Energy Levels in Electron-Bombarded Silicon

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Electron bombardment of n- and p-type silicon reduces the lifetime of minority carriers and decreases the carrier concentration. This paper presents evidence that: (a) an electron trapping level is located 0.16 ev below the conduction band and a hole-trapping level 0.29 ev above the valence band, (b) the recombination centers responsible for the reduction of lifetime in n-type are located 0.31 ev from a band edge, and those in p-type approximately 0.24 ev from a band edge, (c) lattice imperfections are produced at a rate of 0.18 per electron-cm of bombardment at 700 kev.

INTRODUCTION

THE results of the study of bombardment effects in semiconductors (and metals) during the past ten years have recently been summarized in a number of review articles.[1–3] Considerable information on the effect of neutron,[4] gamma,[5] alpha,[6] electron,[7] deuteron,[8] and ion[9] bombardment of germanium has become available, but the literature on silicon is still limited. It has been shown, however, that neutron bombardment decreases the carrier concentration in both n- and p-type silicon,[10] and that electron bombardment reduces carrier lifetime. The latter effect has been used[11] to examine the threshold for damage in both semiconductors.

The interpretation of bombardment effects is based on the model of James and Lark-Horovitz,[12] who assume that they are due to lattice vacancies and interstitials. A vacancy is thought to be capable of existing in a number of states, unoccupied or occupied by one or more electrons; it is therefore either neutral or negatively charged and acts like an acceptor. An interstitial, on the other hand, consists of a neutral atom which may lose one or more electrons, and corresponds to a donor. It is suggested that the first energy level of the vacancy in silicon lies in the lower half of the band, while the first energy level of the interstitial lies in the upper half, and that the second vacancy level lies above the second interstitial level. If the Fermi level lies below the first donor level its electron will drop to the first acceptor level and the empty donor level may now act as a net-acceptor. The second vacancy level may also act as an acceptor. The effect of bombardment on lifetime may be interpreted in terms of the same model on the assumption that certain of these levels act as temporary trapping or recombination centers for minority carriers.

The similarity of results obtained under bombardment with a variety of projectiles (α, β, electron, neutron, γ) follows from this model, since all produce lattice vacancies and interstitials, but there are some significant differences: neutron-induced transmutations produce chemical donors and acceptors as well; fast neutrons produce clusters or tracks of damage rather than single vacancy-interstitial pairs; heavy charged particles have limited penetration and concentrate the defects in a thin surface layer. From the point of view of uniformity of damage and absence of multiple damage, gamma rays are to be preferred. However, monoenergetic gamma rays are absorbed by both Compton and photoelectric effects, yielding primary electrons of all energies below the Compton maximum as well as photoelectrons with the full energy of the incident photon. It is consequently difficult to relate the magnitude of the damage to the bombarding energy in a meaningful manner. For this experiment, electrons seemed the most satisfactory choice. Although their penetration is limited, reasonably uniform damage in depth may be assured by the use of thin targets. Multiple damage may be minimized by the choice of a bombarding energy at which, in the most favorable collision, the electron can transfer to the lattice atoms no more than a few times the threshold energy for damage.

Bombardment damage in semiconductors is known to anneal at sufficiently high temperature. The anneal of room-temperature electron-bombardment damage in germanium has been described in some detail[7]; low-temperature bombardment produces other trapping centers which partially anneal below room temperature.[13] Room-temperature electron-bombardment damage in silicon is stable for extended periods up to 450°K.[14] Evidence suggest that the damage consists of vacancies and interstitials in equal concentration, and that

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[3] G. H. Kinchin and R. S. Pease, Repts. Progr. Phys. **18**, 1 (1955).
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[10] K. Lark-Horovitz, *Reading Conference on Semiconducting Materials* (Butterworth Publications, London, 1951), pp. 47–69.
[11] J. J. Loferski and P. Rappaport, Phys. Rev. **98**, 1861 (1955).
[12] H. M. James and K. Lark-Horovitz, Z. physik. Chem. **198**, 107 (1951).
[13] Brown, Fletcher, and Wright, Phys. Rev. **96**, 843(A) (1954).
[14] G. Bemski (private communication).

annealing takes place by the recombination of a vacancy and an interstitial.[14]

PROCEDURE

Single-crystal rods (0.020×0.100×0.75 in.) of n- and p-type silicon were bombarded at 60°C ($10^3/T = 3.00$) with 700-kev electrons from a Van de Graaff accelerator. Bombardments were made through an 0.003 in. aluminum foil window located $\frac{5}{8}$ in. from the sample in order to scatter the electrons sufficiently to produce a uniform distribution over the exposed $\frac{3}{16}$ in. length of the sample. The distribution of damage was determined by a resistivity traverse which indicated a variation of ±5% over the surface. The uniformity in depth was examined indirectly by bombarding 0.010 in. rods through a silicon wedge with a 10% gradient. The results indicate that damage produced by 700-kev electrons drops by 30% at a depth of 0.020 in.

Electrical contacts to the silicon were made by the electroless-nickel process.[15] Samples were completely plated and the unwanted nickel removed with nitric acid after suitable masking. Some four-contact conductivity bridges were made by this process, but for low-temperature work the voltage probes were made by bonding gold or aluminum wires into the body of a heated specimen.

The samples were soldered to a copper frame, which in turn was attached to a metal Dewar having provisions for heating and cooling. The sample temperature was measured by a thermocouple on the sample at the point of attachment to the copper frame. The sample chamber was maintained at forepump vacuum during measurement and bombardment. As a precaution against the anneal of thermally unstable damage during measurements the samples were heated to 180°C for 10 minutes before temperature-dependent phenomena were examined. No change in sample characteristics was produced by this process.

Resistivities were measured with a conventional four-contact setup. Lifetimes were obtained with the pulsed Van de Graaff bombardment-conductivity decay method.[16]

RESULTS AND DISCUSSION

(1) 7 ohm-cm, *n*-Type Silicon

(*a*) *Conductivity*

The conductivity of a standard specimen was measured as a function of bombardment at 60°C. From the data the electron concentration was derived on the assumption that the electron mobility remains constant. Values of mobility were taken from Morin and Maita.[17] The fractional decrease in the electron concentration, $(n_0-n)/n_0$, as a function of bombardment is given in Fig. 1. In the linear region the data may be represented by

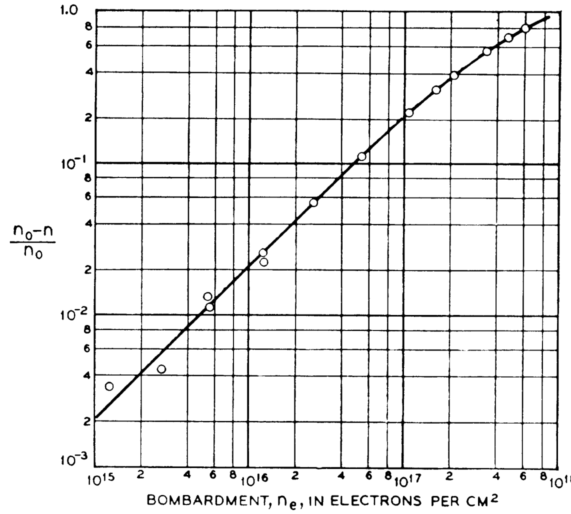

FIG. 1. Fractional decrease in electron concentration as a function of bombardment; 7 ohm-cm, n-type silicon.

$$n = n_0(1-2.1\times10^{-18}n_e),$$

where n_e is the bombardment in electrons/cm². It will be shown that the acceptors are only partially filled at this temperature, so that the cross section for the production of bombardment centers cannot be obtained at this point. At low bombardment the filling remains constant, and the straight, unity slope part of the curve shows that acceptors are introduced in proportion to bombardment. At higher bombardment other effects enter. At 10^{17} electrons/cm² the movement of the Fermi level associated with the changing conductivity begins to decrease the fractional filling of the acceptors; as a result the electron concentration drops more slowly beyond this point.

If the electron mobility decreases with bombardment, the computed $(n_0-n)/n_0$ may be too large. We have no direct evidence to show that the mobility remains unchanged in these experiments, but if mobilities in neutron-bombarded germanium[4] may be taken as a guide, the effect should be small. In making this comparison, it must be borne in mind that the damage done by 700 kev electron bombardment is of the order of 100 times smaller than the damage produced by the same flux of fast neutrons. In the following discussion the effect of possible changes in mobility will be neglected.

(*b*) *Lifetime*

The observed lifetime in a rod of 0.020 in. thickness as a function of bombardment is shown dotted in Fig. 2. Measurements as well as bombardments were made at 60°C. (The 180°C anneal was omitted.) The suggestion[11]

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[16] G. K. Wertheim (to be published); also G. K. Wertheim, Bull. Am. Phys. Soc. Ser. II, 1, 128 (1956).
[17] F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).

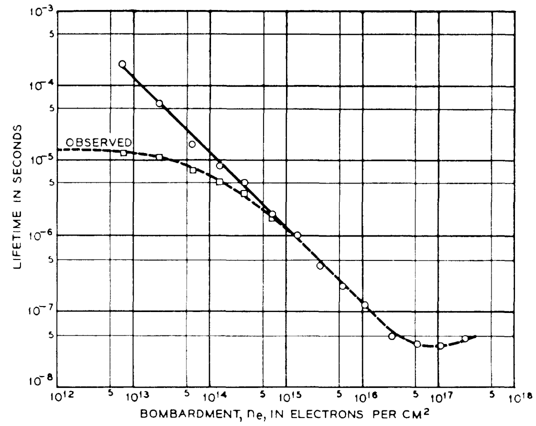

FIG. 2. Measured and bombardment lifetimes as a function of bombardment; 7 ohm-cm, n-type silicon.

that the lifetime at a given temperature may be a more sensitive index of damage than the resistivity is borne out here. It should be noted that 10^{15} electrons/cm² were required to produce a significant change in conductivity, Fig. 1, whereas 3×10^{13} electrons/cm² produced a clearly discernible decrease in the observed lifetime, Fig. 2.

The lifetime in the thin rod is initially dominated by diffusion-limited surface recombination. Little, if any, increase in the measured decay time can be obtained by surface treatment, since the lifetime remains diffusion-limited for the dimensions used. The data shown in Fig. 2 were obtained from a sample with a sand-blasted surface. It was assumed in the analysis that the reciprocal of the measured lifetime τ_m may be expressed as the sum of the three contributions,

$$\frac{1}{\tau_m}=\frac{1}{\tau}+\frac{1}{\tau_b}+\nu, \tag{1}$$

where τ is the lifetime due to bombardment, τ_b the bulk lifetime characteristic of the initial crystal impurities and imperfections, and ν the surface decay constant. The bombardment lifetime may then be obtained on the assumption that $(1/\tau_b+\nu)$ remains constant independent of bombardment. The result, Fig. 2, solid line, indicates that τ is inversely proportional to bombardment up to 3×10^{16} electrons/cm².

The effect of bombardment on lifetime follows from the equations of Hall or Shockley and Read[18]:

$$\tau=\tau_{p0}\frac{n_0+n_1}{n_0+p_0}+\tau_{n0}\frac{p_0+p_1}{n_0+p_0}, \tag{2}$$

and

$$1/\tau_{n0}=N_t\sigma_{n0}v;\quad 1/\tau_{p0}=N_t\sigma_{p0}v, \tag{3}$$

where τ_{p0} and τ_{n0} are the minority carrier lifetimes in highly n- and p-type material, n_0 and p_0 are the thermal equilibrium carrier concentration, n_1 and p_1 the electron and hole concentration when the Fermi level is at the level of the recombination center, N_t the concentration of these centers, σ_{n0} and σ_{p0} their cross section for electron and hole capture, and v the thermal velocity of free carriers. For n-type material in the extrinsic range Eq. (2) takes one of two possible forms, depending on whether $\tau_{p0}n_1$ is either larger or smaller than $\tau_{n0}p_1$:

$$\tau=\tau_{p0}+\tau_{p0}n_1/n_0,\quad\text{or}\quad \tau=\tau_{p0}+\tau_{n0}p_1/n_0. \tag{4}$$

These may both be written

$$\tau=\tau_{p0}+(\tau_0/n_0)N_0\exp(-\Delta E/kT), \tag{5}$$

where $\tau_0=\tau_{p0}$, $N_0=N_c$, and $\Delta E=E_c-E_t$ if the trapping level is near the conduction band, and $\tau_0=\tau_{n0}$, $N_0=N_v$, and $\Delta E=E_t-E_v$ if it is near the valence band.

For bombardments up to 3×10^{16} electrons/cm² the change in the carrier concentration n_0 is small, so that Eq. (5) may be written in the form

$$\tau=\left[\frac{1}{\sigma_{p0}v}+\frac{N_0\exp(-\Delta E/kT)}{n_0\sigma_0 v}\right]\frac{1}{N_t}, \tag{6}$$

where the term in square brackets is a constant independent of bombardment. Equation (6) confirms that at any temperature and bombardment where n_0 has not changed appreciably, the lifetime will be inversely proportional to the trap concentration N_t and hence to bombardment n_e.

In the region where the fractional change in n_0 exceeds 0.05, the behavior of $\tau(n_e)$ may be readily seen in terms of the following approximations. We assume that

$$N_t=\eta n_e,\quad n=n_0-\beta n_e, \tag{7}$$

and that

$$\frac{1}{\sigma_{p0}v}\ll\frac{N_0\exp(-\Delta E/kT)}{n_0\sigma_{n0}v}, \tag{8}$$

i.e., that the temperature-dependent part of the expression for τ dominates in Eq. (6) [Eq. (8) is valid at 60°C in the sample under consideration, Fig. 3], and obtain

$$\tau=C/[n_e(n_0-\beta n_e)]. \tag{9}$$

This equation may be differentiated to show that τ has a minimum when $n_e=n_0/2\beta$, at which point $n=n_0/2$. According to this calculation the minimum in lifetime should occur at $n_e=3\times10^{17}$ electrons/cm², whereas the minimum was actually observed at 1×10^{17} electrons/cm². In view of the approximations made above and the inherent variability of samples this agreement is considered satisfactory.

(c) *Recombination Centers*

To locate the energy level of the above recombination center the bombardment-conductivity decay was measured as a function of temperature. Lifetimes were

[18] R. N. Hall, Phys. Rev. 87, 387 (1952); W. Shockley and W. T. Read, Phys. Rev. 87, 835 (1952).

measured in two samples prior to bombardment and after 1.4×10^{14}, 1.4×10^{15}, and 1.1×10^{16} electrons/cm². Good agreement was obtained between the two samples. Figure 3 shows the bombardment lifetime for one of these samples. The difference between τ and τ_m is small for lifetimes less than 10^{-6} second.

The distance of the energy level of the recombination centers from a band edge may be determined from the slope of the high-temperature part of the data according to Eq. (5), and τ_{p0} is given by the constant value of lifetime at low temperature. Additional information may be obtained provided it is possible to distinguish between the two alternate forms of Eq. (4). Having obtained τ_{p0} and ΔE, and knowing n_0 from measurements of conductivity, we may compute $\tau_0 N_0$ and compare it with $\tau_{p0}N_c$ to show whether the level is near the valence band. If $\tau_0N_0\neq\tau_{p0}N_c$, then $\tau_{n0}=\tau_0N_0/N_v$, and the level is located near the valence band. If $\tau_0N_0=\tau_{p0}N_c$, no statement regarding the location of the level may be made. In the case under consideration, $\tau_0N_0\neq\tau_{p0}N_c$.

The cross sections σ_{n0} and σ_{p0} can be obtained provided the concentration of recombination centers can be established from other measurements. We shall assume that this concentration may be taken equal to that of the acceptors determined below from measurements of the temperature dependence of conductivity.

The following values were obtained from the indicated analysis of the data in Fig. 3:

$$\Delta E=0.31 \text{ ev above the valence band},$$

$$\left.\begin{aligned}\tau_{p0}&=1.0\times10^{-7}\text{ sec}\\ \tau_{n0}&=4.0\times10^{-5}\text{ sec}\end{aligned}\right\}\text{at } 1.4\times10^{14}\text{ electrons/cm}^2,$$

$$\sigma_{p0}=2.8\times10^{-14}\text{ cm}^2,$$

$$\sigma_{n0}=1.0\times10^{-16}\text{ cm}^2.$$

The relative magnitude of the cross sections suggests that the center is an acceptor. When one uses these parameters in Eq. (5), the lifetime may be expressed as

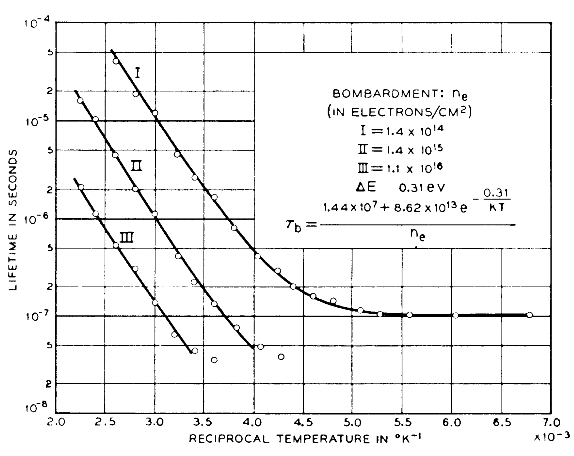

FIG. 3. Bombardment lifetime as a function of reciprocal temperature; 7 ohm-cm, n-type silicon.

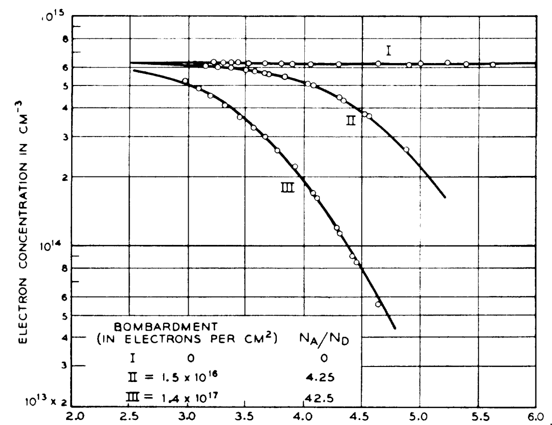

FIG. 4. Electron concentration as a function of reciprocal temperature; 7 ohm-cm, n-type silicon.

a function of temperature and bombardment in 7 ohm-cm, n-type silicon as

$$\tau=\frac{1}{n_e}[1.44\times10^7+8.6\times10^{13}\exp(-0.31/kT)].\quad(10)$$

It has been verified that the bombardment lifetime in n-type silicon of other resistivity may also be obtained in terms of the above parameters. The curves drawn in Fig. 3 were computed from Eq. (10).

(d) *Net Acceptor*

A net acceptor is an energy level which removes conduction electrons from n-type material. It may be an acceptor in the usual sense or else a donor inconjunction with a lower lying acceptor. The energy level of the net acceptor produced by bombardment may be determined from the temperature dependence of conductivity. In the analysis it is assumed that the chemical donors remain fully ionized and that the acceptors exhibit one discrete energy level below that of the chemical donors. It may be shown that under these conditions

$$n=N_d\left(\frac{K+\alpha}{2}\right)\left\{\left[1+\frac{4\alpha}{(K+\alpha)^2}\right]^{\frac{1}{2}}-1\right\},\quad(11)$$

where

$$K=\frac{N_t}{N_d}-1,$$

$$\alpha=\frac{N_c}{N_d}\exp\left(-\frac{E_c-E_t}{kT}\right),$$

and N_d signifies the uncompensated chemical donor.

In the region where $\alpha\gg1$ and $\alpha\gg|K|$, the energy E_c-E_t may be determined from the slope of $\ln[1-(n/N_d)]$ as a function of reciprocal temperature. This may be shown by expanding the square root in

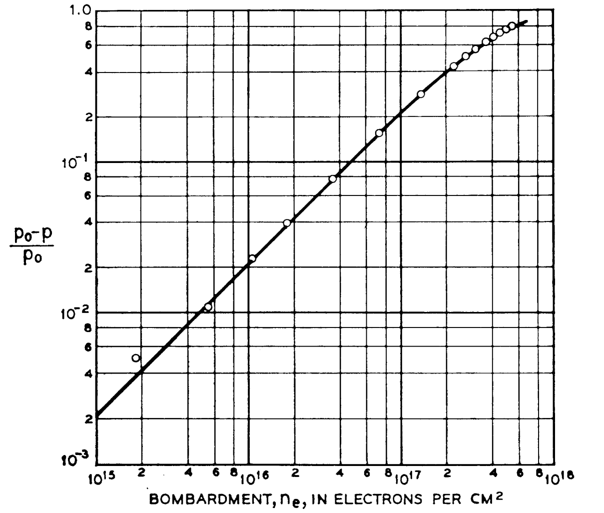

FIG. 5. Fractional decrease in hole concentration as a function of bombardment; 5 ohm-cm, p-type silicon.

Eq. (11) to the first order to obtain

$$\ln\left|1-\frac{n}{N_d}\right| \approx \frac{E_c-E_t}{k}\left(\frac{1}{T}\right)+\ln\left(\frac{N_t-N_d}{N_c}\right). \quad (12)$$

The data relating to conductivity as a function of temperature were treated in the same manner as outlined in Sec. 1(a) and then plotted in the form of $\ln|1-(n/N_d)|$ *vs* $1/T$ (not shown) to allow determination of E_c-E_t. The final determination was made by fitting the data in the form of $\ln n$ *vs* $1/T$ as shown in Fig. 4. The solid lines in this figure were computed from Eq. (11) using the following parameters:

$$E_c-E_t=0.16 \text{ ev},$$

$$\eta=dN_t/dn_e=0.18 \text{ acceptors/electron-cm}.$$

The good agreement between the computed curve and the data suggests that the model is valid, and confirms that only one net-acceptor level is produced in or below that part of the band gap traversed by the Fermi level.

(2) 5 ohm-cm, *p*-Type Silicon

(*a*) *Conductivity*

A similar series of measurements was made on a crystal of 5 ohm-cm, p-type silicon. The results, although similar, differ in a number of respects.

The fraction of holes removed as a function of bombardment at 60°C, Fig. 5, is practically identical with that obtained in the 7 ohm-cm, n-type specimen. This is a coincidence occasioned by the choice of temperature at which the data were taken and by the choice of resistivities. Since the initial hole concentration is 3.5 times the initial electron concentration, the rate of hole removal is also 3.5 times the rate of electron removal in the n-type crystal. This is in the same direction as in the case of neutron bombardment reported by Lark-Horovitz[12] although the difference in rates is less pronounced here. It is interesting to note that fast neutron bombardment removed 5 carriers per neutron in highly p-type material whereas only 0.005 donor/cm^3 were produced per electron per square centimeter here. (The data may not be strictly comparable but the ratio of 5 to 0.005 suggest that the centers observed here may be due to multiple damage.)

(*b*) *Net Donor*

A net donor is an energy level which removes holes from p-type material. The energy level of the net donor responsible for the reduction in hole concentration was obtained from the temperature dependence of the conductivity. The hole concentration in Fig. 6 was de-

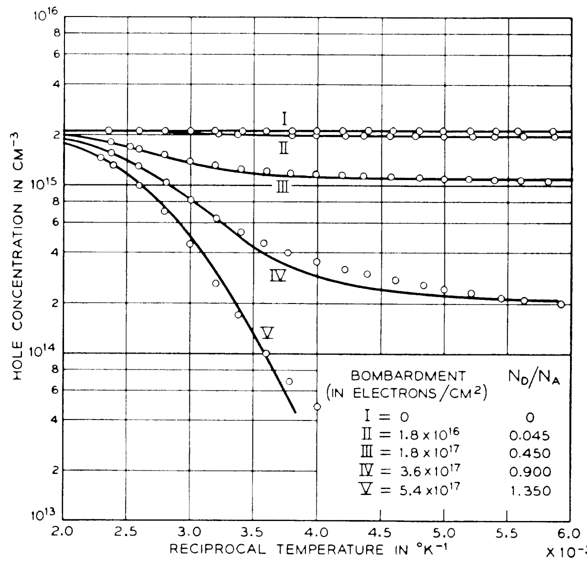

FIG. 6. Hole concentration as a function of reciprocal temperature; 5 ohm-cm, p-type silicon.

rived from the conductivity on the assumption of bombardment-independent mobility. The energy level was determined as in Sec. 1(d), but the fit here is not entirely satisfactory. In particular, the hole concentration appears to continue to decrease at low temperature where the single net donor would be completely ionized. Most likely the assumption of bombardment-independent mobility is not valid at low temperature where the number of charged scattering centers is large. This interpretation is consistent with the fact that the deviation of the data from the computed function increases with bombardment. A possible interpretation in terms of a multiple-level model is under consideration.

The small discrepancy between data and theory at low temperature does not seriously affect the determination of the energy level of the donor centers, which were found to lie 0.29 ev above the valence band. It is possible that these centers are the same as those which were found to dominate the lifetime in *n*-type material. The latter were located 0.31 ev above the valence band, but the precision of the determinations is not great enough to rule out the possibility that they are the same centers which appear in the present case. The rate of introduction of these centers is 0.005 per electron-cm; this is very much lower than that observed for the net acceptor in *n*-type, and suggests that these centers may be associated with multiple damage. Bombardments at other energies or annealing experiments may serve to clear up this question.

(*c*) *Lifetime*

The measured lifetime in the *p*-type crystal as a function of bombardment is shown in Fig. 7. A subtraction of the type employed in the *n*-type case indicates that τ is inversely proportional to bombardment only up to 3×10^{14} electrons/cm², and decreases more slowly beyond that point. At this value of bombardment the change in resistivity is 0.06% and therefore should have no effect on lifetime. The lifetime has a minimum at 2×10^{17} electrons/cm², corresponding to the

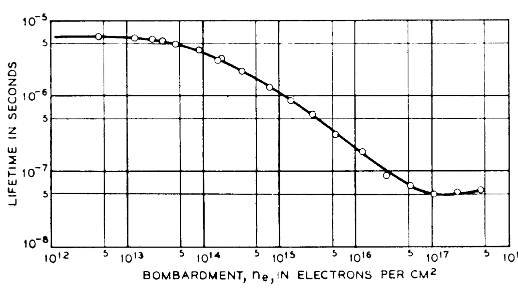

FIG. 7. Measured lifetime as a function of bombardment; 5 ohm-cm, *p*-type silicon.

point at which the hole concentration has been reduced to half its initial value, in agreement with the theory of Sec. 1(b).

An examination of the decay of the bombardment conductivity indicates that the lack of proportionality between reciprocal lifetime and bombardment may be due to a temporary trapping process. It was noted that the decay could not be represented by a single exponential in all ranges. A slower component was evident in the intermediate range of bombardment, and although an attempt was made to subtract its contribution, it may have falsified the decay times in the range of small

TABLE I. Energy levels in electron-bombarded silicon. The cross sections were obtained for $\eta=0.18$ centers/electron-cm.

Nature of center	*n*-type	*p*-type
Net acceptor	0.16 ev below conduction band; 0.18 centers/electron-cm	...
Net donor	...	0.29 ev above valence band; 0.005 center per elec.-cm
Recombination	0.31 ev above valence band $\sigma_{p0}=2.8\times10^{-14}$ cm² $\sigma_{n0}=1.0\times10^{-16}$ cm²	(0.24 ev)

bombardments where it could not be separated from the decay curve. The deviation from proportionality is nowhere greater than a factor of two and could readily be produced by such a mechanism. The same difficulty manifests itself in the temperature dependence of the bombardment lifetime in this crystal. A value of 0.24 ev has been obtained for the distance of the recombination centers from a band edge, but this value is not firmly established.

CONCLUSIONS

Electron bombardment of single-crystal silicon rods at relatively low energy allows the controlled, homogeneous introduction of defects and facilitates the study of energy levels associated with vacancies and interstitials. Measurements of conductivity, by the conventional method, and of lifetime, with the pulsed Van de Graaff technique, have served to locate the energy levels which control carrier concentration and lifetime in *n*- and *p*-type silicon of moderately high resistivity. A search for energy levels in other regions of the forbidden gap is contemplated. A study of mobility in bombarded crystals will be made in order to clarify the questions raised in the study of the *p*-type crystal.

The results so far obtained are summarized in Table I.

ACKNOWLEDGMENTS

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