Activation enthalpy of recombination-enhanced vacancy migration in Si

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As reported by Watkins and co-workers, recombination-enhanced migration is observed in Si for positively charged vacancies, but not for negatively charged vacancies. Although there is a component of the recombination-enhanced vacancy migration that is independent of temperature (athermal), we show that there is another component which obeys a simple Arrhenius behavior with an activation enthalpy of 0.07 eV. These facts are rather mysterious if one believes that the normal thermal activation enthalpies for vacancy migration measured at the temperatures used in these experiments are relevant parameters for the recombination-enhanced migration process. We show that if, instead, one accepts as relevant parameters the ballistic model values for the enthalpy of vacancy migration at high temperatures, then a simple explanation of the facts is readily apparent. At high temperatures, thermally generated carriers recombine at vacancies even in the absence of electrical or optical injection. The implications of this on the temperature dependence of the vacancy contribution to self-diffusion are discussed.

Watkins and co-workers have inferred[1] values for the activation enthalpy for normal thermal migration ΔH_m of the single vacancy V in Si in three of its five charge states as follows:

$$\Delta H_m(V^{2-}) = 0.18 \pm 0.02 \text{ eV} ,\qquad (1)$$

$$\Delta H_m(V^0) = 0.45 \pm 0.04 \text{ eV} ,\qquad (2)$$

$$\Delta H_m(V^{2+}) = 0.32 \pm 0.02 \text{ eV} .\qquad (3)$$

All of the experiments from which these values were inferred used temperatures T below 250 K. Both deep-level transient spectroscopy (DLTS) experiments and electron paramagnetic resonance (EPR) experiments were employed to deduce these values. Some of these data are shown in Fig. 1, which has been adapted from Ref. 1. It is most likely that the values of ΔH_m for V^- and for V^+ are intermediate between those for V^{2-} and V^0 and for V^0 and V^{2+}, respectively.

Although there should be no doubt of the validity of the values of ΔH_m just given for low temperatures, the author has for several years argued that they do not apply at much higher temperatures.[2-6]

The crux of the author's previously published arguments is that at high T $\Delta H_m(V)$ is dominated by the kinetic energy of the atom that actually moves when we say the vacancy hops; potential energy may dominate at low T. Indeed, in Ref. 2, the approximate magnitude of $\Delta H_m(V) \sim 0.36$ eV was derived from consideration of the minimal distortion energy required to move a Si atom from one site to another around a single vacancy cavity. However, such values are too small to allow the Si atom to make its transit in one period of a zone-boundary phonon. The kinetic energy alone required for a Si atom to hop the nearest-neighbor distance in a zone-boundary phonon period is

$$H_k(T > \Theta_D) = 1.18 \text{ eV} ,\qquad (4)$$

where $\Theta_D = 670$ K for Si is the Debye temperature. The zone-boundary period is the characteristic time for the fluctuations of the instantaneous potential in any particular unit cell of the specimen when T is great enough that such phonons are excited with high probability. This occurs roughly when T is greater than Θ_D.

As T is reduced below Θ_D, the characteristic time for thermal fluctuations of the potential slows until, at $T = 0$ K, it ceases altogether. It may approximately be scaled as $(\Theta_D)/T$. Thus, we might estimate, that for normal
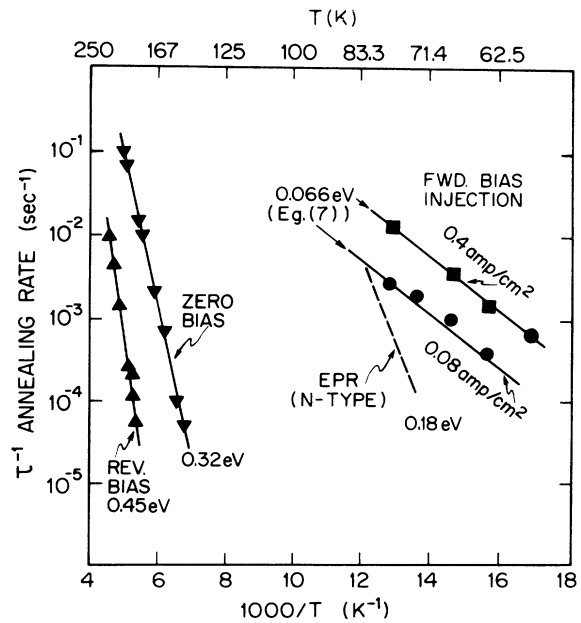

FIG. 1. Annealing kinetics for vacancy in Si determined by DLTS and EPR studies reviewed by Watkins (Ref. 1). The 0.18-eV Arrhenius is from EPR studies of n-type Si. All other data is for p-type Si. The two Arrhenius lines for forward bias are according to Eq. (7).

thermal conditions (i.e., no injection of excess carriers by light or currents), the minimum kinetic energy that a Si atom must have at the onset of a successful hop to a nearest-neighbor vacancy site is

$$H_k(T < \Theta_D) = (T/\Theta_D)^2 \times 1.18 \text{ eV} . \tag{5}$$

For $T = 250$ K, Eq. (5) gives $H_k = 0.164$ eV. As this is less than the empirical value for ΔH_m obtained for all of the charge states of V when $T < 250$ K, one might conclude that the activation enthalpy is dominated by potential energies in this regime. Evidently, this is so. It also seems that the potential energy contributions must be equal to or less than these empirical values. But then these potential energies are negligible compared with H_k when $T \gg \Theta_D$, as is the case for most atomic diffusion and device-processing experiments.

The physical picture is as follows. At high T the thermal vibrations of atoms surrounding a vacancy, or any other point defect where atomic migration can occur, fluctuates with a characteristic period given approximately by the bulk zone-boundary-phonon period. Periodically these thermal fluctuations of the surrounding atoms conspire to provide a path for a particular atom to hop from its initial site to that occupied by the vacancy at the cost of little potential energy. However, the venue for this circumstance is quite limited (to the zone-boundary-phonon period). Thus, the atom that is to make the jump must have sufficient kinetic energy to finish the jump before this easy path is closed off by the continuing thermal motion of the surrounding atoms. On the other hand, at low T when the zone-boundary phonons are not excited, the jumping atom may take much more time and the measured activation barrier may be dominated by the potential energy. The identification of $\Delta H_m(V)$ with H_k is called the "ballistic model" of vacancy migration.

The reader must realize that the ballistic model is a massive simplification of what is inherently a very complicated many-body phenomenon. In reality all the atoms of the solid are in motion and the various migration events that occur must involve some motion of the surrounding atoms, as well as the flight of the hopping atom from its initial to its final position. As such, the only justification for the ballistic model can be empirical. As has been discussed particularly in Refs. 5 and 6, with only one empirically adjusted parameter, that was fixed in 1975 (Ref. 3) to data for Ge at a value identical to that used for fcc structure noble-gas solids, the ballistic model has been found to work much better than one would initially expect in several semiconductor applications and for O vacancy migration in MgO. The reader is referred to Refs. 3–6 for the details of that justification. Here we briefly note several facts that can be cited as evidence for the assumption that kinetic energies dominate vacancy hopping activation energies at high temperatures. In the first place, in Ref. 3 it was shown that the simple kinetic-energy expression,

$$H_k = Mv^2/2 . \tag{6}$$

where M is the mass of the mass of the atom that jumps and v is its velocity assuming it moves from its initial lattice site to its final lattice site in a zone-boundary-phonon

period, gives good agreement with the available experimental values of vacancy migration enthalpies in almost all cases of elemental crystals (metals and insulators as well as semiconductors) where values have been determined (at high temperatures). The values for Si and Ge obtained from (6) are 1.18 and 1.11 eV, respectively, which are in agreement with high-temperature values obtained for those crystals. The case is particularly clear in the instance of Ge where host-isotope-diffusion experiments have been done[7,8] to determine the isotopic mass dependence of the rate of diffusion. These experiments show $\Delta H_m(V_{Ge})$ to be about 85% kinetic energy in character. (There is in Ge a discrepancy between vacancy migration activation energy at low T and at high T that is very similar to the discrepancy for Si, but in the case of Ge the high-T value of about 1.1 eV is much more clearly established. See Refs. 2 and 3 and references therein.) The analogies between Si and Ge are so close and the chemical trends in material parameters are so clear that it is difficult for this author to believe that vacancy behavior could be radically different in the two cases. The assumption of the kinetic energy dependence of vacancy hopping energies has also been tested in group III-V compounds such as InP, where it gives predicted values for In-vacancy hopping and for P-vacancy hopping that differ from each other by a factor of 4 and are both in quantitative agreement with observed values.[5,6] [It should be noted that values consistent with the analog of Eq. (4), not of Eq. (5), have been found also for experiments[5,6] with $T < \Theta_D$ in InP. We return to this point later.] Moreover, analysis of the distribution of E centers, V-P_{Si} pairs, in Si produced by rapid quenching from temperatures close to (but below) the melting point have been interpreted[9] to conclude an activation energy for single vacancy migration of order 1.2 eV.

Consideration of the kinetic energy also provides a simple explanation for the dominance[5] of vacancy–first-nearest-neighbor hopping over second-nearest-neighbor hopping in III-V compounds, despite the cost of forming the antisite defects. The formation of antisite defects would be avoided if the vacancy were to hop to a second-nearest-neighbor site, i.e., one on its own sublattice. However, $\frac{8}{3}$ more kinetic energy would be required to accomplish this (in the same time) because the second-nearest-neighbor distance is a factor of $(\frac{8}{3})^{1/2}$ greater than the nearest-neighbor distance. Thus, for Si it would require 3.2 eV to hop to a second-nearest-neighbor site if it costs 1.2 to hop to a first-nearest-neighbor site.

Returning now to low-T phenomena in Si and to Fig. 1, we see that when a p-type Si DLTS sample is put into forward bias, so that electrons are injected into the conduction band (e_c^-), there is a very great enhancement of the vacancy annealing rate. Evidently the rate of vacancy migration is enhanced by the same large factor. The effect is called recombination-enhanced vacancy migration (REVM).

It is often stated in the literature regarding REVM that the process is independent of T and therefore athermal. However, we see in Fig. 1 a clear variation in the REVM rate with T; for a constant injection current $j = 0.4$ A/cm^2 it varies by a factor of approximately 20 as T

varies from 60 to 80 K. Indeed, the lines in Fig. 1 associated with the forward bias data are the simple Arrhenius expression

$$R(T,j,) \propto j \exp(-\Delta H_{\text{REVM}}/kT) , \qquad (7)$$

where $\Delta H_{\text{REVM}} = 0.066$ eV. Due to inexactitude of the method, this value should probably be quoted as 0.07 eV. We see that only one datum, that for the lowest T and lower j, deviates appreciably from Eq. (7). It should be kept in mind that this result was obtained in p-type Si and is almost certainly dependent upon the charge state of the vacancies. It is not clear whether Eq. (7) pertains to recombination at V^{2+} or at V^{+}; the former is the more prevalent in thermal equilibrium, particularly because of the negative-U character[1] of the donor levels of vacancies in Si, but the injection of electrons in the experiment produces a nonequilibrium population of V^{+}, which can also trap injected electrons and produce REVM. The conversion of V^{+} to the more stable V^{2+} is rather slow.[1]

REVM is also observed in DLTS experiments with n-type Si and, until recently, this was accepted as evidence that there was an effective REVM mechanism for V^{2-}, or for V^{-}. However, as described in Ref. 1, there is now convincing evidence that what REVM does occur in n-type samples is occurring at positively charged vacancies, V^{2+} or V^{+}, which are created as a consequence of the injection of holes (h^{+}'s), and not at the V^{2-}'s or V^{-}'s at all. It seems possible that REVM might also be occurring at neutral vacancies, but there is no firm evidence of this.

In fairness to those who have called the Si REVM effect[1] athermal, it should be noted that there is in fact a detectable rate of REVM even at $T = 4$ K where Eq. (7) implies $R(T,j)$ should be effectively zero. It seems that the net REVM effect must have two distinct components.

Discussions of REVM distinguish two classes of mechanism. (1) A "kick" mechanism[10-13] in which the energy of recombination of an electron e^{-} and a hole h^{+} at the defect H_R site dumps substantial energy into local modes of the lattice at the defect site in some manner that provides either part or all of the enthalpy required for the defect to migrate. (2) A charge-state fluctuation or "Bourgoin" mechanism[12] in which the defect has different configurations in two (or more) charge states and the passage of the current j (with or without recombination) causes transitions among these. If the stable configuration for one charge state is at or near the saddle point for migration of another, fluctuations of the charge state may induce the migration.

The Bourgoin charge-state fluctuation mechanism is usually said to be athermal but might be thermal (with an activation enthalpy less than that without injection) if some thermal energy must be combined with the fluctuation in equilibrium configuration to achieve the migration event. Problems associated with attempts to explain the data for vacancies in Si with the Bourgoin mechanism are discussed in Ref. 1 in terms of the Jahn-Teller configurations of the vacancy in its various charge states, which have been determined by EPR. The problems seem to be severe.

The "kick" mechanism will be thermal provided that H_R, or that fraction $F \leq 1$ of it that is delivered to the mode that is effective in moving the vacancy, is less than that required for the interesting event ΔH_m in this case. Thus,

$$\Delta H_{\text{REVM}} = \Delta H_m - F H_R , \qquad (8)$$

because an extra amount of thermal enthalpy H_{REVM} must be obtained from the background phonon bath. When the "kick" mechanism occurs and a finite ΔH_{REVM} is measured in compound semiconductors, it is often found[10,11] that the normal thermal-activation-enthalpy barrier is reduced by an amount essentially equal to H_R. Of course, this implies that essentially all of H_R went into the mode that knocks the vacancy over to the next site. In Si, Watkins et al. have shown[13] interstitial Al double donors, which was created by electron irradiation, exhibit recombination-enhanced migration with an F factor greater than 90%. Thus,

$$F \simeq 1 , \qquad (9)$$

is usually found, although it is not yet clear why.

Let us now consider how large H_R is. The band gap enthalpy $\Delta H_{cv} = 1.170$ eV for Si at $T = 0$. It increases[14] slowly with T; at 70 K, the midpoint of the REVM Arrhenius in Fig. 1,

$$\Delta H_{cv}(T = 70 \text{ K}) = 1.173 \text{ eV} . \qquad (10a)$$

At the melting point of Si, 1685 K,

$$\Delta H_{cv}(T = 1685 \text{ K}) = 1.329 \text{ eV} . \qquad (10b)$$

H_R is generally less than ΔH_{cv} because true band-to-band recombination is extremely rare and is unlikely to affect vacancy hopping when it does occur. Two modes of recombination that might affect kick REVM can be distinguished. (1) The e^{-} and h^{+} may form an exciton and the exciton may annihilate itself at a vacancy which itself might be in any of its five charge states because the exciton itself is neutral. The annihilation would be facilitated by and well coupled to the vacancy because the localized electronic states of the V break the symmetry of the Si lattice. (As Si is an indirect-gap semiconductor, band-to-band recombination cannot occur in the perfect lattice without phonon emission or absorption to conserve crystal momentum.) The binding energy of the exciton at the vacancy is probably quite close to that in the bulk crystal, which is[14] 14.7 meV. Thus, for the exciton mechanism we have for exciton annihilation

$$H_R(\text{exc}, T = 70 \text{ K}) = 1.173 - 0.015 \text{ eV} = 1.158 \text{ eV} . \qquad (11)$$

(2) The other mode is ion annihilation. Either e^{-} in the conduction band, e_c^{-}, or h^{+} in the valence band h_v^{+} can annihilate one of the corresponding charges at an ionized vacancy. The ionized vacancy may be regarded as having trapped one or two e^{-}'s or h^{+}'s with a binding energy equal to the depth of the corresponding ionization level E_i away from the appropriate band edge. For V^{-} and V^{2-} the appropriate band edge is that of the conduction band, which we denote H_c and recall it is the enthalpy

gap[4,14] and not the more commonly discussed (free energy) band gap ΔE_{cv} that is relevant when calculating the slope of an Arrhenius plot. (However, with $T < 100$ K, the difference between enthalpies and free energies is not large on the scale of experimental and theoretical uncertainties. The difference will be significant when we consider high-T effects.) For V^+ and V^{2+} the appropriate band edge is that of the valence band, which we denote H_v. Thus, the enthalpy released when a $h_v{}^+$ annihilates a trapped electron at a V^{i-}, with $i = 1$ or 2, is

$$H_R(\text{ion}, V^{i-}, T) = \Delta H_{cv}(T) - [H_c(T) - E_i(V^{i-}, T)] \quad (12)$$

and correspondingly when an e_c^- annihilates a trapped hole at a V^{i+}, again with $i = 1$ or 2,

$$H_R(\text{ion}, V^{i+}, T) = \Delta H_{cv}(T) - [E_i(V^{i+}, T) - H_v(T)] . \tag{13}$$

Van Vechten and Thurmond have discussed[4,15] the problem of the variation of the vacancy ionization levels relative to the band edges. For $T < 100$ K this variation is insignificant. The following values are taken literally from Watkins' ionization level diagram:

$$E_i(V^+) - H_v = 0.05 \text{ eV}, \quad H_c - E_i(V^-) = 0.65 \text{ eV} ,$$
$$E_i(V^{2+}) - H_v = 0.13 \text{ eV}, \quad H_c - E_i(V^{2-}) = 0.29 \text{ eV} . \tag{14}$$

However, Watkins warns that the two acceptor levels have not been determined with precision; one can be sure that they are both more than 0.17 eV below E_c, but beyond this there is uncertainty. Despite this caveat, we here take these literal values in order to illustrate clearly the points of the discussion. The qualitative points of the low-T discussion are not affected by the precise values of these acceptor levels, so long as they are deeper than 0.17 eV. The quantitative consequences of the level positions will be seen when we discuss the high-T vacancy migration enthalpy. We will find no conflict with experiment in the high-T data when we use the literal values. These same values were used successfully to account for positron annihilation lifetimes in thermally generated vacancies in Ref. 16.

Accepting these values, we calculate from (12) and (13) that

$$H_R(\text{ion}, V^+, T = 70 \text{ K}) = 1.123 \text{ eV} , \tag{15a}$$

$$H_R(\text{ion}, V^{2+}, T = 70 \text{ K}) = 1.043 \text{ eV} , \tag{15b}$$

$$H_R(\text{ion}, V^-, T = 70 \text{ K}) = 0.523 \text{ eV} , \tag{15c}$$

$$H_R(\text{ion}, V^{2-}, T = 70 + \text{K}) = 0.883 \text{ eV} . \tag{15d}$$

Obviously, there is an uncertainty attached to each of these values which probably exceeds 0.02 eV. (The last digit is shown only for clarity to remind the reader of the increase in ΔH_{cv} with increasing T.)

If one assumes that the normal thermal values of the activation enthalpies at $T = 70$ K, the ΔH_m's is given in Eqs. (1)–(3), are relevant to REVM around $T = 70$ K, then one is faced with a rather mysterious situation. All the various H_R's are much larger than any of the ΔH_m's for the various charge states of the vacancy. Thus, with

the common experience that $F \simeq 1$ in Eq. (8), we would expect REVM to occur for all charge states of vacancy and to be athermal, i.e., independent of T, because the enthalpy being dumped into the local models at the vacancy is much more than required to produce the hop. To account for the absence[1] of REVM for V^- and V^{2-}, we must have $F(V^-) < 0.34$ and $F(V^{2-}) < 0.20$ for the ion modes and $F(V^{i-}) < 0.16$ for the exciton mode; these are uncharacteristically small values. To account for the presence of REVM with $\Delta H_{\text{REVM}} = 0.07$ eV at either V^+ or V^{2+}, we have to have for the ion modes $F(V^+) = 0.226$, so that $FH_R = \Delta H_m - 0.07$ eV, or $F(V^{2+}) = 0.240$. If the 0.07-eV activation enthalpy pertains to the exciton mechanism, we need $F = 0.216$ for a positively charged vacancy or $F(V^0) = 0.328$ for the neutral vacancy. All these values are uncharacteristically small and mysterious. We would further have to account for the truly athermal REVM process, which requires a slightly larger value of F for one of the modes at either V^0, V^+, or V^{2+}. No explanation of any of this is given in Ref. 1 nor, to this author's knowledge, anywhere else.

However, suppose instead that we assume the high-T ballistic model value $\Delta H_m(V) = 1.18$ eV, from Eq. (4) is at least approximately the value relevant to the REVM effect for $T = 70$ K. This assumption is justified by the considerations that (1) the recombination event occurs in a time short compared with the zone-boundary-phonon period and the H_R released from it is rapidly dissipated in a similar time; and (2) the zone-boundary phonons must certainly be excited by the recombination if an atomic hop is to be produced. Let us also assume that for each one of the possible modes and charge states,

$$F = 1.0 . \tag{16}$$

Furthermore, although the high-T ballistic-model value of ΔH_m was never fixed with great precision and although the attribution of that value to REVM at 70 K must certainly be regarded as approximate, let us for the moment assume the relevant value of ΔH_m is exactly 1.180 eV. Then we calculate that for the exciton mode at any charge state of the vacancy

$$\Delta H_{\text{REVM}}(\text{exc}) = 1.180 - 1.158 \text{ eV} = 0.022 \text{ eV} \tag{17}$$

and for the ion annihilation mode we calculate

$$\Delta H_{\text{REVM}}(\text{ion}, V^+, T = 70 \text{ K}) = 1.180 - 1.123 \text{ eV}$$
$$= 0.057 \text{ eV} ; \tag{18a}$$

$$\Delta H_{\text{REVM}}(\text{ion}, V^{2+}, T = 70 \text{ K}) = 1.180 - 1.043 \text{ eV}$$
$$= 0.137 \text{ eV} ; \tag{18b}$$

$$\Delta H_{\text{REVM}}(\text{ion}, V^-, T = 70 \text{ K}) = 1.180 - 0.883 \text{ eV}$$
$$= 0.657 \text{ eV} ; \tag{18c}$$

$$\Delta H_{\text{REVM}}(\text{ion}, V^{2-}, T = 70 \text{ K}) = 1.180 - 0.523 \text{ eV}$$
$$= 0.297 \text{ eV} . \tag{18d}$$

We immediately see that if we reduce our previous esti-

mate of the relevant value of ΔH_m by only as much as 2%, from 1.180 eV to 1.158 eV, Eq. (17) becomes $\Delta H_{REVM}(\text{exc})=0$ for whichever charge state of vacancy may be the site of the exciton annihilation mode of REVM. This is just what is required to account for the truly athermal component of REVM that occurs at either V^0, V^+, or V^{2+}. (This author favors the assumption that the V^0 is the site of the athermal REVM.) Such a 2% adjustment is obviously well within the uncertainty of the hypothesis. If the downward adjustment is any more than 2%, then we still have an explanation for the athermal component of REVM. The only remaining point is the apparent absence of this mode at V^- and V^{2-}.

If the assumed relevant value for ΔH_m is to be reduced slightly from 1.180 eV in Eq. (17), then the same adjustment should be made in Eqs. (18). We could bring the calculated value of $\Delta H_{REVM}(\text{ion}, V^{2+})$ into agreement with the observed value $\Delta H_{REVM}=0.07$ eV by making the adjustment 0.067 eV or 5.7% instead of 2%. This would also make $\Delta H_{REVM}(\text{ion}, V^+)<0$, i.e., give us an alternative or an additional explanation for the athermal component of REVM, provided we retain Eq. (16). It is easy to believe the 1.180 eV estimate is uncertain to 5.7% also. However, the empirical value of ΔH_{REVM} and perhaps also the deviation of the lowest-T datum from the Arrhenius in Fig. 1 might also be explained by the effect of the combination of ion annihilation at V^+ and at V^{2+}; the one gives a contribution with a slightly smaller enthalpy while the other gives a contribution with a slightly larger enthalpy.

Now consider what our calculation implies for V^- and for V^{2-}. We see that the activation enthalpies for the ion annihilation mode of REVM at V^{2-} and at V^- are larger than the activation enthalpy for normal thermal migration (at least for V^{2-} since the value for V^- is not well established). A little consideration shows that if the normal thermal process, which is always occurring in competition to any recombination-enhanced process, has a smaller activation enthalpy it will almost certainly swamp out the recombination-enhanced process. The normal thermal-migration event can occur at any moment at any of the V^{2-}'s while the REVM event can only occur when and where there is recombination at V^{2-}. Thus, the preexponential factor, or attempt frequency, should be greater for the thermal process. When the thermal process has a larger preexponential factor as well as a much larger exponential factor (due to the lower activation enthalpy), the product must be much larger than that for the REVM process. As noted above REVM indeed is not observed at V^{2-}'s. The same conclusion follows for V^-.

Recall that we noted above that for InP values for the activation enthalpy for In and P vacancy diffusion were measured[5,6] that were in close agreement with those calculated with the ballistic model for high T and that these same values were also found even when $T \ll \Theta_D$. One might think that observation would cast doubt upon Eq. (5) if it were not for the fact the data used for those low-T studies involved electrical or optical injection. Thus, instead the observation is further evidence for the validity

of the assumption that it is the high-T–kinetic-energy value for ΔH_m that should be used to estimate the total enthalpy required for the REVM activation enthalpy.

Finally let us consider what implications REVM may have on the behavior of vacancies at high T. The issue arises because minority carriers are generated thermally and will recombine at vacancies even in the absence of electrical or optical injection and because positron annihilation experiments[17] firmly demonstrate that vacancies with static properties very similar to those observed at low temperature are present for $T > 1200$ K in thermal equilibrium in Si at significant concentrations (greater than 10^{16} cm^{-3}). To appreciate that REVM should be a significant effect under high-T thermal conditions, we will now make two points via simple estimates: (1) The minority-carrier density, and thus the thermal rate of recombination, is much higher for such thermal experiments than for the low-T REVM experiments;[1,13] and (2) the "attempt frequency" for thermal REVM is at least comparable to that for the ordinary thermal process in which the enthalpy is obtained from the phonon bath with no assistance from the free carriers.

(1) The intrinsic carrier concentration in Si at its melting point, 1685 K, is about[14] 2×10^{19} cm^{-3}. (This value is typical of most tetrahedral semiconductors at their melting points.) This value is large enough to overwhelm the doping in all but the most heavily doped samples studied at high temperatures. Thus, the minority carrier concentration may be estimated at the intrinsic carrier concentration for most high-T studies. On the other hand, a forward bias current of 0.4 A/cm^2 into a sample with a minority-carrier diffusion length of 5 μm and a minority-carrier lifetime of 1 μsec implies a minority-carrier density in the junction region of order 5×10^{15} cm^{-3}.

(2) To estimate the "attempt frequency" for REVM, we may first note that the thermal velocity of a carrier at $T = 1685$ K is 2.8×10^7 cm/sec and the Coulomb-capture cross section[18] of a singly charged vacancy is 8.7×10^{-14} cm^2 so the rate at which one of the 2×10^{19} cm^{-3} oppositely charged carriers impinge on any one of the singly charged vacancies is, according to the Coulomb cross-section criterion, 4.8×10^{13} sec^{-1}. This may be compared with the normal thermal attempt frequency which is usually taken to be $k\Theta_D/h = 1.4 \times 10^{13}$ sec^{-1}. As the Coulomb-capture cross section for a doubly charged vacancy is four times that for a singly charged vacancy, the thermal REVM attempt frequent at such vacancies will be correspondingly greater. However, the Coulomb cross-section criterion is probably something of an overestimate under these conditions. There are so many carriers of both signs that a single vacancy may interact with more than one simultaneously and the time the carrier spends falling into the Coulomb well may not be negligible compared with the time it spends thermally diffusing before it reaches the point that the attractive Coulomb potential of the charged vacancy exceeds the $\frac{1}{2}kT$ radial thermal average value. To quantify this caveat we note that the radius of the coulomb cross section is 1.66 nm so the corresponding volume is 1.93×10^{-20} cm^3 and the random probability of a carrier being in that volume is about 10% for either type. We

conclude that the attempt frequency for thermal REVM is at least comparable to, if not larger than, the ordinary thermal phonon attempt frequency.

Given that thermal REVM, TREVM, is occurring with a frequency comparable to ordinary thermal-phonon attempt frequency, we must conclude that TREVM makes a significant contribution to the migration of vacancies at processing temperatures which becomes dominant as T approaches 1685 K, the melting point. This follows because the probability of a hop actually occurring at each and any attempt is much larger for TREVM, due to the kick gained from the recombination, than for thermal-phonon-activated vacancy migration TPAVM. If one accepts that this author is correct in that the total enthalpy required for vacancy migration at $T > 670$ K is about 1.18 eV [Eq. (4)] and not the values measured with $T < 250$ K [Eqs. (1) to (3)], then at 1685 K the TRAVM hop occurs only for one hop in a number of order $\exp(1.18 \text{ eV}/1685k) = 3.4 \times 10^3$ attempts. The uncertainty is due to the entropy-of-migration factor, which cannot be larger[2,3] than about 10 (not the entropy-of-vacancy-formation factor). By contrast, we see that, due to the increase in ΔH_{cv} with T, the exciton provides enough kick to boost the vacancy through a 1.18-eV hop with no need for added enthalpy from the thermal bath. That is, from Eq. (10b) we have

$$H_R(\text{exc}, T - 1685) = 1.329 - 0.015 \text{ eV} = 1.314 \text{ eV} \quad (19)$$

so that

$$\Delta H_{\text{TREVM}}(\text{exc}) < 0 . \quad (20)$$

Furthermore, according to the estimate[15] of Van Vechten and Thurmond, the variation of the vacancy ionization levels is such that H_R is increased for each of these by the same amount, 0.159 eV, as is the ΔH_{cv}, and is H_R for the exciton. Thus, all the ΔH_{TREVM} for ion annihilation modes of all the charge states of the vacancy are also 0.159 eV less at $T = 1685$ K than the corresponding values of ΔH_{REVM} at $T = 70$ K, Eqs. (18a) and (18b). This implies $\Delta H_{\text{TREVM}} < 0$ for the ion annihilation mode at V^+ and at V^{2+}; we thus expect a factor of order 3.4×10^3 increase (over the extrapolation of the ordinary TPAVM rate from T's low enough that TREVM is not important due to the scarcity of minority carriers in the absence of injection) in the rate of V^{2+} and/or V^+ migration and in the rate of V^0 migration if indeed the exciton-annihilation mode is effective at V^0's.

In addition, we also expect to see at high T's a TREVM effect on V^- and V^{2-}, despite the evident absence of a REVM effect at low T, as noted above and in Ref. 1. This is because the competing strictly thermal process TPAVM is (at least by this author) assumed to have a total activation enthalpy, 1.18 eV, that is so large that the thermal process does not swamp the recombination enhanced process (as we have argued occurs at low T). However, for the negative vacancies we have positive values for ΔH_{TREVM}

$$\Delta H_{\text{TREVM}}(\text{ion}, V^-, T = 1685 \text{ K}) = 0.498 \text{ eV} , \quad (21)$$

$$\Delta H_{\text{TREVM}}(\text{ion}, V^{2-}, T = 1685 \text{ K}) = 0.138 \text{ eV} . \quad (22)$$

Consider now the corresponding changes in the slopes of the Arrhenius plots of vacancy migration in the five charge states due to the TREVM effect. Any change in slope must be positive, i.e., correspond to a larger net activation enthalpy because the effect is to increase the net rate of migration to an increasing degree as T increases. Looking at this another way, we note that it must always cost enthalpy to create the e^- and the h^+ that can recombine to make the vacancy hop and we will never get all this enthalpy back in a reduction of the hopping activation enthalpy. With a little consideration one sees that indeed the slope increases by just $\Delta H_{cv} - FH_R$, i.e., the amount of the cost of the e^--h^+ pair that was not regained in the mode that boosts the vacancy in its hop. As we are assuming $F = 1$ to a good approximation (as is usually found), the increase in slope for the exciton-annihilation mode is only the exciton binding energy about 0.015 eV, which would be hard to detect. For the ion modes at V^+ the increase in slope would be only $E_i(V^+) - H_v$, about 0.05 eV, which also could probably not be detected. At V^{2+} the corresponding increase would be about 0.13 eV. [Recall Eq. (14).] However, at V^- and at V^{2-} the slope would increase by 0.65 and by 0.29 eV, respectively, due to the ion mode. Note that if we are to assume somewhat different values for the accepter ionization levels at Eq. (14), these values would change by the same amounts. As was noted above, the exciton annihilation does not seem to occur at V^- and V^{2-}, so the net slope for V^- and V^{2-} migration should increase by these amounts.

Now it is well established that the rate of self-diffusion in Si does not obey[19] a simple Arrhenius. Around $T = 1200$ K the slope for self-diffusion (which contains the enthalpy of formation of the defect mediating the self-diffusion as well as the enthalpy of migration of that defect) is (according to Demond et al., who seem to have the very best experiment[19] in the field) 4.15 ± 0.25 eV, while around 1600 K the slope is about 5.0 eV. There is a corresponding increase in the preexponential factor for self-diffusion from a value between 0.3 and 30 cm²/sec at 1200 K to about 2×10^3 cm²/sec at 1600 K. Particularly in view of the fact that positron annihilation experiments show large concentrations of single vacancies to be present in thermal equilibrium at these T's, there is also firm evidence that at least a substantial fraction of the self-diffusion in Si is mediated by single vacancies. (Please note that recent studies of the growth of stacking faults[20,21] favor a dominance of vacancy mechanisms over any self-interstitial mechanism.) Furthermore, the most prevalent[16] charge state of vacancy in lightly doped Si with 1200 K $< T <$ 1685 K, is V^-. Thus, a large fraction, if not all, the increase in the slope of the Si self-diffusion Arrhenius plot can be attributed to the 0.65 eV increase that occurs with the ion annihilation mode TREVM effect at V^-'s, provided we take Watkins' ionization-level diagram literally. Moreover, a large fraction, if not all, of the increase in the preexponential factor for Si self-

diffusion can be attributed to the TREVM effect at vacancies in all their charge states. Of course, similar thermal recombination enhancements are expected for divacancies,[21] and for any other point defect that may contribute significantly to Si self-diffusion, provided they also have a recombination-enhanced migration mechanism.

[1]The latest comprehensive review is in G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), Chap. 3, p. 147.

[2]J. A. Van Vechten, Phys. Rev. B **10**, 1482 (1974).

[3]J. A. Van Vechten, Phys. Rev. B **12**, 1247 (1975).

[4]J. A. Van Vechten, in *Handbook on Semiconductors*, edited by S. P. Keller (North-Holland, Amsterdam, 1980), Vol. 3, Chap. 1.

[5]J. A. Van Vechten and J. F. Wager, Phys. Rev. B **32**, 5259 (1985).

[6]M. T. Juang, J. F. Wager, and J. A. Van Vechten, J. Electrochem. Soc. **135**, 2019 (1988); **135**, 2023 (1988).

[7]D. R. Campbell, Phys. Rev. B **12**, 2318 (1975).

[8]D. Shaw, Phys. Status Solidi B **72**, 11 (1975).

[9]A. Chantre, M. Kechouane, and D. Bois, Physica **116B**, 547 (1983).

[10]J. D. Weeks, J. C. Tully, and L. C. Kimerling, Phys. Rev. B **12**, 3286 (1975).

[11]A. M. Stoneham and R. H. Bartram, Solid State Electron. **21**, 1325 (1978).

[12]J. C. Bourgoin and J. W. Corbett, Radiat. Eff. **36**, 157 (1978).

[13]G. D. Watkins, A. P. Chatterjee, R. D. Harris, and J. R. Troxell, Semicond. Insul. **5**, 321 (1983).

[14]C. D. Thurmond, J. Electrochem. Soc. **122**, 1133 (1975).

[15]J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B **14**, 3539 (1976).

[16]J. A. Van Vechten, Phys. Rev. **33**, 2674 (1986).

[17]S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. **56**, 2195 (1986).

[18]M. Lax, Phys. Rev. **119**, 1502 (1960).

[19]F. J. Demond, S. Kalbitzer, H. Mannsprenger, and H. Damjantschitsch, Phys. Lett. **93A**, 503 (1983).

[20]J.-I. Chikawa, in *Defects and Properties of Semiconductors: Defect Engineering*, edited by J. Chikawa, K. Sumino, and K. Wada (KTK Scientific, Tokyo, 1987), p. 143.

[21]K. Wada and N. Inoue, in *Defects and Properties of Semiconductors: Defect Engineering*, Ref. 20, p. 169.