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Theory of electronically stimulated defect migration in semiconductors

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We develop a theory for carrier-capture-enhanced, recombination-enhanced, and athermal defect migration in semiconductors. Contrary to assumptions made recently in describing such processes in Si, we find that knowledge of energy levels or even total energies at only the initial equilibrium and saddle points is not sufficient to determine barrier reductions. We obtain quantitative criteria for athermal migration and new insights in the enhanced migration of interstitial Al in Si, where we find a recombination channel that may significantly slow down the overall migration rate.

Defect migration and other defect reactions normally involve potential barriers that need to be overcome. Under equilibrium conditions at finite temperatures, the necessary energy is usually supplied by the lattice in the form of phonons. Typically, a local fluctuation of the phonon distribution allows a defect to absorb an adequate number of phonons and overcome a particular barrier. Such processes are called thermal.

In addition to the phonons, the electron gas is another potential source of energy, since it stores energy in the form of elementary electronic excitations. In semiconductors and insulators, electronic energy can be transferred to a defect by capture of a minority carrier into a state in the gap or by electron-hole recombination (successive capture of a minority and a majority carrier), resulting either in enhanced thermal migration (i.e., reduction in the thermal activation energy), or athermal migration (i.e., migration that can occur even at 0 K). Electronically stimulated processes have not been observed under equilibrium conditions, presumably because local fluctuations in the minority-carrier concentration are normally too small to yield a measurable rate. They have, however, been observed in cases where the electron gas is driven out of equilibrium by electron irradiation, laser illumination, or injection of minority carriers at a *pn* junction.[1]

The mechanisms for electronically stimulated processes have so far been described mostly in general terms:[2] charge-state change, recombination enhancement due to local excitation or local heating, the Bourgoin-Corbett[3] mechanism for athermal migration, etc. Explicit calculations for individual defects exhibiting such effects have been lacking.

Two systems have recently attracted theoretical attention. The self-interstitial in Si,[4-7] which migrates athermally[8] under irradiation conditions, and the Al interstitial in Si,[5] which undergoes enhanced migration when electrons are injected in *p*-type material.[9] Baraff, Schluter, and Allan[5] based their analysis on the premise that knowledge of the total energies of various charge states at *only* the initial equilibrium and saddle points along a path is sufficient to determine barrier reductions caused by minority-carrier capture. They, in fact, derived an expression for the barrier reduction in terms of the energy levels at the two points of the path.

In this Rapid Communication, we develop a detailed theory of the energetics of electronically stimulated processes and obtain a number of significant new results. Our main result is that, contrary to the assumption of Ref. 5, knowledge of the energy levels or even the total energy at *only* the initial equilibrium and saddle points is not sufficient to determine barrier reductions caused by carrier capture or electron-hole recombination. We have already used this theory in our recent report[7] of total-energy calculations for the self-interstitial in Si, where we found that athermal migration is possible along several paths. Here, we give the essential elements of the theory, illustrate the results in terms of examples, and describe the consequences of the theory in the case of the enhanced migration of interstitial Al in Si.

We consider *p*-type material with the Fermi level at the top of the valence bands and a defect whose total energy along a given path is given by $E_0(Q)$, where Q is the coordinate along the path, $Q=0$ is the equilibrium site, and $Q=X$ is the saddle point. We first consider defects which, at each Q, can capture an electron at a level[10] $\epsilon_1(Q)$ in the gap, so that

$$E_1(Q)=E_0(Q)+\epsilon_1(Q) \quad , \tag{1}$$

is the total energy of the new charge state when the defect is stationary at Q.

The basic premise of Ref. 5 is that the new barrier is given by $E_1(X)-E_1(0)$. Hence, the barrier reduction ΔV is given in terms of the one-electron energy levels at 0 and X. In this case, using our notation, $\Delta V=\Delta\epsilon_1=\epsilon_1(X)-\epsilon_1(0)$. A closer examination of Eq. (1), however, reveals that the problem is, in general, far more complicated. We note that $E_0(Q)$ *increases* from 0 to X and, for barrier reduction, $\epsilon_1(Q)$ must *decrease* from 0 to X. Thus, $E_1(Q)$ *may not be a monotonic function in that interval.* As a result, one must consider the variation of $E_0(Q)$ and $\epsilon_1(Q)$ along the entire path. In addition, as we shall see, one must also consider the rate at which a migrating defect can loose kinetic energy to the lattice.

In order to illustrate the consequences of the above observation, we define two "interpolation" functions, $f(Q)$ and $g(Q)$, by the following:

$$E_0(Q)=Vf(Q) \quad , \tag{2}$$

$$\epsilon_1(Q)=\epsilon_1(0)-\Delta\epsilon_1 g(Q) \quad . \tag{3}$$

We have $f(0)=g(0)=0$ and $f(X)=g(X)=1$, so that V is the initial barrier in *p*-type material. In addition, $f(Q)$ has a quadratic dependence near both 0 and X. Finally, we also find it convenient to define a *critical index* η_c by

$$\eta_c=\min[g'(Q)/f'(Q)] \quad . \tag{4}$$

In what follows, we shall derive general results in terms of the above quantities and illustrate them by choosing

$$f(Q)=[1-\cos(\pi Q/X)]/2\ , \qquad (5)$$

and two different forms of $g(Q)$: (a) $g(Q)$ having a quadratic dependence[11] near both $Q=0$ and $Q=X$ (this occurs when the state occupied by the captured electron is not orbitally degenerate at either $Q=0$ or $Q=X$ and these two points have higher symmetry than points along the path); and (b) $g(Q)$ having a linear dependence[11] near $Q=0$ and quadratic dependence near $Q=X$ (this occurs when the state occupied by the captured electron is orbitally degenerate, so that, by the Jahn-Teller theorem, motion away from $Q=0$ leads to a splitting of the state and linear gain in energy). For example, a number of atoms occupying a tetrahedral interstitial site have a triply degenerate state of T_2 symmetry which is empty in *p*-type material, but can capture one or more excess electrons.[4-7]

We first consider capture of a single electron. We identify the following cases.

(1) Absolute Athermal Migration. If $V<\eta_c\Delta\epsilon_1$, $E_1(Q)$ has a maximum at $Q=0$ and decreases monotonically to a minimum at $Q=X$, as illustrated in Figs. 1(a) and 1(b) for two different choices of $g(Q)$. Under these conditions, if the defect can retain its kinetic energy without transferring it to the lattice via phonon emission for at least one full step [dashed line in Figs. 1(a), 1(b)], we have ballistic athermal migration. If, on the other hand, some or all of the kinetic energy is dissipated, athermal migration will proceed via the Bourgoin-Corbett[3] mechanism: After electron capture, the defect "rolls down" to X, captures a hole and converts to the initial charge state, rolls down to the next site, captures another electron, etc.

(2) Conditional Athermal Migration-Enhanced Migration. If $\eta_c\Delta\epsilon_1<V<\Delta\epsilon_1$, $E_1(Q)$ has maxima at both $Q=0$ and $Q=X$ and a minimum somewhere *between* these two points, as illustrated in Fig. 1(c). We note three different possibilities: if the kinetic energy is not dissipated, we have ballistic athermal migration [horizontal dashed line in Fig. 1(c)]; if dissipation occurs slowly so that the defect's total energy is between the horizontal and the slanted dashed lines in Fig. 1(c), we have Bourgoin-Corbett athermal migration; if dissipation is fast so that the defect's total energy is given by $E_1(Q)$ in Fig. 1(c), the defect rolls down to Q_0, where a number of possibilities exist. For example, it may capture a hole, switch to the E_0 curve and roll back to 0 (no migration); or, it may overcome the small barrier at X and then capture a hole so that it will then "roll forward" to the next site equivalent to 0 (recombination-enhanced migration). Clearly, in order to compare with experimental data, it is necessary to calculate the actual barrier heights *and* the relative rates of the various processes.

(3) Capture-Enhanced Migration. If $V>\Delta\epsilon_1$, $E_1(Q)$ has a maximum at $Q=X$ and a minimum either at 0 or somewhere between 0 and X depending on the form of $\epsilon_1(Q)$, as illustrated in Fig. 1(d). Thus, carrier capture results in enhanced migration. The new barrier is given by $E_1(X)-E_1(0)=\Delta\epsilon_1$ if $\eta_c\geqslant 1$. If $\eta_c<1$, the new barrier is given by $E_1(X)-E_1(0)$ if kinetic-energy dissipation is slow and by $E_1(X)-E_1(Q_0)$ if dissipation is fast. In practice, both processes will occur with different rates so that the effective barrier will be somewhere between these two extremes. In addition, hole capture at Q_0 may reduce or quench the migration rate.

The above analysis can easily be extended to more general cases. For example, electron capture may not be feasible at $Q=0$, i.e., $\epsilon_1(Q)$ emerges in the band gap at some $Q>0$. Migration can then begin thermally in the initial state and capture can occur along the path, reducing the barrier for the rest of the way, as illustrated in Fig. 1(e).

We now address the question of two-electron capture. We define

$$E_2(Q)=E_0(Q)+\epsilon_2(Q)\ , \qquad (6)$$

where $\epsilon_2(Q)=2\epsilon_1(Q)+U(Q)$ is the energy of a stationary defect at Q when two electrons are captured in gap states. Here, $U(Q)$ is the electron-electron repulsion (Hubbard U). The analysis follows along the same lines as in the one-electron capture, except for one important complication, illustrated in Fig. 1(f): In addition to $E_0(Q)$, $E_1(Q)$, and $E_2(Q)$, we also show the total energy of the defect in the initial charge state plus a free electron at the bottom of the conduction band (curve labeled E_0+E_g). At points

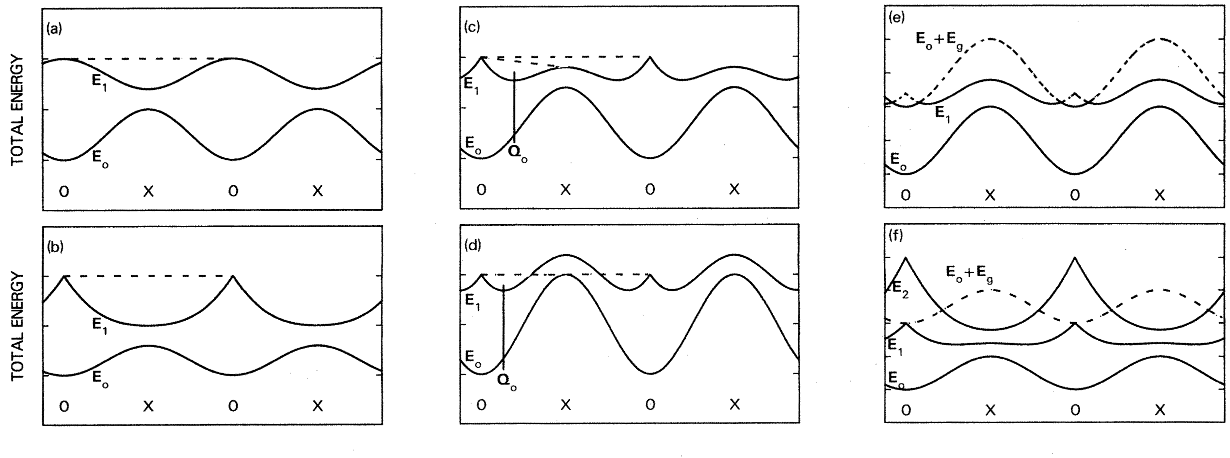

FIG. 1. Total-energy curves for various types of electronically stimulated defect migration. The curves are calculated using the functional forms of $E_0(Q)$, $E_1(Q)$, and E_2 given in the text. In (a) $g(Q)=f(Q)$; in the rest, $g(X)=\sin(\pi Q/2X)$.

along the path where the total energy of the defect is greater than or equal to E_0+E_g, an Auger-like process is possible: the defect may revert to its original charge state by ejecting one electron into the conduction bands and the other into the valence bands (hole capture). Such processes may reduce the migration rate by reducing the value of the preexponential, competing with the enhancement arising from the lowering of the activation energy. We will see an example of this effect below. It is also possible that the Auger-like recombination may quench the migration altogether, even though the barrier is actually lowered by two-electron capture.

As we noted already, the above theory was used in our recent report of the Si self-interstitial, which we found to migrate athermally along several paths by the capture of one or two electrons.[12] Here, we conclude with an application of the above theory to the case of interstitial Al in Si.

By using the energy levels at the tetrahedral (T) and hexagonal (H) sites as reported in Ref. 5, an appropriate interpolation for the variation of these energy levels along the TH path, *and* the experimental value for the initial barrier, we get the curves shown in Fig. 2. In Fig. 2(a), we show the total-energy curves that correspond to the schematic curves drawn in Ref. 5. According to these curves, an $\mathrm{Al}^+(T)$ captures an electron, vibrates toward an H site, captures a second electron, and moves through the H site by having to overcome a smaller barrier. It then continues migrating by successively changing from Al^0 to Al^- and back to Al^0. Note that this type of enhanced migration does not entail recombination of carriers, i.e., holes are not involved.

In Fig. 2(b), we include holes and draw the same curves as before, plus a new one. We note that the total-energy curve of Al^- lies *above* the curve labeled $\mathrm{Al}^+ + e$ except in a small region near H. Thus, for most of the path, Al^- is unstable against an Auger-like process consisting of emitting one electron into the conduction bands and the second electron into the valence bands (hole capture). Two possibilities exist: some Al^-'s may indeed convert to Al^+ and return to the original T site; some others may manage to pass through without converting, but inevitably convert after one or more jumps. Clearly, energetic considerations alone, without any rate calculations, are not sufficient to *predict* enhancement. In this particular case, the experimental data[9] exhibit enhanced migration upon electron injection, suggesting that the Auger-like recombination channel discussed above does not stifle migration altogether. More specifically, the data reveal that, upon electron injection, the activation energy for migration is reduced from 1.2 to 0.3 eV *and* that the preexponential is also reduced by more than seven orders of magnitude.[9] The observed reduction of the activation energy is most likely a consequence of the two-electron capture process first suggested in Ref. 5. The large reduction in the preexponential indicates that the enhanced migration is limited by an electronic rather than a thermal process.[9] However, a detailed model including rate calculations of the various competing processes has yet to be worked out.

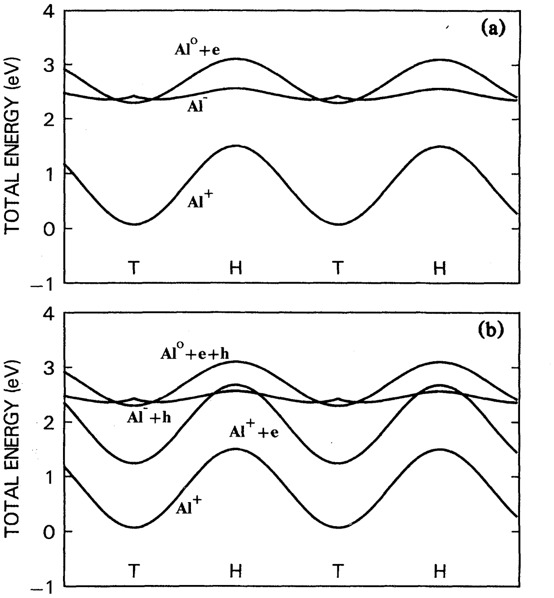

FIG. 2. (a) Total-energy curves for interstitial Al in Si, calculated as described in the text, corresponding to the schematic curves given in Ref. 5. (b) Same as (a), with an added curve, as discussed in the text.

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[9] J. R. Troxell, A. P. Chatterjee, G. D. Watkins, and L. C. Kimerling, Phys. Rev. B **19**, 5336 (1979).

[10] If, at given Q's, the relaxation of the surrounding lattice is independent of charge state, $\epsilon_1(Q)$ is the eigenvalue of the single-particle Schrödinger equation with half an electron in the bound state (Slater's transition-rate rule).

[11] If $g(Q)=f(Q)$, $\eta_c=1$. If $g(Q)$ is linear near 0, $\eta_c=0.4$–0.64 depending on the interpolation used.

[12] For the Si self-interstitial, the T_2 state at the T site lies at the conduction-band edge, $\Delta\epsilon_1=E_g$, and $\eta_c \sim 0.4$–0.64, depending on the form of $\epsilon_1(Q)$. For the TB path, $V=0.6$ eV so that athermal migration is assured by two-electron capture ("athermal" migration is actually also possible by single-electron capture because, even if $\eta_c<0.6$, the resulting barrier at B is only a few meV). For the TH path, $V=1.4$, eV so that the condition for absolute athermal migration is not satisfied for either one- or two-electron capture. Athermal migration is barely possible by two-electron capture, because, in that case, the barrier at H is only a few meV. See Fig. 3 of Ref. 7. More details will be published elsewhere.