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Diffusion and carrier recombination by interstitials in silicon

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We analyze a model of the electronic structure of the silicon interstitial, consistent with full local-density approximation (LDA) calculations. The model assumes three charge states: neutral (0), singly (+), and doubly ionized (++). The (0) interstitial is stable in a shared site, the (++) stable in a tetrahedral site, and the (+) state has energy nearly independent of position. In thermal equilibrium the relative occupation of the (0) and (++) states, each near its stable position, depends upon the electronic Fermi energy. The (+) state has much lower probability than either the (0) or the (++), making this a negative-U center. Nevertheless, the predicted diffusion constant for dopant atoms is dominated by motion of the interstitial in the (+) state. It has an activation energy of about one-half the band gap and is also proportional to the total interstitial density. If the interstitial density is established at some high annealing temperature, it depends strongly upon the Fermi energy at that temperature, and is much higher for p-type silicon. The moving interstitial also provides radiationless recombination of excess carriers, at a rate calculated using matrix elements derived from the full LDA electronic structure. The recombination rate does not contain an important Boltzmann factor, in contrast to a Huang-Rhys mechanism, but is proportional to the interstitial density and, at high carrier densities, to the square root of the product of the electron and hole densities. This recombination causes an enhancement of the diffusion rate, given near equilibrium by a factor $[N_e\tau_h/N_e^0+N_h\tau_e/N_h^0]/[\tau_e+\tau_h]$, with N_e, N_e^0, and τ_e the density of electrons, the equilibrium density, and an electron emission time, and h indicating the corresponding parameters for holes. For high carrier densities, the enhancement can greatly exceed the equilibrium diffusion. [S0163-1829(98)02816-1]

I. INTRODUCTION

In an earlier study, Harrison and Wills[1] made an all-electron local-density approximation (LDA) super-cell calculation of the electronic structure and total energy of the silicon self interstitial in a tetrahedral site and in a shared site (the so-called [110] dumbbell). Bar-Yam and Joannopoulos[2] had earlier found that the latter geometry had lower energy for the neutral interstitial, and calculations by Blöchl, Smargiassi, Car, Laks, Andreoni, and Pantelides[3] and by Wills[1] confirmed this. Wills and Harrison also pointed out that, as an interstitial moves from the tetrahedral site to the shared-site geometry, an electronic level associated with the interstitial drops from the conduction band into the valence band and that because of this electrons can be carried from the conduction band to the hole band, constituting carrier recombination. The present study is an effort to understand and predict the properties of such a system and the roles it plays in recombination and diffusion.

We should recognize that although these LDA calculations suggest the diffusion path from shared site through tetrahedral site, that is not experimentally established. It could be that a direct shift from one shared site to the next by motion along the bond direction is of lower energy and dominant. However, it seems likely that again only in the shared site would the electronic level lie in the bonding (valence) band so the properties of the system would be similar.

We proceed by first defining a model electronic structure that corresponds approximately to the calculations made by Wills.[1] Certainly there are major uncertainties in the accuracy of even the best LDA calculations, but the fact that the independent calculations of Refs. 1, 2, and 3 are consistent on the scale of tenths of an electron volt for the level energies, indicates their validity *within the context* of LDA on that scale. There are further sizable corrections to the LDA approximation, such as the enhancement of the gap from Coulomb correlations, which we take to be 0.64 eV. These are clearly large compared to the accuracy of the LDA calculations themselves, so the straight LDA calculation without corrections would be of little value. However, we believe that our corrections—mostly from Ref. 1—are also accurate on a scale of tenths of an electron volt. Thus we have reason to proceed with our model, recognizing that there may be errors of this size in the numerics.

In terms of this model we calculate the distribution of interstitials in various states in thermal equilibrium. By extending this to a system with a concentration gradient we obtain the diffusion constant. We then calculate the rate of carrier recombination when there are excess electrons and holes, using emission and capture rates obtained by Harrison and Wills[1] and, finally, we calculate the additional diffusion induced by such recombination.

II. MODEL OF THE INTERSTITIAL ELECTRONIC STRUCTURE

We imagine the minimum-energy path that an interstitial follows between the shared site (position $s=0$) and the tetrahedral site (position $s=\pi$) and of course, it can continue to a second shared-site position (position $s=2\pi$), etc. We associate an electronic energy level with the interstitial which is doubly occupied for the neutral interstitial, designated by (0), singly occupied (+), or empty (++). We write that energy level $\varepsilon(s)$, which we take to be the energy (+,++) at which an electron is removed from the (+) state. For the neutral state (0) the electron is taken from a shallower level

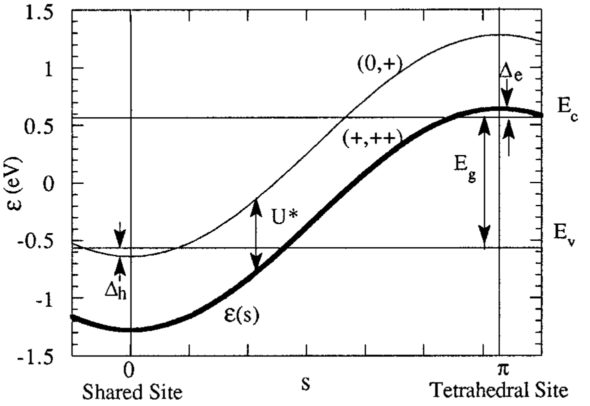

FIG. 1. A schematic representation of the interstitial energy level for electrons in an interstitial as it moves from $s=0$ at the shared site to $s=\pi$ at the tetrahedral site. The levels (0,+) and (+,++) are taken as $\varepsilon_1 \cos(s) \pm U^*/2$, respectively, with $\varepsilon_1 = 0.96$ eV, as described in the text.

(0,+), $\varepsilon(s)+U^*$, with $U^*=0.64$ eV an effective Coulomb energy,[4] equal to the atomic Coulomb energy of 7.64 eV divided by the dielectric constant of 12. The total energy of the interstitial depends upon the charge state and is written as an energy $E_{++}(s)$ for the interstitial in the (++) state, plus an energy $\varepsilon(s)$ if it is in the (+) state, plus another $\varepsilon(s)+U^*$ if it is in the neutral state, with two electrons in the level including the Coulomb repulsion between them.

We may now learn about the energies $E_{++}(s)$ and $\varepsilon(s)$ from Wills'[1] results, as corrected for Coulomb and finite-cell-size effects.[5] The energy level for the neutral interstitial at the shared site was at the valence-band maximum, corresponding to $\varepsilon(0)+U^*$ equal to the valence-band maximum. Wills found the level for the tetrahedral site, containing 0.9 electrons, at 1.22 eV above the valence-band maximum. Adding $0.1U^*$ (because only 0.9 electrons were present in the calculation) brings it to the energy (+,++) at which an electron is removed from the (+) state, or $\varepsilon(\pi)=1.22+0.1U^*=1.27$ eV above the valence-band maximum, and well above the conduction-band minimum at $E_g=1.13$ eV. (This 1.13 eV is U^* above the LDA gap of 0.49 eV[1,4]). This is shown schematically in Fig. 1.

We found[5] the total energy change for an isolated neutral interstitial in going from the shared site to the tetrahedral site was 0.78 eV, corrected from Wills' super-cell calculations.[1] At the tetrahedral site the two electrons were put in a shallow level below the conduction band, lower in energy than two electrons at the conduction-band edge by 0.12 eV. In terms of our model this 0.78 eV equals the change in $E_{++}(s)$ plus the change in energy of the two electrons, $2E_c-0.12$ eV $-[2\varepsilon(0)+U^*]=2E_g+U^*-0.12$ eV$=2.78$ eV. Thus the change $E_{++}(\pi)-E_{++}(0)=0.78-2.78=-2.00$ eV.

Now for convenience in our model we shall take both $\varepsilon(s)$ and $E_{++}(s)$ to vary sinusoidally from zero to π, as in Fig. 1. Then with $\varepsilon(s)$ measured from midgap as in Fig. 1 and $E_{++}(s)$ measured from $E_{++}(\pi/2)$ we can write

$$\begin{aligned} \varepsilon(s) &= \bar{\varepsilon} - \varepsilon_1 \cos(s), \\ E_{++}(x) &= E_0 \cos(s). \end{aligned} \tag{1}$$

Setting $\varepsilon(s)$ in the first to $\varepsilon(0)=-E_g/2-U^*$ [so that $\varepsilon(0)+U^*$ is at the valence-band maximum] and $\varepsilon(\pi)=-E_g/2+1.27$ eV, we obtain $\varepsilon_1=[\varepsilon(\pi)-\varepsilon(0)]/2=0.96$ and $\bar{\varepsilon}=-0.25$ eV, and we have $E_0=[E_{++}(0)-E_{++}(\pi)]/2=1.00$ eV. The accuracy of these estimates is probably not enough to really distinguish them from the simpler symmetric arrangement $\bar{\varepsilon}=-U^*/2=-0.32$ eV again with $\varepsilon_1=0.96$ eV. This is the form that was illustrated in Fig. 1. We have

$$\varepsilon(s) = -\frac{U^*}{2} - \varepsilon_1 \cos(s) \tag{2}$$

and the energy of the (0,+) level is $U^*/2-\varepsilon_1\cos(s)$ measured from midgap. Note that for this symmetric case we require

$$\varepsilon_1 = 0.96 \gtrsim (E_g+U^*)/2 = 0.89 \text{ eV} \tag{3}$$

if the (+,++) level is to dip into the conduction band and the (0,+) level is to enter the valence band.

The predicted difference of 0.04 between ε_1 and E_0 is also not significant and we take $E_0=\varepsilon_1=0.96$ eV for our analysis. Note that for $E_0=\varepsilon_1$ the total energy of the (+) interstitial is $E_0\cos(s)-\varepsilon_1\cos(s)=0$ independent of s. This is a considerable simplification, and certainly not exactly true. However, it is true as close as we can predict from our calculations and we will indicate where it makes a difference in our discussion.

With this $E_0=\varepsilon_1=0.96$ eV, with $E_g=1.13$ eV, and $U^*=0.64$ eV we have all the parameters we need. This leads to interstitial levels moving into the bands by the $\Delta_e=\Delta_h=0.075$ eV, as shown in Fig. 1. This provides a very clear model and we proceed directly with it. At the same time we should note that we have indicated accuracies for the energy levels only on a scale of tenths of an electron volt, so we are not really guaranteed that this interstitial level moves into the bands as we have assumed. The calculations suggest it, and our models assume it, but it remains to be tested experimentally. Hopefully our calculation of the properties of this model will aid in that test.

III. EQUILIBRIUM DISTRIBUTIONS

In equilibrium the probability of any particular state of the interstitial in an interval ds will be proportional to ds and to $\exp(-E/kT)$, with E the energy of that state. When we compare states with different numbers of electrons we must consider the energy μ of the reservoir to or from which electrons are taken. This μ is of course the electronic Fermi energy for the system in equilibrium. Thus, the energy, for example, of the (+) state relative to the (++) state is given by $-U^*/2-\varepsilon_1\cos(s)-\mu$ using Eq. (2).

A. The relative probabilities of different charge states

Taking all energies from our model we have the probabilities

$$P_{++}(s)ds = Ae^{-[E_0\cos(s)]/kT}ds = Ae^{-\varepsilon_1\cos(s)/kT}ds,$$

$$P_{+}(s)ds = 2Ae^{-[E_0\cos(s)-U^*/2-\varepsilon_1\cos(s)-\mu]/kT}ds = 2Ae^{(U^*/2+\mu)/kT}ds,$$

$$P_0(s)ds = Ae^{-[E_0\cos(s)-U^*-2\varepsilon_1\cos(s)+U^*-2\mu]/kT}ds = Ae^{[\varepsilon_1\cos(s)+2\mu]/kT}ds. \quad (4)$$

The factor of 2 in $P_+(s)$ came because there are two spin states available, whereas there is only a single (0) state and a single $(++)$ state. We take equal *a priori* probabilities of equal intervals in s, so that A is a normalization constant, which is obtained by setting

$$\int_{0,2\pi}[P_{++}(s)+P_+(s)+P_0(s)]ds = 1, \quad (5)$$

normalizing the path along one period. We will need to relate this to a number of interstitials per unit volume when we discuss diffusion.

Since $\varepsilon_1 \gg kT$, the first and third integrals are heavily dominated by the region of s near the minimum energy. For $P_{++}(s)$ we expand the cosine around $s=\pi$ and perform the integration noting $\int_{-\infty,\infty}e^{-(\varepsilon_1/2kT)s^2}ds = \sqrt{2\pi kT/\varepsilon_1}$ to obtain the integral equal to $A\sqrt{2\pi kT/\varepsilon_1}e^{\varepsilon_1/kT}$. We similarly expand $P_0(s)$ around $s=0$ and integrate. We shall find that the integral over $P_+(s)$ is always much smaller than the sum of these so that we may add and solve for A to obtain

$$A = \left(\frac{\varepsilon_1}{2\pi kT}\right)^{1/2}\frac{e^{-\varepsilon_1/kT}}{1+e^{2\mu/kT}}. \quad (6)$$

This may be substituted into Eq. (5) to obtain each $P(s)$. We also have the integrated probability P_{++} of finding the $(++)$ state (with that probability concentrated at $s=\pi$) and the integrated probability P_0 of finding the (0) state (with that probability concentrated at $s=0$),

$$P_{++} = \frac{e^{-\mu/kT}}{e^{\mu/kT}+e^{-\mu/kT}}$$

and

$$P_0 = \frac{e^{\mu/kT}}{e^{\mu/kT}+e^{-\mu/kT}}. \quad (7)$$

Note that if $\mu=0$, corresponding to the electronic Fermi-energy midgap, there is an equal probability of having two electrons in the interstitial or no electrons in the interstitial in our symmetric model. If we raise the Fermi energy above midgap we increase the probability of the neutral state in the shared-site geometry and reduce the probability of the $(++)$ state in the tetrahedral geometry.

We may also substitute Eq. (6) into Eq. (4) and obtain the integrated probability P_+ of finding the $(+)$ state (equally likely at any s for our choice of parameters),

$$P_+ = 4\pi\left(\frac{\varepsilon_1}{2\pi kT}\right)^{1/2}\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{e^{\mu/kT}+e^{-\mu/kT}}. \quad (8)$$

From Eq. (3), $\varepsilon_1 - U^*/2$ is greater than $E_g/2$, half the band gap, and this probability is always tiny, as we noted before. This behavior is frequently described as a ‘‘negative-U center’’ because the tendency to bifurcate into systems with zero and two electrons, and no systems with one, would occur for an attraction between electrons in place of the usual Coulomb repulsion U.

We may note that this is really a three-dimensional problem and we could redo the problem allowing the interstitial to move in the y and z directions perpendicular to the minimum energy path that we followed with the s coordinate. Then the probabilities of Eq. (4) are replaced by a $P\,ds\,dy\,dz$. We would again expand for small y and z and integrate to obtain the normalization. If the $\partial^2E/\partial y^2 + \partial^2E/\partial z^2$ varied along the path we would obtain an s-dependent factor, equivalent to letting A become a function $A(s)$. This complicates the algebra but leaves a one-dimensional problem as we have done, so it is not an important feature.

B. Total atom fraction of interstitials

Up to this point we have addressed only the *relative* probability of interstitials having the three charge states. At any temperature there will be an equilibrium density of interstitials, minimizing the free energy by compromising between the energy of formation of the interstitials and the entropy increase due to their presence. Shockley and Moll,[6] using a statistical analysis similar to ours by Shockley and Last,[7] showed that the equilibrium concentration of neutral defects depends only upon temperature, but that of charged defects depends strongly also upon Fermi energy. Their argument was based upon defects diffusing through a pn junction. In equilibrium there can be no net flux of any species and since the neutral interstitials feel no force from the field of the junction, there must be no density gradient causing diffusion. The density remains the same across the junction though the Fermi energy shifts from the valence band to the conduction band. This same independence of Fermi energy must apply to uniform equilibrium systems. On the other hand a $(++)$ interstitial will feel a strong force toward the p-type region and correspondingly the density of $(++)$ interstitials must be much higher where the Fermi energy is near the valence-band maximum. This same ratio of $(++)$ to (0) interstitials follows directly from Eq. (7), but we now see it arises from many extra $(++)$ interstitials rather than a decrease in the number of (0) interstitials.

The total density of interstitials may be very slow to equilibrate when the temperature is changed, freezing in interstitials with a concentration appropriate to a high temperature in quenched systems, but the relative numbers in different charge states can equilibrate quickly. Thus it may usually be appropriate to estimate the concentration of interstitials for the high temperature, which we denote by T_h, at which the concentration was fixed, and use that density with the relative probabilities given above at the temperature and Fermi energy at which the system is operating.

We begin with the atom fraction of neutral interstitials, X_0, the ratio of the density of neutral interstitials to the density of bulk atoms. The density of neutral interstitials is lower by a factor $e^{-E_{\text{form}}/kT_h}$, with E_{form} the energy of formation of a neutral interstitial (in the shared site) relative to an atom in the bulk, estimated by Blöchl *et al.*[3] as 3.3 eV. However, that extra atom can lie in any of the 12 [110] directions relative to the site it shares so this atom fraction of neutral interstitials in equilibrium is

$$X_0 = 12e^{-E_{\text{form}}/kT_h}. \tag{9}$$

This corresponds to about $3\times10^{14}/\text{cm}^3$ for silicon at the melting temperature of 1683 K. There are also differences in the entropy associated with the interstitial atom, which Blöchl *et al.*[3] estimated as $6k$, increasing this estimate by a factor of $e^6 = 403$. The atom fraction of the $(++)$ interstitials will be much higher if the Fermi energy is near the valence-band maximum. The atom fraction of interstitials including all charge states will be

$$X_{\text{tot}} = \frac{X_0}{P_0} = 12(e^{\mu/kT_h} + e^{-\mu/kT_h})e^{-(E_{\text{form}}+\mu)/kT_h}, \tag{10}$$

which can be much larger than X_0.

IV. DIFFUSION

We return to a system at some lower temperature T and may use the probabilities we have obtained to write the flux of interstitials, equal in both directions for an equilibrium distribution. The flux will depend upon the interstitial atom fraction, and if we then allow a small gradient in the atom fraction of interstitials, we may infer a net flux and the diffusion constant for interstitials. We may also see how the moving interstitials move dopant atoms to derive a diffusion constant for dopants.

We first relate our normalization from Eq. (5) to the interstitial atom fraction. In the equilibrium state we have seen that the *neutral* interstitials are predominantly in the shared-site geometry, vibrating around $s=0$, and a diffusion of the neutral occurs only if it crosses a neighboring tetrahedral site. Note that each (shared) site is surrounded by four neighboring unoccupied (if the interstitial atom fraction is not too high) tetrahedral interstitial sites. That means that the shared site is a part of six paths such as we are discussing (one between each pair of nearest neighbors), which cross this site. Each of these six paths connects two (at $\pm[110]a/2$ for example) of the 12 second-neighbor possible shared sites. Thus the probability of finding a neutral interstitial with $0 < s < 2\pi$ on any one path is one-sixth of the atom fraction of neutral interstitials present, $P_0X_{\text{tot}}/6$, with P_0 from Eq. (7) and X_{tot} from Eq. (10). Almost all of these interstitials will lie at or above $s=0$ or will lie at or below $s=2\pi$. Similarly a fraction $P_{++}X_{\text{tot}}/6$, with P_{++} given in Eq. (7), of the interstitials along any path will be in a state $(++)$ and predominantly near $s=\pi$. $P_+X_{\text{tot}}/6$ will be in the charge state $(+)$ and be equally distributed along $0<s<2\pi$.

A. Equilibrium flux

We calculate contributions to diffusion from interstitials in each of the charge states, beginning with (0). We need now consider the distribution of velocities along the path, which we may do just as we considered displacements of the path (in the y and z directions) following Eq. (8). We take the path length between equivalent sites, $\Delta s = 2\pi$, to be the distance between such sites, $a/\sqrt{2}$, with a the cube edge $a = 4d/\sqrt{3} = 5.43$ Å for silicon. Then the real velocity of an interstitial is

$$v = \frac{a}{2\pi\sqrt{2}}\frac{ds}{dt} \tag{11}$$

and the probability of finding a neutral interstitial in the range ds on the path with velocity v along the path in a range dv is

$$P_0(s,v)\,ds\,dv = P_0(s)\left(\frac{M}{2\pi kT}\right)^{1/2}\exp(-\tfrac{1}{2}Mv^2/kT)\,ds\,dv \tag{12}$$

since $\int_{-\infty,\infty}\exp(-\frac{1}{2}Mv^2/kT)dv = \sqrt{2\pi kT/M}$ and M is the mass of the interstitial, the silicon-atom mass. The number of interstitials, in a velocity range dv, which will cross a given point in a time dt, is the number in a range of s equal to $ds = (ds/dt)dt$. We divide that number by dt to get the rate of crossing. Then the rate R_0 neutral interstitials are crossing the barrier at $s=\pi$ in the direction of increasing s on a particular path is $X_{\text{tot}}/6$ times $\int_{0,\infty}P_0(\pi,v)(ds/dt)dv$, or

$$\begin{aligned} R_0 &\pm \left(\frac{4\pi M}{kT}\right)^{1/2}\frac{X_{\text{tot}}}{6a}\int_{0,\infty}P_0(\pi)\exp(-\tfrac{1}{2}Mv^2/kT)v\,dv \\ &= \left(\frac{4\pi kT}{M}\right)^{1/2}\frac{X_{\text{tot}}}{6a}P_0(\pi) \\ &= \frac{X_{\text{tot}}}{6}\left(\frac{2\varepsilon_1}{Ma^2}\right)^{1/2}\frac{e^{\mu/kT}}{e^{\mu/kT}+e^{-\mu kT}}e^{-2\varepsilon_1/kT} \end{aligned} \tag{13}$$

where we have used Eqs. (4) and (6) for $P_0(\pi)$ to obtain the final form. We similarly calculate the rate the $(++)$ interstitials cross $s=0$ in the same direction, which is the same but with $e^{\mu/kT}$ in the numerator replaced by $e^{-\mu/kT}$ so the rate for interstitial motion for the two charge states is

$$R_0 + R_{++} = \frac{X_{\text{tot}}}{6}\left(\frac{2\varepsilon_1}{Ma^2}\right)^{1/2}e^{-2\varepsilon_1/kT}. \tag{14}$$

Of course, in equilibrium an equal number flow in the opposite direction. The form is as expected for our symmetric model. Either species must overcome an activation barrier $2\varepsilon_1$. The leading factor is proportional to the number of interstitials and the square root has units of the reciprocal of time, sometimes called an attempt frequency. In our simple model, the vibrational frequency at the minimum turns out to be exactly $\omega/2\pi = \sqrt{2\varepsilon_1/Ma^2}$ but these two constants would not be the same if the model included a variation of $A(s)$ as discussed after Eq. (8).

The rate for $(+)$ interstitials is simpler to estimate. The number of interstitials in the 0 to 2π range on a particular path is given by $X_{\text{tot}}/6$ times the P_+ of Eq. (8) and is independent of s. The rate they cross in one direction is this number times the velocity

$$\sqrt{M/2\pi kT}\int_{0,\infty}dv\ v\ \exp(-Mv^2/2kT) = \sqrt{kT/2\pi M}$$

divided by the path length $a/\sqrt{2}$, or

$$R_{+}=2\,\frac{X_{\mathrm{tot}}}{6}\left(\frac{2\varepsilon_1}{Ma^2}\right)^{1/2}\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{e^{\mu/kT}+e^{-\mu/kT}}. \tag{15}$$

This differs from Eq. (12) by a factor $e^{(\varepsilon 1+U^*/2)/kT}/\cosh(\mu/kT)$, which is always so large that this contribution dominates the diffusion, recalling that μ is measured from midgap so the cosh will ordinarily be near one. Even if μ is near a band edge so $\cosh(\mu/kT)\approx\exp(E_g/2kT)/2$, the factor is of order $2\exp(U^*/kT)$, using Eq. (3). Thus we may neglect the contributions R_0 and R_{++} to the flux of interstitials.

B. Interstitial diffusion

The diffusion constant for interstitials D_{int} is defined such that the interstitial flux equals minus D_{int} times the gradient of the interstitial density. D_{int} is isotropic in a cubic crystal so we evaluate it for gradients in a [100] direction. Again in equilibrium, with X_{tot} constant, the flow of (+) interstitials from the left would equal that from the right given by Eq. (15). If however $\partial X_{\mathrm{tot}}/\partial s$ is nonzero, there will be an additional term from the left given by Eq. (15) with X_{tot} replaced by $-\partial X_{\mathrm{tot}}/\partial s\times 2\pi\nu$ if the interstitial acquired the singly charged state (+) ν periods before ($s=-2\pi\nu$), and did not scatter after that. Clark and Ackland[8] have suggested on the basis of molecular-dynamics calculations that such successive correlated jumps occur even when the energy is not independent of position as we have assumed here for the (+) interstitial. We shall keep ν as a parameter in our calculation, thinking of it being 3 to 5, though further study is required to give a good estimate. Similarly, the flow from the left will be reduced by the same expression if ν is the same. Since the period in s of 2π for a path along a $[\pm 1,\pm 1,0]$ or $[\pm 1,0,\pm 1]$ direction corresponds to a distance in the x direction of $(a/\sqrt{2})\cos 45°=a/2$, it is more convenient to replace $-\partial X_{\mathrm{tot}}/\partial s\times 2\pi\nu$ by $-\partial X_{\mathrm{tot}}/\partial x\times \nu a/2$ for two-thirds of the six paths per interstitial, and zero for the other third $[0,\pm 1,\pm 1]$. Furthermore, the number of interstitials per unit volume is $N_{\mathrm{tot}}=(8/a^3)X_{\mathrm{tot}}$. We need also to divide by the area per interstitial $a^2/2$ in a (100) plane, but double the result to account for the paths crossing this plane at a tetrahedral site. We obtain an interstitial flux of

$$\tfrac{2}{3}6(\nu a^2/4)(R_+/X_{\mathrm{tot}})\partial N_{\mathrm{tot}}/\partial x$$

or a diffusion constant of

$$D_{\mathrm{int}}=\nu a^2 R_+=\frac{2\nu a^2}{3}\left(\frac{2\varepsilon_1}{Ma^2}\right)^{1/2}\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{e^{\mu/kT}+e^{-\mu/kT}}. \tag{16}$$

ν again is the average number of periods a (+) interstitial moves before changing charge. It is interesting that there is a Boltzmann factor with an activation energy slightly larger than half the gap [see Eq. (3)] which we may associate with the formation energy of the (+) interstitial, since the motion is without an activation energy. The denominator, equal to $2\cosh(\mu/kT)$ is also interesting. Since μ is measured from midgap, the denominator equals 2 for intrinsic silicon, but increases greatly for doping of either sign, suppressing diffusion.

We should note at this point that our symmetric model has let the interstitial move along its path with kinetic energy independent of position, whereas certainly there will be some variation, perhaps of the order of the $\varepsilon_B=0.04$ eV, which we obtained from our estimate at the end of Sec. II. This would reduce the probability of the interstitial overcoming the highest barrier along the path by a factor such as $\exp(-\varepsilon_B/kT)$. Since this barrier is certainly very small on the scale of $\varepsilon_1-U^*/2$, which itself is uncertain, this aspect of our model is not a serious problem.

C. Dopant diffusion

Of more interest is the diffusion constant for dopants, which we assume to move the same as host silicon atoms. Of course a dopant interstitial will have slightly different energy than a silicon interstitial, but we take that difference to be small as we took the variation in energy with s of the (+) interstitial to be small. Each time an interstitial moves through a site occupied by a dopant, it displaces that dopant by one period ($s=2\pi$) along the path. Thus the flux (in a [100] direction) of dopants across a (100) plane to the right is equal to the flux of interstitials to the right times the atom fraction of dopants in the plane immediately to the left, at a distance $a/4$. For the diffusion of dopants we take the interstitial density to be independent of position, but the dopant density to vary in the [100] direction so that instead of $-\partial X_{\mathrm{tot}}/\partial x\times\nu a/2$ we have $-X_{\mathrm{tot}}\partial X_{\mathrm{dop}}/\partial x\times a/4$ in the flux of dopants. The diffusion constant for dopants becomes

$$D_{\mathrm{dop}}=\frac{a^2}{3}\left(2\frac{\varepsilon_1}{Ma^2}\right)^{1/2}\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{e^{\mu/kT}+e^{-\mu/kT}}\,X_{\mathrm{tot}}. \tag{17}$$

Of course there are other mechanisms for diffusion, but this is the contribution from the interstitials present and it is proportional to the atom fraction of interstitials. The Boltzmann factor in the numerator is [using Eq. (3)] of order $e^{-E_g/(2kT)}$. For n-type doping there is an additional factor of about this size from the denominator. For p-type doping, if the same Fermi energy applied during the formation of the interstitials, X_{tot} would be increased relative to the X_0 appropriate to undoped materials by a factor $1/P_0$ from Eq. (7). Then the factor $e^{-(\varepsilon_1-U^*/2)/kT}/(e^{\mu/kT}+e^{-\mu/kT})$ would be replaced by $e^{-(\varepsilon_1-U^*/2+\mu)/kT}$ and for $\mu\approx -E_g/2$ the exponential would be near one. Diffusion is greatly enhanced for p-type materials, because of the positive charge states of the interstitial.

D. Transient enhanced diffusion

An important point has been made by Rafferty, Gilmer, Jaraiz, Eaglesham, and Gossmann[9] concerning the quenching of interstitials, which we discussed in Sec. III B. They indicate that interstitials which arise from ion implantation condense into complexes, the so-called {311} defects. This, of course, occurs because the energy is lower (in their estimate by 1.8 eV) with the extra atom as a part of the complex rather than as a free interstitial. There then arises a quasi-equilibrium between the free interstitials and the complex. This 1.8 eV energy gain in condensing onto the complex is very much less than the 3.3 eV formation energy of an interstitial from the bulk. In this quasi-equilibrium the form of the atom fraction given in Eq. (9) remains correct, but E_{form}

is replaced by this much smaller condensation energy and T_h is replaced by the ambient temperature. The resulting concentration of interstitials can be much higher than in the true equilibrium we have discussed. Rafferty, Gilmer, Jaraiz, Eaglesham, and Gossmann[9] indicate that this gives a good account of the familiar transient enhanced diffusion following ion implantation. Eventually, through equilibration at surfaces, the {311} defects will evaporate and the interstitial density drop to its true equilibrium value signaling the end of the transient-enhanced diffusion.

V. CARRIER RECOMBINATION

Our calculation of equilibrium distributions among the interstitial charge states implicitly assumes that carriers can be emitted and absorbed in order to reach that equilibrium, but does not depend upon the rate. However, when the system is *not* in equilibrium the rates themselves are of interest. The changes in charge state can lead to radiationless recombination of carriers, which is the subject of a major text by Abakumov, Perel, and Yassievich[10] and we address only a small part of the subject. However, the interstitial provides a model for radiationless recombination, which seems quite different from all of those they considered. It is perhaps closest to the Huang-Rhys mechanism[11] in which a local electronic level is shifted by a harmonic oscillator, corresponding to some defect in the system. An electron can be captured when the oscillator has sufficient amplitude for the level to move into the conduction band. However, the resulting rate inevitably has an activation energy ε_{act} associated with such a large excursion of the oscillator, and the corresponding $e^{-\varepsilon_{\text{act}}/kT}$ appears in the result. We shall see here that no large activation energy appears in the final result, Eq. (32).

Recombination such as we discuss here will show up as leakage current in diodes and Liu, Lu, Sung, Pai, and Tsai[12] have recently suggested that their observations of excess leakage current are consistent with recombination arising from vacancies or interstitials quenched into silicon mosfets. Our study of the interstitial provides a detailed mechanism for such recombination.

A. Emission and capture rates

The emission rates can be directly calculated using the familiar Golden Rule of quantum mechanics, but we require a matrix element between the electronic state of the interstitial and the band states for the free electron. These matrix elements can be obtained indirectly from Wills' super-cell calculation.[1] This was done for the $(++)$ interstitial by fitting the density of states arising from the interstitials in the super-cell calculation to a tight-binding band of p-like interstitial levels, through matrix elements $V_{pp\sigma}$ and $V_{pp\pi}$ between adjacent interstitials. These were in turn treated as indirect couplings from interstitial $|p\rangle$ to interstitial $|p\rangle$ through the conduction-band states $|\mathbf{k}\rangle$ as $V_{ppm} = \Sigma_{\mathbf{k}} \langle p|H|\mathbf{k}\rangle\langle\mathbf{k}|H|p'\rangle/(\varepsilon_p - \varepsilon_{\mathbf{k}})$ following the theory of Wills and Harrison.[6] In that theory the couplings are of the form

$$\langle\mathbf{k}|H|p\rangle = \left(\frac{4\pi r_p}{3\Omega}\right)^{1/2} \frac{\hbar^2 k}{m} Y_{1m}(\mathbf{k}), \tag{18}$$

with Ω the volume of the system and r_p a ''p-state radius'' characteristic of the interstitial electronic state. This leads[13] to coupling between interstitial states separated by R of $V_{pp\sigma} = \hbar^2 r_p/(\pi m R^3)$ and $V_{pp\pi} = -\frac{1}{2} V_{pp\sigma}$, so that r_p could be obtained by fitting the calculated density of states. The variation with R could be tested by comparison of fits to different super-cell sizes. Wills' fit of the bands[1] gave $r_p = -9.5$ Å. The corresponding state for the (0) interstitial, in the shared site, was expected to have symmetry more like that of a d state and the formula corresponding to Eq. (18) was $\langle\mathbf{k}|H|d\rangle = \sqrt{4\pi r_d^3/(3\Omega)}(\hbar^2 k^2/m) Y_{2m}(\hat{\mathbf{k}})$ and Wills' fit[1] gave $r_d = -1.2$ Å. Using these matrix elements, and representing the conduction band as a parabolic band with effective mass $m_e = 0.33$ m, we obtain an emission rate from the p-like interstitial state to an energy conserving state of wave number k as

$$\frac{1}{\tau_e(k)} = \frac{2\pi}{\acute{h}} \sum{}_{\mathbf{k}} |\langle p|H|\mathbf{k}\rangle|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_p) = \frac{4\hbar k^3 |r_p|}{3m_e} \tag{19}$$

Similarly, the emission rate into the hole band was found to be

$$\frac{1}{\tau_h(k)} = \frac{4\hbar k^5 |r_d|^3}{3m_h}, \tag{20}$$

and we take $m_h = 0.42$ m. These lead to values at the energy Δ_e in our model (Fig. 1) of $\tau_e = 4.3\times10^{-15}$ sec. and at Δ_h for holes $\tau_h = 2.5\times10^{-12}$ sec. These numbers are extremely uncertain, largely from the uncertainty in the real magnitude of Δ_e and Δ_h, but also from the fitting of the coupling using Eq. (18), which could easily lead to errors of factors of ten in the rates in Eqs. (19) and (20).

If the probability of occupation of the interstitial state, when it is in the conduction band, is given by $f(p)$ and the probability of the conduction-band state being empty is $1 - f(\mathbf{k})$, then the rate of emission is $f(p)[1 - f(\mathbf{k})]/\tau_e(k)$. The rate of capture must contain the same statistical factors with $\mathbf{k}$ and p interchanged, and since they must be equal when both f's are the equilibrium distribution, it follows from detailed balance that the factor $1/\tau_e(k)$ must be the same. Thus we have estimated emission and capture rates for carriers in terms of the distribution functions. Again, the values for the $\tau_e(k)$ at Δ_e above the conduction-band edge and the corresponding $\tau_h(k)$ are quite uncertain. The form, however, allows us to proceed.

B. Rates in equilibrium

We first calculate the rate at which $(++)$ interstitials capture electrons from the conduction band. The probability that an interstitial in the state $(+)$ captures an electron is negligibly smaller because the fraction of interstitials in the $(+)$ state is so small. We consider first an equilibrium situation, but distinguish the Fermi energy μ_i, which enters the probabilities $P_{++}(s)$ from Eq. (4) and P_{++} from Eq. (7) and the Fermi energy μ_e, which determines the occupation of the electronic states in the conduction band. We shall see, of course, that they are the same in equilibrium, but they are not the same when there are excess carriers. The probability that a given interstitial has this charge state is P_{++} given in Eq. (7) as $e^{-\mu_i/kT}/[e^{\mu_i/kT}+e^{-\mu_i/kT}]$. It then sits with high probability near $s=\pi$ and we write the corresponding $\tau_e(s=\pi)$ corresponding to the k for an electron with the energy of the $(+,++)$ interstitial state at $s=\pi$ (see Fig. 1). The rate electrons are being captured into this empty level is $1/\tau_e$ times the probability of band states at that energy being occupied, $f_0=1/[e^{(\varepsilon_1-U^*/2-\mu_e)/kT}+1]$ with the electron energy and the Fermi energy for the electrons μ_e measured from midgap (again, see Fig. 1). It will be adequate to take the exponential in the Fermi distribution to be large to write this probability as $f_0\approx e^{-(\varepsilon_1-U^*/2-\mu_e)/kT}$. Thus the capture rate by an individual interstitial is

$$R_{++\to+}=\frac{e^{-(\varepsilon_1-U^*/2+\mu_i-\mu_e)/kT}}{[e^{\mu_i/kT}+e^{-\mu_i/kT}]\tau_e(s=\pi)}. \tag{21}$$

Similarly, the probability of the $(+)$ state is given by Eq. (8) and since the energy is independent of s, all s values are equally likely. Thus, taking the occupation of the conduction-band states as much less than one, the rate becomes $P_+/\langle\tau_e\rangle$ with $1/\langle\tau_e\rangle=1/2\pi\int ds\,1/\tau_e(s)$, integrated over the region where the level $(+,++)$ is in the conduction band. Using Eq. (8), this is

$$R_{+\to++}=\frac{4\pi}{\langle\tau_e\rangle}\left(\frac{\varepsilon_1}{2\pi kT}\right)^{1/2}\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{e^{\mu_i/kT}+e^{-\mu_i/kT}}. \tag{22}$$

We see immediately that in equilibrium, with $\mu_i=\mu_e$, the exponential factors are the same for Eqs. (21) and Eq. (22) and the multiplicative factors differ only because we have used different approximations in the evaluation of the integrals and for the occupation probabilities for the two cases. $1/\langle\tau_e\rangle$ is much smaller than $1/\tau(s=\pi)$ because the integral extends only over a small range of s, as seen in Fig. 1, and $1/\tau_e(s)\leqslant 1/\tau_e(s=\pi)$ over that range. This is compensated for by the large ratio of ε_1/kT in the square root in Eq. (22). We enforce the exact equality of the two rates at equilibrium by using the simpler form for the leading factor from Eq. (21) to replace Eq. (22) by

$$R_{+\to++}\approx\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{[e^{\mu_i/kT}+e^{-\mu_i/kT}]\tau_e}, \tag{23}$$

identical to Eq. (21) without the factor $e^{-(\mu_i-\mu_e)/kT}$. We also simplified the notation by writing $\tau_e=\tau_e(s=\pi)$, the value at the maximum.

For our symmetric model the same analysis applied to the emission and capture of holes (or electrons) from the valence band yields

$$R_{0\to+}\approx\frac{e^{-(\varepsilon_1-U^*/2-\mu_i+\mu_h)/kT}}{[e^{\mu_i/kT}+e^{-\mu_i/kT}]\tau_h} \tag{24}$$

with τ_h evaluated at $s=0$. The difference in the sign before the Fermi energies in the exponent of course is as expected since a *lowering* of the Fermi energy for the holes μ_h, *increases*, the number of holes and similarly a shift in the Fermi energy μ_i, which increases the number of interstitials in the state $(++)$ reduces the number in the state (0). The rate $R_{+\to0}$ is the same without the factor $e^{(\mu_i-\mu_h)/kT}$. We have again forced the net rates to be exactly zero in equilibrium.

If we now move out of equilibrium, but assume that what electrons are present in the conduction band are in thermal equilibrium *with each other*, and the holes are in equilibrium with each other, we may use the same formulas, but with the three different Fermi energies, μ_i defining the relative occupation of the $(++)$ and (0) states, and μ_e and μ_h representing the density of carriers in the conduction and valence bands. The relation between the density of electrons N_e and the corresponding Fermi energy μ_e measured from midgap is given by[14]

$$N_e=2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}e^{-(E_g/2-\mu_e)/kT}\equiv C_e e^{-(E_g/2-\mu_e)/kT}, \tag{25}$$

obtained by summing the occupied states for the conduction band, expanding the Fermi distribution function for a Fermi energy far from the band edge compared to kT. The corresponding expression for holes is $N_h=C_h e^{-(E_g/2+\mu_h)/kT}$. Thus we could rewrite the equations in terms of N_e, N_h, and the density of interstitials in each charge state to obtain the rate equations for the changes in carrier concentrations in each interstitial charge state with time. We shall not do this here but go immediately to steady-state equations.

C. Steady state

In steady state the number of electrons leaving the conduction band must equal the number arriving in the valence band, and the occupation of the two charge states (0) and $(++)$ will shift until that is the case, then becoming independent of time. That is, we set $R_{++\to+}-R_{+\to++}=R_{+\to0}-R_{0\to+}$ to obtain

$$\frac{e^{-(\mu_i-\mu_e)/kT}-1}{\tau_e}=\frac{e^{(\mu_i-\mu_h)/kT}-1}{\tau_h}, \tag{26}$$

which is the steady-state condition determining μ_i in terms of μ_e and μ_h, or correspondingly N_e and N_h. We may solve for $e^{\mu_i/kT}$ and evaluate the rate electrons are disappearing from the conduction band, $R_{++\to+}-R_{+\to++}$, which is equal to the rate they appear in the valence band. We also have $R_{+\to++}$ equal to $R_{++\to+}$ except for the factor $e^{-(\mu_i-\mu_e)/kT}$. Using Eq. (21) and (26) we obtain the recombination rate for a single interstitial of

$$R_{eh}=\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{[e^{\mu_i/kT}+e^{-\mu_i/kT}]}\times\frac{[(\tau_e-\tau_h)^2+4\tau_e\tau_h e^{(\mu_e-\mu_h)/kT}]^{1/2}-\tau_e-\tau_h}{2\tau_e\tau_h}. \tag{27}$$

We have not inserted the solution for $e^{\mu_i/kT}$ in the denominator, which seems to yield too complicated a form to be of interest.

This may be written in terms of carrier concentrations N_e and N_h and the corresponding equilibrium concentrations N_e^0 and N_h^0 for an equilibrium Fermi energy μ_0 by using Eq. (25) to write

$$e^{(\mu_e-\mu_h)/kT}=\frac{N_eN_h}{N_e^0N_h^0}. \tag{28}$$

Still the dependence of the recombination upon concentration is quite unfamiliar. It is interesting to consider two limits.

First, if the system is close to equilibrium then the Fermi energies are close to each other and we may expand the exponential under the square root in Eq. (27), and the square root itself, to lowest order in $\mu_e-\mu_h$ to obtain

$$\begin{aligned} R_{eh}&\approx\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{2\cosh(\mu_0/kT)}\frac{\mu_e-\mu_h}{(\tau_e+\tau_h)kT}\\ &=\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{2\cosh(\mu_0/kT)}\frac{\delta N_e/N_e^0+\delta N_h/N_h^0}{\tau_e+\tau_h} \end{aligned} \tag{29}$$

with the last form obtained from Eq. (25) using $\delta N_e=N_e-N_e^0$ and $\delta N_h=N_h-N_h^0$. This dependence upon the δN may also look unfamiliar but it would also follow from a mass-action law that the recombination rate was proportional to $N_eN_h/N_e^0N_h^0-1$ near equilibrium.

We may finally obtain the rate far from equilibrium, when $N_e\gg N_e^0$ and $N_h\gg N_h^0$. Then Eq. (27) becomes

$$\begin{aligned} R_{eh}&\approx\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{[e^{\mu_i/kT}+e^{-\mu_i/kT}]}\frac{e^{(\mu_e-\mu_h)/2kT}}{\sqrt{\tau_e\tau_h}}\\ &=\frac{e^{-(\varepsilon_1-U^*/2)/kT}}{\tau_he^{\bar{\mu}/kT}+\tau_ee^{-\bar{\mu}/kT}}\left(\frac{N_eN_h}{N_e^0N_h^0}\right)^{1/2} \end{aligned} \tag{30}$$

with, of course, $\bar{\mu}=(\mu_e+\mu_h)/2$. This dependence upon concentrations is the square root of the mass-action form, and follows because the recombination is sequential. Such dependences were also found by Abakumov, Perel, and Yassievich.[10] Because of the form of the first denominator in the final form, the longest relaxation time τ_h, which we estimated as 2.5×10^{-12} sec, completely dominates the recombination.

We may obtain a more meaningful form using Eq. (25) for the equilibrium concentrations to obtain

$$(N_e^0N_h^0)^{1/2}=2\left(\frac{\sqrt{m_em_h}kT}{2\pi\hbar^2}\right)^{3/2}e^{-E_g/2kT}. \tag{31}$$

We then use Eq. (3) to take $E_g/2\approx\varepsilon_1-U^*/2$ and with excess carriers in both bands, the individual Fermi energies are at the band edges and $\bar{\mu}\approx0$. We multiply by the number of interstitials per unit volume N_{tot} to obtain a recapture rate per unit volume of

$$\begin{aligned} \frac{R_{eh}}{V}&=\frac{1}{2(\tau_e+\tau_h)}\left(\frac{2\pi\hbar^2}{\sqrt{m_em_h}kT}\right)^{3/2}N_{\text{tot}}\sqrt{N_eN_h}\\ &\approx0.7\times10^{-7}N_{\text{tot}}\sqrt{N_eN_h}\,\frac{\text{cm}^3}{\text{sec}}, \end{aligned} \tag{32}$$

where V stands for volume.

It is interesting that all of the Boltzmann factors have disappeared (if we don't count the one that determines N_{tot}), except a $e^{-(\Delta_e+\Delta_h)/2kT}$ with $\Delta_h=\Delta_e\approx0.07$ eV in our model, which we have dropped by using the approximation in Eq. (3). In addition, the factor $1/T^{3/2}$ increases with decreasing temperature. The principal Boltzmann factor also disappears in Eq. (29) near equilibrium, because $1/N_e^0$ and $1/N_h^0$ contain factors analogous to that in Eq. (31). This is a very remarkable aspect of this mechanism for radiationless recombination, which distinguishes it from the Huang-Rhys mechanism.[11] This would, nevertheless, seem to be a rather low capture rate: if N_{tot} equals the 3×10^{14} interstitials/cm^3 we estimated after Eq. (9), the decay rate for carriers is 2×10^7 per second. However, the very long τ_h we have used is a very uncertain number. Further if the material were p type when the density of interstitials was fixed, the concentration of interstitials would increase by a factor $e^{E_g/kT_h}\approx1500$. [$P_{++}/P_0=e^{-2\mu/kT_h}$ from Eq. (7), with $\mu\approx-E_g/2$.] This would raise our estimate to 3×10^{10} /sec.

VI. RECOMBINATION-INDUCED DIFFUSION

When there are excess carriers present, the rate at which $(++)$ interstitials capture electrons from the conduction band to become $(+)$ increases, as does the capture of holes in the valence band by (0) interstitials to produce $(+)$ interstitials. This increases the fraction of $(+)$ interstitials in the steady state, thereby enhancing diffusion.

We may readily calculate the increase by noting that the rates of formation of $(+)$ interstitials from Eq. (21) and (24), respectively, increase by factors of $e^{\delta\mu_e/kT}$ and $e^{-\delta\mu_h/kT}$. Noting the many common factors in the two equations we obtain an increase of the total rate of production of $(+)$ interstitials by a factor of f given by

$$f=\frac{\dfrac{e^{\delta\mu_e/kT}}{\tau_e}+\dfrac{e^{-\delta\mu_h/kT}}{\tau_h}}{\dfrac{1}{\tau_e}+\dfrac{1}{\tau_h}}=\frac{\tau_h\dfrac{N_e}{N_e^0}+\tau_e\dfrac{N_h}{N_h^0}}{\tau_e+\tau_h}. \tag{33}$$

In a steady state, the fraction of interstitials in the $(+)$ state must increase by just this factor, and both diffusion constants we defined must also increase by the same factor. The final form in Eq. (33) may thus be multiplied by the diffusion constant of Eq. (17) to obtain the recombination enhanced diffusion constants for dopants. Since in devices N_e can be considerably larger than the equilibrium value N_e^0 the enhancement may be considerably larger than the original diffusion rate. Note that these formulas also obtain if there is a suppressed number of carriers, δN_e or δN_h negative, leading to a carrier-generation-suppressed diffusion.

Finally, we should note in addition that recombination of carriers liberates an energy approximately equal to the band gap for each pair combined. This occurs, for example, when an interstitial has acquired an electron from the conduction band to become (+) with a thermal kinetic energy, but then deposits it in the valence band to become (++) with a potential energy of the order of the gap. As it falls to the tetrahedral site it acquires the corresponding kinetic energy, which ultimately arrives as heat in the lattice. This also occurs in equilibrium but is then rare enough that these high-kinetic-energy interstitials are a normal part of the equilibrium distribution. This will be true also in a steady state if the system remains fairly close to equilibrium. However, when there are net recombinations the energy shows up as heat and can also modify the diffusion through the temperature dependence of Eqs. (16) and (17).

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