Annealing of Bombardment Damage in a Diamond-Type Lattice: Theoretical

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The annealing of isolated interstitial-vacancy pairs presumably introduced by bombardment is considered theoretically with special attention paid to the diamond-type lattice. It is proposed that the annealing can be divided into three stages. First, those vacancy-interstitial pairs having a small initial separation will recombine under the influence of short-range elastic forces. Second, vacancies located initially farther from their companion interstitials will wander according to a random walk process, some of them wandering back within the range of the elastic forces and recombining but some escaping from the vicinity of their interstitials. Finally, vacancies which have escaped in the second stage will continue to wander until captured on surfaces or dislocations or by interstitials other than their own. Approximate analytic expressions are derived for these various stages. An outline is given of a more complete treatment with a quantitative solution for one particular phase of the annealing in the diamond-type lattice.

I. INTRODUCTION

HEN crystals are bombarded with high-energy particles (neutrons, deuterons, alpha particles, electrons, etc.) the mechanical and electrical properties have been found to change.¹ Heating tends to restore the original properties of the crystal. These irradiation effects are believed to be caused by displacement of atoms from their normal lattice sites into interstitial positions. After bombardment the interstitial atoms tend to return to their original positions in the lattice, particularly if the crystal is heated.

In this paper we consider the annealing mechanism of the simplest type of irradiation damage. It is believed that many of the essential details of more complicated types of damage will be exhibited by this simple type. The case which we will consider is that of a single interstitial atom associated with each vacancy. In the case of heavy particle bombardment, clumps of such interstitial-vacancy pairs will undoubtedly be present, but the simplest case may actually be realizable in bombardment with electrons with energies near to the threshold for interstitial-vacancy production.

We have also given special attention to a particular crystal structure, the diamond-type lattice, so that annealing of germanium, silicon, and diamond can be analyzed directly. The same general procedures can be applied to other crystal structures.

II. DIFFUSION OF VACANCIES

We shall begin by assuming that the interstitial remains fixed and examine the behavior of a vacancy. In order for the vacancy to be stable each of its neighboring atoms must find itself in a potential energy trough. Each must therefore overcome a potential barrier E in order to jump into the vacancy. The average time τ required for one of them to make such a jump under thermal excitation is given by²

$$\tau = \nu_0^{-1} e^{E/kT},\tag{1}$$

where ν_0 is interpreted as the average lattice frequency (ca 10¹³ cps), T is the absolute temperature, and k is Boltzmann's constant. When an adjacent atom jumps into the vacancy, the vacancy moves to the former position of the jumping atom. Hence the vacancy can be said to jump with an average jump time τ given by (1).

If the vacancy is close to an interstitial atom, the energy barrier and hence the jump time will be altered.



FIG. 1. Effect of elastic deformation around an interstitial on the nearest neighbor atoms of a vacancy. The distortion due to the vacancy has been neglected. Notice how the atom between the interstitial and the vacancy has been pushed toward the vacancy.

One reason for this is that the lattice is deformed by the interstitial. The atoms around the interstitial are forced away from the interstitial. This causes the lattice to be compressed in a direction radially outward from the interstitial and to be expanded in directions perpendicular to the radial direction. This effect is shown schematically in Fig. 1 for a two-dimensional simple cubic lattice. If a vacancy is located in this deformed region, its neighboring atoms which are located along the radial line from the interstitial are pushed toward

¹For a review of the literature, see G. J. Dienes, "Radiation Effects in Solids," Annual Reviews of Nuclear Science (Annual Reviews, Inc., Stanford, 1952), Vol. II. ² N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford University Press, London, 1940).

the vacancy, while those perpendicular to this line are pushed away. This lowers the potential barrier E for radial jumps and increases it for lateral jumps. Since the atoms closest to the interstitial are affected most, the jumps toward the interstitial have the lowest barrier. Thus a vacancy within a distorted lattice around the interstitial has a preference for jumping towards the interstitial and an average jump time which decreases the closer it is to the interstitial.

If we assume the vacancy to be fixed and the interstitial atom to move, in the undistorted lattice the average jump time is given by (1), where the barrier energy E is now interpreted as the energy required by an interstitial to squeeze between neighboring atoms to an adjacent interstitial site. Within the region distorted by the vacancy, however, the situation is more complicated than before. The germanium lattice surrounding the vacancy moves towards the vacancy, the radial distance between atoms increasing and the tangential distance decreasing. Thus interstitial jumps along the line to the vacancy are more difficult. Motion toward or away from the vacancy will therefore be accomplished by diagonal jumps. This possibility has not been fully explored, although we do not believe it will change our general conclusions significantly. We shall consider here only the vacancies as moving.

III. STAGES OF ANNEALING

For those vacancies located within the deformed lattice around the interstitial, the vacancy jumps mainly towards the interstitial with jump times which become progressively smaller as the vacancy approaches the interstitial. Thus, the time required for recombination of these vacancies is approximately the time in which the vacancy jumps from its initial position.

For those vacancies which are located outside this deformed region, the probability of jumping in any direction is the same. Thus these vacancies wander according to a random-walk process, some wandering back within the deformed region where they are subsequently captured, and the rest wandering off through the crystal. The vacancies which wander off are "liberated" from their original interstitials. These will eventually be captured on dislocations or on the surface or may recombine with other interstitials.

These different processes correspond to different stages of the annealing, since they occur at different times. First to recombine will be those vacancies initially located within the deformed lattice surrounding the interstitial, since the time of recombination is less than the average jump time in the undistorted lattice. Second to recombine will be those which are initially located outside of the deformed lattice around the original interstitial, but which wander back after a small number of jumps of time τ and are captured at their original interstitials. Finally, because they must wander throughout the crystal, those vacancies which were

liberated from their original interstitials will recombine or be captured after a large number of jump times τ .

IV. APPROXIMATE TIME DEPENDENCE OF ANNEALING

We shall consider the functional dependence on time of these various stages of annealing. Let us designate Nas the number of unrecombined vacancy-interstitial pairs per unit volume and number the vacancy sites in order of their distance from the interstitial. Let N_i be the number of vacancies which were originally in the *i*th site. The expression for the annealing will be obtained from the expression for a particular initial site *i*, multiplied by N_i , and summed over all the sites.

For a vacancy initially within the distorted region around the interstitial, the rate of recombination of vacancies in site i will be approximately proportional to the number of unrecombined pairs:

$$dN/dt = -N/\tau_i,\tag{2}$$

where τ_i is the average jump time from the site *i* towards the interstitial. This leads to an exponential dependence on time characteristic of a monomolecular law of recombination. We shall designate by subscript M this first stage of the annealing, which is thus given by

$$N_M = \sum_{i} N_i e^{-t/\tau_i},\tag{3}$$

where \sum_{1} indicates summation over all of the sites within the region distorted by the interstitial.

A vacancy located initially outside this distorted region will be governed by a random-walk process. As a first approximation, we shall treat this as diffusion in an isotropic medium. Let $P(r_i, r, t)$ be the probability per unit volume of finding a vacancy at a distance r from the interstitial at a time t after it was initially located at r_i . There is spherical symmetry around the interstitial so that the differential equation governing the diffusion can be written

$$\frac{\partial P}{\partial t} - \frac{D}{r^2} \frac{\partial}{\partial r} \frac{\partial P}{\partial r} = 0, \qquad (4)$$

where D is the diffusion constant. This equation can be solved under the boundary conditions that P must vanish at infinity and also at $r=r_c$, where r_c is the radius of the deformed region around the interstitial:³

$$P(r_{i}, r, t) = \frac{1}{8\pi (Dt)^{\frac{1}{2}}} \frac{1}{rr_{i}} \left[\exp\left[-\frac{(r-r_{i})^{2}}{4Dt}\right] - \exp\left[-\frac{(r+r_{i}-2r_{o})^{2}}{4Dt}\right] \right].$$
(5)

The integration of this expression over the volume gives

⁸ H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids (Oxford University Press, London, 1947).

the total probability of finding a vacancy unrecombined. The integrated expression contains two parts: one which vanishes with time and the other which does not. The vanishing part corresponds to the vacancies which recombine during this second stage and the constant part corresponds to the vacancies which are liberated, eventually to recombine in the final stage. By multiplying the time-dependent part by the initial number of vacancies in site i and summing over all the sites, we obtain the expression for the second stage of the annealing, indicated by a subscript L for liberation:

$$N_{L} = \sum_{2} N_{i} \frac{r_{c}}{r_{i}} \operatorname{erf}\left[\frac{r_{i} - r_{c}}{(4Dt)^{\frac{1}{2}}}\right].$$
 (6)

Here \sum_2 indicates summation over all of the sites outside r_c and erf refers to the error function. The diffusion constant is related to the jump time by the expression⁴

$$D = \langle b^2 \rangle / 2\tau, \tag{7}$$

where b is the magnitude of the change in the radius r during a single jump, and the brackets indicate the average over all possible jumps. Equation (6) can be rewritten in terms of (7) to give

$$N_{L} = \sum_{2} N_{i} \frac{r_{c}}{r_{i}} \operatorname{erf} \left[\frac{(r_{i} - r_{c})}{(2\langle b^{2} \rangle)^{\frac{1}{2}}} \left(\frac{\tau}{t} \right)^{\frac{1}{2}} \right].$$
(8)

For the diamond-type lattice it is not difficult to show that $\langle b^2 \rangle = a^2/16$, where *a* is the cube edge of the unit cell.

The time dependence of the final stage of the annealing will depend on whether capture occurs at dislocations or on the surface or whether the liberated atom recombines with other interstitials besides the one with which it was originally associated. We shall present expressions for all three. Let us introduce N_F (F for final) for the number of vacancies which are still free during the final stage of the annealing. The initial number of such vacancies N_{F0} is found from the constant part of the integration of Eq. (5). By multiplying this by N_i and summing, we find

$$N_{F0} = \sum_{2} N_{i} [1 - (r_{c}/r_{i})].$$
(9)

We shall assume that these are initially distributed uniformly through the volume of the crystal.

If these vacancies are captured on the surface, we must solve the transient diffusion equation.³ For a rectangular parallelepiped of dimensions of u, v, w, this leads to

$$N_{F} = N_{F0} \frac{2^{9}}{\pi^{6}} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{e^{-\alpha_{lmn}t}}{(2l+1)^{2}(2m+1)^{2}(2n+1)^{2}}, \quad (10)$$

where

$$\alpha_{lmn} = \pi^2 D \bigg[\frac{(2l+1)^2}{u^2} + \frac{(2m+1)^2}{v^2} + \frac{(2n+1)^2}{w^2} \bigg]. \quad (11)$$

⁴ M. C. Wang and C. E. Uhlenbeck, Revs. Modern Phys. 17, 333 (1945).

A fair approximation to (10) is obtained by taking only the first term of the summation, so that if $w \ll u, v$, (10) can be rewritten

$$N_F \doteq N_{F0} \exp\left[-\frac{\pi^2 \langle b^2 \rangle}{2w^2} \left(\frac{t}{\tau}\right)\right], \qquad (10a)$$

where expression (7) for the diffusion constant has been used. The approximate expression (10a) is correct at t=0, but becomes 20 percent too high at long times.

For capture at dislocations we shall solve the same equation with the requirement that the vacancy density vanish at a distance r_d from each dislocation. Inside r_d we assume that the lattice is distorted in such a way that capture is certain to follow. By symmetry the flow of vacancies vanishes midway between adjacent dislocations. We shall simplify this problem by assuming that cylindrical symmetry exists around each dislocation. The boundary conditions are then (a) the vacancy density vanishes at $r=r_d$, and (b) the vacancy flow vanishes at $r=R_d$, where $2R_d$ is approximately the average distance between dislocations. With these simplifying assumptions, the annealing is given by³

$$N_{F} = 4N_{F0} \sum_{n} \frac{1}{(\alpha_{n}R_{d})^{2}} \frac{J_{1}^{2}(\alpha_{n}R_{d}) \exp(-D\alpha_{n}^{2}t)}{J_{0}^{2}(\alpha_{n}r_{d}) - J_{1}^{2}(\alpha_{n}R_{d})}, \quad (12)$$

where the J's and Y's are the Bessel and Neuman functions, respectively, and the α_n 's are the roots of

$$J_{0}(\alpha_{n}r_{d})Y_{1}(\alpha_{n}R_{d}) - J_{1}(\alpha_{n}R_{d})Y_{0}(\alpha_{n}r_{d}) = 0.$$
(13)

An approximate expression can be obtained for (12) if we take only the first term of the summation and assume $R_d \gg r_d$. For this case, the smallest solution of (13) is obtained when $\alpha_0 r_d \ll \alpha_0 R_d \ll 1$, so that we may expand the Bessel Functions around their arguments and obtain for the smallest root of (13):

$$\frac{1}{\alpha_0^2} \doteq \frac{R_d^2}{2} \left[-\gamma + \ln \frac{2}{\alpha_0 r_d} \right].$$
(13a)

Here γ is Euler's constant=0.577. With this approximation and the use of (7), Eq. (12) can be written

$$N_F \doteq N_{F0} \exp\left[-\frac{1}{2}\alpha_0^2 \langle b^2 \rangle (t/\tau)\right].$$
(12a)

If the final stage consists of a direct recombination of vacancies with interstitials, we shall obtain a secondorder or bimolecular process. This can be seen by the following consideration: The number of vacancies which recombine in a jump time will be equal to the number of vacancies multiplied by the fraction of lattice sites available to the vacancy from which recombination is practically certain. This fraction is equal to the density of interstitials N_F divided by the total density of lattice sites N_{atom} and multiplied by the number of sites within the deformed region surrounding each interstitial which can be reached in a single jump from a site outside the deformed region. On the average the number of such sites will be equal to $4\pi r_c^2 \langle b \rangle N_{\text{atom}}$, where r_c is the same capture radius previously introduced and $\langle b \rangle$ is the magnitude of the change in the separation of interstitial and vacancy during one jump averaged over all possible jumps. Thus the rate of change of vacancies with time is

$$\frac{dN_F}{dt} = -\frac{N_F}{\tau} \times \frac{N_F}{N_{\text{atoms}}} \times 4\pi r_c^2 \langle b \rangle N_{\text{atoms}}, \qquad (14)$$

giving a differential equation which is easily integrable:

$$N_F = \frac{N_{F0}}{1 + 4\pi r_o^2 \langle b \rangle N_{F0}(l/\tau)}.$$
 (15)

For a diamond-type lattice the indicated average can be performed to give $\langle b \rangle = (\sqrt{3}/16)a$.

The total number of vacancies present after an annealing time t is given by the summation

$$N = N_M + N_L + N_F. \tag{16}$$

It should be noted that the annealing time t in all the above expressions only appears in the ratio t/τ . By comparing the times at which the same degree of annealing occurs for different temperatures, the barrier energy can be determined without an actual fit of the theoretical expressions to experimental data. The barrier energy, so determined, will be constant in the stages of the annealing governed by N_L and N_F but will decrease with decreasing time (or temperature) in the stage governed by N_M .



FIG. 2. The diamond lattice surrounding an interstitial site place at the origin. Only the details of the two essentially different octants are shown. All the octants with the same label (+ or -) have identical symmetry with respect to the interstitial. Numbers indicate site numbers (*i*) arranged in an increasing sequence with their distance from the interstitial.

V. ANNEALING IN A DISCRETE LATTICE

In the last section we developed expressions for the time dependence of the annealing by approximating the discrete lattice outside the capture radius r_e with a continuum in which diffusion takes place, and by idealizing the discrete lattice inside the capture radius by permitting vacancy jumps only toward the interstitial. In this section we shall present a set of differential equations which describe the annealing without using the above approximations.

To begin with, lattice symmetry enables us to reduce the number of sites which we must consider. Vacancies in sites which have the same symmetry with respect to the interstitial have exactly the same probability of escaping or recombining with the interstitial. Let us introduce P_i as the probability of finding the vacancy in any of these identical sites.

We next need to consider those sites of different symmetry which are adjacent to the *i*th site. Let us introduce b_{ji} for the number of *j* sites adjacent to the *i*th site. Also let $1/\tau_{ji}$ be the probability per unit time that a vacancy located in the *i*th site will jump to a particular one of the adjacent *j* sites. The total probability of a vacancy jumping from the *i*th site is thus $\sum_{j} b_{ji}/\tau_{ji}$. This leads us to the differential equation governing the rate of change of P_i with time,

$$\frac{dP_i}{dt} = -P_i \sum_j \frac{b_{ji}}{\tau_{ji}} + \sum_j \frac{b_{ij}}{\tau_{ij}} P_j.$$
(17)

This actually represents an infinite set of linear homogeneous differential equations for which the solution is

$$P_i = \sum_n A_n \Psi_{in} e^{-\gamma_n t}, \qquad (18)$$

where γ_n are the eigenvalues of the matrix

$$\left\|\delta_{ij}\left(\gamma_n - \sum_k \frac{b_{ki}}{\tau_{ki}}\right) + \frac{b_{ij}}{\tau_{ij}}\right\|,\tag{19}$$

in which δ_{ij} is the Kronecker delta, Ψ_{in} are the eigenvectors of the matrix (19), and A_n are constants determined from the initial distribution of P_i . Equation (18) thus represents the general solution for the first two stages of the annealing, providing the b_{ij} and τ_{ij} are known, and the initial values of P_i are given.

VI. ANNEALING IN THE DIAMOND-TYPE LATTICE

To illustrate how this method works we have obtained the b_{ij} for a diamond-type lattice and solved the equations for the special case where τ_{ij} is constant independent of i, j. This corresponds to the liberation stage of the annealing.

In the diamond-type lattice there exist "natural" interstitial sites such that an atom located in such a site is the same distance from its four nearest neighbors as the separation between nearest neighbors in the normal lattice sites. If we place the interstitial at the origin of the coordinate system and place one of its nearest neighboring interstitial sites at the (111) position (measured in units of one-fourth the cube edge of the unit cell), this will locate the germanium atoms or vacancy sites. Thus the four neighboring vacancy sites will be $(\overline{111})$, $(\overline{111})$, $(1\overline{11})$, and $(11\overline{1})$. The next six nearest neighbors will be (200), (020), (002), (200), $(0\overline{2}0)$, and $(00\overline{2})$. All other sites can be obtained from these first two by adding or subtracting integral multiples of the fundamental translation vectors (022), (202), and (220). All sites in the nearest position to the interstitial and all progeny of these sites obtained by translation have neighboring vacancy sites in the same directions, namely $(\overline{111})$, $(\overline{111})$, $(1\overline{11})$, and $(11\overline{1})$. Similarly all sites in the next nearest position to the interstitial and their progeny will have their neighboring vacancy sites in the directions (111), (111), (111), and (111). This enables us to locate easily the nearest neighbors and hence to determine the b_{ij} .

Since around each coordinate axis there is twofold rotational symmetry, of the eight octants around the origin only two will be essentially different (see Fig. 2). For instance, we may choose for the two octants those whose indices are all positive or all negative. Thus the four nearest sites to the interstitial have identical symmetry and are characterized by the $(\overline{111})$ position in the negative octant. In each octant there is a threefold rotational axis along the cube diagonal, so that all sites whose indices are related by a simple permutation have identical symmetry. Thus (200), (020), and (002) have the same symmetry. In fact since at least one of the indices is zero, they are on the edge of the octant and are common to the positive and negative quadrants, so that all six next nearest neighbors to the interstitial have the same symmetry. The four nearest neighbors thus represent site i=1, and six next nearest neighbors represent site i=2. The first few sites are shown in Fig. 2.

A scheme for representing all the vacancy sites in the vicinity of the interstitial is shown in Fig. 3. Here the nearest neighbors are connected by lines and the numbers on the lines indicate the b_{ij} . For convenience the sites are plotted with their distance from the interstitial on the vertical axis and their distance from the nearest coordinate plane on the horizontal axis. Position in the positive octant is plotted to the right and position in the negative octant to the left. The areas of the circles are drawn proportional to the number of sites with the same symmetry.

We have attempted the solution of Eqs. (19) with two different boundary conditions, capture at i=1 and i=2, and initial location of the vacancy successively at each of the nine closest sites. Because the determinations of γ_n , Ψ_{in} , and A_n are laborious if many sites are considered, we did not use this method. Instead we used three separate approximate methods whose regions of accuracy overlapped enough to determine the complete solution. For the early stages of the annealing we considered only the first twelve sites and permitted no return from sites outside these. The Eqs. (19) were then solved on an analog computer for P_1 and P_1+P_2 for the two stated boundary conditions, respectively. After enough time elapses (ca 5τ) these computed values will fall below the actual values because of the neglect of vacancies diffusing back from outside the first twelve positions. In order to correct this error, we would have to consider more sites than the computer could handle. To extend the solution to longer times we replaced the continuous differential equation of (19) by a discontinuous jump equation in which after a time τ the increase in P_i is given by



FIG. 3. Representation of the vacancy sites relative to an interstitial located at the origin. Sites with the same symmetry are lumped together, the area of each circle being arranged proportional to the number of individual sites. Lines connect nearest neighbors, and the number of these (b_{ji}) is indicated. Notice that the sites occur in shells of about the same radius.

The factor $\frac{1}{4}$ appears here because there are four sites to which a vacancy may jump; i.e., $\sum_{j} b_{ij} = 4$ and $\tau_{ij} = 4\tau$. It was not difficult to solve this equation taking into consideration the first one hundred sites. This allowed sixteen jump times τ before the influence of sites outside the first one hundred could be felt. For times longer than this enough sites were involved so that we felt the continuum differential equations should be applicable and we could use an equation of the type (8), where r_c and r_i were regarded as adjustable parameters to tie smoothly onto the solutions obtained from (19a).

The complete solutions for two particular initial conditions are shown in Fig. 4. Here on the vertical axis is plotted the probability that a vacancy has recombined



FIG. 4. The annealing in an undistorted discrete diamond-type lattice [Eq. (19)] compared with the annealing in an isotropic homogeneous medium [Eq. (6)] for two particular initial conditions. The light lines indicate how the three approximate curves used in solving Eq. (19) depart from the actual curve. The two cases shown represent the largest departures of the continuum solution from the discrete solution.

with an interstitial, $1 - (N/N_i)$, at a time *t* after starting in position *i*. The heavy line for each curve represents the final solution and the light lines show the departure



FIG. 5. The probability that a vacancy and interstitial have recombined a time i after starting in the ith site of a diamond-type lattice. The heavy line represents the complete solution for a lattice which is undeformed outside the first site (i=1). The light and the dashed lines indicate how the three approximate curves used in the solution depart from the actual curve.

of the approximate solutions from this in the range of time where the approximation begins to break down. The approximate solution of Sec. IV, Eq. (6), in which r_c and r_i were not adjusted is shown as a dashed curve. The two boundary conditions shown represent the largest departures of the approximate solution of Eq. (6) from the more complete solution of all the boundary conditions investigated. The approximate solutions of Eq. (6) can be made coincident with the complete solution for long times by adjustment of r_c and r_i . The effective values of these radii for coincidence for these two cases are marked on the curves. Even though the approximate solution, only a small adjustment of r_c and r_i is required for coincidence of the curves.



FIG. 6. Same as Fig. 3 except that the lattice is assumed to be deformed out to the second site (i=2).

The complete solutions for all of the boundary conditions investigated are shown in Figs. 5 and 6. The effective value of r_c/r_i is marked on the curves. This represents the asymptotic value for the annealing probability at long times. The value for $(r_c)_{eff}$ could be chosen the same for all curves with the same capture site. The value for $(r_i)_{eff}$ approached the true value as r_i increased. In no case did these radii have to be adjusted by more than 15 percent. Use will be made of the analysis in this section in the interpretation of the observed annealing of bombarded germanium in the following paper.

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