

General Treatment of the Effect of Stress on Defect Diffusion in Si

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1 ABSTRACT

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 Jahn-Teller distorted vacancies in Si, which we predict to show isotropic diffusion for (100) grown uniaxially strained films, but strong anisotropic diffusion for (111) films.

Keywords: Defects, diffusion, pressure effects

2 INTRODUCTION

The effect of stress on dopant diffusion in Si 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 MOS device characteristics. [1], [2]

Most of the theoretical work regarding the effect of stress on diffusion assumes only a hydrostatic state of stress in the substrate. [3] However, stresses caused by dislocations, deposition processes, thermal and geometric effects all add to a complex stress state under a multi-layered 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. [4], [5]

The only fundamental theoretical treatment of diffusion in a general stress field to date is given in the work of Dederichs and Schroeder (D&S), [6] 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 for the first time in order to be able to describe diffusion in more complicated situations like the diamond lattice. Using common as-

sumptions of transition state theory, D&S derived from microscopic lattice hops a continuum diffusivity tensor,

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

where p_h is the jump rate and \underline{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 saddlepoint configuration to the local stress tensor; in this way, the symmetry of the saddlepoint determines, in addition to the stress field, the symmetry of the diffusivity tensor.

The limitations of Eq. (1) are not noted in D&S. In fact, it is easy to find simple examples like diffusion along a zig-zag chain or vacancy diffusion in Si, [9] which illustrate that this equation involves implicit assumptions about the crystal symmetry.

3 DIFFUSION TENSOR

As in D&S, we assume that there are well-defined states (*i.e.*, energy valleys) which the system can occupy and that the rate of jumping from one state to another is controlled by the difference in energy from the initial valley to the saddlepoint. The energy difference, of course, must account for the additional work done against an external stress field. We 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.) We assume throughout that there is no trapping or dissociation of the defects.

3.1 Defects with simple basis

In this case, the state is specified completely by the spatial location of its primitive cell, A . We can describe the system by a concentration c on each site A ,

$$\begin{aligned} p[A \rightarrow B] &= p_0 \exp \left[-\beta \left(\varepsilon_{c(s)}^{[AB]} - \varepsilon_{c(v)}^A \right) \right] \\ &\equiv M_{[AB]}/S_A; \end{aligned} \quad (2)$$

$$M_{[AB]} = M_{[BA]} \equiv p_0 \exp\left(-\beta \varepsilon_{c(s)}^{[AB]}\right), \quad (3)$$

$$S_A \equiv \exp\left(-\beta \varepsilon_{c(v)}^A\right), \quad (4)$$

where $\beta = 1/(k_B T)$ and p_0 is a basic hop rate. Here, 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 one phase in equilibrium with another.)

In a uniform host, the concentration on site A develops in time by

$$\dot{c}_A = -c_A \sum_B p[A \rightarrow B] + \sum_B c_B p[B \rightarrow A]. \quad (5)$$

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

$$c_B = \int_{BZ} u(\underline{k}, t) \exp(i\underline{k} \cdot \underline{R}_B) d^3k. \quad (6)$$

Matching Fourier components of the rate equation then gives

$$\begin{aligned} \dot{u}(\underline{k}, t) &= \gamma(\underline{k}) u(\underline{k}, t) / S; \\ \gamma(\underline{k}) &= \sum_B M_{[0B]} [\exp(i\underline{k} \cdot \underline{R}_{B0}) - 1], \end{aligned} \quad (7)$$

where the site 0 has been chosen arbitrarily and $\underline{R}_{JI} \equiv \underline{R}_J - \underline{R}_I$. 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} ,

$$\gamma(\underline{k}) = - \left(\sum_B M_{[0B]} \underline{R}_{B0} \otimes \underline{R}_{B0} \right) : (\underline{k} \otimes \underline{k}) / 2 + O(k^4) \quad (8)$$

(The dyad $\underline{a} \otimes \underline{b}$ defines a matrix with components $a_i b_j$). The symbol “:” means 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, $\gamma(\underline{k} = 0) = 0$. There are no terms linear in \underline{k} because $\sum_B M_{[0B]} \underline{R}_{B0} = 0$ (in a solid with a simple basis, for every neighbor there is an opposite neighbor which cancels).

When we substitute the series expansion of $\gamma(\underline{k})$ (Eq. (8)) into the equations of motion (Eq. (7)) 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 $\underline{k} = 0$ will have physical significance in the resulting diffusion equation. We therefore define a “solid permeability tensor”

$$\underline{\underline{P}} = -\frac{1}{2} \left. \frac{\partial^2 \gamma(\underline{k})}{\partial \underline{k} \partial \underline{k}} \right|_{\underline{k}=0}, \quad (9)$$

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

$$\underline{\underline{D}} = \frac{1}{S} \sum_B M_{[0B]} \underline{R}_{B0} \otimes \underline{R}_{B0} \quad (10)$$

as obtained by D&S.

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

$$\dot{c}(\underline{x}, t) = \nabla \cdot \left[\underline{\underline{P}}(\underline{x}, t) \cdot \nabla \left(\frac{c(\underline{x}, t)}{S(\underline{x}, t)} \right) \right]. \quad (11)$$

Our notation now is somewhat different than D&S. 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[8]. 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. (4)), the solid permeability factor depends only on the saddlepoint energy (Eqs. (3), (8), and (9)), and the solid diffusivity depends on the migration energy (difference between saddlepoint and valley, Eq. (10)).

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.

3.2 Defects with degenerate 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. 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} .

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

$$\begin{aligned} p[Aa \rightarrow Bb] &= p_0 \exp\left(-\beta(\varepsilon_{c(s)}^{[AaBb]} - \varepsilon_{c(v)}^{Aa})\right) \\ &= M_{[AaBb]} / S_{Aa}; \end{aligned} \quad (12)$$

$$M_{[AaBb]} = M_{[BbAa]} \equiv p_0 \exp\left(-\beta \varepsilon_{c(s)}^{[AaBb]}\right) \quad (13)$$

$$S_{Aa} \equiv \exp\left(-\beta \varepsilon_{c(v)}^{Aa}\right). \quad (14)$$

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

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

Matching Fourier components of the rate equation then gives

$$\begin{aligned} \dot{u}_a(\underline{k}, t) &= \sum_b \Gamma_{ab}(\underline{k}) u_b(\underline{k}, t) / S_b \\ \Gamma_{ab}(\underline{k}) &= \sum_B M_{[0aBb]} e^{i\underline{k} \cdot \underline{R}_{Bba}} - \delta_{ab} \sum_{Bc} M_{[0aBc]}, \end{aligned} \quad (15)$$

where the cell $A = 0$ has been chosen arbitrarily. Note that number conservation is expressed as $\sum_a \Gamma_{ab}(\underline{k} = 0) = 0$.

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 $\underline{k} = 0$ because of number conservation. We expect generally that only one eigenvalue vanishes for $\underline{k} = 0$. This is because a conserved quantity is associated with each vanishing eigenvalue at $\underline{k} = 0$. 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} , then only the slowest mode is relevant. All the other modes are fast and correspond to short-range relaxation among the members of the primitive cell.

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 $\underline{k} = 0$ (and also because we know the eigenvector there—see below), we can use perturbation theory to obtain the permeability. This approach is described in detail elsewhere. [9]

As an 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

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

with $q \equiv \sum_B M_{[01B2]}$, $\underline{Z} \equiv \sum_B M_{[01B2]} \underline{R}_{B201}$, and $\underline{Y} \equiv \sum_B M_{[01B2]} \underline{R}_{B201} \underline{R}_{B201}$. 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

$$\underline{P} = \frac{1}{2} \left[\underline{Y} - \frac{\underline{Z} \otimes \underline{Z}}{q} \right]. \quad (16)$$

Only the first term will be recognized from Eq. (1), whereas the second term arises from the general treatment described above.

Finally, we note that for a degenerate basis, the appropriate solubility factor is the average solubility over all states. This is the form expressed by D&S (implied by their Eq. (36); our notation is somewhat different). The general proof is given in Ref. [9].

4 EFFECT OF STRESS ON DIFFUSION

When a defect is created in a host which is uniform in the absence of stress, 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,

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

where “ 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.

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

$$\varepsilon_{c(v)}^{Aa}(\underline{\sigma}) = \varepsilon_{c(v)}^{Aa}(0) + \underline{\Omega}_{c(v)}^{(a)} : \underline{\sigma} \quad (17)$$

where the stress is evaluated locally. We have assumed here that the 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 $\underline{\Omega}_{c(v)}^{(a)}$ relative to the stress tensor. These values of $\varepsilon_{c(v)}(\underline{\sigma})$ are used to determine the solubility factor S (Eq. (14)).

The creation quantities for the saddlepoint, $[AaBb]$, are defined in an analogous way. The values of $\varepsilon_{c(s)}(\underline{\sigma})$ are used to determine the permeability tensor \underline{P} (Eqs. (9), (13), and (15)).

5 VACANCY IN Si

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

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

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

$$\begin{aligned}\Omega_{ch} &\equiv \Omega_{cl} + 2\Omega_{ct}, \\ \Omega_{ca} &\equiv \Omega_{cl} - \Omega_{ct}.\end{aligned}$$

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

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

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

where $p = Tr[\underline{\sigma}]/3$. 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 saddlepoint configuration has a symmetry axis along a $\{111\}$ direction,[7] and once again the two transverse volumes are equal. Defining

$$\begin{aligned}\underline{\alpha} &\equiv 2\beta\sigma\underline{\Omega}_{c(s)a}/3, \\ \delta &\equiv e^{-(\alpha_{yz} + \alpha_{zx} + \alpha_{xy})} + e^{-(\alpha_{yz} - \alpha_{zx} - \alpha_{xy})} \\ &+ e^{-(\alpha_{yz} + \alpha_{zx} - \alpha_{xy})} + e^{-(\alpha_{yz} - \alpha_{zx} + \alpha_{xy})},\end{aligned}$$

we find the components of the permeability tensor to be

$$\begin{aligned}P_{xx} &= 2e^{-\beta p \Omega_{c(s)h}} [\cosh(2\alpha_{xy}) + \cosh(2\alpha_{zx})] / \delta, \\ P_{xy} &= -2e^{-\beta p \Omega_{c(s)h}} \sinh(2\alpha_{xy}) / \delta.\end{aligned}\quad (18)$$

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.

The anisotropy caused by a saddlepoint 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 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

$$\frac{P_{\perp}}{P_{\parallel}} = 4/(1 + 3 \exp(\chi)) \quad (19)$$

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

6 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, whose previous work was valid only for the case of defect states with non-degenerate basis. The present work shows the proper way to calculate the permeability tensor for the most general case of intact diffusion in a crystal, and we have applied our results to the vacancy in Si. 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 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.

7 ACKNOWLEDGMENTS

We would like to thank Michael Aziz, Wilhelm Wolfer, Stephen Foiles, Neil Carlson, and Michael Masquelier for useful discussions concerning this work.

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