Recombination Properties of Bombardment Defects in Semiconductors*

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The theory of recombination via defects having energy levels in the forbidden gap is reviewed. Emphasis is given to those aspects which complicate interpretation of lifetime data, such as the inherent difference between steady state and transient measurements, large-signal behavior, competing recombination mechanisms, trapping, the possible existence of strongly temperature-dependent cross sections, and the properties of multilevel defects. A summary of the known recombination properties of bombardment-produced defects is given.

INTRODUCTION

CRYSTALLINE defects give rise to energy levels in the forbidden gap of semiconductors. The location of such defects is usually determined from measurements of the Hall effect taken over a range of temperature. When such measurements are combined with those of conductivity the state of charge of the defect can sometimes be inferred as well. Additional information can be obtained from measurements of the lifetime of nonequilibrium carrier concentrations, which yield capture cross sections of defects for minority carriers, and under some circumstances for majority carriers. Since the magnitude and temperature dependence of these cross sections are related to the state of charge of the capturing defect, lifetime measurements can help to define the nature of crystalline imperfections.

The basic aspects of the recombination of excess carriers in semiconductors are now familiar and have been recently treated in a number of review articles.[1–4] Further details on many of the subjects which will be mentioned only briefly here can be found in these articles. There are four chief recombination mechanisms: (1) recombination via levels or states in the forbidden gap, (2) recombination via surface states, (3) recombination by the Auger effect, and (4) band-to-band recombination in which the excess energy is radiated as a photon, sometimes accompanied by phonons. For the study of crystalline defects, the first mechanism is the most important, since the measurements are here directly related to the properties of the defects. We will consequently confine ourselves almost entirely to this subject.

The second mechanism, recombination via surface states, often adds complications which may mask the volume effect, especially since the surface recombination velocity may depend on the bombardment of the specimen. This field has been explored to only a slight extent although changes in device parameters ascribable to surface changes are well known. Recombination via the Auger effect[5] has recently been invoked to explain the lifetime in InSb which is inherently short (10^{-7} sec at room temperature). Here radiation effects on lifetime have not been studied, probably because the inherently short lifetime makes measurements difficult, and also because the preparation of high purity material with controlled lifetime is not very far advanced. Radiative band-to-band recombination[6] has been studied in many semiconductors. The change in the fraction of carriers recombining by this mechanism could be used as an index of the imperfections introduced by bombardment.[7] This, however, does not appear to be a powerful tool.

Theory of Recombination via Defect Levels

Recombination via levels in the forbidden gap was first discussed by Hall and by Shockley and Read.[8] The general result of their analysis is that the net capture rates of a given defect for electrons and holes are given by

$$U_n=C_n[N^0\delta n-(n_0+n_1+\delta n)\delta N],\quad U_p=C_p[N^-\delta p+(p_0+p_1+\delta p)\delta N]. \tag{1}$$

The terms are defined in Table I. To discuss a particular recombination process we then need solutions to a set of coupled differential equations

$$(d\delta n/dt)=g_n-U_n,\quad (d\delta p/dt)=g_p-U_p, \tag{2}$$

subject to the neutrality condition

$$\delta p-\delta n=\delta N. \tag{3}$$

Relatively simple solutions are obtained only in restricted cases; a general solution has not been obtained and would be of dubious value because of its complexity.

We will consider steady state and transient solutions separately. In either case the desired solution is the free time of a minority carrier, i.e., the time spent by an excess minority carrier in the minority band before

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

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TABLE I. Definition of symbols.

U_n, U_p	net capture rates of a defect for electrons and holes.
C_n, C_p	the capture constants for electrons and holes equal to $\langle\sigma_n v_n\rangle$ and $\langle\sigma_p v_p\rangle$.
σ_n, σ_p	capture cross sections for electrons and holes.
v_n, v_p	thermal velocities of electrons and holes.
δn, δp	deviations from the thermal equilibrium carrier concentrations, n_0 and p_0.
N^0, N^-	the thermal equilibrium density of empty and filled defect states, $N^0+N^-=N$.[a]
δN	deviation from the thermal equilibrium defect population.
n_1, p_1	carrier concentrations when the Fermi level is at the defect level.
g_n, g_p	the volume rate of generation of electrons and holes by external means.

[a] $N^0=N[n_1/(n_0+n_1)]=N[p_0/(p_0+p_1)]$; $N^-=N[n_0/(n_0+n_1)]=N[p_1/(p_0+p_1)]$.

it is annihilated. In the steady state case this is taken to be the excess minority carrier concentration divided by the net capture rate which is equal to the generation rate. This is not the lifetime obtained from a measurement of the diffusion length. It should also be noted that the free time of excess majority carriers is in general not equal to that of minority carriers.

The minority carrier lifetime is given by

$$\tau=\frac{\tau_{p0}(n_0+n_1)+\tau_{n0}(p_0+p_1)+a}{n_0+p_0+N^0N^-/N} \qquad (4)$$

where

$$a=\begin{cases}\tau_{n0}N^- & \text{in } p\text{-type}\\ \tau_{p0}N^0 & \text{in } n\text{-type.}\end{cases}$$

If the recombination center density is sufficiently small this reduces to the familiar form

$$\tau_0=\frac{\tau_{p0}(n_0+n_1)+\tau_{n0}(p_0+p_1)}{n_0+p_0}, \qquad (5)$$

which also applies generally to the diffusion length. If the recombination center density is sufficiently small and the injection level sufficiently large so that the excess hole and electron densities are equal, we obtain for the large signal case

$$\tau=\frac{\tau_{p0}(n_0+n_1+\delta n)+\tau_{n0}(p_0+p_1+\delta n)}{n_0+p_0+\delta n}. \qquad (6)$$

In the transient case[9–11] the solution is the characteristic time of the decay of the excess carrier concentration. If the density of injected carriers is sufficiently small so that the differential equations are linear this is the time constant of an exponential. The result then is similar to Eq. (4),

$$\tau=\frac{\tau_{p0}(N^0+n_0+n_1)+\tau_{n0}(N^-+p_0+p_1)}{n_0+p_0+N^0N^-/N}, \qquad (7)$$

which for small recombination center densities becomes identical with the steady state solution, Eq. (5). An approximate solution valid only in the region of transition from small to large signal has also been given.[11] For very large deviations from equilibrium the decay is not exponential and is given by the following equation[12]:

$$\delta n=\delta n_0\exp\left(\frac{-t}{\tau_{n0}+\tau_{p0}}\right)\times\left(\frac{1+(n_0+p_0)/\delta n_0}{1+(n_0+p_0)/\delta n}\right)^{1-[\tau_0/(\tau_{n0}+\tau_{p0})]}. \qquad (8)$$

In the intermediate region solutions in closed form have not been obtained. In certain cases, such as the one which arises when the recombination level and the Fermi level are in the same half of the energy gap, it may be experimentally impossible to realize an injection level small enough to operate in the linear region. This comes about since the injection level in n type should be small compared to $(N^-+p_0+p_1)$. Some machine calculations applicable to this situation have recently been reported.[13]

Detailed discussions and extensions of various aspects of these equations have been given in a number of publications.[14–17] An extension to degenerate semiconductors has been given by Rose.[18]

The idealization made in the foregoing discussion that only a single species of defect contributes to recombination is seldom met in real situations. The multitude of levels usually found in bombarded material should serve as adequate warning that single level solutions may not be applicable. The independent multilevel steady state case has been discussed by Kalashnikov and Okada[19] and the transient case by Wertheim.[11] In both cases it turns out that it is not proper to add recombination rates of the individual species of defects unless certain restrictive conditions are met. These are that the concentrations and the cross sections for carrier capture of both defects be such that no appreciable fraction of the injected carriers is trapped.

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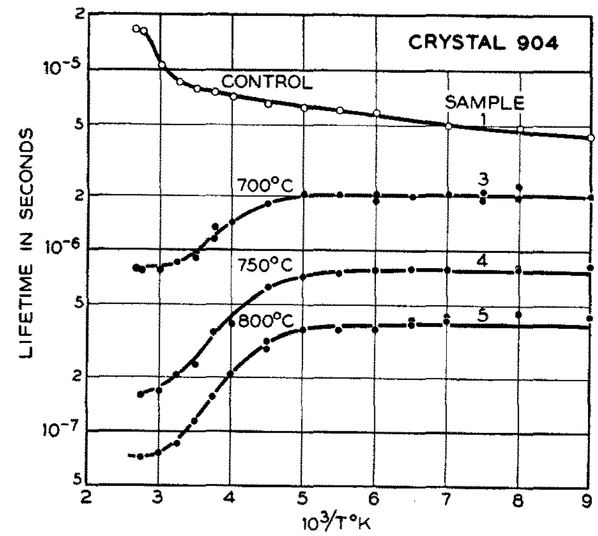

FIG. 1. Lifetime in a multilevel system (p-type germanium containing nickel).

The case where one of the defects communicates only with the minority carrier band, i.e., acts as a minority carrier trap, has been treated by Haynes and Hornbeck[20] and others.[11,21] This case is particularly applicable to bombarded germanium at low temperature. Another case, not usually met in the elemental semiconductors, is that discussed by Rose[22] which deals with continuous energy level spectra.

More important than the case of multiple independent levels is that where two or more levels belong to the same defect, i.e., they correspond to successive stages of ionization, rather than to the ground and excited states of one electronic level. This case applies to most of the well known chemical recombination centers in germanium and silicon, and also to radiation damage in germanium. The most important chemical recombination centers in germanium, copper, and nickel, have three and two levels, respectively, while the most important one in silicon, namely gold, has two. The equilibrium statistics are easily generalized for such defects,[23–25] but the nonequilibrium recombination case leads to considerable difficulty. The general situation has recently been discussed by Sah and Shockley.[26] The examination of experimental results in terms of this picture has just begun.

An illustration may be drawn from the study of chemical impurities in germanium. One of the most thoroughly studied systems, nickel in germanium, offers an instructive example of recombination through two levels belonging to the same atom. These levels correspond to successive added electrons. In p type the temperature dependence of lifetime was found to have the behavior shown in Fig. 1.[27] This behavior cannot be realized in terms of single level recombination statistics, unless one of the captured constants has an exponential temperature dependence with an activation energy of 0.2 ev. In terms of the double level model of the simplest kind, where only small changes from the thermal equilibrium concentration are allowed, this behavior follows directly from the fact that a level exists only if the atom is in either of the two states of charge adjoining that level. Specifically an atom exhibiting two levels exists in three states of charge Fig. 2. The lower level exists only if the atom is in either of the lower two states of charge, and the upper only if the atom is in either of the two higher states. The levels of nickel in germanium fall as shown in Fig. 2. In p type the Fermi level may pass through the lower level as the temperature is changed, producing large changes of lifetime by modulating the density of the upper level.

In a situation such as this, the lifetime equation may be written

$$\tau = 1/(C_{n1}N^{(0)} + C_{n2}N^{(-)})$$

where we have assumed that electron capture will be the time limiting step in recombination via both the lower and upper level. Figure 3 shows measurements of lifetime in another p-type specimen, together with a fit made using experimentally measured concentrations of the various charge states of nickel and substituting in the foregoing equation, assuming that the capture constants are independent of temperature. This assumption seems to be borne out by the fit obtained.

Capture Cross Sections

The usefulness of lifetime measurements depends ultimately on our ability to relate the measured magnitude and temperature dependence of a cross section to

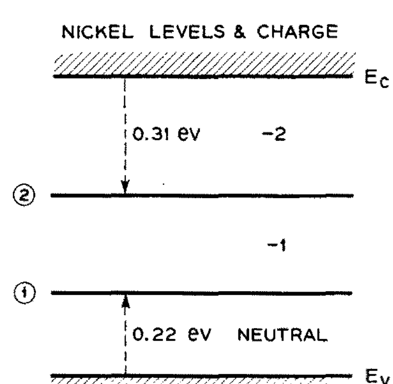

FIG. 2. The level scheme and states of charge of a multilevel impurity.

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[21] H. Y. Fan, Phys. Rev. **92**, 1424 (1953); Fan, Navon, and Gebbie, Physica **20**, 855 (1954).
[22] A. Rose, Phys. Rev. **97**, 322 (1955).
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[24] W. Shockley and J. T. Last, Phys. Rev. **107**, 392 (1957).
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[27] G. K. Wertheim, Bull. Am. Phys. Soc. Ser. II, **4**, 27 (1959).

values derived from a model of a crystalline defect. There are three types of capture processes, those involving capture by a neutral defect, those involving capture by a defect whose charge is opposite to that of the carrier, and those where the charge is the same. Recombination always involves one Coulomb-attractive process and either a neutral or a repulsive one. The Coulomb-attractive capture process is seldom observed in conventional lifetime measurements since the other, slower process usually determines the lifetime.

A theoretical treatment of the capture process has been given only for the Coulomb-attractive case where the capture process depends on the Coulomb potential and not on the details of the electronic structure of the defect. The cross section for this process is very large at low temperature and decreases rapidly as the temperature increases. Characteristic values observed experimentally are 10^{-13} cm^2 at 78°K and 10^{-15} cm^2 at 300°K. In the neutral case there is no long-range attractive potential so that cross section should be related to the characteristic atomic dimension. The capture constant may well be independent of temperature. Characteristic values obtained experimentally at room temperature are in the vicinity of 10^{-16} cm^2. They do not exhibit a strong temperature dependence. In the repulsive case, cross sections smaller than 10^{-16} cm^2 are to be expected. These may exhibit an exponential temperature dependence of the form $\exp(-E/kT)$ where E may be as large as a few tenths of an electron volt. This behavior could arise from a potential barrier surrounding the defect which can be overcome only by carriers which have an energy greater than that corresponding to the band edge. The experimental evidence supporting this model has recently been challenged. Experimentally cross sections greater than 10^{-16} cm^2 have been observed for repulsive defects.

It is apparent that the distinction among the three capture processes cannot be made on the basis of room temperature cross sections alone, since values ranging from 10^{-15} to 10^{-16} cm^2 have been obtained in all cases. At low temperature, 78°K, the results should be less ambiguous. These facts indicate that the temperature dependence of the cross section is an important parameter which can help to determine the charge of the recombination defect. No attempt has so far been made to use this parameter in the study of bombardment damage.

EXPERIMENTAL

Three types of measurement are usually made: (1) lifetime as a function of defect density at fixed temperature, (2) lifetime as a function of temperature at fixed defect density, and (3) lifetime as a function of carrier concentration at fixed temperature and defect density. The first two methods have the advantage that considerable information can be obtained from a single specimen. In addition, measurements made at fixed temperature avoid the complication which may arise

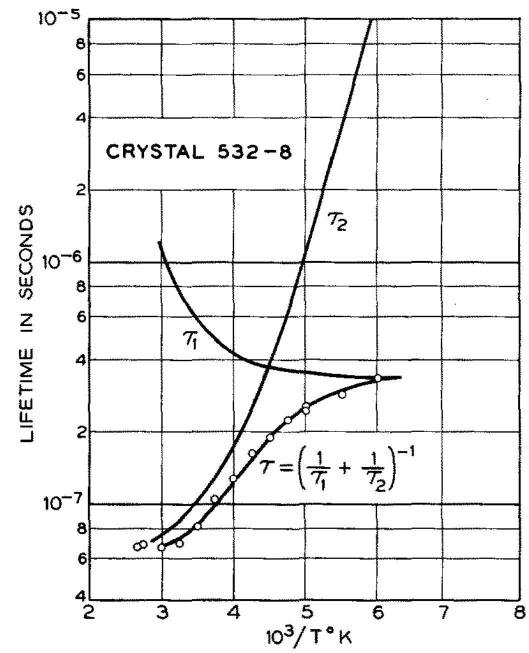

FIG. 3. Comparison of measured lifetime with that computed from experimentally obtained charge state of the impurity.

from temperature-dependent capture constants and from the anneal of the damage introduced. On the other hand, since energy levels can be determined only if a range of Fermi level positions is examined, the third method is in some ways the most advantageous. However, if this method is used, the assumption must be made that all the specimens are sufficiently similar that the rate of introduction of damage will be the same and, more important, that there are no Fermi level dependent annealing processes.

There are a large number of methods for measuring lifetimes. These have been discussed in a recent review article.[3] We would only repeat that transient and steady state methods may give different answers when the defect concentration is high [see Eqs. (4) and (7)]. Steady state methods using the diffusion of carriers have the advantage that they measure the free time of minority carriers directly. Included among these methods are simple diffusion length measurements from an injecting source to a collector and the PME effect, but not the PME–PC null method, which is very sensitive to small trapping effects. Transient methods, utilizing injection by a pulse of light or radiation, do not readily distinguish between trapping and lifetime effects, although auxiliary experiments can usually establish the presence of trapping.

REVIEW OF THE LITERATURE

Most of the work dealing with bombardment effects on lifetime in semiconductors has been concentrated on germanium, probably because this material is the one most readily available in controlled purity, and because its bombardment induced levels are better known than

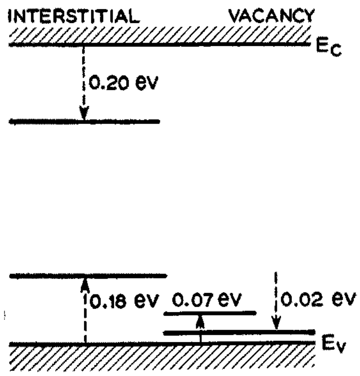

FIG. 4. Energy level scheme of neutron bombardment damage in germanium.

those of any other semiconductor. It has been found that the defects introduced by heavy particle bombardment of germanium differ significantly from the defects produced by electrons or gamma rays, although certain similarities in the two cases have also been found. Heavy particles such as fast neutrons, protons, deuterons, or alpha particles, will produce clustered defects or disordered regions, while electrons and gamma rays may be expected to produce vacancy-interstitial pairs, or, under some conditions, isolated vacancies and interstitials. We will therefore discuss the two types of bombardment separately.

I. Germanium

(a) *Heavy Particle Bombardment*

The energy level scheme produced by fast neutron[28] bombardment at room temperature is shown in Fig. 4. Recombination in n-type germanium has been studied both as a function of defect density and temperature.[29] The results are compatible with recombination via the level 0.23 ev below the conduction band. These studies were made using uniform bars of a variety of resistivities and injection at a surface barrier contact. The hole-capture cross section of the defect was found to be 3×10^{-15} cm^2 (revised value). An analogous study using the base region of a *pnp* transistor and pile neutron bombardment has been reported by Messenger and Spratt.[30] Their results are in reasonable agreement with those of Curtis and co-workers. The recombination level was found to be 0.23 ev below the conduction band and the hole-capture cross section 1×10^{-15} cm^2. In addition they give a value for the electron capture cross section of 4×10^{-15} cm^2. The difference between the two reported hole-capture cross sections may have arisen from different ways of estimating the defect concentration and the neutron flux, and is probably not significant. The similarity in magnitude of the hole- and electron-capture cross sections tends to rule out the assignment of the 0.23-ev level to a transition between a singly and doubly charged state.

Measurement after bombardment with neutrons of higher energy (14 Mev) have been reported by Vavilov and co-workers.[31] They did not locate the defect level, but give a cross section for hole capture of 1×10^{-15} cm^2 based on theoretical, computed defect densities. These may not be applicable if the recombination level is not one of major defect levels. Moreover, the cross section represents only a lower limit since the occupancy of the defect is not known. Similar measurements have been reported by Curtis and Cleland,[32] using 14.5-Mev neutrons. They conclude that recombination proceeds via a level close to the middle of the gap which exhibits acceptor nature. The density of this defect was not determined.

Results in p-type germanium are much more complicated. Some of the difficulty may arise from known annealing processes which take place readily between room temperature[33] and 80°K after some types of bombardment. We will consider only the high temperature region where trapping is not significant. In this region measurements have been reported by Curtis *et al.*[34] The behavior here indicates that the level 0.23 ev below the conduction band is still the dominant recombination center, but it appears that it is the second level of a defect which has its first level in the lower half of the gap. Under these circumstances the passage of the Fermi level through the lower level will strongly modify the lifetime in a manner similar to that discussed for nickel in germanium above. In particular the 0.23-ev level does not exist when the Fermi level is more than a few kT below the lower level, so that the lifetime in p type at low temperature is much longer than would be computed on the basis of the 0.23-level alone. (A fuller account of this work appears elsewhere in this issue.) The assumption of a double level defect leads to good agreement between the cross section for hole capture determined in n- and p-type material.

A study of the effects of deuteron bombardment on lifetime[35] has not yielded cross sections or energy levels which may be compared to those given in the foregoing. The general agreement among the various papers dealing with pile neutron bombardment is gratifying. The results indicate that the recombination center is identical with the defect which controls carrier concentration in n-type germanium.

(b) *Electron and Gamma Bombardment*

Bombardment of germanium with cobalt-60 gamma rays (1.17 and 1.33 Mev) has yielded the following

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[29] Curtis, Cleland, Crawford, and Pigg, J. Appl. Phys. **28**, 1161 (1957).
[30] G. C. Messenger and J. P. Spratt, Proc. Inst. Radio Engrs. **46**, 1038 (1958).
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energy level scheme[36] (Fig. 5). One may expect that electron bombardment will produce the same defects, since the displacement of germanium atoms is due to the intermediate Compton electrons and photoelectrons produced by the gamma rays. The maximum energy of the Compton electrons is 0.817 and 0.964 Mev, respectively. The contribution of photoelectrons is small.

In n type the dominant recombination level was found to be located 0.20 ev below the conduction band,[34] close to the level found after pile neutron bombardment, but the cross section for hole capture in this case was only 4×10^{-16} cm^2, smaller by a factor of eight than that found after neutron bombardment. This is surprising, since the existence of the same level in the two cases suggests that the damage configuration is identical. Experiments in p type again indicate that the recombination level is the second level of a defect whose first level is in the lower half of the gap, giving further support to the notion that a similar defect is involved in both cases. The difference in cross sections may be due to clustering of defects in the neutron case.

Electron bombardment effects in n type also have been reported by Smirnov and Vavilov.[37] They used 0.55- and 0.75-Mev electrons, and obtained cross sections of 5×10^{-17} and 1×10^{-16} cm^2, respectively. The energy level of the defect was not determined, but we may assume that it is identical with that found above. However, since the Fermi level position in these samples is not given, it is not possible to deduce whether a correction for the filling of the defect should be applied to obtain the true cross section. The values quoted would then represent only lower limits.

A more detailed study of electron bombardment effects has been reported by Rappaport and Loferski,[38] using 1-Mev electrons, and by Baruch,[39] using a 2.0-Mev electrons. In both cases germanium samples with a wide range of resistivities were measured after the same amount of bombardment. The lifetimes were measured at room temperatures. No specific results are given in reference 38. Baruch found the recombination level to be 0.18 ev below the conduction band, with a hold-capture cross section of 1.6×10^{-15} cm^2 and an electron-capture cross section of 1.6×10^{-16} cm^2. The electron-capture cross section is based on limited data.

The agreement among these papers is satisfactory in insofar as the recombination level is found to be located about 0.20 ev below the conduction band. The cross sections are in less satisfactory agreement. The reported value ranges from 1.0×10^{-16} to 16.0×10^{-16} cm^2. Some of this difference may again be due to incomplete knowledge of the defect density in the actual specimens under consideration.

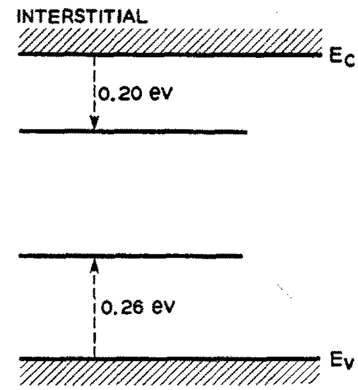

FIG. 5. Energy level scheme of gamma bombardment damage in germanium.

In addition to the high temperature recombination behavior of bombardment defects, the low temperature trapping aspects have also been investigated. Shulman[40] has reported hole traps located 0.28 ev above the valence band in n-type electron bombarded germanium. The cross section of these traps for holes was reported to be 6.0×10^{-16} cm^2; the cross section is of the activation energy type with $\Delta E\sim0.05$ ev. Other studies[41] have shown hole trapping below 225°K with a trap located 0.11 ev above the valence band. In p type the trapping behavior depends on the bombarding temperature and annealing of the crystal. Samples electron bombarded at 80°K exhibit traps which anneal rapidly at temperatures above 225°K. These traps are apparently located somewhat below the middle of the gap. In general it is clear that trapping dominates the recombination processes in bombarded germanium at temperatures below 200°K.

II. Silicon

The extent of work on recombination in bombarded silicon is very much smaller than that in germanium. Possible reasons for this have been suggested in the foregoing.

(a) *Neutron Bombardment of Silicon*

Recombination in silicon bombarded with neutrons from a fission plate has shown that the dominant recombination level is located close to the middle of the energy gap.[42] (This is in sharp contrast to the electron bombardment results discussed in the following.) The recombination process shows a strong dependence on the injection level, suggesting that the recombination level is not discrete. A detailed analysis has not been given. The effect of pile neutrons on transistors has also been analyzed to obtain a measure

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[37] L. S. Smirnov and V. S. Vavilov, Zhur. Tekh. Fiz. **27**, 427 (1957); Soviet Phys. Tech. Phys. **2**, 387 (1957).
[38] P. Rappaport and J. J. Loferski, Bull. Am. Phys. Soc. Ser. II, **3**, 141 (1958).
[39] P. Baruch, Proceedings of the International Conference on Semiconductors, Rochester, 1958; J. Phys. Chem. Solids **8**, 153 (1959).
[40] R. G. Shulman, Phys. Rev. **102**, 1451 (1956).
[41] G. K. Wertheim (unpublished); see also W. L. Brown, J. Appl. Phys. **30**, 1320 (1959), this issue.
[42] G. K. Wertheim, Phys. Rev. **111**, 1500 (1958).

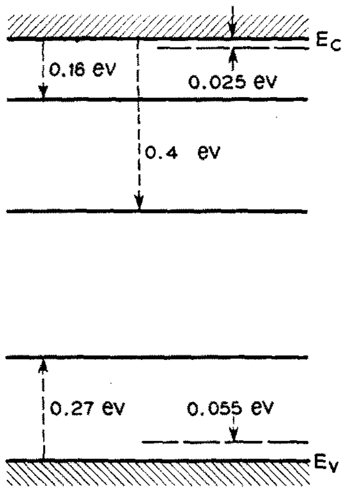

FIG. 6. Energy level scheme of electron bombardment damage in pulled silicon containing oxygen.

of the radiation effect.[43] Cross sections were not obtained but the lifetime has been expressed as a function of flux as $3.0\times10^6\Phi^{-1}$ in n type and as $2.0\times10^6\Phi^{-1}$ in p type. The lifetimes obtained from these equations are greater by factors of eight and five in n and p type than those of reference 42. The differences may arise from differences in neutron dosimetry or from differences in the neutron spectrum.

(b) *Electron Bombardment*

Hall effect and conductivity measurements in electron bombarded silicon have shown three levels well within the forbidden gap[44–46] (Fig. 6). These are responsible for carrier concentration changes in material of moderate resistivity and, on the basis of the recombination statistics, should have the dominant effect on carrier lifetime. Other levels close to the band edges, found in some experiments,[46] should have little or no effect on recombination. In n-type material the recombination behavior is entirely in accord with the single level model. A good fit to the data is obtained using temperature independent hole- and electron-capture constants for the level 0.27 ev above the valence band.[11,44] The room temperature cross sections were found to be 8.0×10^{-13} cm^2 and 9.5×10^{-15} cm^2 for holes and electrons, respectively. The hole-capture cross section is extremely large, and suggests that capture must take place to a Coulomb-attractive defect. This indicates that the defect is an acceptor. On the other hand, carrier removal experiments indicate that this level has no effect on carrier concentration when the Fermi level is above it. This in turn means that the damage site is over-all neutral. A consistent picture is obtained on the assumption that the damage site contains two defects, having opposite unit charge when the Fermi level is above the 0.27-ev level. The magnitude of the Coulomb-attractive cross section suggests that the two defects must be separated by a distance of perhaps 50 A.

In p type the behavior of the lifetime is in accord with recombination through the level 0.16 ev below the conduction band. In this case the cross sections were both found to be approximately 2×10^{-15} cm^2. Since one of the two must be a Coulomb-attractive capture cross section which may be expected to be larger, we are led to the conclusion that the damage site must contain a pair of close-spaced defects of opposite charge. Certain difficulties which remain in this picture have been discussed.[45] The anneal of these lifetime effects has been studied by Bemski and Augustyniak.[47] Recombination via the level 0.45 ev below the conduction band has not been observed.

III. Other Investigations

A number of other studies concerned with recombination in bombarded material have also been reported in recent years. Loferski and Rappaport[48] have used the short circuit current of a diode under bombardment to determine the threshold for the production of damage. In the case of a step junction the short circuit current is a direct measure of the diffusion length near the junction, and consequently a measure of the lifetime. The thresholds in germanium and silicon were found to be 14.5 ev and 12.9 ev, respectively. No information about the location or cross sections of the defects produced was given. Electron bombardment has also been used to reduce the carrier storage time in switching diodes,[49,50] and to increase the turn-on current of *pnpn* cross points.[51] In both cases the desired effect arises from the reduction of lifetime in a region into which carriers are injected. Bombardment effects in transistors ascribable to changes in lifetime in the base region have also been reported.[52,53]

IV. Other Semiconductors

Studies of the effects of bombardment on lifetime in other semiconductors have not yet been reported. As a matter of fact the systematic study of recombination properties in these substances is itself not far advanced. In the III–V compounds where the production of high purity single crystal material is more advanced than in any but the elemental semiconductors, long lifetimes have not yet been achieved. In the large gap II–VI compounds the emphasis has been on luminescent

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[44] G. K. Wertheim, Phys. Rev. **105**, 1730 (1957).
[45] G. K. Wertheim, Phys. Rev. **110**, 1272 (1958).
[46] D. E. Hill, thesis, Purdue University (unpublished); Bull. Am. Phys. Ser. II, **3**, 142 (1958).
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[48] J. J. Loferski and P. Rappaport, Phys. Rev. **98**, 1861 (1955); **111**, 432 (1958).
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[50] R. Gorton, Nature **179**, 864 (1957).
[51] G. Backenstoss (unpublished).
[52] Florida, Holt, and Stephen, Nature **173**, 397 (1954).
[53] J. W. Easley, Proc. Inst. Radio Engrs. WESCON (1958); J. J. Loferski, J. Appl. Phys. **29**, 35 (1958).

TABLE II. A summary of recombination properties of bombardment defects in germanium and silicon.

Author(s)	Sample type	Irradiation	Defect level	Cross section $\times 10^{16}$ cm²
Curtis, Cleland, Crawford, and Pigg[a]	n-type Ge	pile neutrons and Co[60] gammas	$E_c-E=0.23$ $E_c-E=0.23$	$40(\sigma_p)$ $5(\sigma_p)$
Messenger and Spratt[b]	n-type Ge	pile neutrons	$E_c-E=0.23$	$10(\sigma_p)$ $40(\sigma_n)$
Vavilov, Spitsyn, Smirnov, and Chukichev[c]	n-type Ge	14-Mev neutrons	not determined	$10(\sigma_p)$
Curtis and Cleland[d]	n-type Ge	14.5-Mev neutrons	$E-E_v=0.32$	$[\sigma_p/\sigma_n=300]$
Curtis, Cleland, and Crawford[e]	n-type Ge	pile neutrons and Co[60] gammas	$E_c-E=0.20$ $E_c-E=0.20$	$30(\sigma_p)$ $4(\sigma_p)$
	p-type Ge	pile neutrons and Co[60] gammas	multilevel behavior $E_c-E=0.2$	
Smirnov and Vavilov[f]	n-type Ge	0.55 Mev 0.75-Mev electrons	not determined not determined	$0.5(\sigma_p)$ $1.0(\sigma_p)$
P. Baruch[g]	n- and p-type Ge	2-Mev electrons	$E_c-E=0.18$	$16(\sigma_p)$ $1.6(\sigma_n)$
G. K. Wertheim[h]	n-type Si p-type Si	fission plate neutrons	middle of gap	$\left[\begin{array}{l}\tau=3.9\times10^5\Phi^{-1}\\ \tau=4.3\times10^5\Phi^{-1}\end{array}\right]$
G. C. Messenger[i]	n-type Si p-type Si	pile neutrons	not determined	$\left[\begin{array}{l}\tau=3\times10^6\Phi^{-1}\\ \tau=2\times10^6\Phi^{-1}\end{array}\right]$
G. K. Wertheim[j]	n-type Si	0.7-Mev electrons	$E-E_v=0.27$	$8000(\sigma_p)$ $95(\sigma_n)$
	p-type Si	0.7-Mev electrons	$E_c-E=0.16$	$18(\sigma_p)$ $19(\sigma_n)$
J. W. Easley[k]	n-type Si	fission plate neutrons	not determined	$[\tau=5.7\times10^5\Phi^{-1}]$

[a] See reference 29. [b] See reference 30. [c] See reference 31. [d] See reference 32. [e] See reference 34. [f] See reference 37. [g] See reference 39. [h] See reference 42. [i] See reference 43. [j] See reference 45. [k] See reference 53.

rather than conductive processes. These usually reflect trapping rather than recombination processes. Radiation effects on luminescence in these substances are known.

V. Other Imperfections

Dislocations are the only other nonchemical defects whose lifetime effect has been thoroughly studied. The major fraction of the work in this field has been done in germanium. A review of this work has recently been given by Haasen and Seeger.[54] Good agreement has been obtained by two entirely different approaches.[55,56] The major difference between these and an earlier paper can now be attributed to difficulties in the measurement of the dislocation density.

An interesting extension of radiation damage study is possible in view of the suggestion that the defects produced by the annealing of a crystal supersaturated with copper or nickel are vacancies.[57] Vacancies can also be produced by quenching from temperatures near the melting point[58] and by plastic deformation.[59] A comparison between the defects produced in these three ways with those produced by bombardment may show which of the bombardment levels are to be assigned to an isolated vacancy. Some thoughts along this line have been put forward by Seeger,[60] and a number of other experiments are possible.

CONCLUSIONS

It is apparent from the preceding as well as from the summary in Table II, that our understanding of the recombination effects of radiation damage in germanium and silicon has made considerable progress. Difficulties usually arise when it proves impossible to associate the recombination level with one otherwise identified. This situation is similar to our experience with chemical impurities where proper interpretation of lifetime data became possible only after the level scheme had been established by other means; the difficulties are not surprising in view of the luxuriant complexity of the multilevel recombination problem. The conceptually simple

[54] P. Haasen and A. Seeger, *Halbleiter Probleme, IV* (Friedrich Vieweg und Sohn, Braunschweig, 1958), pp. 68.
[55] J. P. McKelvey, Phys. Rev. **106**, 910 (1957).
[56] G. K. Wertheim and G. L. Pearson, Phys. Rev. **107**, 694 (1957).
[57] P. Penning, Philips Research Repts. **13**, 17 (1958).
[58] R. A. Logan, Phys. Rev. **101**, 1455 (1956).
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[60] A. Seeger, Proceedings of the Brussels Conference, 1958 (to be published).

equations for the net capture rates of individual defects lead to differential equations which have useful solutions only in the simplest cases. One well-known solution is the single level case, but unfortunately most known recombination centers are not of this type. Multilevel defects give rise to an entirely new class of effects which may readily be confused with temperature dependent capture constants and may suggest erroneous energy levels. Determinations of cross sections can usually be made with confidence only if both the level scheme and the charge state of the defect are known from Hall or conductivity measurements.

The lack of consistency that has been noted among various measurements of similar systems can arise in a variety of ways. In the case of neutron damage the chief source of discrepancy may well lie in the neutron dosimetry since the total integrated flux is often used to compute the defect density using introduction rates measured elsewhere or computed from theory. It appears desirable to determine the defect density as directly as possible, when meaningful cross sections are needed. Under certain favorable conditions it can be obtained from lifetime measurements alone.[11] When this is not possible Hall measurements are called for. Complications may also arise from radiation annealing.[61] A possible mechanism here is that energetic carriers give up energy to the damage configuration, facilitating rearrangement. Additional complications may be due to the failure of the reciprocity law[62]; i.e., the amount of damage may depend not only on the integrated flux, but also on the rate at which it is administered. Finally, the suggestion has also been put forth that annealing and rearrangement of the microscopic defect structure may depend on the electronic state of charge of the defect, that is to say on the Fermi level.[28,63] If this is correct it may not be proper to assume that a given bombardment will necessarily produce the same defects in an n- and a p-type crystal. Some of these intriguing ideas may be amenable to investigation using the recombination process.

The principal achievement of the papers discussed here has been to show that bombardment defects have measurable, reproducible recombination properties. Cross sections and energy levels have been established in a number of cases. Little has been done so far to use this information to establish the detailed structure of bombardment defects, which is, after all, the central problem in the study of radiation effects.

[61] Mac Kay, Klontz, and Gobeli, Phys. Rev. Letters 2, 146 (1959).

[62] J. W. Mac Kay (private communication); W. L. Brown (private communication).

[63] W. L. Brown, J. Appl. Phys. 30, 1320 (1959), this issue.

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Radiation Effects on Recombination in Germanium

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The properties of recombination centers in germanium are obtained on the basis of lifetime data in conjunction with other information available. For recombination centers introduced by Co^{60} gamma rays and fission neutrons, the recombination energy level position is placed at 0.20 ev below the conduction band. The room temperature hole-capture cross sections resulting are 1.1×10^{-15} cm^2 and 6×10^{-15} cm^2 for Co^{60} gamma-ray and fission neutron irradiation, respectively. For the case of 14-Mev neutron irradiation the energy level is located 0.32 ev above the valence band. The room temperature hole and electron cross sections are $\sim6\times10^{-15}$ cm^2 and 2.2×10^{-17} cm^2, respectively. The capture probabilities are assumed to be independent of temperature except for the case of gamma irradiation, for which there is apparently a fairly strong variation corresponding to a change in the activation energy of 0.07 ev. The selection of the values given above is not entirely unique. The assumptions made in their determination are discussed. The values given are directly applicable only in the case of n-type material, the situation in p-type material being more complex.

I. INTRODUCTION

MINORITY carrier lifetime measurements are being used to an increasing extent as a sensitive detector of radiation damage. That lifetime is very sensitive to radiation was recognized as early as 1953 when measurements were made on diodes irradiated in the Oak Ridge graphite reactor.[1] Lifetime changes in transistors as well as bulk samples were reported at about the same time by others,[2] but the low initial lifetimes made fairly large irradiation necessary for measurable effects. Several investigators have used the properties of devices to study the effect of irradiation on lifetime. For instance, some of the earlier measurements depended upon relating the lifetime to the short-circuit current of the photovoltaic effect,[3] and the reverse

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[1] B. R. Gossick (personal communication).

[2] Florida, Holt, and Stephen, Nature 173, 397 (1954).

[3] J. J. Loferski and P. Rappaport, Phys. Rev. 98, 1861 (1955).