstitial atoms are in fact extremely mobile[13] and after a certain length of path, are soon fixed by impurities in the crystal. During their brief paths, they have a probability of encountering a D site, this probability evidently increasing with the concentration N of the latter. The number of D sites formed follows the differential equation:

$$\frac{dN}{d\phi}=\alpha-\frac{\sigma_D\alpha' N}{\sigma_c C_0-(\alpha-\alpha')\phi\sigma_c+(\sigma_D-\sigma_c)N}$$

in which C_0 is the density of the C sites capable of fixing I defects during a period of time greater than the duration of irradiation, α is the rate of formation of D defects per unit of flux, α' is the rate of formation of I defects per unit of flux, and σ_D and σ_c are the capture cross sections of I defects for a D and C site.

Figure 6 shows the curve obtained with:

$$C_0=6.3\times10^{14}/\text{cm}^3,$$
$$\alpha=1.5\times10^{-4}\ \text{defect/photon/cm},$$
$$\alpha'=1.35\times10^{-3}\ \text{defect/photon/cm},$$
$$\sigma_D=5.1\sigma_c.$$

In the assumption of a constant rate of divacancy formation a model of this type explains the variations in the rate of D site introduction by annealing during irradiation.

It is to be noted that researchers who have used higher irradiation doses observe smaller average introduction rates than ours. Vitovskii *et al.*[5] find $\eta=6\times10^{-5}$ defect/photon/cm^2 at doses between 10^{17} and 10^{18} photons/cm^2 while Sonder and Templeton[8] find $\eta\leqslant10^{-5}$ at doses greater than 10^{19} photons/cm^2.

(e) Variations of energy position from level 270 meV to 210 meV: As this variation occurs more rapidly when defects are produced in clusters, we attribute it to association of divacancies with another defects in the lattice. In a cluster of defects, as those formed by irradiation with thermal neutrons, thirty or so elementary motions are sufficient for a D site to become associated with another defect.

We observe that Sonder and Templeton[8] find energy levels at about 0.21 eV almost exclusively, in heavily doped samples poor in oxygen, using strong irradiation doses. The rate of introduction of these energy levels is slower than that of our D sites. This, in our opinion, confirms that the new D' sites result from associations with the D sites.

Can any other assumption explain the nature of the D sites?

The annealing mechanisms and the energy shift of the levels may also be explained, for instance, by assuming that the D sites are formed by associations between vacancies and lattice impurities (boron for example). However, considering that formation of sites BV competes with the formation of other sites (V-0 etc.), their rate of formation should depend on the boron concentration. The results we have obtained do not confirm this assumption. Moreover, it is possible to introduce many more D defects than the initial acceptor density.

V. LOW-TEMPERATURE IRRADIATION

We are not at all sure that the defects produced by low-temperature irradiation are directly related to the D sites. We have, however, mentioned these defects, since they influence the rate of formation of D defects. This influence may however be indirect; the unstable positive defects created at low temperature raise the position of the Fermi level, if produced in a large number, and this may affect the conditions governing the formation of the D sites.

Meanwhile we have found no entirely satisfactory explanation for the variation in the rate of formation of the D sites with irradiation temperature.