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Entropy of migration for atomic hopping

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The entropy of migration of an atom undergoing an atomic hop into a nearest-neighbor vacancy is calculated under the assumption that the entropy is translational at the saddle-point configuration and vibrational at the initial, equilibrium state prior to the hop. These contributions to the entropy of migration are calculated using standard statistical thermodynamic expressions, assuming that the translational entropy is given by the particle-in-a-box approximation and the vibrational entropy is that of a simple harmonic oscillator vibrating at the Debye frequency. This formulation of the entropy of migration is then quantitatively applied to explain the abnormal prefactors experimentally deduced in InP drain-current–drift measurements, in deep-level-defect–transformation kinetic studies of the metastable *M* center in InP, and in Si and Ge self-diffusion experiments.

I. INTRODUCTION

The kinetics of solid-state processes such as diffusion and defect-transformation reactions are often found to exhibit the Arrhenius form,[1]

$$k = A \exp(-E_a/k_B T) , \tag{1}$$

where k is the rate constant, A is the prefactor, E_a is the activation energy, and k_B is Boltzmann's constant. Adopting the thermodynamic formulation of rates,[1] it is possible to make the following identifications:

$$A = A_0 \exp(\Delta S_a/k_B) , \tag{2}$$

$$E_a = \Delta H_a , \tag{3}$$

where A_0 can loosely be interpreted as an attempt frequency and ΔS_a and ΔH_a are, respectively, the entropy and enthalpy of activation. These activation quantities represent the difference of the reactant at its saddle-point configuration with respect to its initial configuration.

The prefactor A has often been observed experimentally to be abnormally large, or alternatively, abnormally small, in a variety of solid-state processes such as self-diffusion[2–7] and deep-level–defect transformations.[8–14] The unusual magnitude of the prefactor is attributed to the correspondingly abnormal magnitude of the entropy of activation. The physical reason for the unusual magnitudes of these empirically determined activation entropies (i.e., $\Delta S_a/k_B > 5$ or $\Delta S_a/k_B < -5$) is generally controversial or unexplained in the prior literature and the subject of this work.

Three contributions to the entropy of activation have been discussed in the literature: (1) A vibrational contribution due to a modification of the vibrational frequencies of the lattice when the reactant achieves its saddle-point configuration,[15,16] (2) a configurational entropy due to the different multiplicity of bonding configurations (e.g., Jahn-Teller distortion) at the saddle point compared to the initial state,[17] and (3) the entropy of ionization due to the softening of the lattice when an electron or hole is emitted from a defect state compared to when it is localized at that state.[16,18]

Note that ionization must occur concomitant with the process of interest for mechanism 3 to appear in the corresponding activation barrier. In the prior literature, the first two mechanisms are generally regarded as producing a $\Delta S_a/k_B < 5$ and the third mechanism is usually either neglected or argued not to contribute on the ground that ionization is not correlated with the process. It has often been said a value of $\Delta S_a/k_B > 5$ for a simple point-defect migration process is "unphysical;" see, for example, Refs. 4 and 5.

The purpose of the work discussed herein is to propose a physical mechanism associated with atomic migration which is capable to explaining the very large magnitudes of the activation entropies $\Delta S_a/k_B \gg 5$. The proposal is motivated by our own observation of $\Delta S_a/k_B \sim 15$ for certain defect-transformation processes in InP.

Our explanation is based upon the ballistic-model (BM)[16,19,20] hypothesis that atomic migration into a vacancy on a nearest-neighbor site may be calculated by assuming that the migration energy is kinetic in origin. Within the context of this model, the migrating atom must attain a sufficient kinetic energy to successfully transverse the saddle-point configuration. In the spirit of the BM, we propose that the activation entropy of a process involving atomic migration (e.g., diffusion, metastable defect transformations) will be determined (at least to a large extent) by the difference of the translational entropy of the hopping atom in its saddle-point configuration and the vibrational entropy of the hopping atom in its equilibrium position prior to the hop. These two contributions to the activation entropy are calculated using standard statistical thermodynamic expressions.

Using this formulation for the entropy of activation of atomic migration, we provide quantitative justifications for experimentally obtained prefactors for the activation entropy for phosphorus-vacancy nearest-neighbor hopping contributions to drain-current drift in InP metal-insulator-semiconductor (MIS) capacitors and field-effect transistors,[13,14] for the prefactors found in defect-transformation experiments involving the M center[8–12] in InP, and for the self-diffusion[4–7] of Si and Ge.

II. ENTROPY OF MIGRATION FOR NEAREST-NEIGHBOR HOPPING

The physical picture adopted in the BM is as follows. At temperatures above the Debye temperature θ_D, the thermal vibrations of the atoms surrounding a vacancy fluctuate with a characteristic frequency given approximately by the Debye frequency $\nu_D = k_B\theta_D/h$, where h is Planck's constant. Periodically these thermal fluctuations conspire to provide a path for an atom to hop into the vacancy at a cost of very little potential energy. The venue for this path is limited by the thermal motion of the surrounding atom to a period of order the zone-boundary phonon period of the host lattice, which is proportional to the Debye period ν_D^{-1}. For an atom to successfully migrate it must make the hop in a time less than the lifetime of the favorable venue. This requires a minimum velocity of the hopping atom to be

$$v = \nu_D d \ , \tag{4}$$

where d is the distance between lattice sites. This velocity corresponds to a kinetic energy

$$E_{\mathrm{kin}} = \tfrac{1}{2}mv^2 \ , \tag{5}$$

where m is the mass of the hopping atom. Thus, since the potential energy that the atom must overcome is assumed to be quite small during this favorable venue, the enthalpy of migration is given by

$$\Delta H_m = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m(Fd\nu_D)^2 \tag{6}$$

where F is a geometric constant equal to 0.9 in the case of a diamond or zinc-blende lattice.[19]

In order to calculate the entropy of migration, we extend the BM treatment. At temperatures above the Debye temperature an atom on a normal lattice site can be modeled as a simple harmonic oscillator vibrating at the Debye frequency. The entropy associated with this vibrating atom can be calculated from statistical thermodynamics and is given by[21]

$$\frac{S_v}{k_B} = 3\left\{ \frac{h\nu_D/k_BT}{\exp(h\nu_D/k_BT)-1} - \ln\left[1-\exp\left[\frac{-h\nu_D}{k_BT}\right]\right]\right\} , \tag{7}$$

where the factor 3 is due to the three degrees of freedom of the oscillating atom.

According to the BM, during the limited venue that the atomic migration actually occurs, i.e., when an atom moves through the saddle-point configuration, the hopping atom is essentially a free particle moving ballistically. Thus, for this brief period of time the vibrational modes are replaced by a translational mode. We can calculate the translational entropy using the particle-in-a-box approximation,[21]

$$\frac{S_t}{k_B} = \ln\left[\frac{(2\pi emk_BT)^{3/2}}{h^3}V\right] , \tag{8}$$

where $e = 2.718$ and V is the volume of the box which we take to be the volume occupied by two nearest-neighbor atoms. In the present work we estimate the volume of the box as the atomic volume of two atoms as defined by the Van Vechten–Phillips tetrahedral radii.[22] There are other equally reasonable ways of approximating the box volume, such as a narrow channel geometry in which the hopping atom is restricted in directions perpendicular to the migration path. We note that either method of calculation yields approximately the same estimate of the box volume. Furthermore, it is clear from Eq. (8) that the entropy depends weakly (i.e., logarithmically) on the box volume.

The entropy of migration of an atom hopping into a vacancy is thus given by,

$$\Delta S_m = S_t - S_v \ . \tag{9}$$

Therefore, our formulation for the entropy of atomic migration is given by Eqs. (7)–(9). We will now employ these equations to explain the abnormal activation entropies found experimentally in defect-transformation reactions and self-diffusion.

We note that our formalism is implicitly based on a constant volume ensemble, whereas the experimental data we wish to consider are obtained under constant pressure. Thus, it is necessary to distinguish between constant volume and constant pressure entropies.[23] We do not correct for this difference since these corrections are rather small, less than k_B, for the semiconductors of interest in this work.

We also note that our formulation for the migrational entropy differs from that normally employed,[15,23]

$$\frac{\Delta S_m}{k_B} = \sum_i \ln\left[\frac{\omega_i}{\omega_i'}\right] , \tag{10}$$

where ω_i and ω_i' are the normal-mode frequencies on the initial and saddle-point configurations, respectively. Equation (10) is valid only in the context of the harmonic or quasiharmonic approximation and is deduced assuming that the migrational barrier is best calculated assuming it is potential energy in origin. Thus, the essential difference between our approach and the conventional approach is whether the migrational barrier is more readily calculated as a potential or kinetic energy barrier. It is difficult to believe that modifications of the vibrational frequencies of atoms surrounding a vacancy during atomic hopping could be of a sufficient magnitude to account for migrational entropies as large as $15k_B$.

III. ENTROPY OF MIGRATION EXAMPLES

A. Phosphorus-vacancy nearest-neighbor hopping

Phosphorus-vacancy nearest-neighbor hopping (PVNNH) has been linked[13,14] to drain current drift (DCD) in InP metal-insulator-semiconductor field-effect transistors (MISFET's). Consider an InP MISFET or

MIS capacitor which has P vacancies in the channel region under its gate. Nearest-neighbor hopping of an In atom into the P vacancy can be described by the following defect reaction:

$$\mathrm{In_{In}} + V_{\mathrm{P}}^{+} + 4e^{-} = V_{\mathrm{In}}^{-}\mathrm{In_{P}^{-2}} \; . \tag{11}$$

Application of the law of mass action to this defect reaction results in

$$\frac{[V_{\mathrm{In}}^{-}\mathrm{In_P^{-2}}]}{[V_{\mathrm{P}}^{+}][\mathrm{In_{In}}]}\alpha[e^{-}]^{4} \; . \tag{12}$$

The application of a positive gate bias to an InP MIS capacitor or MISFET induces an accumulation of electrons in the channel and hence an increase in $[e^{-}]$ which shifts the equilibrium to the right-hand side of the defect reaction. Four of the accumulated channel electrons are captured for every P vacancy annihilated. DCD in MISFET's or flatband voltage shift in MIS capacitors is attributed to the loss of these electrons from the channel.

From the BM an activation enthalpy of $\Delta H_m(V_{\mathrm{P}}) = 1.2$ eV was predicted[13] which was found to be in good agreement with experimental values[14] deduced from variable-temperature bias-stress measurements of InP MIS capacitors. Additionally, a computer simulation of the effect of the PVNNH mechanism on flatband voltage shift versus bias stress measurements was performed.[14] In the kinetic analysis it was found that the rate-limiting step in the total reaction given by Eq. (11) was

$$V_{\mathrm{P}}^{0} + e^{-} = (V_{\mathrm{In}}\mathrm{In_P})^{-} \tag{13}$$

and an entropy of activation ΔS_a was used as an adjustable parameter (the only adjustable parameter) in the computer simulation to fit the experimental data. A value $\Delta S_a^{\mathrm{expt}}/k_B = 15.3$ was deduced from the computer simulation[14] compared to that originally estimated[13] by Van Vechten and Wager from

$$\Delta S_a / k_B = \ln(8D_0/a^2\nu_D) \; , \tag{14}$$

where D_0 is the prefactor of the diffusion constant for in self-diffusion in InP. Using an experimental value of $D_0 = 1\times10^{5}$ cm/s as reported[3] by Goldstein gives $\Delta S_a/k_B = 17.5$.

To calculate the entropy of activation we recognize that the rate-limiting reaction given by Eq. (13) involves both In hopping and ionization so that the activation entropy is given by

$$\Delta S_a = \Delta S_m + \Delta S_i \tag{15}$$

where ΔS_i is the entropy of ionization. We calculate ΔS_i using[16,18,23]

$$\Delta S_i(T) = \Delta S_{CV}(T) = \frac{\alpha T(T+2\beta)}{(T+\beta)^2} \; , \tag{16}$$

where ΔS_{CV} is the entropy of the band gap (i.e., the entropy of formation of free-electron-hole pairs) and for InP (Ref. 24) $\alpha = 6.63\times10^{-4}$ eV/K and $\beta = 162$ K. ΔS_m is calculated using Eqs. (7)–(9) which results in an activation entropy $\Delta S_a^{\mathrm{theor}}/k_B = 8.2 + 6.8 = 15.0$ (the parameters used in this calculation are summarized in Table I). In the calculation 325 K was used because it is the average temperature at which the activation energy was extracted in the computer simulation. We regard the close agreement between experiment (15.3) and theory (15.0) as strong support for the importance of the translational and ionization entropies in determining the total activation entropy.

B. The metastable *M* center

The metastable *M* center[8–12] is an electron-irradiation-induced defect complex in InP which exhibits two distinct configurations denoted *A* and *B*. There is a reversible transformation between the configurations which exhibits the following kinetics[8,9] as deduced from Arrhenius plots:

$A \rightarrow B$ stage 1:

$$k = 10^{18}\exp[-(0.40\ \mathrm{eV})/k_B T], \quad T = 110\ \mathrm{K} \tag{17}$$

$A \rightarrow B$ stage 2:

$$k = 10^{11}\exp[-(0.42\ \mathrm{eV})/k_B T], \quad T = 160\ \mathrm{K} \tag{18}$$

$$B \rightarrow A: \quad k = 10^{7}\exp[-(0.24\ \mathrm{eV})/k_B T], \quad T = 140\ \mathrm{K} \; . \tag{19}$$

We have proposed[12] an atomic model for the *M* center. In terms of this atomic model, the reversible transformation $A = B$ may be written as follows:

$$(V_{\mathrm{In}}^{-}\mathrm{P_{In}^{+}})^{0} + 3e^{-} \underset{\mathrm{P\ hop}}{=} \mathrm{P_{In}^{+}} + V_{\mathrm{P}}^{+} + \mathrm{P_{In}^{+}} \; , \tag{20}$$

where the parentheses around the first term denotes a Coulombic attractive interaction between the initial point defects and *P* hop identifies P atomic migration to a nearest-neighbor vacancy as the transformation mechanism. We have discussed[12] the atomic model in some detail; it is our present objective to offer a quantitative explanation for the three widely divergent prefactors found in the kinetic equations.

First note that the reversible transformation between configurations as specified by Eq. (20) involves the capture or emission of three electrons as well as a P hop. We propose that the wide range of empirically deduced prefactors results from differences in the rate-limiting step in the defect complex transformation. We now individually treat each of the kinetic equations.

1. A → B stage 1

The process occurs at a temperature of 110 K with a prefactor $A_0^{\mathrm{expt}}(110\ \mathrm{K}) = 10^{18}$. We assume that the rate-limiting step is a process involving a P hop and emission of a single electron,

$$(V_{\mathrm{In}}^{-}\mathrm{P_{In}^{+}})^{0} \underset{\mathrm{P\ hop}}{\rightarrow} \mathrm{P_{In}^{+}} + V_{\mathrm{P}}^{0} + \mathrm{P_{In}^{0}} + e^{-} \; . \tag{21}$$

For this rate-limiting defect reaction the prefactor can be written as

$$A_0 = \nu_D \exp[(\Delta S_m + \Delta S_i)/k_B] \; . \tag{22}$$

The parameters used to calculate A_0 are summarized in Table I. The calculated prefactor $A(110\ \mathrm{K}) = 1.2 \times 10^{18}$ is an excellent agreement with that found experimentally. Note the very large value of the activation entropy, $\Delta S_a / k_B = 12.2$ and that the translational entropy $S_t / k_B = 8.0$ is a dominant contribution.

2. *A→B stage 2*

This process occurs at 160 K with a prefactor $A_0^{\mathrm{expt}}(160\ \mathrm{K}) = 10^{11}\ \mathrm{s}^{-1}$. We assume that the rate-limiting step is due to the emission of a single electron,

$$(V_{\mathrm{In}}^- P_{\mathrm{In}}^+)^0 \rightarrow (V_{\mathrm{In}}^- P_{\mathrm{In}}^+)^+ + e^- \ . \tag{23}$$

The prefactor of the rate-limiting step corresponds to electron emission and can be written,

$$A_0 = v_{\mathrm{th}} \sigma N_c \exp(\Delta S_i / k_B) \ , \tag{24}$$

where v_{th} is thermal velocity, σ is the capture cross section, and N_c is the conduction-band effective density of states. Assuming $\sigma = 10^{-15}\ \mathrm{cm}^2$, which is a typical capture cross section, we obtain $A_0^{\mathrm{theor}}(160,\ \mathrm{K}) = 9.6 \times 10^{11}\ \mathrm{s}^{-1}$ (see Table I) again in good agreement with experiment.

3. *B→A*

At a temperature of 140 K the prefactor of the $B \rightarrow A$ transformation is found to be $A_0^{\mathrm{expt}}(140\ \mathrm{K}) = 10^7\ \mathrm{s}^{-1}$. In accordance[9] with Levinson *et al.* we assume that the reverse reaction occurs in one stage with the capture of three electrons as well as a P hop,

$$P_{\mathrm{In}}^+ + V_{\mathrm{P}}^+ + P_{\mathrm{In}}^+ + 3e^- \xrightarrow[\text{P hop}]{} (V_{\mathrm{In}}^- P_{\mathrm{In}}^+)^0 \ . \tag{25}$$

The prefactor of this process can be written as,

$$A_0 = \nu_D \exp[(\Delta S_m - 3\Delta S_i)/k_B] \ , \tag{26}$$

where the negative sign before the ionization entropy arises because of electron capture and a concomitant hardening of the lattice. As summarized in Table I, this re-

TABLE I. InP parameters used in the phosphorus vacancy nearest-neighbor hopping and metastable *M* center calculations.

	Lattice constant a (Å)	5.868 75
	Debye temperature θ_D (K)	292
	Debye frequency ν_D (s^{-1})	6.1×10^{12}
	Mass m (kg)	$\mathrm{In} = 1.91 \times 10^{-25}$, $\mathrm{P} = 5.14 \times 10^{-26}$
	Tetrahedral radius r (Å)	In=1.405, P=1.128
	Volume V (m^{-3})	1.76×10^{-29}
	Phosphorus vacancy nearest-neighbor hopping	
	Temperature T (K)	325
	Vibrational entropy S_v / k_B	3.4
	Translational entropy S_t / k_B	11.6
	Migrational entropy $\Delta S_m / k_B$	8.2
	Ionization entropy $\Delta S_i / k_B$	6.8
	Activation entropy $\Delta S_a / k_B$	15.0
	Metastable *M* center	
$A \rightarrow B$ stage 1		
	Temperature T (K)	110
	Vibrational entropy S_v / k_B	0.8
	Translational entropy S_t / k_B	8.0
	Migrational entropy $\Delta S_m / k_B$	7.2
	Ionization entropy $\Delta S_i / k_B$	5.0
	Activation energy $\Delta S_a / k_B$	12.2
	Prefactor A_0 (s^{-1})	1.2×10^{18}
$A \rightarrow B$ stage 2		
	Temperature T (K)	160
	Thermal velocity v_{th} (cm/s)	3.1×10^7
	Capture cross section σ (cm^2)	10^{-15}
	Density of states N_c (cm^{-3})	1.04×10^{17}
	Ionization entropy $\Delta S_i / k_B$	5.7
	Prefactor A_0 (s^{-1})	9.6×10^{11}
$B \rightarrow A$		
	Temperature T (K)	140
	Vibrational entropy S_v / k_B	1.3
	Translational entropy S_t / k_B	8.4
	Migrational entropy $\Delta S_m / k_B$	7.1
	Ionization entropy $\Delta S_i / k_B$	−5.5
	Activation entropy $\Delta S_a / k_B$	−9.4
	Prefactor A_0 (s^{-1})	5.0×10^8

sults in a prefactor $A_0^{\text{theor}}(140\text{ K})=4.0\times10^8\text{ s}^{-1}$ in reasonable agreement with that found experimentally. Note that in this case, the large entropy of three captured electrons dominates, yielding a negative activation entropy.

C. Self-diffusion in Si and Ge

Let us now test our proposal for the entropy of atomic hopping by applying it to the experimentally deduced prefactors for self-diffusion in Ge and Si. The prefactor for self-diffusion D_0 for Ge over a temperature range of 766–928 °C was found to be[2]

$$D_0^{\text{expt}}(\text{Ge})=7.8\text{ cm}^2/\text{s} . \tag{27}$$

The prefactor for Si self-diffusion when the self-diffusion data has been fit to a simple Arrhenius plot, has been reported[6] over a very wide range (1–9000 cm^2 s). Demond *et al.* have shown, however, that the rate of self-diffusion in Si does not obey[6] a simple Arrhenius law. They have interpreted this as due to the superposition of two activated processes. For the temperature range 830–1200 °C the dominant process has a prefactor that falls within the range,

$$D_0^{\text{expt}}(\text{Si,low }T)=0.2\text{–}20\text{ cm}^2/\text{s} . \tag{28}$$

For temperatures greater than 1200 °C the dominant process has a prefactor of order

$$D_0^{\text{expt}}(\text{Si,high }T)\simeq2000\text{ cm}^2/\text{s} . \tag{29}$$

We assume that self-diffusion in Ge and low-temperature self-diffusion in Si proceeds via neutral monovacancy diffusion. The prefactor for self-diffusion is given by[4,5,25]

$$D_0=\tfrac{1}{8}a^2 f \nu_D \exp[(\Delta S_m+\Delta S_f)/k_B] , \tag{30}$$

where a is the lattice constant, f is the correlation factor (equal to $\frac{1}{2}$ for self-diffusion by vacancy migration in diamond lattices[25]), and ΔS_f is the entropy of formation of a vacancy. ΔS_m is calculated using Eqs. (7)–(9). Note that ΔS_m is temperature dependent so that the average temperature over the experimental range is used to calculate ΔS_m. The parameters used to calculate ΔS_m for Si and Ge are summarized in Table II. The entropies of formation were taken[26,27] to be $\Delta S_f(\text{Si})/k_B=3.0$, $\Delta S_f(\text{Ge})/k_B=2.6$. Using Eq. (30), we find

$$D_0^{\text{theor}}(\text{Ge})=11\text{ cm}^2/\text{s} , \tag{31}$$

$$D_0^{\text{theor}}(\text{Si,low }T)=24\text{ cm}^2/\text{s} \tag{32}$$

which are in reasonable agreement with that found experimentally, particularly when it is realized that precise values for ΔS_f are not well established and there is a large spread in the experimental data in the case of Si self-diffusion. Note that the total activation entropy of the prefactor (i.e., $\Delta S_a=\Delta S_m+\Delta S_f$) is quite large for both Ge and Si, $\Delta S_a^{\text{theor}}(\text{Ge})/k_B=8.9$ and $\Delta S_a^{\text{theor}}(\text{Si})=9.2$.

An alternative mode of vacancy migration that yields the same theoretical prefactor for low-temperature Si self-diffusion is that singly ionized vacancies, rather than neutral vacancies, are the mediators of self-diffusion and that they are deionized through capture of free carriers concomitant with the hopping event, i.e.,

$$V_{\text{Si}}^{+}+e^{-}\xrightarrow[\text{hop}]{}V_{\text{Si}}^{x} \tag{33}$$

or

$$V_{\text{Si}}^{-}+h^{+}\xrightarrow[\text{hop}]{}V_{\text{Si}}^{x} . \tag{34}$$

The activation entropy for both of these self-diffusion mechanisms is the same as in Eq. (30), namely $(\Delta S_m+\Delta S_f)/k_B$, since the ionization entropy contribution from the singly ionized vacancy is canceled by the ionization entropy associated with the free-carrier capture. Note that Eqs. (33) and (34) for Si are similar to Eqs. (13), (21), and (25) for InP in that our prefactor analysis suggests that carrier capture or emission often occurs concomitant with atomic hopping.

The prefactor for high-temperature self-diffusion in Si

TABLE II. Parameters used to calculate the entropy of migration for Si and Ge self-diffusion. The values in parentheses refer to high-temperature self-diffusion in Si.

Parameter	Silicon	Germanium
Lattice constant a (Å)	5.430 72	5.657 54
Debye temperature θ_D (K)	648	374
Debye frequency ν_D (s^{-1})	1.35×10^{13}	7.79×10^{12}
Mass m (kg)	4.66×10^{-26}	1.21×10^{-25}
Tetrahedral radius r (Å)	1.173	1.225
Volume V (m^{-3})	1.35×10^{-29}	1.54×10^{-29}
Temperature T (K)	1288 (1573)	1120
Vibrational entropy S_v/k_B	5.1 (5.7)	6.3
Translational entropy S_t/k_B	11.3 (11.6)	12.6
Migrational entropy $\Delta S_m/k_B$	6.2 (5.9)	6.3
Formation entropy $\Delta S_f/k_B$	3.0	2.6
Ionization entropy $\Delta S_i/k_B$	(5.0)	
Activation entropy $\Delta S_a/k_B$	9.2 (13.9)	8.9
Prefactor D_0 (cm^2/s)	24 (2708)	11

can be justified in accordance with our activation entropy formulation if the total activation entropy used in Eq. (30) is given by

$$\Delta S_a = \Delta S_m + \Delta S_f + \Delta S_i \ . \tag{35}$$

Using an average temperature of 1573 K and Eq. (16) to evaluate ΔS_i with[16] $\alpha = 4.73\times 10^{-4}$ eV/K and $\beta = 636$ K yields $\Delta S_i / k_B = 5.0$. This leads to (see Table II) $\Delta S_a / k_B = 13.9$ and a prefactor for high-temperature Si self-diffusion

$$D_0^{\text{theor}}(\text{Si}, \text{high } T) = 2708 \text{ cm}^2/\text{s} \tag{36}$$

which is in reasonable agreement with that deduced by Demond *et al.* There are various mechanisms for self-diffusion which would result in this prefactor: neutral vacancies which ionize concomitant with the hop to become singly ionized, singly ionized vacancies which hop without changing their ionization state, or doubly ionized vacancies which undergo free-carrier capture during the hop to become singly ionized. The situation becomes further complicated if the negative U character[28] of V_{Si} is brought in to consideration.

IV. CONCLUSIONS

We propose the entropy of atomic migration may be calculated from a difference of the translational and vibrational entropy as calculated using Eqs. (7)–(9). It is found that in a kinetic process involving atomic hopping is often dominated by the effects of the migrational and ionization entropies. We have been able to quantitatively account for the prefactors, or equivalently, the activation entropies, of PVNNH in InP MIS devices, transformations in the metastable M center in InP, and self-diffusion in Si and Ge. Prefactors with magnitudes as large as those exhibited in the processes discussed were previously considered to be anomalous. We believe that analysis of the magnitudes of prefactors, along the lines of that discussed herein, may be a powerful approach for the microscopic identification of defects and defect-related processes.

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