

Effect of stress on dopant and defect diffusion in Si: A general treatment

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We present a theoretical treatment of the effect of stress on dopant and defect diffusion in Si. A prior treatment [P. H. Dederichs and K. Schroeder, Phys. Rev. B **17**, 2524 (1978)] of vacancy diffusion in strained fcc metals is extended to include more general defects and crystallinity. The new method is applied to two examples in Si: (1) a vacancy, including Jahn-Teller distortions, and (2) a B-I pair. Both are predicted to show isotropic diffusion for (100) grown uniaxially strained film, but strong anisotropic diffusion for (111) films.

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The effect of stress on dopant diffusion in silicon has recently taken on more importance for microelectronics. The introduction of new materials frequently causes higher stresses, both because of mismatches in the properties and also because of high deposition stresses in some cases. In addition, shrinking device dimensions can cause significant stress gradients, which act as driving forces for diffusion. Stress effects on dopant diffusion have been blamed for significant deviations in the device characteristics for both *n*-type and *p*-type metal-oxide semiconductor transistors.^{1,2}

On the experimental side, contradictory results for the qualitative influence of stress on boron diffusion further motivate a fundamental investigation of stress effects on diffusion: Whereas the measurements of Aziz and co-workers^{3,4} suggest that compression enhances diffusivity, other work⁵⁻⁸ finds the reverse.

Much of the theoretical work regarding the effect of stress on diffusion assumes a hydrostatic state of stress in the substrate, which is of course only a special case.⁹⁻¹¹ Stresses caused by dislocations, deposition processes, and thermal and geometric effects all add up to a complex stress state under a multilayered gate stack. Additionally, a stress concentration typically exists at the gate edge caused by the peeling stress peak at the free edge of the gate stack. The resulting stress concentration can produce stress magnitudes approaching the material strength even at low temperatures.^{12,13}

The only fundamental theoretical treatment of diffusion in a general stress field (that we have been able to find) is given in the work of Dederichs and Schroeder¹⁴ (DS), who derived the effect of stress on diffusivity of vacancies in simple face-centered-cubic crystals. However, their derivation from microscopic lattice hops is a special case of a more general solution that we derived in the present work in order to be able to describe diffusion in more complicated situations such as the diamond lattice.

Using common assumptions of transition state theory, DS showed how to derive the continuum diffusivity tensor from the microscopic lattice hops on a primitive Bravais lattice:

$$D_{\alpha\beta} = \frac{1}{2} \sum_{\text{hops}} R_{\alpha}^h R_{\beta}^h p^h, \quad (1)$$

where p_h is the jump rate and R^h is the jump vector for a hop h . The effect of stress on a jump rate depends (through p_h)

on the relationship of the saddle-point configuration to the local stress tensor; in this way, the symmetry of the saddle-point determines, in addition to the stress field, the symmetry of the diffusivity tensor. DS noted instances where the diffusion in the presence of stress is anisotropic, depending on the detailed symmetry of the saddlepoint configuration.

In the same work, DS considered how to extend their treatment to more complex defects, focusing on oriented defects (such as a dumbbell self-interstitial) in cubic lattices with one atom per unit cell. Labeling the orientational states (of which there are s) within the cell by index μ , their result was

$$D_{\alpha\beta} = \frac{1}{2} \sum_{\text{hops}} R_{\alpha}^h R_{\beta}^h \left(\frac{1}{s} \sum_{\mu\nu} p_{\mu\nu}^h \right), \quad (2)$$

where the hop vectors are Bravais lattice vectors and the effective jump rate is an average over internal jumps within the cell [the sum over (μ, ν)]. This result is valid for the cases considered by DS, but is not general, and in particular is not valid for a diamond lattice under stress. For the purposes of this work, we must derive the general expressions.

A relevant example illustrates the need for a more general treatment. Consider, in Fig. 1(a), the motion of a vacancy on a stressed diamond lattice. If a uniaxial stress is applied along a bond axis, say the (111) axis, then there will be two different kinds of saddle points (assuming for simplicity that the saddle point is midway between two lattice sites). Long-range diffusion along the (111) axis involves hops through both types of saddle points in series, whereas diffusion perpendicular to (111) involves only one type of saddlepoint. We will see in this paper how to treat such general topology in a systematic way. However, we expect in general that hops in series give different behavior than that predicted by Eq. (2). As a very simple example, consider diffusion along an alternating chain, illustrated in Fig. 1(b), where long-range diffusion along the chain must combine two rates (p_I and p_{II}) in series. A steady current j flowing along the chain requires that the differences in concentrations on the sites (c_i) obey $j = (c_2 - c_1)/p_I = (c_{1'} - c_2)/p_{II} = (c_1 - c_{1'})/p_{\text{eff}}$, which gives $p_{\text{eff}} = p_I p_{II} / (p_I + p_{II})$, thus combining the rates in series. The difference between this result and Eq. (2) becomes especially clear for strongly different rates such as $p_I \gg p_{II}$. In this case, our result finds that $p_{\text{eff}} \sim p_{II}$, i.e., the slower rates determines the overall diffusion, which is physically sensible, whereas Eq. (2) finds the opposite result.

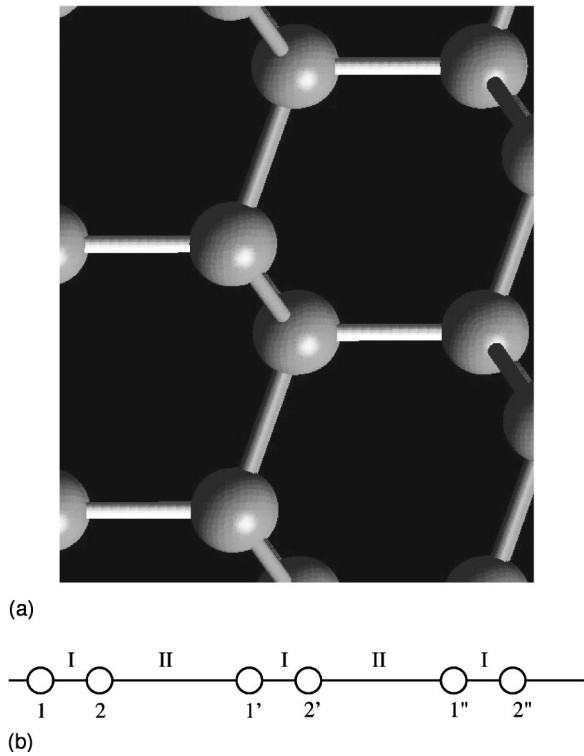


FIG. 1. (a) Diamond lattice, with bonds along a particular (111) direction highlighted. If a uniaxial stress is placed along this (111) axis, the bonds along the (111) direction are no longer equivalent to the bonds in the other directions. A vacancy hopping on this lattice will see two types of saddle points. Long-range diffusion in the (111) direction then involves hopping through both types of saddle points in series. Diffusion perpendicular to the (111) direction is accomplished by hops only through the second type of saddle point. (b) Ideal alternating chain, a one-dimensional analog to the structure presented in (a). The sites are successively labeled 1, 2, 1', 2', etc. The hops between sites are of two types, with rates p_I and p_{II} . Long-range diffusion occurs in series, so that the resulting diffusivity is limited by the slower of rates p_I and p_{II} .

The more universal methodology presented in this paper admits for treatment of arbitrarily complex defects in external fields. The derivation here establishes the generic relationship between detailed atomistic microscopic diffusion processes and long-range diffusivity, thus enabling a complete first-principles calculation of diffusion, within the limitations of the underlying transition state theory.

As an application of the theory, we will determine the specific form of the diffusion equation in the presence of stress for two examples: (1) Si vacancy with Jahn-Teller distortion, and (2) boron–self-interstitial pair. These equations require the microscopic parameters associated with the defects; the practical means of calculating these parameters from first-principles electronic structure theory is left to a subsequent paper.¹⁵ In this paper, we present only one aspect of the problem: the local bulk diffusion equation in the presence of stress. As we explore further in the Discussion section, a complete treatment of the effect of stress on dopant diffusion in Si (or virtually any application, for that matter) needs to include also boundary conditions on the diffusion equation. This we also defer to a later paper.

We present here the derivation of the diffusion equation in the presence of stress for defects in Si. We begin in Sec. I with a derivation of the diffusion tensor from microscopic parameters, along the same lines but broader than given by DS. In Sec. II, we connect the results of Sec. I to stress. The resulting framework is applied in Sec. III to the two defects mentioned above.

I. DERIVATION OF THE DIFFUSION TENSOR FROM MICROSCOPIC PARAMETERS

Our formulation is very much the same as done by DS: microscopic jump rates are combined statistically to give long-range diffusivity. We express the formulation in terms of stress, while DS worked in terms of strain (of course there is an easy mapping between the two).

We assume that there are well-defined states (i.e., energy valleys) that the system can occupy. The concept of state here is quite general. A state can be simply a defect, such as a vacancy, located on a particular lattice site, so that a state is distinguished entirely by specifying its location; this is clearly the case for vacancies in elemental metals, and is treated in Sec. I A. More generally, however, the defect can have other degrees of freedom. For example, the primitive cell in Si has a two-atom basis. In that case, one must specify on which basis site the defect is located, in addition to which primitive cell. Or, for another example, a vacancy in Si might undergo a Jahn-Teller distortion, which has three independent orientations. In that case, one must specify orientation in addition to location. An even more complex example would be a cluster of impurity atoms that migrate together—the internal degrees of freedom in this case would be numerous. The general case—where there are internal degrees of freedom—is treated in Sec. I B.

We assume furthermore that the rate of jumping from one state to another is controlled by the difference in energy from the initial valley to the saddle point. The energy difference, of course, must account for the additional work done against an external stress field. We find it convenient to introduce a *local* reference, which is the perfect system subjected to the local value of the external stress. We then introduce a defect into the local reference and measure changes in the system relative to that reference. We have coined the word “creation” for values calculated with respect to this local reference, in order to avoid confusion with other common terms (“formation,” “migration,” “defect,” etc.) For example, the “creation energy” is the energy required to insert a defect into the perfect, stressed lattice; likewise “creation volume” describes the change in volume during that process. This choice of local reference allows a clean treatment of diffusion in the presence of a nonuniform stress field.

We do not consider any trapping, reaction, or dissociation of the defects; we take only hops that maintain the unity of the defect. A treatment of stress effects on reactive diffusion would be beyond the scope of this paper.

A. Defects with simple basis

An example in this category is a simple (unreconstructed) vacancy in a metal having a primitive cell with one atom

(e.g., simple cubic, body-centered cubic, and face-centered cubic). In this case, the state is specified completely by designating the spatial location of its primitive cell, A . We can describe the system by a concentration c on each site A ,

$$p[A \rightarrow B] = p_0 \exp[-\beta(\varepsilon_{c(s)}^{[AB]} - \varepsilon_{c(v)}^A)] \equiv M_{[AB]}/S_A \quad (3)$$

with

$$M_{[AB]} = M_{[BA]} \equiv p_0 \exp(-\beta\varepsilon_{c(s)}^{[AB]}), \quad (4)$$

$$S_A \equiv \exp(-\beta\varepsilon_{c(v)}^A), \quad (5)$$

where $\beta = 1/(k_B T)$ and p_0 is a basic hop rate. In these definitions, we separate the ‘‘solubility factor’’ S of the defect in the valley, S_A , from the ‘‘mobility factor’’ $M_{[AB]}$. (The ‘‘solubility factor’’ S is not to be confused with the ‘‘solubility limit.’’ The former is a property of a single phase, the latter of two phases in equilibrium.)

We will begin the treatment by assuming a uniform host, and then extend the results at the end to a nonuniform host. In a uniform host, all valleys have the same energy, so that $\varepsilon_{c(v)}^A = \varepsilon_{c(v)}$ and $S_A = S$. The saddle-point energies $\varepsilon_{c(s)}^{[AB]}$ do not depend on the absolute positions A and B , but only on the relative position. (The saddle-point energies are not all the same because the host is not assumed to be isotropic. In the presence of stress, even a cubic crystal is not isotropic.)

The concentration on site A develops in time by

$$\dot{c}_A = -c_A \sum_B p[A \rightarrow B] + \sum_B c_B p[B \rightarrow A]. \quad (6)$$

We can make use now of the translation symmetry of the host by expanding the solutions in plane waves within the Brillouin zone (BZ) into a Bloch form,

$$c_B = \int_{\text{BZ}} u(\underline{k}, t) \exp(i\underline{k} \cdot \underline{R}_B) d^3k. \quad (7)$$

Matching Fourier components of the rate equation then gives

$$\dot{u}(\underline{k}, t) = \gamma(\underline{k}) u(\underline{k}, t) / S \quad (8)$$

with

$$\gamma(\underline{k}) = \sum_B M_{[0B]} [\exp(i\underline{k} \cdot \underline{R}_{B0}) - 1],$$

where the site 0 has been chosen arbitrarily and $\underline{R}_{Jl} \equiv \underline{R}_J - \underline{R}_l$. Because we are looking for the long-time and macroscopic, i.e., long-wavelength evolution of the system, we expand $\gamma(\underline{k})$ in powers of \underline{k} ,

$$\gamma(\underline{k}) = - \left(\sum_B M_{[0B]} \underline{R}_{B0} \otimes \underline{R}_{B0} \right) : (\underline{k} \otimes \underline{k}) / 2 + O(k^4) \quad (9)$$

(the dyad $\underline{a} \otimes \underline{b}$ defines a matrix with components $a_i b_j$). The symbol $:$ is introduced for convenience to mean the double dot product; i.e., $\underline{a} : \underline{b} = \text{Tr}[\underline{a} \cdot \underline{b}]$. There are no terms of order unity because, by number conservation, $\gamma(\underline{k} = \underline{0}) = 0$. There

are no terms linear in \underline{k} because $\sum_B M_{[0B]} \underline{R}_{B0} = \underline{0}$ (in a solid with a simple basis, for every neighbor there is an opposite neighbor that cancels).

When we substitute the series expansion of $\gamma(\underline{k})$ [Eq. (9)] into the equations of motion [Eq. (8)] and transform back to real space, each power of \underline{k} in γ will be associated with a spatial derivative. Thus the second derivative of $\gamma(\underline{k})$ at $\underline{k} = \underline{0}$ will have physical significance in the resulting diffusion equation. We therefore define a ‘‘solid permeability tensor’’

$$\underline{\underline{P}} = - \frac{1}{2} \frac{\partial^2 \gamma(\underline{k})}{\partial \underline{k} \partial \underline{k}} \Big|_{\underline{k} = \underline{0}}, \quad (10)$$

and the resulting diffusion equation is $\dot{c} = (1/S) \underline{\underline{P}} : \underline{\nabla} \underline{\nabla} c = \underline{\underline{D}} : \underline{\nabla} \underline{\nabla} c$, where the diffusion tensor $\underline{\underline{D}}$ is obtained from the microscopic hop parameters by

$$\underline{\underline{D}} = \frac{1}{S} \sum_B M_{[0B]} \underline{R}_{B0} \otimes \underline{R}_{B0} \quad (11)$$

as obtained by DS.

In the case of a nonuniform host (as would exist, for example, if an applied stress field was nonuniform), then the hop rates are dependent on position. A careful derivation (see DS) shows that the diffusion equation becomes

$$\dot{c}(\underline{x}, t) = \underline{\nabla} \cdot \left[\underline{\underline{P}}(\underline{x}, t) \cdot \underline{\nabla} \left(\frac{c(\underline{x}, t)}{S(\underline{x}, t)} \right) \right]. \quad (12)$$

Our notation now is somewhat different than that of DS. We have introduced explicitly the solid solubility factor S because it illustrates clearly that the equilibrium condition is $c(\underline{x}, t) \propto S(\underline{x}, t)$, and also that a gradient in the solubility factor acts as a driving force for diffusion.¹⁶ [It is often conventional to use the local chemical potential $\mu = (1/\beta) \ln(c/S)$ instead of S .] Also, we have introduced the tensor quantity $\underline{\underline{P}}$, which is the product of the diffusivity and solubility factor. In analogy to gaseous and liquid systems, we have chosen to call this the ‘‘solid permeability factor’’; in an anisotropic medium, the permeability factor in general is a tensor quantity. The solid solubility factor depends only on the valley energy [Eq. (5)], the solid permeability factor depends only on the saddle-point energy [Eqs. (4), (9), and (10)], and the solid diffusivity depends on the migration energy [difference between the saddle point and valley, Eq. (11)].

Clearly the choice of a local reference for the energies discussed previously does not affect the diffusivity (which depends on differences in energy), but does affect the solubility factor. In comparing the relative solubility factors of a defect at two different (stressed) locations, one must calculate the energy required to insert the defect into each (stressed) location. Thus, using the stressed but otherwise perfect Si as a local reference is natural for the diffusion problem.

B. Defects with nonsimple basis

In this category are crystals with primitive cells having more than one atom in the basis, or defects with internal

(e.g., orientational) degrees of freedom. For example, the diamond and hexagonal-close-packed (hcp) structures have a two-atom basis. Also, complex defects, such as a dumbbell self-interstitial or vacancy with Jahn-Teller distortion, have an orientation which must be specified in addition to the site. Some care is required in this derivation beyond the previous section.

We identify now a lattice site by $\{Aa\}$, with its cell index A and the index a which denotes the state within the cell. The number of states in the basis is N_{states} . For a symmetric vacancy in diamond, as an example, $N_{\text{states}}=2$, because there are two sites in the primitive cell. However, if we admit Jahn-Teller distortions, then on each of two atomic sites a vacancy can have one of three orientations, so that in this case $N_{\text{states}}=6$. It is easy to imagine more complex defects (clusters, for example) where the number of states could be quite large.

In this more general case, we must be careful to keep track of all the degrees of freedom of the system when taking the continuum limit. The situation is analogous to the calculation of the elastic constants for crystals with more than one atom in the primitive cell: the internal coordinates (“internal strain”) must be treated explicitly—one must account for optical modes in addition to the acoustic modes.¹⁷ There is also a formal parallel to the calculation of the energy levels of a tight-binding solid: in the case of multiple-atom primitive cells, multiple solutions (bands) occur. We will see that multiple solutions occur likewise in the general solution to the migration equation, though once we identify the general solutions, we will throw out all but the long-time and long-wavelength terms to get the diffusion equation.

The rate of jumping from state $\{Aa\}$ to state $\{Bb\}$ through the saddle point $[AaBb]$ is given by

$$p[Aa \rightarrow Bb] = p_0 \exp[-\beta(\varepsilon_{c(s)}^{[AaBb]} - \varepsilon_{c(v)}^{Aa})] \\ = M_{[AaBb]}/S_{Aa} \quad (13)$$

with

$$M_{[AaBb]} = M_{[BbAa]} \equiv p_0 \exp(-\beta \varepsilon_{c(s)}^{[AaBb]}), \quad (14)$$

$$S_{Aa} \equiv \exp(-\beta \varepsilon_{c(v)}^{Aa}). \quad (15)$$

The concentration of state a in cell A develops in time according to

$$\dot{c}_{Aa} = -c_{Aa} \sum_{Bb} p[Aa \rightarrow Bb] + \sum_{Bb} c_{Bb} p[Bb \rightarrow Aa].$$

Making use of the translation symmetry of the host yields

$$c_{Bb} = \sum_{\underline{k}} u_b(\underline{k}, t) \exp(i\mathbf{k} \cdot \mathbf{R}_{Bb}). \quad (16)$$

Matching Fourier components of the rate equation then gives

$$\dot{u}_a(\underline{k}, t) = \sum_b \Gamma_{ab}(\underline{k}) u_b(\underline{k}, t) / S_b$$

with

$$\Gamma_{ab}(\underline{k}) = \sum_B M_{[0aBb]} \exp(i\mathbf{k} \cdot \mathbf{R}_{Bb0a}) - \delta_{ab} \sum_{Bc} M_{[0aBc]}, \quad (17)$$

where the cell $A=0$ has been chosen arbitrarily. Note that number conservation is expressed as

$$\sum_a \Gamma_{ab}(\underline{k}=\underline{0}) = 0. \quad (18)$$

The complete dynamics of the system are contained in $\Gamma_{ab}(\underline{k})$, which is a symmetric rate matrix of size $N_{\text{states}} \times N_{\text{states}}$. The eigenvalues are the rate constants of the relaxation process. At least one eigenvalue vanishes at $\underline{k}=\underline{0}$ because of number conservation [Eq. (18)]. We expect generally that only one eigenvalue vanishes for $\underline{k}=\underline{0}$. This is because a conserved quantity is associated with each vanishing eigenvalue at $\underline{k}=\underline{0}$. We anticipate that the only conserved quantity associated with diffusion will be the total defect number (we have assumed that the defects diffuse intact). For small \underline{k} , we have then only one relevant mode (that is, the slowest). All the other modes are fast and correspond to short-range relaxation among the members of the primitive cell.

There is an easy analogy to the vibrational modes of a solid with more than one atom in the primitive cell: in the vibrational spectrum near $\underline{k}=\underline{0}$ there are three low-frequency acoustic modes (corresponding to three components of conserved momentum) and the rest are higher-frequency optical modes. The difference is that in the diffusion problem, of course, the modes are all exponentially decaying, and so only the slowest mode is relevant.

Consider, for example, the alternating chain discussed in the Introduction. In this system, the primitive cell consists of two sites, so that Γ is a 2×2 matrix:

$$\Gamma(\underline{k}) = \begin{pmatrix} -p_I - p_{II} & p_I e^{[ik(x_2 - x_1)]} + p_{II} e^{[ik(x_2 - x_1 - a)]} \\ p_I e^{[ik(x_1 - x_2)]} + p_{II} e^{[ik(x_1 - x_2 + a)]} & -p_I - p_{II} \end{pmatrix}$$

where x_1 and x_2 are the site positions within the unit cell, a is the periodicity of the chain, and p_I and p_{II} are the rates associated with transitions over the two different saddle points. The two eigenvalues are $\gamma_{\pm} = -p_I - p_{II} \pm \sqrt{p_I^2 + p_{II}^2 + 2p_I p_{II} \cos(ka)}$. The relaxation mode associated with γ_- (the “optical mode”) has finite lifetime even when $k=0$. This corresponds to a relaxation within the primitive cell, which occurs very quickly to bring the sublattice into equilibrium. The rate γ_+ of the other (“acoustic”) mode vanishes at $k=0$ (that is, small, long-wavelength deviations from

uniformity take a very long time to relax) and so this is the only relevant mode. The leading order term for small k is $a^2 k^2 p_{\text{I}} p_{\text{II}} / (p_{\text{I}} + p_{\text{II}})$, which, when we transform to real space, will become the operator $P \partial^2 / \partial x^2$. Thus, $P = (a^2/2) p_{\text{I}} p_{\text{II}} / (p_{\text{I}} + p_{\text{II}})$, as we expect for processes in series.

In general, N_{states} is potentially large, and it is not possible to obtain an analytical form for the relevant eigenvalue. However, because we want only the behavior near $k=0$ (and also because we know the eigenvector there—see below), we can use perturbation theory to obtain the permeability. Because we are only interested in the diffusive behavior, we want the second-order coefficient of the relevant eigenvalue in an expansion in k . If we expand Γ to second order in k , we get

$$\begin{aligned} \Gamma_{ab}(k) &= \underbrace{q_{ab} - q_a \delta_{ab}} + \underbrace{ik \cdot \underline{Z}_{ab}} - \underbrace{\frac{1}{2} k \otimes k : \underline{Y}_{ab}} + \mathcal{O}(k^3), \\ &= \Gamma_{ab}^{(0)} + \Gamma_{ab}^{(1)} + \Gamma_{ab}^{(2)} + \mathcal{O}(k^3) \quad (19) \end{aligned}$$

where $\Gamma^{(0)}$, $\Gamma^{(1)}$, and $\Gamma^{(2)}$ are the zeroth-, first-, and second-order terms and

$$q_{ab} \equiv \sum_B M_{[0aBb]},$$

$$q_a \equiv \sum_b q_{ab},$$

$$\underline{Z}_{ab} \equiv \sum_B M_{[0aBb]} \underline{R}_{Bb0a},$$

$$\underline{Y}_{ab} \equiv \sum_B M_{[0aBb]} \underline{R}_{Bb0a} \otimes \underline{R}_{Bb0a}.$$

Note that $\Gamma^{(1)} \sim \mathcal{O}(k)$ and $\Gamma^{(2)} \sim \mathcal{O}(k^2)$. In order to establish the relevant eigenvalue to $\mathcal{O}(k^2)$, we need to carry the perturbation out to *first* order in $\Gamma^{(2)}$ and *second* order in $\Gamma^{(1)}$.

We can see that $v_b = 1/\sqrt{N_{\text{states}}}$ is the relevant eigenvector of $\Gamma_{ab}^{(0)}$, with zero eigenvalue, because [from Eq. (19)]

$$\sum_b \Gamma_{ab}^{(0)} v_b = \frac{1}{\sqrt{N_{\text{states}}}} \sum_b \Gamma_{ab}^{(0)} = 0.$$

Again this is number conservation [Eq. (18)].

If we know the complete eigensystem of $\Gamma^{(0)}$,

$$\sum_b \Gamma_{ab}^{(0)} u_b^{(m)} = \gamma_m(0) u_a^{(m)},$$

we can apply Rayleigh-Schrödinger perturbation theory¹⁸ in a straightforward way. We label the relevant eigenvalue “1,”

$$\begin{aligned} \gamma_1(k) &= \frac{1}{N_{\text{states}}} \sum_{ab} \Gamma_{ab}^{(2)} - \frac{1}{N_{\text{states}}} \\ &\quad \times \sum_{m>1} \frac{\left| \sum_{ab} u_a^{(m)} \Gamma_{ab}^{(1)} \right|^2}{\gamma_m(0)} + \mathcal{O}(k^3). \quad (20) \end{aligned}$$

(The *first-order term* involving $\Gamma^{(1)}$ vanishes by symmetry; that is, $\sum_{ab} \Gamma_{ab}^{(1)} = 0$.) In the case of a simple basis, $\Gamma^{(1)}$ is a number and it vanishes by symmetry [see discussion following Eq. (9)]. For the general case of a nonsimple basis, the matrix $\Gamma^{(1)}$ does not vanish.

We note that the first term alone adds rates in parallel. In some cases (for instance, those considered by DS), the second term vanishes. In general, the second term, which we will term the “cell correction,” is nonvanishing. To illustrate the role of the cell correction, we examine again our simple example of the alternating chain. The first term of Eq. (20) alone gives the result discussed in the Introduction, which adds the rates in parallel:

$$a^2(p_{\text{I}} + p_{\text{II}})/8$$

The cell correction [i.e., second term of Eq. (20)] gives

$$-a^2(p_{\text{I}} - p_{\text{II}})^2/[8(p_{\text{I}} + p_{\text{II}})]$$

which gives in sum the correct total result where the rates add in series. It is clear from this simple example that Eq. (20) is the more general result.

It is impractical, in general, to obtain the complete eigensystem of $\Gamma^{(0)}$ for systems where $N_{\text{states}} > 2$. Instead, it is more useful to apply the perturbation method of Dalgarno and Lewis,¹⁸ because this circumvents the diagonalization. In this method, one defines the vector w_b by the equations

$$\sum_b \Gamma_{ab}^{(0)} w_b = - \sum_b \Gamma_{ab}^{(1)} v_b \quad \forall a.$$

Once these are solved for w_b , the second term in Eq. (20) is computed as $\sum_{ab} v_a \Gamma_{ab}^{(1)} w_b$, which is second order in $\Gamma^{(1)}$. One must take care because $\Gamma^{(0)}$ has a zero eigenvalue. The singularity can be dealt with easily in one of two equivalent ways. One way is to form $\Gamma_{\Lambda}^{(0)} \equiv \Gamma^{(0)} + \Lambda \mathbf{v} \otimes \mathbf{v}$, then $w_a = -\lim_{\Lambda \rightarrow \infty} \sum_{bc} (\Gamma_{\Lambda}^{(0)})_{ab}^{-1} \Gamma_{bc}^{(1)} v_c$. Another way is to solve for $w_2, w_3, \dots, w_{N_{\text{states}}}$ in terms of w_1 , where it can be shown that the contribution to γ_1 is independent of w_1 . Either method gives a solution which has the proper meaning.

After the relevant eigenvalue (γ_1) has been determined, the permeability factor tensor follows from its definition [Eq. (10)], using γ_1 .

As a more interesting example, the rate matrix Γ for a vacancy on a diamond lattice (ignoring Jahn-Teller distortions and taking only nearest-neighbor hops) has the structure

$$\Gamma(\underline{k}) = \begin{pmatrix} -q & q + ik \cdot \underline{Z} - \frac{1}{2} k \otimes k : \underline{Y} \\ q - ik \cdot \underline{Z} - \frac{1}{2} k \otimes k : \underline{Y} & -q \end{pmatrix},$$

where

$$q \equiv \sum_B M_{[01B2]},$$

$$\underline{Z} \equiv \sum_B M_{[01B2]} \underline{R}_{B201},$$

$$\underline{Y} \equiv \sum_B M_{[01B2]} \underline{R}_{B201} \underline{R}_{B201},$$

and the sums cover nearest-neighbor hops.

This system has two eigenvalues:

$$\gamma_{\pm}(\underline{k}) = -q \pm q \left[1 + \frac{1}{2q^2} (\underline{k} \cdot \underline{Z})^2 - \frac{1}{2q} \underline{k} \cdot \underline{Y} \cdot \underline{k} + \mathcal{O}(k^3) \right].$$

The relevant mode is γ_+ , and

$$\underline{P} = \frac{1}{2} \left[\underline{Y} - \frac{\underline{Z} \otimes \underline{Z}}{q} \right]. \quad (21)$$

Again, the first term will be recognized from Eq. (2), and the second term is the cell correction.

A technical note: the Bloch form [Eq. (16)] for a non-primitive cell has some arbitrary choice implicit in it. That is, the phase factor attributed to each site may be arbitrarily changed. Instead of the phase factor $\exp(i\underline{k} \cdot \underline{R}_{Bb})$ used in Eq. (16), we could equally well have chosen $\exp(i\underline{k} \cdot \underline{R}_B)$, where the phase factor does not depend on the position within the unit cell, but only on the position of the whole cell. This amounts to only a unitary transformation, of course; it changes the value of the matrix elements of Γ , but not the eigenvalues. Such a transformation, because it involves the wave vector, will change the values of the perturbation terms in Eq. (19), so that $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are altered by the transformation, but the combination which gives the eigenvalue [Eq. (20)] is invariant.

Finally, we note that for a degenerate basis, the appropriate solubility factor is the average solubility over all states; that is, the proper solubility to use in the diffusion equation [Eq. (12)] is

$$\bar{S}_A \equiv \frac{1}{N_{\text{states}}} \sum_a S_{Aa} = \frac{1}{N_{\text{states}}} \sum_a \exp(-\beta \varepsilon_{c(v)}^{(A)}). \quad (22)$$

This is the form expressed by DS [implied by their Eq. (36); our notation is somewhat different]. The general proof is left for the Appendix.

II. EFFECT OF STRESS ON DIFFUSION

It remains to relate the distortions in the energy surface to the applied stress. That is, we must specify how stress affects the valley and saddle-point energies in the hop rates [Eq. (13)]. We will assume that the host, in the absence of stress, is uniform.

When a defect is created, the solid changes shape from its original condition. In linear elasticity, the change in the shape of a volume can be expressed as a real, symmetric tensor. For example, a sphere is distorted into an ellipsoid, and the difference can be described in complete generality (within linear elasticity) by three principal values and axes:

$$\underline{\underline{\Omega}}_c = \Omega_{c1} \hat{t}_1 \otimes \hat{t}_1 + \Omega_{c2} \hat{t}_2 \otimes \hat{t}_2 + \Omega_{c3} \hat{t}_3 \otimes \hat{t}_3,$$

where the subscript c is again for ‘‘creation.’’ The symmetry of the shape change is determined by the symmetry of the defect, i.e., the principal axes will be symmetry axes of the defect. If the defect has an orientation (for example, a dumbbell self-interstitial or a Jahn-Teller distorted vacancy), the principal axes will be directed accordingly, but the set of principal values will be the same for all orientations. A defect with cubic symmetry will have three degenerate principal values, of course. A defect with an orientation may have one eigenvalue unequal to the other two.

We will call the creation energy in the absence of external stress $\varepsilon_{c(v)}^{Aa}(0)$. In the presence of an external stress, the creation energy must include the work required to distort the solid in opposition to that stress, so that

$$\varepsilon_{c(v)}^{Aa}(\underline{\underline{\sigma}}) = \varepsilon_{c(v)}^{Aa}(0) + \underline{\underline{\Omega}}_{c(v)}^{(a)} : \underline{\underline{\sigma}} \quad (23)$$

where the stress is evaluated locally. We have assumed here that all of the defect internal states are energetically degenerate in the absence of stress. (It is easy to remove that assumption in the following.) The stress can break the degeneracy, depending on the orientation of the principal axes of $\underline{\underline{\Omega}}_{c(v)}^a$ relative to the stress tensor. These values of $\varepsilon_{c(v)}^a(\underline{\underline{\sigma}})$ are used in determining the solubility factor S [Eqs. (15) and (22)].

Similarly, when the system is at the saddle point [$AaBb$], the shape is different from the reference condition (the perfect, stressed lattice), which is represented by the saddle-point volume tensor $\underline{\underline{\Omega}}_{c(s)}^{[AaBb]}$ and the energy at the saddle point becomes, under stress,

$$\varepsilon_{c(s)}^{[AaBb]}(\underline{\underline{\sigma}}) = \varepsilon_{c(s)}^{[AaBb]}(0) + \underline{\underline{\Omega}}_{c(s)}^{[AaBb]} : \underline{\underline{\sigma}}, \quad (24)$$

where the subscript s is for ‘‘saddle point.’’ It is important to keep in mind that the reference state for the saddle point volume is the perfect, stressed crystal, just as it was for the valley volume. $\underline{\underline{\Omega}}_{c(s)}$ is the change in volume/shape imposed on the perfect, stressed crystal by placing the defect at the saddle point. It is *not* the distortion caused in going from valley to saddle point; this latter is commonly called the ‘‘migration volume.’’ The values of $\varepsilon_{c(s)}(\underline{\underline{\sigma}})$ are used in determining the permeability tensor $\underline{\underline{P}}$ [Eqs. (10), (14), and (17)].

It is revealing to separate the effects of hydrostatic stress (pressure) from those due to deviatoric stress. The deviatoric stress is defined as the traceless part of the stress:

$$\begin{aligned} \underline{\underline{\sigma}} &= p \underline{\underline{I}} + \underline{\underline{\sigma}}_{\text{dev}}, \\ p &\equiv \text{Tr}[\underline{\underline{\sigma}}]/3. \end{aligned} \quad (25)$$

Similarly, for the volume tensor,

$$\begin{aligned} \underline{\underline{\Omega}} &= (\Omega_h/3) \underline{\underline{I}} + \underline{\underline{\Omega}}_a, \\ \Omega_h &\equiv \text{Tr}[\underline{\underline{\Omega}}], \end{aligned} \quad (26)$$

where Ω_h would be identified as the total scalar volume change and $\underline{\underline{\Omega}}_a$ is the traceless part of $\underline{\underline{\Omega}}$. We can see that the

work against the external stress has two terms: one couples the pressure to the total volume change, and the other couples the deviatoric stress to the anisotropic part of the saddle-point volume:

$$\underline{\underline{\sigma}}:\underline{\underline{\Omega}} = p\underline{\underline{\Omega}}_h + \underline{\underline{\sigma}}_{\text{dev}}:\underline{\underline{\Omega}}_a. \quad (27)$$

From this it is clear that the permeability factor in general will have an overall scalar factor that depends on the pressure and the isotropic saddle-point volume [$\exp(-\beta p \Omega_{c(s)h})$]. The anisotropic part of the saddle-point volume, along with the deviatoric part of the stress tensor, will determine the anisotropic part of the permeability tensor (sum over terms involving $\exp[-\beta \text{Tr}[\underline{\underline{\Omega}}_{c(s)a} \cdot \underline{\underline{\sigma}}_{\text{dev}}]]$).

Specific examples of the permeability tensor in the presence of stress are worked out and displayed in Sec. III.

III. TWO EXAMPLES

In this section, we apply the above theory to two examples of dopant diffusion in Si which are important for microelectronics. The first one, the neutral vacancy, is complicated by the existence of the Jahn-Teller distortion and the dependence of that distortion on stress and charge state.¹⁹ The second example is the diffusion of a B-self-interstitial (B-SI) pair.

In both of the examples treated here, symmetry will dictate that two of the eigenvalues of all of the volume tensors will be degenerate. In the case of such degeneracy, we find it convenient to represent the volume tensor of a defect with orientation along direction \hat{d} by

$$\underline{\underline{\Omega}}_c = \Omega_{cl} \hat{d} \otimes \hat{d} + \Omega_{ct} (\underline{\underline{I}} - \hat{d} \otimes \hat{d})$$

with ‘‘longitudinal’’ (Ω_{cl}) and ‘‘transverse’’ (the doubly degenerate Ω_{ct}) values. We can then describe the volume tensor by two parameters, either the combination Ω_{cl} and Ω_{ct} , or

$$\Omega_{ch} \equiv \Omega_{cl} + 2\Omega_{ct},$$

$$\Omega_{ca} \equiv \Omega_{cl} - \Omega_{ct}.$$

The latter pair measures the overall (scalar) volume and the anisotropic part.

We also note that the jump direction is not generally the same as the symmetry axis of the saddle point, although for simple defects, such as the vacancy treated here, the two *are* the same (the nearest neighbor hop also defines the symmetry axis of the saddle point). However, this is not true for the second example, the B-SI pair.

A. Vacancy (with Jahn-Teller distortion) in Si

As noted above, the vacancy in Si may or may not undergo a Jahn-Teller distortion, depending on the charge state *and* the stress.^{10,15,19} In the absence of a Jahn-Teller distortion, the results derived for the perfect diamond lattice apply [see Eq. (21)].

In the presence of a Jahn-Teller distortion, the vacancy in the valley has three possible orientations. Each orientation is

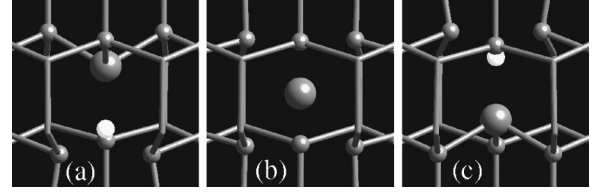


FIG. 2. Projection of a Si crystal containing a migrating Jahn-Teller distorted vacancy on the $(\bar{1}21)$ plane. The migrating Si atom (which moves in the opposite direction as the vacancy) is shown as a large dark ball, the vacancy in (a) and (c) by a small white ball. The small dark balls show the other Si atoms surrounding the two involved vacancy sites. (a) is the initial configuration, (b) the saddle point with a threefold symmetry around the migration direction (111) which lies in the paper plane, and (c) the final configuration.

symmetric around a $\langle 100 \rangle$ axis, so that the two transverse volumes are equal. The three orientations combined with two lattice sites in the primitive cell makes $N_{\text{states}} = 6$.

The solubility factor for the case with Jahn-Teller distortion is

$$S = e^{-\beta p \Omega_{c(v)h}} [e^{-\beta \Omega_{c(v)a} (-2\sigma_{xx} + \sigma_{yy} + \sigma_{zz})} + e^{-\beta \Omega_{c(v)a} (\sigma_{xx} - 2\sigma_{yy} + \sigma_{zz})} + e^{-\beta \Omega_{c(v)a} (\sigma_{xx} + \sigma_{yy} - 2\sigma_{zz})}] / 3,$$

where $p = \text{Tr}[\underline{\underline{\sigma}}]/3$. The case of no Jahn-Teller distortion is obtained by taking $\Omega_{c(v)a} \rightarrow 0$, in which limit the solubility factor becomes $S = e^{-\beta p \Omega_{c(v)h}}$.

The vacancy hops by a jump to a nearest-neighbor site; the saddle-point configuration has a symmetry axis along a $\{111\}$ direction,¹⁵ and once again the two transverse volumes are equal (see Fig. 2). Defining

$$\underline{\underline{\alpha}} \equiv 2\beta \underline{\underline{\sigma}} \Omega_{c(s)a} / 3,$$

$$\delta \equiv e^{-(\alpha_{yz} + \alpha_{zx} + \alpha_{xy})} + e^{-(\alpha_{yz} - \alpha_{zx} - \alpha_{xy})} + e^{-(\alpha_{yz} + \alpha_{zx} - \alpha_{xy})} + e^{-(\alpha_{yz} - \alpha_{zx} + \alpha_{xy})},$$

we find the components of the permeability tensor to be

$$P_{xx} = 2e^{-\beta p \Omega_{c(s)h}} [\cosh(2\alpha_{xy}) + \cosh(2\alpha_{zx})] / \delta,$$

$$P_{xy} = -2e^{-\beta p \Omega_{c(s)h}} \sinh(2\alpha_{xy}) / \delta. \quad (28)$$

The other components can be obtained by cyclic permutation of the Cartesian components x, y, z . The Jahn-Teller distortion of the vacancy in its equilibrium position has no effect on the permeability factor.

B. Boron-self-interstitial pair in Si

The B-SI pair results in more complex forms for the solubility and permeability factors. The defect in the valley has a $\langle 111 \rangle$ symmetry axis, with the B-SI bond aligned so that the (substitutional) B lies along the line between the SI and a Si lattice atom [Fig. 3(a)].²⁰ The threefold symmetry around the $\langle 111 \rangle$ axis fixes the two transverse volumes as equal.

There are four orientations for the B-SI pair on each site, and two lattice sites per primitive cell, so that $N_{\text{states}} = 8$. The solubility factor for the boron-self-interstitial pair is

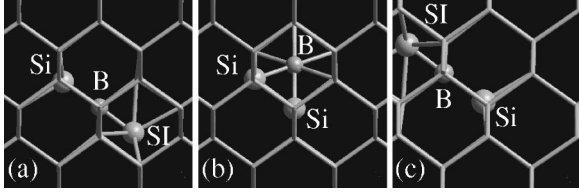


FIG. 3. Projection of a Si crystal containing a migrating B-SI pair on the (110) plane. The atoms involved in the diffusion process are marked as balls, the rest as stick-only network. Substitutional Si atoms are labeled Si, interstitial ones SI, and B atoms with a B. (a) shows the initial configuration, (b) one possible quasi-hexagonal saddle point, and (c) one possible final configuration.

$$S = e^{-\beta p \Omega_{c(v)h}} (e^{-\omega_{yz} - \omega_{zx} - \omega_{xy}} + e^{-\omega_{yz} + \omega_{zx} + \omega_{xy}} + e^{+\omega_{yz} - \omega_{zx} + \omega_{xy}} + e^{+\omega_{yz} + \omega_{zx} - \omega_{xy}}) / 4,$$

where $\underline{\omega} \equiv 2\beta\Omega_{c(v)a}\sigma/3$.

The migration in p -type Si occurs when the SI pushes into the lattice site occupied by the B, which is displaced to a nearby hexagonal or quasi-hexagonal site [Fig. 3(b)]; since the hexagonal interstitial is a saddle point for the positive, and a local minimum close to the saddle point for the neutral charge state,²⁰ it is assumed to be the dominant saddle point in p -type Si in this paper. The quasi-hexagonal site has a $\langle 111 \rangle$ symmetry axis. The B in the quasi-hexagonal site is surrounded by 6 Si atoms, anyone of which may now be displaced by the B, leading again to a B-SI pair. The resulting hops can be $1nn$, $2nn$, or even $3nn$. There are a total of 768 paths that contribute to the reduced rate matrix [Eq. (17)]. The symmetry between the two sites of the sublattice can be used to block diagonalize $\Gamma^{(0)}$, $\Gamma^{(1)}$, and $\Gamma^{(2)}$ [from Eq. (19)] to 4×4 and the resulting parts can be handled in a straightforward, if tedious, way. The resulting permeability tensor is

$$\underline{\underline{P}} = c_1 \underline{\underline{\rho}} + c_2 \underline{\underline{\chi}}, \quad (29)$$

which corresponds to the first- and second-order perturbation terms [as in Eq. (20)]:

$$\begin{aligned} c_1 &\equiv \zeta / (4\lambda_x \lambda_y \lambda_z), \\ \rho_{xx} &\equiv (1 + \lambda_y^2 \lambda_z^2 + \lambda_z^2 \lambda_x^2 + \lambda_x^2 \lambda_y^2), \\ \rho_{xy} &\equiv -5(1 - \lambda_y^2 \lambda_z^2 - \lambda_z^2 \lambda_x^2 + \lambda_x^2 \lambda_y^2) / 11, \\ c_2 &\equiv \zeta / (132\lambda_x \lambda_y \lambda_z (1 + \lambda_y^2 \lambda_z^2 + \lambda_z^2 \lambda_x^2 + \lambda_x^2 \lambda_y^2)), \\ \chi_{xx} &\equiv -(1 + \lambda_y^2 \lambda_z^2 - \lambda_z^2 \lambda_x^2 - \lambda_x^2 \lambda_y^2)^2, \\ \chi_{xy} &\equiv -1 + 2\lambda_x^2 \lambda_y^2 + \lambda_y^4 \lambda_z^4 + \lambda_z^4 \lambda_x^4 - \lambda_x^4 \lambda_y^4 - 2\lambda_x^2 \lambda_y^2 \lambda_z^4, \\ \zeta &\equiv \exp(-\beta p \Omega_{c(s)h}), \\ \lambda_z &\equiv \exp(2\beta \Omega_{c(s)a} \sigma_{xy} / 3), \\ \Omega_{c(s)h} &\equiv \Omega_{c(s)l} + 2\Omega_{c(s)t}, \\ \Omega_{c(s)a} &\equiv \Omega_{c(s)l} - \Omega_{c(s)t}. \end{aligned} \quad (30)$$

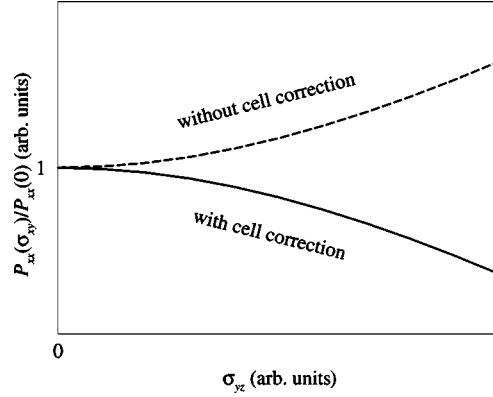


FIG. 4. Influence of the cell correction term on the solid permeability of a vacancy in an uniaxially [011] strained Si crystal: The cell correction predicts a decrease of the diffusion along the x axis, whereas without cell correction, the opposite behavior is predicted.

IV. DISCUSSION

With specific examples in hand, we are now able to discuss certain aspects of the results. First, we will examine the importance of the so-called cell correction [the second term in Eq. (20)]. Second, we will look at the qualitative aspects of the predictions for a very feasible situation—a strained Si film. Since the significant aspect of the present work deals with the deviatoric part of the stress, which produces anisotropic diffusion, we will not be concerned with the hydrostatic (isotropic) part.

The cell correction is very significant in the case of the vacancy in Si. Take, as a specific example, a state of stress where σ_{yz} is the only nonvanishing component, which corresponds to uniaxial stress along a [011] direction. In this state, the permeability tensor has these principal axes: [011], [01 $\bar{1}$], and [100]. The correct answer for the diffusion along the x axis is [from Eq. (28)]

$$P_{xx} \propto \text{sech}(2\beta \Omega_{c(s)a} \sigma_{yz} / 3),$$

whereas without cell correction, we would find

$$P_{xx} \propto \cosh(2\beta \Omega_{c(s)a} \sigma_{yz} / 3)$$

(see Fig. 4). We see from this, that compression along [011] should *suppress* the diffusion along the x axis, whereas without the cell correction, we would have found the opposite behavior. The same is not true for the B-SI pair, Eq. (30), where the cell correction is limited to less than 3% for the case cited.

In both examples given here, a state of deviatoric stress can produce considerable anisotropy in the resulting diffusion. Generally one expects that the anisotropy will be largest at low temperatures and high stresses. Both examples are characterized by having saddle points with $\langle 111 \rangle$ symmetry, which results in a permeability tensor which depends only on the stress components σ_{yz} , σ_{zx} , and σ_{xy} (relative to the cube axes). The anisotropy of the permeability tensor in these two examples is proportional to $\beta \Omega_{c(s)a} \sqrt{\sigma_{yz}^2 + \sigma_{zx}^2 + \sigma_{xy}^2}$ at small stress or small β .

The anisotropy caused by a saddle point with $\langle 111 \rangle$ symmetry is best illustrated by considering a simple state of stress which could be produced in a thin film of Si grown coherently with a substrate of different lattice constant (for example, SiGe). If the growth axis is $\langle 100 \rangle$, then the stress tensor is diagonal in the cube orientation, and the diffusion of vacancies or B-SI pairs is isotropic. However, for a growth direction of $\langle 111 \rangle$, the diffusion perpendicular to the film will be very different than the diffusion within the plane. For vacancy diffusion, the ratio of out-of-plane to in-plane diffusivity is

$$\frac{P_{\perp}}{P_{\parallel}} = 4[1 + 3 \exp(\chi)] \quad (31)$$

with $\chi = -\frac{8}{3}\beta\Omega_{c(s)a}[(C_{11} + 2C_{12})C_{44}]/[C_{11} + 2(C_{12} + C_{44})](\Delta a/a)$ and Δa is the difference in in-plane lattice constants. The anisotropy ratio approaches 4 or 0, depending on the sign of $\Omega_{c(s)a}\Delta a$. For the B-SI pair,

$$\frac{P_{\perp}}{P_{\parallel}} = \frac{4 \exp(\chi)[3 + 8 \exp(\chi)]}{4 + 19 \exp(\chi) + 21 \exp(2\chi)} \quad (32)$$

which approaches 32/21 or 0, depending on the signs.

We emphasize again that the quantities used in the definition of creation energy and volume are entirely local: no reference is made to remote reservoirs as could be done if the bulk were in equilibrium with a free surface, for example. That is, we are not concerned with where the point defect originates. Instead, we are explicitly treating the motion of an existing point defect from one region to another within the bulk, resulting in a change of energy given by differences in the local energies of Eq. (23). The full treatment should include interaction with surfaces and interfaces, and the possibility of equilibration, like in the form of boundary conditions. This is implicit in the ‘‘nonlocal’’ volume of Aziz *et al.*,^{3,4} for example. Many of the related experiments^{3–8} involve diffusion near a free surface or an interface with an oxide or nitride. The results, comparison, and interpretation of those various experiments must take into account the effects of the boundary conditions. For example, the resolution of the apparent contradictions as to stress effects on boron diffusion may lie with the different types of boundaries present in the experiments; certainly such considerations are important. Likewise, the idea of the nonlocal activation volume introduced by Aziz²¹ depends on the location of vacancy sources (such as a free surface). What we present here is only one aspect of the problem — the local bulk diffusion equation in the presence of stress. A proper treatment, including boundary conditions on the differential equations and reactions between diffusing species (for example, B, SI, and B-SI), will be left to a later paper.

V. CONCLUSIONS

In an effort to examine the effect of stress on defect and dopant diffusion in Si, we have had to generalize the results of Dederichs and Schroeder. We have found it convenient in this work to define the solid-state solubility factor and permeability factor (tensor), which are easily applied to the

cases of nonuniform host or interfaces between uniform hosts. The present work shows the proper way to calculate the so-called cell corrections to the permeability tensor for the most general case of intact diffusion in a crystal, and we have worked out two specific examples for Si: a vacancy (with Jahn-Teller distortion), and a B-SI pair. Specific conclusions are drawn regarding the qualitative form of the diffusion in a strained film: If the growth axis of the film is $\langle 100 \rangle$, the diffusion of vacancies or B-SI pairs is isotropic; for $\langle 111 \rangle$ films, however, strong anisotropies can exist between the diffusivity tensor components in growth direction and perpendicular to it, depending on the magnitude of the creation volume anisotropy and the strain. In a subsequent paper,¹⁵ we will obtain the microscopic parameters (volumes) from first-principles electronic structure calculations.

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APPENDIX A: DERIVATION OF SOLUBILITY FACTOR FOR DEGENERATE BASIS

We want to establish the equation of motion in the diffusive limit from the master equation (in reciprocal space),

$$\dot{u}_a = \sum_b \Gamma_{ab}(\underline{k}) u_b / S_b, \quad (A1)$$

where the sum is over states within the cell. $\Gamma(\mathbf{k})$ (a matrix of order N_{states}) has exactly one eigenvalue which approaches zero as $k \rightarrow 0$; the eigenvector for this eigenvalue is $v_a = 1/\sqrt{N_{\text{states}}}$. This is the mode relevant to diffusion. The other $N_{\text{states}} - 1$ eigenvalues are all nonvanishing as $k \rightarrow 0$; they account for the rate of local equilibration among the states within the cell. As far as the diffusive behavior is concerned, the exact values of the faster rates are unimportant. Instead, it is sufficient to look for the leading behavior in k in both space and time. In that limit, Γ is adequately represented by

$$\Gamma_{ab} = \gamma v_a v_b + \Lambda(\delta_{ab} - v_a v_b), \quad (A2)$$

where γ is the relevant eigenvalue (vanishes as $k \rightarrow 0$) and Λ is some finite value that will drop out of the diffusion equation. Defining $r_a \equiv \sqrt{S_a}$, $\chi_a(t) \equiv u_a(t)/r_a$, and $\Phi_{ab} \equiv \Gamma_{ab}/(r_a r_b)$, we can rewrite the master equation [Eq. (A1)] as

$$\dot{\chi}_a = \sum_b \Phi_{ab} \chi_b. \quad (A3)$$

Taking the Laplace transform [$\chi_a(t) \rightarrow \tilde{\chi}_a(s)$] gives

$$\sum_b [s\delta_{ab} - \Phi_{ab}] \tilde{\chi}_b(s) = \chi_a(0). \quad (\text{A4})$$

We only need to solve this set of equations in the limit that $\gamma \ll \Lambda$. We can accomplish this by perturbing the solution away from $\gamma=0$. We first find the eigensystem of $\Phi_{ab}^{(0)} \equiv \Lambda(\delta_{ab} - v_a v_b)/(r_a r_b)$. This matrix has one eigenvalue at 0 and $N_{\text{states}} - 1$ eigenvalues at $\bar{\Lambda} \equiv \Lambda(\sum_a 1/S_a)/N_{\text{states}}$. The eigenvector for the mode with eigenvalue 0 is r_a (this is just the equilibrium condition: $[\chi_a \propto r_a] \rightarrow [u_a \propto S_a]$). Now we can calculate the shift in the 0 eigenvalue due to the perturbation $\Phi_{ab}^{(1)} \equiv \gamma/(N_{\text{states}} r_a r_b)$. The first-order shift in the eigenvalue is $\bar{\gamma} = \sum_{ab} r_a \Phi_{ab}^{(1)} r_b / (\sum_c r_c^2) = \gamma/\bar{S}$, where $\bar{S} \equiv (\sum_a S_a)/N_{\text{states}}$. In the appropriate limit, the inverse of

the matrix $[s\delta_{ab} - \Phi_{ab}]$ is then $(s - \bar{\gamma})^{-1} r_a r_b / (\bar{S} N_{\text{states}}) + (s - \bar{\Lambda})^{-1} [\delta_{ab} - r_a r_b / (\bar{S} N_{\text{states}})]$. This formally separates the short-time behavior (second term) from the long-time behavior (first term), and we can safely drop the second term.

Finally, summing over all states within a cell gives the concentration in the cell, $\tilde{u}(s) \equiv \sum_a \tilde{u}_a(s)$, and the solution (in Laplace space) is $\tilde{u}(s) = (s - \bar{\gamma})^{-1} [\sum_a u_a(0)]$ which is simply a restatement of the diffusion equation in the text.

The appropriate time constant for the diffusion equation is then $\bar{\gamma} = \gamma N_{\text{states}} / (\sum_a S_a)$; or, equivalently, the proper solubility factor in the diffusion equation is $\bar{S} \equiv (\sum_a S_a)/N_{\text{states}}$ [see Eq. (22)].

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