Electron-Bombardment Damage in Silicon*

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The nature of 1-Mev electron-bombardment damage in silicon is investigated by using Hall effect, conductivity, and carrier-lifetime measurements. It is shown that the bombardment imperfections consist of sites containing at least two electrically active point defects. The connection between these sites and the energy levels in the forbidden gap found in an earlier investigation is established. The state of charge, the electron and hole-capture cross sections, and the temperature dependence of the energy levels of these imperfections are obtained.

DAMAGE PROCESS

IN the discussion of radiation damage, a distinction must be made between the "primary damage" produced by the collision and the damage observed in subsequent measurements after annealing and diffusion have changed the configuration of the structural disorder. It is in principle possible to observe the primary damage at low temperatures, where the processes of annealing and diffusion are slow, but how low the temperature must be is not known. Evidence has been obtained that significant rearrangements take place in silicon between 77°K and room temperature. Temperatures lower than 77°K have not been investigated, but it may be assumed on the basis of the study of copper[1] and germanium[2] that rearrangement takes place at lower temperatures as well.

However, even the production of the primary damage is not completely understood. The collision process may be treated rigorously and is not subject to theoretical uncertainties; that is, we know the energy spectrum of the struck atoms immediately after the collision. On the other hand, the probability that an atom of given energy, moving in a given direction, will produce a stable displacement is not known.[3] Recent experiments in germanium have shown that the Wigner threshold energy of about 30 ev, although it yields the correct cross section for the production of damage by particles capable of transferring energies much greater than this value, does not in reality correspond to a sharp cutoff in the production of damage.[4] Moreover, a dependence of the cross section on crystal direction has also been observed.[4] Leaving aside these considerations, which have not been explored in silicon, we shall discuss the damage process in terms of a threshold or displacement energy of 28 ev,[5] which corresponds to bombarding electrons of 280-kev energy, and adequately represents the damage rate under deuteron and high-energy electron bombardment.

The experiments to be described were carried out with 0.7- and 1.0-Mev electrons. At 0.7 Mev the maximum energy that can be transferred to a silicon atom in a collision with zero impact parameter is 3.4 times the assumed displacement energy. An atom with this energy is in turn capable of displacing its neighboring atoms as it is ejected from its lattice site. On the average such a collision will result in 2.2 displaced atoms.[6] However, to obtain a true picture of the damage produced, we must average over all impact parameters, from the largest, which results in the transfer of just the displacement energy, to zero, the most favorable. When this is done, the average number of displacements per collision is very close to unity; in other words, we are dealing with a situation where one atom is displaced from its normal lattice site to an interstitial position by each collision, and multiple damage is infrequent. The primary damage then consists of vacancy-interstitial pairs with a range of possible vacancy-interstitial distances.

The stability of these vacancy-interstitial pairs depends on the temperature and perhaps on the purity of the crystal. Annealing has been observed as a crystal bombarded at 77°K is warmed to room temperature. Most of the remaining damage anneals above 450°K.[7] The damage studied here is that remaining after the low-temperature annealing. In practice it may be produced by bombarding at or above room temperature. The damage produced by low-temperature bombardment and subsequent anneal is identical with that produced by high-temperature bombardment, but the effective cross section decreases with decreasing bombarding temperature. The implications of this observation are not clear at this point. The damage stable at room temperature may consist of isolated vacancies or interstitials, vacancy-interstitial pairs with a definite spacing, or complexes involving impurities. The role of crystal imperfections and impurities has not been investigated, but the fact that the same energy level is obtained in all crystals suggests that an impurity atom is not an electrically active part of the damage site.

* This work was supported in part by the Wright Air Development Center of the U. S. Air Force.
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NATURE OF DAMAGE

In the interpretation of bombardment effects, a distinction must be made between the damage sites and the point imperfections which it contains. The damage site is a volume about the point of initial collision which may contain either a grossly disturbed structure or, in the other extreme, only one or two point imperfections. This distinction is essential because some measurements are sensitive to properties of the site, while others detect those of the individual points.

Carrier mobility in the range where charged center scattering is dominant depends primarily on the net charge of the damage site rather than on the point charges which it contains, provided the characteristic dimension of the site is small compared to the spacing of the sites. This is readily seen by making a multipole expansion of the electric field of a site and determining the scattering due to the various terms. The monopole term, involving the net charge, produces the major effect. Dipole scattering has been shown to be weak compared to monopole and neutral impurity scattering[8]; scattering due to higher moments may be neglected.

Carrier concentration and lifetime on the other hand, depend on individual point defects. The properties of these defects may, however, be perturbed by nearby imperfections. Thus, the energy level of a donor may be raised toward the conduction band by a nearby negative charge, or the cross section of a charged center may be reduced by a charge of opposite sign located within its capture radius.

Measurements of these properties can serve to determine the donor or acceptor nature of bombardment defects by determining their state of charge. In this connection it should be noted that the differentiation between donors and acceptors cannot be made on the basis of the ratio of the statistical weight of the empty center to that of the full one, r, in the Fermi function[9]

$$\left[1+r\exp\left(\frac{E-E_f}{kT}\right)\right]^{-1}.$$

For example, a chemical donor can be empty in one way and filled in two (spin up or down) so that $r=\frac{1}{2}$ but an interstitial silicon atom can be empty in two ways (losing a spin-up or a spin-down electron) and filled in only one, so that $r=2$. An interstitial atom, acting in this manner, would also be considered a donor, however, since its two states of charge are neutral and positive.

A further difficulty arises because a linear temperature variation of the energy level cannot be distinguished from the effect of the statistical weight ratio. An energy level of the form $E_0+\alpha T$ results in a Fermi function

$$\left[1+r\exp(\alpha/k)\exp\left(\frac{E_0-E_f}{kT}\right)\right]^{-1}.$$

Consequently we can determine only the combined effect of the statistical weight ratio and the linear energy-level shift. If this is expressed as an effective temperature coefficient, α', we find that

$$\alpha'=\alpha+k\ln r.$$

DISCUSSION OF PREVIOUS WORK

In a previous paper[10] conductivity measurements were used to locate two energy levels in the forbidden gap of electron-bombarded silicon. The introduction of centers was found to be linearly dependent on the number of bombarding electrons per unit area, and independent of the rate of bombardment. A theoretical fit of the carrier concentration over a range of temperature indicated that the damage could be represented by a discrete energy level, that is, that all damage sites of a given type have the same binding energy. This suggests that the damage sites consist either of isolated point imperfections or else of paired imperfections with a definite spacing. The production of two sites spatially separated but of equal density and opposite charge is considered improbable; on the other hand, a damage site may give rise to two or more energy levels widely separated in the forbidden gap, each corresponding to a charged point imperfection, while the site considered as a whole remains neutral. Under moderate bombardment no change in the carrier concentration was found when the Fermi level was $2kT$ further from the band edge than was the bombardment center, indicating that both damage sites are neutral under this condition.

An analysis of lifetime in n-type material indicated the presence of a recombination center in the lower half of the energy gap, exhibiting a characteristic slope of 0.31 ev at high temperature. The reduction of lifetime in p-type material was also noted, and a slope of 0.24 ev obtained. The theory of recombination has recently been extended by Sandiford[11] and by Clarke,[12] taking into account the difference between the steady-state and transient lifetimes in the region where the density of recombination centers is comparable to the other parameters. The results obtained by applying this analysis to bombarded silicon, on the assumption that the product of thermal velocity and cross section is independent of temperature, are[13,14]

$$E-E_v=0.27\text{ ev}, \qquad \sigma_n=9.5\times10^{-15}\text{ cm}^2,$$
$$\eta=5\times10^{-3}\text{ cm}^{-1}, \qquad \sigma_p=8.0\times10^{-13}\text{ cm}^2.$$

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[14] The value of $E-E_v$ was obtained by correcting the slope of 0.31 ev for the temperature variation of the density of states.

TABLE I. Crystal properties and bombardments.[a]

Crystal No.	ρ	N_d-N_a	Impurity	E_e	n_e	η	T_b
I	1-p	-1.2×10^{16}	B R	0.7	5.1×10^{17}	0.008	300
II	12-p	-1.2×10^{15}	Ga	1.0	5.0×10^{16}	0.014	300
III	0.4 -n	1.5×10^{16}	As R	0.7	3.0×10^{16}	0.17	246
IV	15-n	4.0×10^{14}	As R	0.7	6.0×10^{14}	0.11	246
V	70-n	6.0×10^{13}	...	0.7	8.3×10^{14}	0.05	78
VI	2-n	2.2×10^{15}	P NR	1.0	9.7×10^{15}	0.18	193
VII	0.01-n	4.3×10^{18}	As R	0.7	5.6×10^{18}	0.57	246
VIII	0.03-p	-2×10^{19}	B R	0.7	4.2×10^{18}	1.6	246
Reference 10	7-n	6.2×10^{14}	As R	0.7	...	0.16	333
Reference 10	5-p	-2.1×10^{15}	SR	0.7	...	0.005	333

[a] ρ = resistivity and type, ohm-cm; N_d-N_a = uncompensated donor or acceptor concentration, cm^{-3}; E_e = bombarding energy, Mev; n_e = number of bombarding electrons/cm^2; η = rate of introduction of damage, cm^{-1}; T_b = bombarding temperature, °K. R means that the crystal was rotated during growth, NR that the crystal was not rotated during growth, and SR that the crystal was slowly rotated during growth.

The rate of introduction of damage was here obtained from lifetime data alone, utilizing the behavior at a high density of recombination centers. (Note that it is possible to separate the cross section from the density of centers.) The resulting agreement in location and rate of introduction indicates the identity of this recombination center with the net donor found in conductivity measurements.

The present work deals with a number of aspects not considered in the earlier papers. Hall-effect measurements have been made to investigate changes in mobility, which in turn allow determination of the state of charge of the damage sites. The donor or acceptor nature of the various bombardment defects has been identified. Measurements have been made on a number of crystals over a greater range of temperature, to determine the temperature coefficients of the known energy levels and to search for others. Regions of the forbidden gap near the band edges have been investigated.

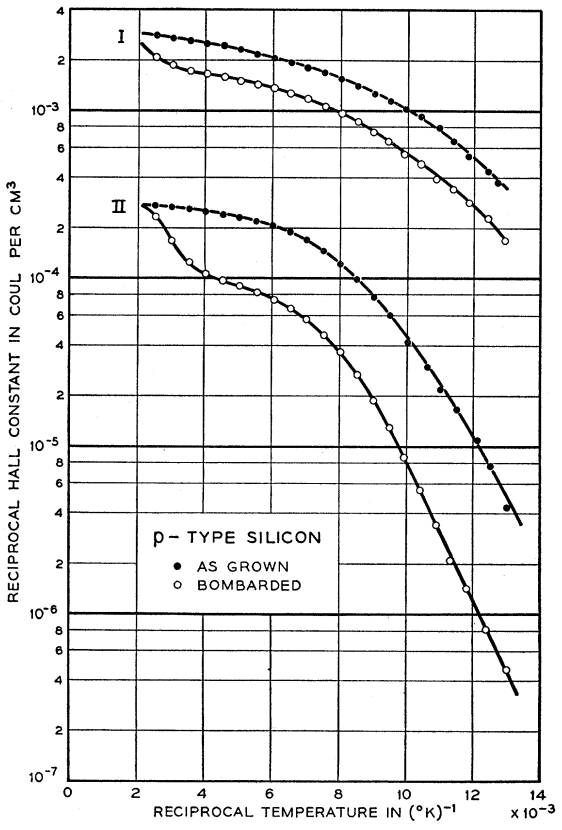

FIG. 1. Reciprocal of the Hall constant before and after bombardment in 1-ohm-cm boron-doped silicon, sample I, and 12-ohm-cm gallium-doped silicon, sample II.

PROCEDURE

The samples studied were in the form of "bridges" cut from pulled single crystals. Each sample was soldered to a copper frame at one end, and was otherwise unsupported. Electron bombardments were made in the vacuum of the Van de Graaff accelerator at a variety of temperatures (Table I) and at bombarding energies of 1.0 and 0.7 Mev. Samples used in carrier concentration and mobility determinations received equal bombardments on the front and rear surfaces; lifetime samples were bombarded from one side only. Bombardment intensities were chosen so that the density of bombardment centers remained smaller than the concentration of uncompensated chemical donors or acceptors, so that the resistivity of the sample would remain low over the range of temperature to be studied. Sample thickness was in the range of 10 to 25 mils. Further details are identical with those of reference 10.

DISCUSSION OF RESULTS

1. The Lower Half of the Energy Gap

(a) *Carrier Concentration*

The reciprocal of the Hall constant (proportional to the carrier concentration and the ratio of conductivity mobility to Hall mobility) for two p-type silicon samples before and after electron bombardment is given in Fig. 1. In the data for the unbombarded samples, the temperature dependence in the region above 150°K is due entirely to changes in the mobility ratio. The ratio changes very little with bombardment in this region where lattice scattering dominates; the displacement of

the data for the bombarded samples is due almost entirely to the filling of an energy level as the sample is cooled. However, the curves for the bombarded samples at low temperature illustrate two additional effects, which manifest themselves as a more rapid drop in the reciprocal Hall constant than was observed in the unbombarded samples. The mobility ratio changes as lattice scattering becomes secondary to scattering by charged impurities produced by bombardment, and the freeze out of carriers on chemical acceptors changes due to the increased compensation. More specifically, the fractional freeze out of the residual carriers on the chemical acceptors takes place more rapidly than the fractional freeze out of the total carriers on the same density of acceptors. This effect is seen clearly in the 12 ohm-cm gallium-doped crystal, sample II, where the slope at low temperature in the bombarded sample corresponds to the energy level of the gallium acceptor.

These data admit of an interpretation in terms of a single discrete energy level having a small temperature coefficient. The equation

$$E-E_v=kT\ln\frac{rN_v}{N_A-\frac{1}{2}N},$$

valid in the region where the chemical acceptors remain fully ionized, was used to determine the position of the energy level at the temperature at which the bombardment centers are half-filled. In sample I the point of half-filling is 459°K, yielding an energy level located at 0.291 ev; in sample II the point of half-filling is 351°K and the energy level 0.286 ev. (A value of 0.29 ev was obtained on the basis of conductivity measurements alone.[10]) These results are consistent with an energy level of the form

$$E-E_v=0.268+5\times10^{-5}\quad(\text{ev}),$$

and a statistical weight ratio of unity, or else with a constant energy level of 0.268 ev and a statistical weight ratio of $\frac{1}{2}$ for holes.

The temperature coefficient of an energy level due to a simple substitutional impurity may be expected to be a fraction of the temperature coefficient of the energy gap, which in silicon is -3.6×10^{-4} ev/°K.[15] If $r=1$, the total effect observed above is ascribed to the temperature coefficient, and we find that as the energy gap decreases, the distance of the bombardment level from the band edge actually increases. The sign of the temperature coefficient reverses only if $r<\frac{1}{2}$.

The motion of this bombardment level is in the same direction as that of the Fermi level in the range investigated. The motion of the latter in this range is given by

$$\frac{d}{dT}(E_f-E_v)=\frac{E_f-E_v}{T}+\tfrac{3}{2}k,$$

and in the samples under study is approximately 10^{-3} ev/°K. The effect of the simultaneous motion of the Fermi level and the energy level is to smooth the curve of carrier concentration when plotted as a function of temperature. This effect is small, however, and was not detected in the earlier investigation.

(b) *Mobility*

In the analysis of mobility the experimental conductivity mobility of Ludwig and Watters[16] was employed in conjunction with ionized impurity scattering mobilities computed from the Conwell-Weisskopf formula.[17] These were combined according to the method of Conwell.[18] The lattice-scattering mobility is known accurately only in the range from 100 to 450°K, making analysis at other temperatures questionable. Further uncertainties arise because the ionized-impurity-scattering mobility and the method of combining lattice and impurity mobility were evaluated for spherical energy surfaces.[17,18]

In the 12-ohm-cm gallium-doped sample, the observed change in mobility with bombardment is small, because the density of bombardment centers is small compared to the density of compensated chemical impurities present in the original crystal. In the 1-ohm-cm sample, compensation is low. The Hall-constant data, Fig. 1, show that the 0.27-ev level remains filled from the lowest temperature studied to well above room temperature, so that a simple analysis of the mobility as a function of temperature is possible. The Hall mobility before and after bombardment is shown in Fig. 2. The mobility of the unbombarded sample is in good agreement with similar data of Morin and Maita.[15] The rise in mobility below 100°K is associated with a decrease in the density of charged scattering centers as the density of ionized acceptors drops. After bombardment this rise is not observed, because the density of charged centers remains equal to at least twice the density of the bombardment centers.

In the analysis below we assume that the fractional change in conductivity mobility is equal to the measured fractional change in the Hall mobility, i.e., that the ratio of conductivity mobility to Hall mobility is independent of bombardment. This approximation is valid provided only small changes in mobility are made. At 100°K the Hall mobility in the 1-ohm-cm sample decreased by 17%. Combining a lattice-scattering mobility of 7500 cm^2/volt-sec with the ionized-impurity mobility for 9×10^{15} charged centers/cm^3, we obtain a conductivity mobility of 3550 cm^2/volt-sec. After bombardment with 5.1×10^{17} electrons/cm^2, the density of charged centers was 1.3×10^{16}, including 4×10^{15} cm^{-3} bombardment defects, which we assume to be singly charged. The computed mobility is now 2880

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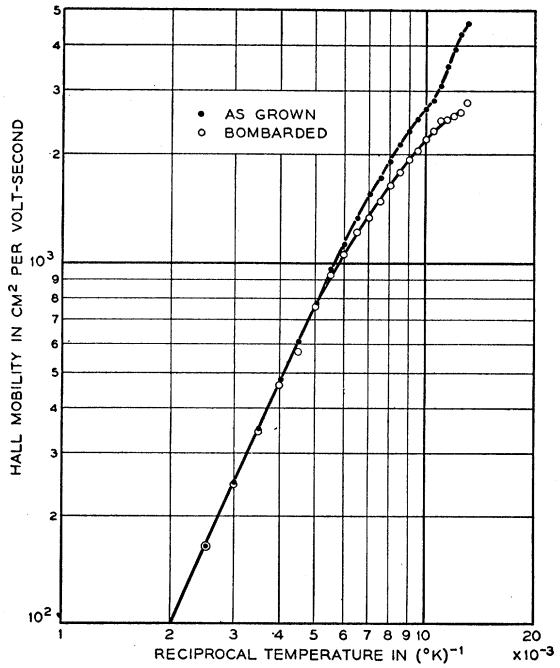

FIG. 2. Hall mobility before and after bombardment in 1-ohm-cm boron-doped silicon, sample I, Fig. 1.

cm²/volt-sec, a decrease of 19%. This is somewhat larger than the observed change, largely because of the simultaneous change of the mobility ratio. This result indicates that the density of charged scattering centers introduced by bombardment is equal to the density of the 0.27-ev level when the latter is occupied by holes. If the center is assumed to be doubly charged, the ionized impurity mobility, which varies inversely with the square of the charge, is much too low to yield agreement with the data.

We conclude that the site containing the 0.27-ev level is singly charged when the Fermi level is below it and that there are no other charged sites of comparable density under these conditions. It may be seen that the charge must be positive. If it were negative, the site would be doubly negative when the Fermi level is above it, requiring in turn the presence of two fixed positive charges to maintain neutrality without changing the carrier concentration. These fixed charges would reduce the mobility and thus contradict the measurements. The conclusion that there are no other charged sites is important, for it indicates that the level found in the upper half of the gap is associated with a neutral site, in this Fermi level position, and that other possible levels, like those seen near the band edges in deuteron-bombarded material, are neutral if present here. The determination of mobility in p type is a particularly sensitive test, in spite of the lower lattice scattering mobility, because the density of the 0.27-ev level is much lower than that of the 0.16-ev level in the upper half of the gap.

A model of the damage site giving rise to the 0.27-ev level must explain three salient facts: (1) lifetime measurements show that the center has unit negative charge when the Fermi level is in the upper half of the gap; (2) mobility determinations demonstrate that the site has unit positive charge when the Fermi level is below the 0.27-ev energy level; and (3) carrier removal experiments indicate that the site is neutral when the Fermi level is above the energy level in question.

These conditions are met by a damage site containing two point defects, one having unit positive charge and the other unit negative charge when the Fermi level is above 0.27 ev. The observed energy level arises from the acceptor member of the pair. (It is termed an acceptor because it exhibits two states of charge, negative and neutral.) The energy level of the accompanying positive charge has not been found, probably because it is located very close to the conduction band edge. It may be recalled that the 0.27-ev level was termed a "net donor" in the preceding paper.[10] This does not contradict its present identification as an acceptor, because the action of the acceptor member of the donor-acceptor pair in which the donor lies above the acceptor is indistinguishable from that of a donor when only carrier concentration is considered. Mobility effects are due to the total charge of the site and are small unless the Fermi level is below the 0.27-ev level.

An estimate of the spacing of the two members of the damage site can be made on the basis of the hole-capture cross section obtained from lifetime measurements. To first approximation, the radius of the charged-center cross section can be no greater than the spacing of the members of the pair, since the Coulomb potential of the capturing center is thoroughly disturbed by a charge of opposite sign. On this assumption we find that the spacing must be at least 50 A, a distance large compared to the nearest-neighbor distance in silicon. The energy of interaction of two unit charges at this distance is 0.025 ev, so that the location of the energy level of the acceptor center is only slightly perturbed by the nearby positive charge. This effect is sufficiently small so that the broadening of the energy level produced by the existence of a range of spacings within the sites may escape detection in measurements of the type described.

2. Upper Half of the Energy Gap

The analysis of data for the upper half of the energy gap parallels that just given. The reciprocal of the Hall constant for three n-type samples, Fig. 3, indicates an energy level,

$$E=0.160+1.1\times10^{-4}T \text{ ev},$$

for $r=1$. The sign of the temperature coefficient is opposite to that expected for a simple substitutional imperfection, in that the level moves away from the band edge as the energy gap decreases.

Mobility data after bombardment for sample III, Fig. 4, are consistent with an added singly charged scattering center equal in concentration to that of the bombardment level. Samples IV and V are heavily compensated, having ionized-impurity concentrations in excess of the uncompensated donor concentration. The change of mobility with bombardment is consequently small. In sample V the observed change of 5% at 100°K is in agreement with the known density of charged centers. Data for crystal VI clearly show the increase in the density of charged scattering centers at

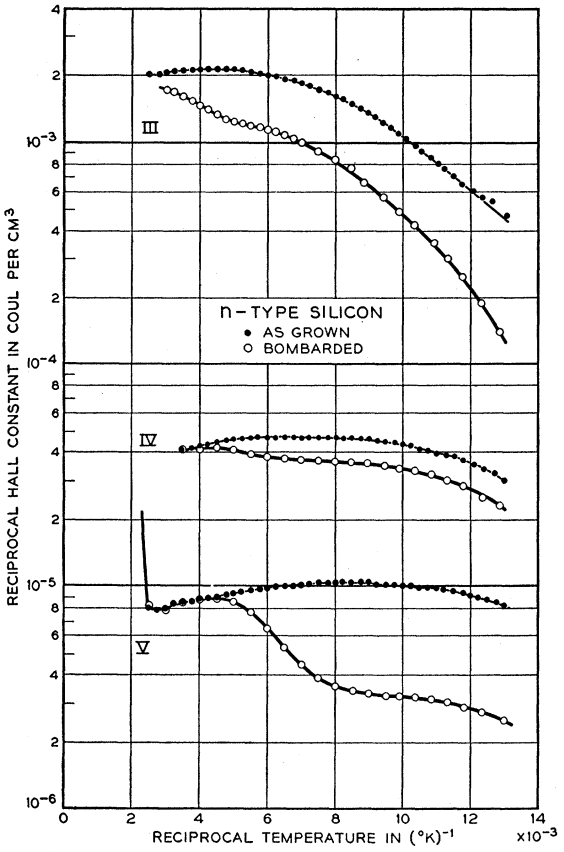

FIG. 3. Reciprocal of the Hall constant before and after bombardment in 0.4-ohm-cm arsenic-doped silicon, sample III, in 15-ohm-cm arsenic-doped silicon, sample IV, and in 70-ohm-cm n-type silicon, sample V.

the temperature where the carrier concentration drops as the sample is cooled (Fig. 5). This confirms directly that the reduction in mobility is due to the bombardment site containing the 0.16-ev level. We also conclude that the site is neutral when the Fermi level is below the 0.16-ev level and negatively charged when it is above. This behavior is that of an acceptor but it is also consistent with that of a donor in conjunction with a nearby positive charge.

Lifetime measurements in 5-ohm-cm p-type silicon indicate that this level in the upper half of the energy gap may act as a recombination center. The data of

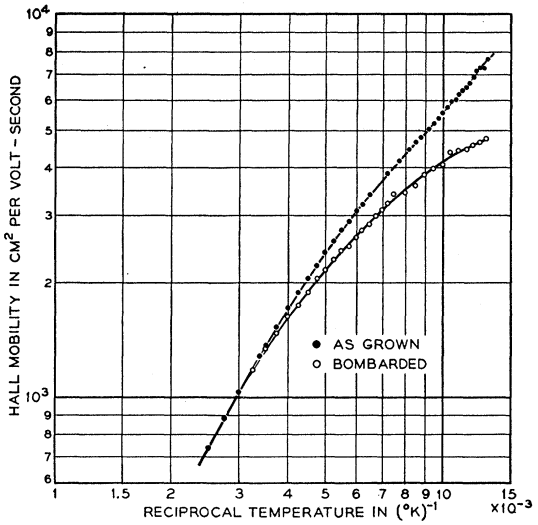

FIG. 4. Hall mobility before and after bombardment in 0.4-ohm-cm arsenic-doped silicon, sample III, Fig. 3.

lifetime as a function of reciprocal temperature, Fig. 6, are compatible with this interpretation. The solid lines were computed assuming: (1) an energy level 0.18 ev below the conduction band, corresponding to the slope of 0.24 ev[10] corrected for the temperature dependence of the density of states; (2) a rate of introduction of 0.18 cm^{-1} obtained from the leveling off of the lifetime in Fig. 7 of reference 10; and (3) cross sections for hole and electron capture of 1.8×10^{-15} and 1.9×10^{-15} cm^2, chosen for optimum fit with the present data. In making the fit, the product of cross section and thermal velocity was again assumed to be independent of temperature, which may account for the difference between the energy-level location obtained here and that obtained from Hall-coefficient measurements. The good agreement in the rate of introduction of damage and in the location of the energy level indicates that the same level is responsible for the reduction of lifetime in p-type and the effect on the carrier concentration in n-type silicon.

The effect of the level in the lower half of the energy

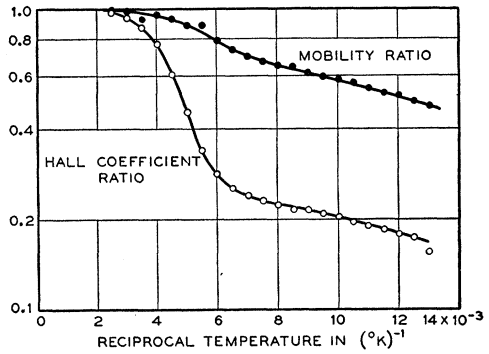

FIG. 5. Ratio of Hall mobility after bombardment to that before bombardment, and ratio of the Hall coefficient before bombardment to that after bombardment in 2-ohm-cm phosphorus-doped silicon, sample VI.

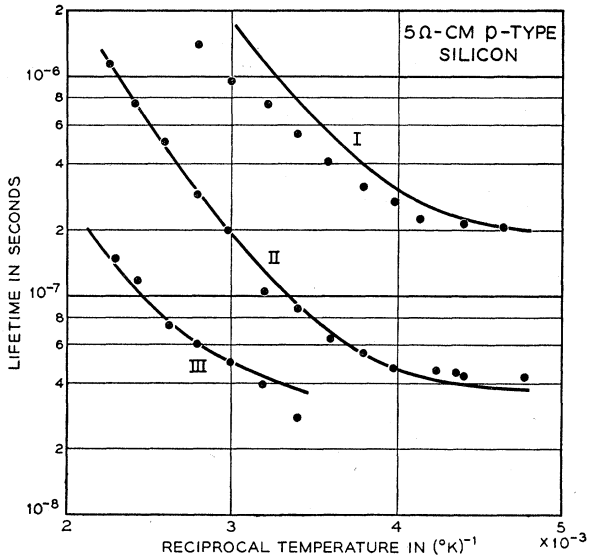

FIG. 6. Minority carrier lifetime in 5-ohm-cm p-type silicon after various amounts of electron bombardment, reference 10. I···1.8×10^{15} electrons/cm², II···1.8×10^{16} electrons/cm², III···1.8×10^{17} electrons/cm².

gap on the lifetime in p-type material must also be considered. Knowing the cross sections and rate of introduction of this level, the expected effect may be readily computed. When small-signal conditions are met, we find the lifetime given by

$$\tau=\left(1+\frac{N+p_1}{p_0}\right)(\sigma_n v_n N)^{-1},$$

valid in the range of temperature and bombardment of Fig. 6. According to this equation, the lifetime should be temperature-independent below 350°K and rise sharply with a slope of 0.3 ev above that point. This is not in accord with the observations, although the magnitude of the lifetime at 350°K is approximately that observed. In the large-signal, nonlinear region, the decay should be nonexponential and the decay time should be a function of the magnitude of the excitation. This again was not observed. The failure to see the action of this center in p-type crystals may be due to a nonadditivity of reciprocal lifetimes[13] or to an increase in the lifetime in the large-signal region. The high-temperature behavior of the curve for 1.8×10^{15} electrons/cm², Fig. 6, may be due in part to the center in the lower half of the energy gap, since the concentration of defects here is sufficiently low so that nonadditivity of reciprocal time constants may not yet be significant.

The hole- and electron-capture cross sections were both found to be approximately equal to a characteristic neutral-center cross section. However, one of the two capture processes must involve a Coulomb attractive center whose cross section is expected to be many orders of magnitude greater. This suggests that the Coulomb cross section is perturbed by a nearby center of opposite charge. Under this condition the cross section can be no greater than πd^2, where d is the spacing of the two charged centers. The above cross sections require a spacing of 2.5 A, a number which should be compared to the smallest vacancy-interstitial spacing of 2.44 A, and to the second smallest vacancy-interstitial distance of 2.71 A. The discreteness of the energy level indicates that the spacing involved can have at most a few allowed values, since the energy of interaction of two unit charges separated by 2.5 A is 0.5 ev.

These results suggest that the damage site contains a vacancy-interstitial pair in, perhaps, the first or second nearest-neighbor position. The 0.16-ev level is then due to the positive member of this close-spaced pair of opposite charges, and is consequently a donor. This inference should be examined in the light of further experiments, such as a study of the kinetics of the anneal of this center, or of the production of this center under bombardment with more energetic electrons or heavy particles.

3. Energy Levels near the Band Edges

Energy levels resulting from high-energy electron and heavy-particle bombardment of silicon have recently

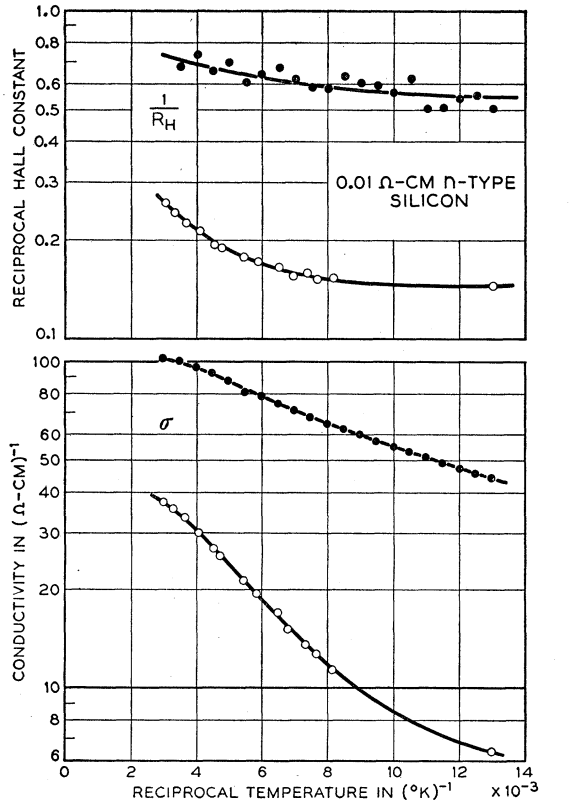

FIG. 7. Reciprocal of the Hall constant and conductivity before and after bombardment in 0.01-ohm-cm arsenic-doped silicon, sample VII.

been reported from two sources. Energy levels produced by deuteron irradiation have been observed near the band edges.[19] A state 0.025 ev below the conduction band was ascribed to an isolated interstitial atom, and a state 0.055 ev above the valence band edge to an isolated vacancy. Evidence was also obtained for levels further inside the gap, which were ascribed to clusters of defects. Measurements of Hall mobility as a function of bombardment have shown a minimum with the Fermi level 0.23 ev below the conduction band, and another with the Fermi level 0.25 ev above the valence band,[20] indicating the presence of two energy levels which may be related to those discussed above. Bombardment with 4.5-Mev electrons has also shown the presence of energy levels near the band edges[21] and given some evidence for levels deeper in the forbidden gap.

In view of these observations, a search of the regions near the band edges was made following 0.7-Mev electron bombardment. The reciprocal Hall constant and conductivity in a 0.01-ohm-cm n-type sample, bombarded at 246°K with 5.6 10^{18} electrons/cm^2, is shown in Fig. 7. No anneal was observed on warming the bombarded sample to room temperature. The data are not consistent with an interpretation in terms of a single discrete energy level. This is not surprising, in view of the high density of centers introduced by bombardment and the high density of donors present in the unbombarded material. More important, however, is the fact that the Fermi level at 333°K, when the bombardment centers are still 86% occupied, is located 0.08 ev below the edge of the conduction band. The data indicate a broad energy level extending from 0.05 ev to the energy level of the isolated defect, suggesting that the observed behavior is due to the same imperfection found in less heavily bombarded material, but with its level broadened by interaction with near neighbors. The rate of introduction of damage in this crystal is 0.57 cm^{-1}, which is higher by a factor of three than that characteristically found in n-type material. The production of damage was monitored during bombardment and found to be linear from 5×10^{16} to 1×10^{18} electrons/cm^2, dropping somewhat beyond that point.

A degenerate p-type sample was also investigated. It received a total bombardment of 4.2×10^{18} electrons/cm^2 at 0.7 Mev. A 26% anneal was observed on warming the sample from the bombarding temperature of 246°K to somewhat above room temperature. The rate of introduction of damage after the anneal was 300 times greater than that characteristically observed in p-type material of lower carrier concentration, and may indicate the presence of an energy level close to the valence band edge.

CONCLUSIONS

It has been shown that the damage remaining in silicon at room temperature following bombardment with 0.7- to 1.0-Mev electrons consists of sites containing paired point imperfections, which give rise to two energy levels. The upper level is a donor in association with a closely spaced negative imperfection, separated by a distance of perhaps 2.5 A; it has an energy level located $(0.160+1.1\times10^{-4}T)$ ev below the conduction band. The lower level is an acceptor in association with a positive charge at a distance greater than 50 A; it has an energy level $(0.268+5\times10^{-5}T)$ ev above the edge of the valence band. These imperfections correctly account for the behavior of the carrier concentration and mobility in the silicon crystals which have been studied. A broadening of the upper energy level has been observed in a low-resistivity crystal. (0.01 ohm-cm). The hole- and electron-capture cross sections of the 0.160-ev level are 1.8×10^{-15} and 1.9×10^{-15} cm^2, respectively, and those of the 0.268-ev level are 8.0×10^{-13} cm^2 and 9.5×10^{-15} cm^2.

No difference in the location of the energy levels was found following bombardment at 0.7 or 1.0 Mev, nor were the levels shifted by bombarding at low temperature and annealing at the customary bombarding temperature, or even by annealing above 500°K. One of the major remaining problems is the variation in the rate of introduction of damage from crystal to crystal, and the variation with temperature in a given crystal. These problems have not been explored sufficiently to attempt an explanation. A useful, independent check on the model proposed in this paper can be made by a study of the kinetics of the anneal of bombardment damage in silicon. The two centers which are introduced should exhibit a strikingly different anneal if one consists of a close-spaced pair which can annihilate with a single jump, and the other consists of a wide-spaced pair which may anneal like an isolated defect.

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