# Diffusion-Limited Annealing of Radiation Damage in Germanium

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The theory of the previous paper in this journal was used to treat the annealing of radiation damage in $n$-type germanium as studied by Fletcher, Brown, and Wright, and by Augustyniak. The damage was produced by 3-Mev electrons to a density of $10^{15}$ defects per cubic centimeter. The damage was assumed to have consisted of vacancy-interstitial pairs which annealed by the diffusion together of interstitials and vacancies. A reasonable fit of the data has been obtained for the initial 50% of the annealing. The data of Augustyniak were fit for all stages of the annealing process. Choice of parameters to fit the data led to the following conclusions: (1) The sum of the diffusion coefficients of interstitials and vacancies is given by $10^{11} r_0^2 \exp(-31.6 \text{ kcal}/RT)$, where $r_0$ is the capture radius; (2) the average separation of the interstitial and the vacancy of the pairs produced by 3-Mev electrons is approximately $1.5\, r_0$, and (3) the first 65% of the annealing occurs by the recombination of each interstitial with the vacancy from which it was originally dislodged. Fair agreement of the activation energy with the previously accepted activation energy for vacancy diffusion suggests vacancy-diffusion annealing. Absence of a more rapid interstitial diffusion indicates that the interstitial does not possess the contracted electron cloud of a positive ion.

## I. INTRODUCTION

WHEN solids are bombarded by high-energy particles, such as electrons, protons, or neutrons, their physical properties are known to change. Upon heating, however, a large number of such radiation-damaged materials are found to recover their original properties. In the simpler cases, the damaging process is believed to be due to the displacement of atoms or molecules from their appropriate crystal sites by the incident radiation, thereby producing large numbers of vacancies and interstitials. These defects are responsible for the change in physical properties observed. The annealing which occurs at high temperatures is believed to be due to a destruction of these defects either by a direct recombination of vacancies and interstitials or by their annihilations at dislocations.

If the radiation damage were produced in such a way as to consist of a fairly low concentration of fairly well-isolated interstitials and vacancies, it would seem that the annealing process would correspond closely to a diffusion-limited chemical reaction, in which the reacting species were vacancies, interstitials, and dislocations. These conditions are just those which Brown, Fletcher, and Wright[1] have shown appear to exist in germanium bombarded by electrons with energies not many times greater than the threshold energy for interstitial-vacancy pair production. Furthermore, these workers have been able to obtain a measure of the number of defects present after bombardment and after annealing. Consequently, an attempt has been made to analyze the results of Brown, Fletcher, and Wright[1] and the preliminary results of Augustyniak[2] on the annealing of radiation damage in germanium, under the assumption that the annealing process is a diffusion-controlled chemical reaction. The treatment is based on the theory developed in the preceding paper in this journal. The diffusion on the germanium lattice is approximated by diffusion in a continuum.

Fletcher and Brown[3] have actually given an excellent theoretical discussion of the annealing process. The present approach differs from that of Fletcher and Brown in that they divided the annealing process into three stages corresponding to three distinct mechanisms of annealing. The present treatment combines the two stages which appear to be the most significant. This reconsideration of the problem seems justified because (1) the data of Augustyniak have further illuminated the problem, (2) some new conclusions are reached, and (3) a test of the theory developed in the previous paper is desirable.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

The experimental technique employed by Brown, Fletcher, and Wright is described in detail in their original report of the work.[1] A brief summary is presented here. Single-crystal samples of 1.4-(ohm cm)$^{-1}$ $n$-type germanium ($\frac{1}{16}$ in.$\times\frac{1}{16}$ in.$\times\frac{1}{2}$ in.) were bombarded with 3-Mev electrons at room temperature. The samples after bombardment and room-temperature annealing were approximately 0.8-(ohm cm)$^{-1}$ $n$-type. The results of auxiliary experiments indicated that the change in conductivity was proportional to the number of defects introduced at the low-defect concentrations studied. The samples were annealed at various temperatures in air. The resistances were measured periodically at room temperature by the four-point-probe technique. The fractions annealed were determined from the conductivity changes by the equation:

$$\varphi(t,T)=(\Delta\sigma_0-\Delta\sigma)/\Delta\sigma_0, \quad (1)$$

where $\Delta\sigma$ is the change in conductivity due to irradiation and annealing at temperature $T$ for time $t$ and $\Delta\sigma_0$ is the initial change in conductivity due to irradiation

[1] Brown, Fletcher, and Wright, Phys. Rev. **92**, 591 (1953).
[2] W. Augustyniak (private communication).
[3] R. C. Fletcher and W. L. Brown, Phys. Rev. **92**, 585 (1953).

TABLE I. Annealing of radiation damage in $n$-type germanium (data of Brown, Fletcher, and Wright[a]).[b]

| Time (sec) \ Anneal temp. (°C): | Fraction annealed (percent) 160 | 180 | 200 | 220 | 240 | 260 | 280 | 300 |
|---|---|---|---|---|---|---|---|---|
| 60 | 1.8 | 2.4 | 15.5 | 29.5 | 42 | 46 | 64 | 76.5 |
| 120 | 2.6 | 6.3 | 22 | 37.4 | 47.5 | 53.5 | 70 | 84 |
| 180 | 3.1 | 9.0 | 27.5 | 40.0 | 48.6 | 58 | 73 | 86 |
| 240 | 3.7 | 10.4 | 30.8 | 41.3 | 49.4 | 62 | 75.3 | 87 |
| 300 | 4.2 | 11.5 | 32.5 | 42.0 | 50.3 | 64.5 | 77 | 87 |
| 360 | 4.7 | 13.3 | 34.3 | | | | | |
| 420 | 4.9 | 14.6 | 36.4 | 45.5 | 51 | 69.5 | 79.5 | 87 |
| 600 | 5.5 | 18.0 | 38.5 | 44.8 | 57.5 | 70.5 | 79.5 | 87 |
| 1200 | 8.8 | 24.6 | 41.6 | 48 | 58.3 | 76 | 85.3 | 89 |
| 1800 | 12.1 | 29.4 | 43.7 | 50.5 | 62 | 78 | 88 | 89.7 |
| 2400 | 14.7 | 32 | 44.8 | 52 | 66 | 79.2 | | 89.7 |
| 3000 | 17.4 | 33.5 | 45.4 | 52.5 | 69.5 | 81.5 | 94.5 | 89.5 |
| 3600 | 18.9 | 34.2 | 45.8 | 56 | 72 | | | |

[a] See reference 1.
[b] Conductivity before bombardment $=1.4$ (ohm cm)$^{-1}$. Conductivity after bombardment $=0.8$ (ohm cm)$^{-1}$. Initial concentration of bombardment defects $=1.05\times10^{15}$ cm$^{-3}$.

and room-temperature annealing only. Their results, in terms of $\varphi$, are summarized in Table I.

Augustyniak[2] has recently conducted similar experiments on 1.5-(ohm cm)$^{-1}$ $n$-type germanium. His technique differed from the above only in that the annealing was carried out in a peanut-oil thermostatic bath and the resistances were measured through four soldered contacts. His preliminary results[2] are summarized in Table II. Augustyniak's work, carried out in the same laboratories as that of Brown *et al.*, was believed to have eliminated some of the major sources of experimental error in the earlier work.

## III. MICROSCOPIC DESCRIPTION OF THE SAMPLES

The interstitials and vacancies produced by displacement of atoms from their appropriate lattice points are, of course, produced in pairs. These pairs are produced by a fairly monochromatic beam of electrons; therefore, one might expect that each interstitial atom would be dislodged about the same distance from the vacancy which is produced simultaneously. Since, however, the collisions of the bombarding electrons with the atoms of the lattice are random and only a portion of the electron energy is transferred on each collision, it seems more appropriate to expect a distribution of displacements of the interstitial atom from the corresponding vacancy. This distribution is, however, unknown.

Further, since the electron energy (3 Mev) is only a few times the threshold energy for interstitial pair production, it seems likely that the pairs will be produced singly rather than in groups as is often believed to be the case with heavier high-energy particles. Since the electron beam was uniform over the sample and the samples were quite thin, it seems reasonable to assume that the pairs were randomly distributed with respect to one another.

The role of dislocations in the annealing process will depend on the relative densities of the radiation defects and the dislocations. The radiation-induced defect densities in these experiments were about $10^{15}$ cm$^{-3}$. The density of dislocation sites in sound crystals is expected to be much less than this, so that the reaction of defects and dislocations may be neglected. This will not be the case, of course, if the radiation-induced defects are oriented along the dislocations as may occur if stable defects are produced much more readily near dislocations than elsewhere. Since no positive evidence that the extent of damage depends on dislocation density has been reported, it has been assumed that the dislocations play no significant part in the processes described here.

## IV. MATHEMATICAL FORMULATION

In order to formulate the problem mathematically, one denotes the $i$th interstitial as $A_i$ and the $j$th vacancy as $B_j$. As in the previous paper, for every pair, $A_iB_j$, one defines a probability distribution $\rho_{ij}$ such that: $\rho_{ij}V^{-2}dV_AdV_B$ gives the probability that $A_i$ is in $dV_A$ at $\mathbf{r}_A$, $t$ and that simultaneously $B_j$ is in $dV_B$ at $\mathbf{r}_B$, $t$. One specifies that for a particular pair $A_iB_j$, the condition $i=j$ indicates that this pair was produced from a single collision of a bombarding electron with the lattice. These pairs will have nonrandom initial distributions given by the distribution of displacements by bombardment of an interstitial from the vacant site which it previously occupied; all other $A_iB_j$ pairs ($i\neq j$) will have a uniform (random) initial distribution such that

$$\rho_{ij}(\mathbf{r}, t=0)=1 \quad \text{for} \quad i\neq j, \tag{2}$$

where $\mathbf{r}=(\mathbf{r}_A-\mathbf{r}_B)$. It would be desirable to determine the form of $\rho_{ii}(\mathbf{r}, t=0)$ from the experimental data.

TABLE II. Annealing of radiation damage in $n$-type germanium (data of W. Augustyniak[a]).

| Time (sec) | Anneal temp. (°C): | Fraction annealed (%) 205.2 | 236.7 |
|---|---|---|---|
| 2 | | 2 | 6 |
| 5 | | 3 | 11.2 |
| 10 | | 4 | 17.5 |
| 20 | | 6 | 25.5 |
| 50 | | 12.2 | 36.5 |
| 100 | | 19 | 43.5 |
| 200 | | 27.5 | 50.5 |
| 500 | | 39 | 56.5 |
| 1000 | | 46.5 | 60.5 |
| 2000 | | 52 | 63 |
| 5000 | | 56.5 | 66 |
| 10 000 | | 58 | |
| 20 000 | | 59.2 | |
| 50 000 | | 60 | |
| Conductivity before bombardment, (ohm cm)$^{-1}$: | | 1.49 | 1.40 |
| Conductivity after bombardment, (ohm cm)$^{-1}$: | | 0.705 | 0.665 |
| Initial concentration of bombardment defects, cm$^{-3}$: | | $1.44\times10^{15}$ | $1.39\times10^{15}$ |

[a] See reference 2.

This is not impossible but the experimental data are not adequate to justify such a process. Therefore, it has been assumed that

$$\rho_{ii}(\mathbf{r}, t=0)=VN\exp\left[-\left(\frac{r}{\lambda r_0}\right)^2\right], \quad r>r_0 \qquad (3)$$

where $\lambda$ is a parameter to be determined from the experimental data and $N$ is a normalization constant. This is equivalent to the assumption that the probability of an interstitial and a vacancy produced as a pair being separated by a distance $r$ is given by

$$\rho(r)dr=N\exp\left[-\left(\frac{r}{\lambda r_0}\right)^2\right]4\pi r^2 dr. \qquad (4)$$

This function is shown in Fig. 1 for various values of the parameter $\lambda$. The normalization constant $N$ is found by requiring the integral of (4) from $r_0$ to infinity to equal unity.

The diffusion-limited reaction is simply $A+B\rightarrow AB$ where $AB$ is a normal lattice point so that $A$ and $B$ are both destroyed upon reaction. The process is irreversible and the equilibrium concentration of vacancies and interstitials is negligible, so that

$$\rho_{ij}\rightarrow 0 \quad \text{as} \quad t\rightarrow\infty. \qquad (5)$$

One does not expect an activation energy for recombination of an interstitial and a vacancy so that the Smoluchowski boundary condition is valid:

$$\rho_{ij}(r\leqq r_0, t)=0. \qquad (6)$$

Equations (2), (3), (5), and (6) provide the boundary conditions on the $\rho_{ij}$. The equations necessary for the complete formulation of the problem are given in Sec. VII A of the preceding paper.

## V. RATE EQUATION

Using Eqs. (36), (39), (40), and (41) of the preceding paper in this journal and the boundary conditions expressed in Eqs. (2), (3), (5), and (6) of this paper, one readily obtains the $\rho_{ij}$ in the following form:

$$\rho_{ij}=\exp\left[\int_0^t f_{ij}dt\right]\left[1-\frac{2r_0}{r}\operatorname{erf}\left(\frac{r-r_0}{2(Dt)^{\frac{1}{2}}}\right)\right] \text{ for } i\neq j, \qquad (7)$$

$$\rho_{ii}=\frac{VN}{\pi}\exp\left\{\int_0^t f_{ii}dt\right\}\left[\frac{1}{r}\int_p^\infty [r+2(Dt)^{\frac{1}{2}}s]\times\exp\{-s^2-a[r+2(Dt)^{\frac{1}{2}}s]^2\}ds - \frac{1}{r}\int_p^\infty [-r+2r_0+2(Dt)^{\frac{1}{2}}s]\times\exp\{-s^2-a[-r+2r_0+2(Dt)^{\frac{1}{2}}s]^2\}ds\right] \qquad (8)$$

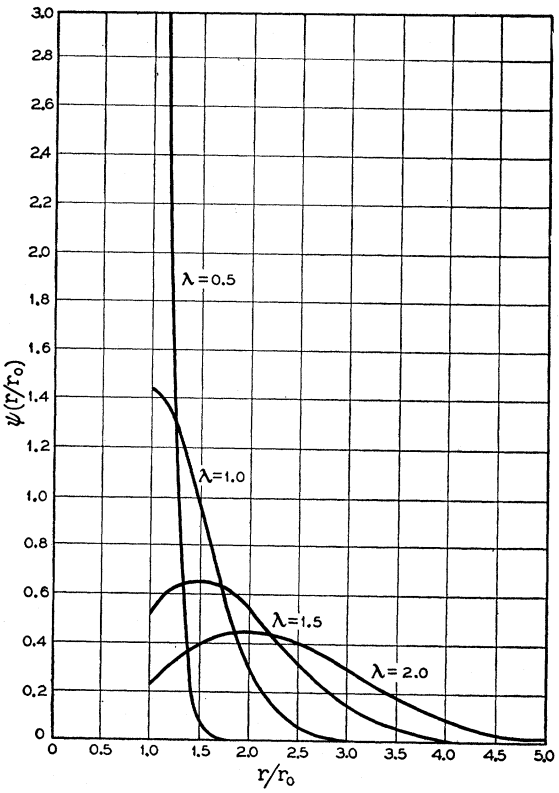



FIG. 1. Postulated one-parameter radial distribution for interstitial about vacancy from which dislodged by 3-Mev electron. ($r_0$=capture radius.)

where

$$\operatorname{erf}(x)=\int_x^\infty \frac{\exp(-\alpha^2)}{\sqrt{\pi}}d\alpha,$$

$$a=1/\lambda r_0^2, \quad p=(r-r_0)/2(Dt)^{\frac{1}{2}},$$

and the $f_{ij}$ and $f_{ii}$ are given by Eq. (37) of the previous paper. One notes that:

$$\rho_{ij}\rightarrow\exp\left[\int_0^t f_{ij}dt\right] \quad \text{as} \quad r\rightarrow\infty \quad \text{for} \quad i\neq j, \qquad (9)$$

$$\rho_{ii}\rightarrow 0 \quad \text{as} \quad r\rightarrow\infty. \qquad (10)$$

One may now evaluate $f_{ij}$ $(i\neq j)$ just as the $f_{ij}$ were evaluated in the previous paper when all of the $\rho_{ij}$ were identical. Substituting (9) and (10) into Eq. (33) of the preceding paper, one obtains

$$\exp\left(\int_0^t f_{ij}dt\right)=\frac{C_A C_B}{C_A^0 C_B^0} \quad \text{for} \quad i\neq j, \qquad (11)$$

and therefore

$$\rho_{ij}=\frac{C_A C_B}{C_A^0 C_B^0}\left[1-\frac{2r_0}{r}\operatorname{erf}\left(\frac{r-r_0}{2(Dt)^{\frac{1}{2}}}\right)\right] \text{ for } i\neq j. \qquad (12)$$

The $f_{ii}$ may now be evaluated directly from the $\rho_{ij}$ $(i\neq j)$ by using Eq. (37) of the preceding paper. The result is

$$f_{ii}=-4\pi r_0^2 D(C_A+C_B)\left[\frac{1}{r_0}+\frac{1}{(\pi Dt)^{\frac{1}{2}}}\right]. \quad (13)$$

By differentiating (8) and (12) with respect to $(r)$ and substituting the results into Eq. (34) of the previous paper, one finds that the rate of the reaction $A+B\rightarrow AB$ is given by

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-4\pi r_0 DC_A^2\left[1+\frac{r_0}{(\pi Dt)^{\frac{1}{2}}}\right]-4\pi r_0^2 DNC_A^0$$

$$\times\exp\left[\int_0^t f_{ii}dt\right]\left\{\frac{\exp(-ar_0^2)}{(\pi DT)^{\frac{1}{2}}}\left(1-\frac{4aDt}{4aDt+1}\right)^2\right.$$

$$+\frac{\exp\left[-ar_0^2\left(1-\frac{4aDt}{4aDt+1}\right)\right]}{(4aDt+1)^{\frac{1}{2}}}\left[\frac{2}{r_0}\left(1-\frac{4aDt}{4aDt+1}\right)\right.$$

$$\left.\left.-4ar^0\left(1-\frac{4aDt}{4aDt+1}\right)^2\right]\operatorname{erf}\left[a^{\frac{1}{2}}r_0\left(\frac{4aDt}{4aDt+1}\right)^{\frac{1}{2}}\right]\right\}. \quad (14)$$

The first term on the right hand side of Eq. (14) gives the rate of the reaction $A_i+B_j\rightarrow AB$ with $i\neq j$. The remaining term gives the rate of the same reaction with $i=j$, that is, it gives the rate of annealing due to the recombination of each interstitial with the particular vacancy from which it was originally dislodged. It is obvious that the second term will be dominant at early times if the initial distance between the interstitial and the vacancy of the pair $A_iB_i$ is small compared to the average distance between pairs.

## VI. TREATMENT OF THE DATA

For early times such that $4Dt\ll(\lambda r_0)^2$, the rate given by Eq. (14) reduces to

$$\frac{dC_A}{dt}=-4\pi r_0^2 DC_A^0 N\exp\left(-\frac{1}{\lambda^2}\right)\left[\frac{1}{(\pi Dt)^{\frac{1}{2}}}\right], \quad (15)$$

in which it has been assumed that $\lambda r_0\ll[1/C_A^0]^{\frac{1}{3}}$. This integrates readily to give

$$\varphi=K(Dt)^{\frac{1}{2}}, \quad (16)$$

where

$$K=8\pi^{\frac{1}{2}}r_0^2 N\exp(-1/\lambda^2) \quad (17)$$

and $\varphi$ is the fraction of the initial defects annealed at the time $t$. The data of Brown, Fletcher, and Wright taken at early times and the data of Augustyniak are are shown in Fig. 2 as a graph of $\varphi$ *versus* $\sqrt{t}$. The curves are linear for early times, in agreement with the theory. The fact that linearity extends to large values of $\varphi$ confirms the assumptions that $\lambda r_0\ll(1/C_A^0)^{\frac{1}{3}}$ and that the initial reaction corresponds to recombination of interstitials with the vacancy from which they were originally dislodged. This follows from Eq. (51) in the previous paper which gives the duration of the transient $t^{\frac{1}{2}}$ dependence due to reaction of $A$'s with randomly distributed $B$'s. This transient is of the order of $\frac{4}{3}\pi r_0^3 C_A^0$ mean lives. This is of the order of $10^{-7}$ mean lives if $r_0$ is of the order of 5 angstroms. The long transient observed here must therefore arise from a strong initial correlation of the $A$'s and $B$'s, i.e., $\lambda r_0\ll(1/C_A^0)^{\frac{1}{3}}$.

The initial slopes of the curves in Fig. 2 give $K$ for each temperature. If one assumes that the capture radius $r_0$ is independent of temperature, then $K$ is temperature-independent and the change of slope with temperature in Fig. 2 gives the temperature dependence of $D$. The value of $D$ is given by the sum of the diffusion coefficients of the interstitials and the vacancies. If one of these is much greater than the other, then $D$ will have the form

$$D=D_0\exp(-E^*/RT). \quad (18)$$

It follows from (16) and (18) that

$$\log(\text{slope of Fig. 2})=\text{const}-E^*/2RT. \quad (19)$$

Equation (19) is shown graphically in Fig. 3. From the slope of the curve in Fig. 3, one obtains:

$$E^*=31.6\text{ kcal/mole}. \quad (20)$$

This is somewhat smaller than the value of 39 kcal obtained by Brown *et al.* in the treatment of their data. This difference is believed to arise from the fact that the present treatment deals exclusively with the early stages of annealing and therefore was restricted to the experiments at temperatures below 250°C. The techniques of Brown *et al.* emphasized the comparison of data for two annealing temperatures only in the range where the annealing process had an easily measurable rate at both temperatures. This range was limited in the work of Brown, Fletcher, and Wright. Both tech-

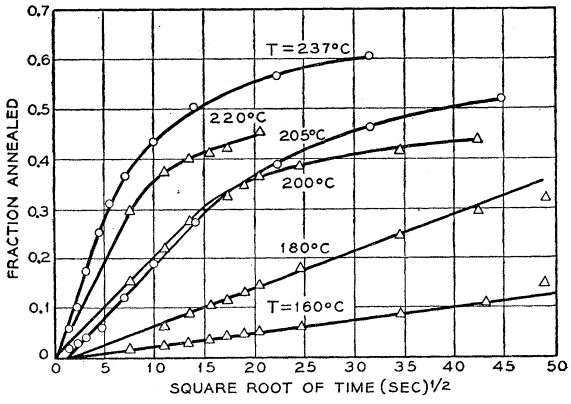



FIG. 2. Initial annealing of radiation damage in germanium. Δ data of Brown, Fletcher, and Wright.[1] O data of Augustyniak.[2]

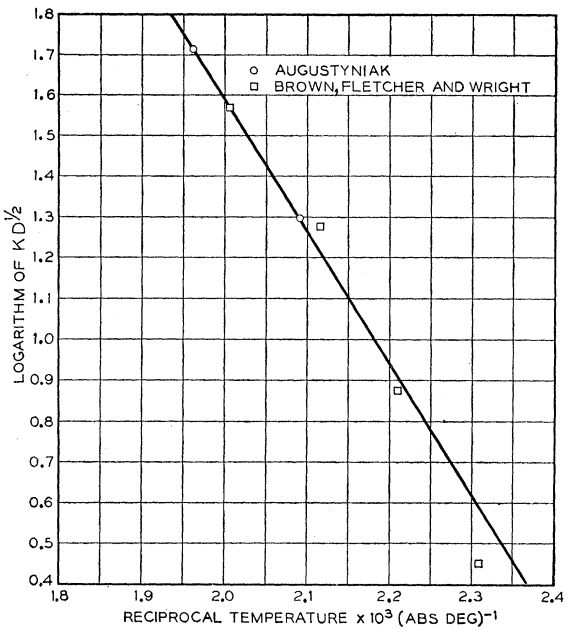



FIG. 3. Initial annealing rate as a function of temperature. $\varphi = K(Dt)^{\frac{1}{2}}$ = fraction annealed.

niques give the same activation energy (31.6 kcal) when applied to the data of Augustyniak for values of $\varphi$ less than 0.6. There is, however, some evidence to indicate that the apparent activation energy increases in the later stages of annealing.

One important fact should be noted with regard to the rate of annealing given by Eq. (14). If one introduces the variable

$$x = Dt \tag{21}$$

into Eq. (14), both $D$ and $t$ are eliminated. It appears, therefore, that the annealing data taken at various temperatures could be reduced to a single curve in a graph of $C_A$ or $\varphi$ *versus* $x$. This assumes, of course, that $r_0$, $C_A{}^0$, $\lambda$, and $D(T)$ are the same for all samples, which is to be expected since they were prepared under nearly identical conditions. A similar conclusion regarding the superposition of the data was reached by Brown, Fletcher, and Wright. All of the data are shown in Fig. 4 [(a) and (b)] on a graph of $\varphi$ *versus* $(Dt)^{\frac{1}{2}}$, under the assumption that $D$ is given by (18) and (20). The data for $\varphi$ less than 0.45 are adequately superimposed. These data correspond to seven samples annealed below 250°C. The data for $\varphi$ greater than 0.45 scatter considerably and the data for particular samples appear to diverge systematically. Qualitatively it appears that the temperature coefficient of annealing increases in the later stages of the annealing process. However, this trend is not quantitative and is obscured by the scatter of the experimental data so as to make its existence uncertain.

The divergence of the data for $\varphi$ greater than 0.45 is not fully understood. It may arise from a failure of the assumptions of the theory which predicts superposition of the curves or it may arise from errors in the experimental preparation of identical samples and in the determination of temperature and $\varphi$. The assumptions necessary to predict superposition of the curves on a reduced plot such as Fig. 4 are less restrictive than those already introduced. It appears sufficient to make the following assumptions:

(1) The rate of annealing is limited by the diffusion together of interstitials and vacancies according to Fick's law.

(2) The only significant forces between reactant entities are short-range attractive forces.

(3) $D$ is given by an equation of the form of (18) with a constant activation energy.

(4) The capture radius is temperature-independent.

(5) The initial distributions are identical for all samples.

It would not be surprising if some of these assumptions were not valid. However, experimental errors appear to be more likely candidates for explaining a good deal of the divergence of data in Fig. 4. There is considerable scatter in the data and there is a lack of agreement between the results of Augustyniak and those of Brown, Fletcher, and Wright for samples annealed at the same temperature. In short, the present data are not sufficient to indicate exactly in what respect the above assumptions fail.

For further treatment of the data, one may introduce new variables into Eq. (14) so as to make it directly comparable with the data in Fig. 4. The result is:

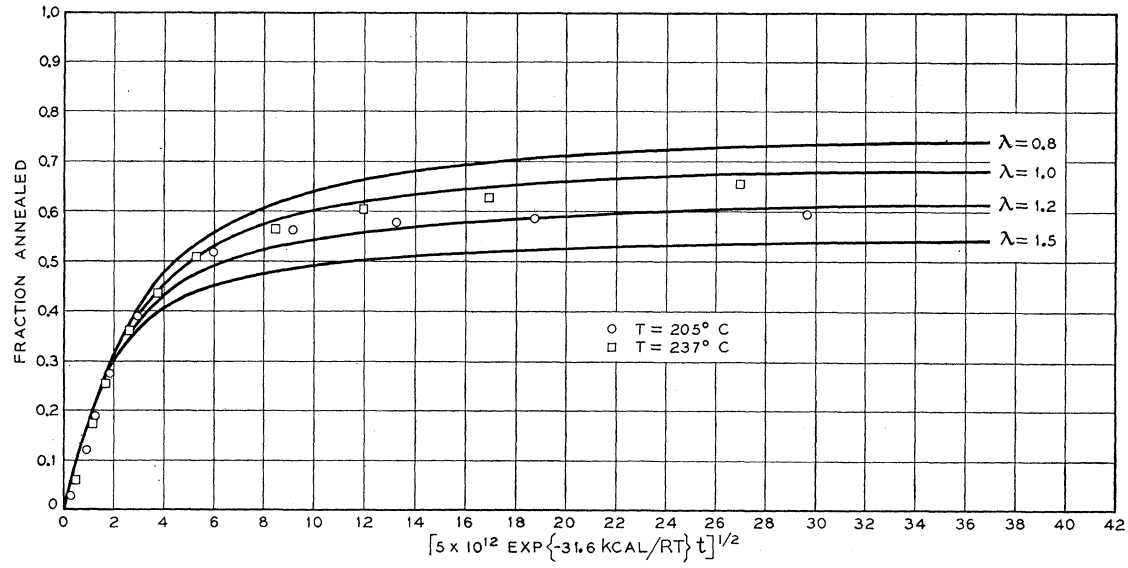
$$\begin{aligned}\frac{d\varphi}{dz} = {} & 2\pi r_0{}^3(1-\varphi)^2 z\left(1+\frac{2}{\pi^{\frac{1}{2}}}z^{-1}\right) \\ & +2\pi r_0{}^3 N\left\{\frac{2\exp(-1/\lambda^2)}{\pi^{\frac{1}{2}}}\left[\frac{\lambda^2}{z^2+\lambda^2}\right]^2\right. \\ & +\frac{z}{\lambda(z^2+\lambda^2)^{\frac{1}{2}}}\exp\left(-\frac{1}{z^2+\lambda^2}\right)\operatorname{erf}\left[\frac{1}{\lambda}\left(\frac{z^2}{z^2+\lambda^2}\right)^{\frac{1}{2}}\right] \\ & \times\left[2\lambda^2\left(\frac{\lambda^2}{z^2+\lambda^2}\right)-4\left(\frac{\lambda^2}{z^2+\lambda^2}\right)^2\right] \\ & \left.\times\exp\left(\int_0^t f_{ii}\,dt\right)\right\},\end{aligned} \tag{22}$$

where

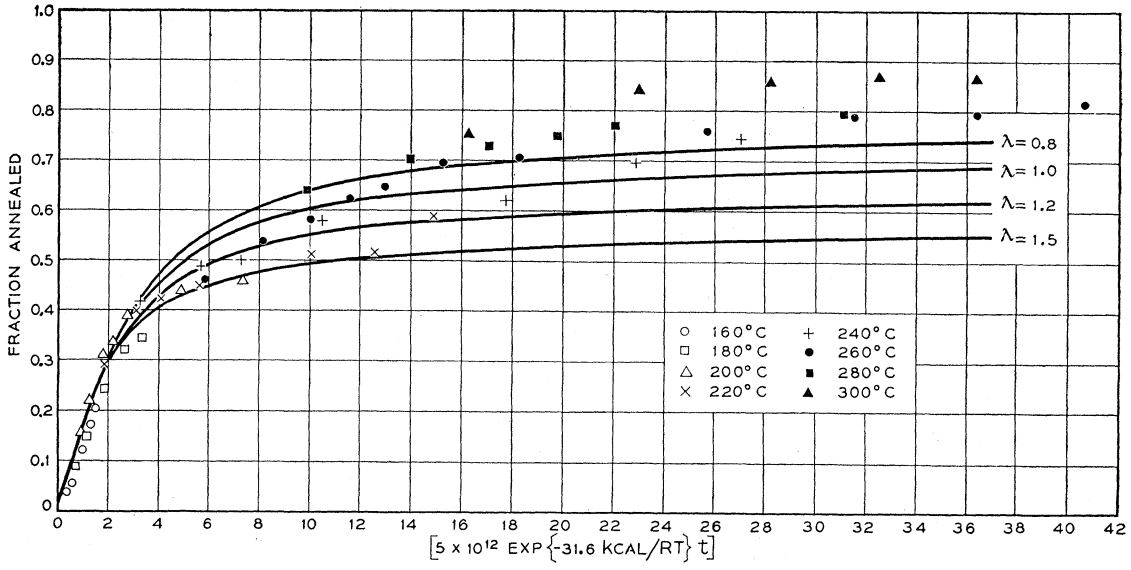
$$\varphi = (C_A{}^0 - C_A)/C_A{}^0, \tag{23}$$

$$z = (4Dt/r_0{}^2)^{\frac{1}{2}}. \tag{24}$$

The only parameter appearing in the first term of (22) is $r_0$. The only parameter in the second term is $\lambda$ (except for $r_0$ appearing in $f_{ii}$) since the normalization constant $N$ is inversely proportional to $r_0{}^3$. There is also an unknown scale factor $D_0/r_0{}^2$ necessary to adjust




(a)




(b)

FIG. 4. Annealing of radiation damage in germanium. Curves given by Eq. (22) of text. (a) Data of Augustyniak.[2] (b) Data of Brown, Fletcher, and Wright.[1]

the variable $z$ in (22) to the independent variable in Fig. 4.

If one assumes that $r_0$ is of the order of $5\times10^{-8}$ cm and that $C^0$ is about $10^{15}$ cm$^{-3}$, as given by the initial change in electron concentration, the coefficient of the first term is found to be about $10^{-6}$. This term, corresponding to $A_i+B_j\rightarrow AB$ $(i\neq j)$, will not make a significant contribution to the annealing process until $z$ is greater than 100. The second term, on the other hand, corresponding to $A_i+B_i\rightarrow AB$, will make its contribution for $z$ equal to or less than $\lambda$. Furthermore, this second term will account for the annealing of 70% of the total damage for $\lambda=1$, but will account for only a few percent or less, if $\lambda$ is five or greater. We are forced to the conclusion, therefore, that the initial rapid annealing in Fig. 4 is due to the first term $(A_i+B_j\rightarrow AB;\ i\neq j)$ or the second term $(A_i+B_i\rightarrow AB)$, but not due to both, unless $r_0$ is orders of magnitude greater than the lattice constant.

If one assumes that the annealing is due primarily to the first term in Eq. (22), the functional dependence of $\varphi$ on $z$ does not agree with the experimental results and the value of $D_0$ required is about 250. This leads to an abnormally high vibrational frequency of $10^{17}$ sec$^{-1}$. The assumption that the annealing is due primarily to the second term in (22) leads to the correct

functional dependence and a reasonable value of $D_0$. Under these conditions the exponential involving $f_{ii}$ is essentially unity. Four curves using slightly different values of the parameters are shown in Fig. 4. The best values of the parameters used were

$$\lambda=1.0, \quad D/r_0^2=7.8\times10^{10}\exp(-31.6\text{ kcal}/RT),$$

and

$$\lambda=1.2, \quad D/r_0^2=1.6\times10^{11}\exp(-31.6\text{ kcal}/RT).$$

If one assumes that the magnitude of $r_0$ is of the order of the jump distance, the vibrational frequency is found to be of the order of $10^{12}$ sec$^{-1}$. It is apparent that an excellent fit of the data for $\varphi<0.5$ can be obtained by using reasonable values of the parameters. The data of Augustyniak are also fitted adequately for all values of $\varphi$.

It appears necessary to conclude from the results of the preceding paragraph that the interstitial recombines with the vacancy from which it was originally dislodged in about 70% of the cases. This is essentially all of the annealing observed in the experiments conducted below 250°C. The data for higher temperature annealing, although it scatters considerably, suggests that the diffusion rate may become more temperature sensitive in these latter stages of annealing. If this is correct, the scale factor $\exp(-31.6\text{ kcal}/RT)$ is not valid for these high-temperature experiments, and the variable $z$ in Eq. (22) may become large enough to permit the first term, corresponding to $A_i+B_j\rightarrow AB$ $(i\neq j)$, to make a significant contribution.

## VII. CONCLUSIONS

### A. Displacement of Atoms by 3-Mev Electrons

It is possible to deduce from the annealing data some information about the probable distribution of an interstitial about the vacancy from which it is dislodged by an incident 3-Mev electron. Comparing those distributions shown in Fig. 1, it appears that the distribution with $\lambda\cong1$ leads to the best fit of the annealing data. Since the annealing is certainly sensitive to the gross features of this initial distribution, it appears safe to conclude that most of the interstitial atoms are displaced to a point just outside the capture radius and that the density of particles falls off very rapidly at greater distances. The average displacement is found to be about one and a half times the capture radius. However, because of the continuum approximation of the lattice and the assumption of an exact reaction sphere, this number has only qualitative significance.

### B. Recombination of Vacancies and Interstitials

The annealing data show that, unless the capture radius of a vacancy for an interstitial is orders of magnitude greater than the lattice spacing, essentially all of the annealing observed in these experiments occurred by recombination of each interstitial with the vacancy from which it was originally dislodged.

### C. Diffusion Coefficients

The diffusion coefficient determined in these annealing experiments is the sum of the diffusion coefficients of the interstitials and the vacancies. Its value will be dominated by whichever of these diffuses most rapidly in the temperature range investigated. Although the present theory gives no method of determining which of these dominates, it is certain that the value obtained provides an approximate upper bound for both diffusion coefficients and is probably a good approximation to one of them. It is, however, the diffusion coefficient of a vacancy very near to an interstitial (or *vice versa*) and therefore may not apply exactly to the isolated defect. It does provide some significant indirect evidence to indicate that the interstitial may not be positively charged in intrinsic germanium (above 160°C) as has been suggested. It would seem that if the interstitial were positively charged it would diffuse much more rapidly than the upper limit indicated by the diffusion coefficient obtained.[4] For example, lithium and copper, which are believed to diffuse interstitially as positive ions, have diffusion coefficients of $25\times10^{-4}\exp(-11.8\text{ kcal}/RT)$ cm$^2$/sec and $3\times10^{-5}$ cm$^2$/sec ($T=700$–$900$°C; $E^*<5$ kcal), respectively, in germanium.[5]

If it were assumed that the diffusion coefficient obtained applied to the vacancy and that this value did not differ greatly from an isolated vacancy, it would be possible to combine this result with that of Letaw, Slifken, and Portnoy[6] on the self-diffusion of germanium to obtain the energy and free energy of formation of a vacancy. The energy of formation calculated under this assumption is 42 kcal/mole. This is to be compared with the results of Mayburg and Rotondi[7] (49 kcal) and of Logan[8] (46 kcal) for the energy of formation of thermally quenched in acceptors, believed to be vacancies.

### D. Interstitial-Vacancy Capture Radius

The present theory offers no way of obtaining the capture radius directly from annealing data on isolated vacancy-interstitial pairs. The capture radius appears only in the combinations $D/r_0^2$. However, Brown[9] has

[4] The possibility exists that the interstitial atoms do diffuse rapidly so as to be annihilated at dislocations and the surface during the bombardment process. If this occurs, the stable defects are isolated vacancies and the annealing process is the reaction of vacancies with dislocations and surfaces. However, the rapid initial annealing indicates that the "reactants" are closely associated. This would require a cluster of more than one hundred vacancies around each lattice point on the edge dislocations, or a clustering at the surface such that the bulk conductivity could not be effected as observed.

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[6] Letaw, Slifken, and Portnoy, Phys. Rev. **93**, 892 (1954).

[7] S. Mayburg and L. Rotondi, Phys. Rev. **91**, 1015 (1953).

[8] R. A. Logan, Phys. Rev. **101**, 1455 (1956).

[9] W. L. Brown (private communication).

reported that experiments with low-energy electrons (less than 0.6 Mev) result in defects stable at room temperature (i.e., vacancies and interstitials separated by more than the capture radius) at electron energies which are not likely to displace the germanium atoms by more than a few lattice spacings.

### E. Confirmation of the Theory

The theory of diffusion-limited chemical reactions developed here and in the preceding paper provides a satisfactory description of a large portion of the annealing data discussed here. The data which are not fitted adequately appear to scatter considerably owing to experimental error, but may indicate that some of the assumptions outlined in Sec. VI are not satisfied. The present annealing problem does not provide a complete test of some aspects of the theory because the competition of many $A$'s for each of the $B$'s and *vice versa* does not appear to be important and, therefore, a less general theory might suffice. However, it does appear safe to conclude on the basis of the present work that the application of diffusion theory to the kinetics of certain reactions in the solid state leads to satisfactory results.

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# High-Frequency Relaxation Processes in the Field-Effect Experiment

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A theoretical treatment is given of two dispersion phenomena in the field-effect experiment: (1) dispersion arising from the finite time required to generate minority carriers, and (2) relaxation of the fast surface states. It is shown that the in-phase part of the field-effect mobility is given (for an $n$-type semiconductor) by $\mu_{FE}=-\mu_n+A/(1+\omega^2\tau_1^2)-B/(1+\omega^2\tau_2^2)$, where $(\omega/2\pi)$ is the frequency of the applied field, $A$ and $B$ are constants, and $\tau_1$ and $\tau_2$ are characteristic times, all four quantities being functions of the body resistivity, surface potential, and of the densities, energy levels, and capture cross sections of the fast states. Under certain conditions, $\tau_1$ is equal to the fundamental decay-mode lifetime of the sample, while $\tau_2$ is expected to be much shorter, and depends primarily on the cross sections and the position of the state level in the gap. A comparison of the theory with recent experimental results of Montgomery shows (1) that reasonable agreement can be obtained, and (2) that the presence of any significant number of states in the region close to the center of the gap is unlikely.

## 1. INTRODUCTION

THE field-effect experiment is the observation of a change in the conductance of a thin slice of material, caused by the application of an external electric field normal to its surface. Such an effect was looked for in metals around the turn of the century, and the failure to detect it was discussed by Thomson.[1] Since the volume density of electric carriers may be many orders of magnitude less in a semiconductor than in a metal, a fresh attempt at the field-effect experiment was made by Shockley and Pearson[2] some ten years ago, using the high-purity silicon then available for the first time. A modulation of conductance was indeed found, but the magnitude of the effect was less than expected. One possible reason for this was suggested by Bardeen[3]: the semiconductor surface has on it electronic trapping levels, which tie up most of the induced charge in localized sites ("surface states"). Since then, many experiments have confirmed the truth of Bardeen's suggestion. Montgomery and Brown[4] have studied the field-effect experiment in germanium, as a function of the height of the surface space-charge barrier. Brattain and Garrett[5,6] have brought the field-effect experiment into reconciliation with a parallel line of work—the study of surface photovoltage and surface recombination.[7] It is now fairly well established (1) that there are two classes of surface states on germanium and silicon, distinguished by having relaxation times[8] of the order of a second or greater (the "slow states"), or a microsecond or less (the "fast

[1] J. J. Thomson, *The Corpuscular Theory of Matter* (Constable and Company, London, 1907), p. 80.
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[7] W. H. Brattain and J. Bardeen, Bell System Tech. J. **32**, 1 (1953).
[8] I.e., times for readjustment of state population, by interchange of charge with whichever band is the more accessible.