Atomistic Calculation of Oxygen Diffusivity in Crystalline Silicon

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A theoretical calculation of the diffusivity of oxygen in crystalline silicon is presented based on constrained path energy minimization and jump rate theory using an empirical interatomic potential, which was recently developed by us for modeling the interactions between silicon and oxygen atoms. The calculations predict that an oxygen atom jumps in a (110) plane from one bond-center site to another. The saddle point configuration is farther away from the starting configuration than the midpoint along the path. The oxygen diffusivity is predicted as $D = 0.025 \exp(-2.43 \text{ eV}/k_B T) \text{ cm}^2/\text{sec}$ and is in excellent agreement with experiments.

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Oxygen is the primary impurity in commercial silicon crystals grown by the Czochralski process. It is typically introduced into the crystal during solidification from the melt because of the dissolution of the quartz crucible used in the Czochraski puller [1,2]. Most oxygen atoms exist in silicon as interstitial impurities that occupy puckered bond-center sites which bridge two neighboring silicon atoms along the $\langle 111 \rangle$ direction [3]. Because the solubility of oxygen in silicon decreases with decreasing temperature, crystal cooling and thermal annealing lead to the precipitation of oxygen clusters that range in size from several nanometers to tens of micrometers. Small clusters of silicon and oxygen containing up to 20 oxygen atoms are electrically active and are referred to as thermal donors. Larger oxygen precipitates, believed to be microphases of silica, play essential roles in the internal gathering of metallic impurities in industrial processing of silicon. The diffusion of oxygen plays a critical role in the formation of these clusters, and, as a result, the experimental measurement of the diffusivity of oxygen in silicon has received much attention. These experiments can be classified either as oxygen transport measurements or as relaxation frequency measurements. Oxygen transport measurements [4–7] performed at temperatures from 1000 to 1500 K measure oxygen concentration profiles which are fitted by predictions for Fickian diffusion to yield the diffusivity as a function of temperature. Other experiments [8,9] performed at 600 to 700 K use stress-induced dichroism of the 9 μm infrared spectrum peak for oxygen in silicon to measure the frequency of relaxation of oxygen after the release of an imposed stress on the crystal. The diffusion constant is calculated from the relaxation rate by assuming that the relaxation of the dichroism has the same underlying mechanism as the diffusion.

Different experiments have yielded quite different fits of the diffusion coefficient by an Arrhenius expression; these differences have been attributed to the limited temperature range of some experiments and to anomalously fast oxygen diffusion in others, probably involving oxygen-oxygen or oxygen-defect interactions [9]. However, most data from these experiments can be consistently fit by a single expression of the form $D = 0.13 \exp(-2.53 \text{ eV}/k_B T) \text{ cm}^2/\text{sec}$, as pointed out by Mikkelsen [10]. He obtained this expression by fitting to data from six independent experiments. This expression is generally believed to be the intrinsic diffusion constant involving oxygen jumping from a bond-center site to one of the six nearest bond-center sites.

Theoretical investigation of oxygen diffusion in silicon is difficult because of the large diffusion barrier and the complicated nature of mixed bonding between oxygen and silicon atoms. Several theoretical efforts have attempted to calculate the diffusion barrier, but have obtained different results. Needles *et al.* [11] found a barrier of 1.8 eV from supercell calculations using a local density functional theory. A similar calculation by Oshiyama and Saito [12] gave 2.0 eV, while earlier cluster calculations by the same authors yielded 1.2 eV [13]. Snyder and Corbett [14] and Kelly [15] computed 2.3 to 2.5 eV from self-consistent calculations. All these calculations assume that the saddle point configuration for diffusion is in a (110) plane and at the midway between the two bond-center sites. No calculations of the prefactor of the diffusion constant have been reported.

In this Letter, we report calculations of oxygen diffusion in silicon using an empirical potential that has recently been developed for oxygen-silicon interactions [16]. The diffusion path is determined by a series of energy minimization calculations performed with the constraint of a constant cone angle θ between the O-Si bond and the axis connecting the two silicon atoms bonded to the oxygen atom at the initial equilibrium configuration; the angle θ is shown in Fig. 1. The diffusion coefficient is calculated using jump rate theory [17,18].

The empirical interatomic potential for the O-Si system is constructed using the Stillinger-Weber (SW) silicon potential [19] and the silica potential of van Beest, Kramer, and van Santen [20]. Three new components are introduced to describe the charge-transfer and mixed bonding between oxygen and silicon atoms. These ingredients include (a) a charge-transfer function, (b) a bond-softening function, and (c) an ionization energy.

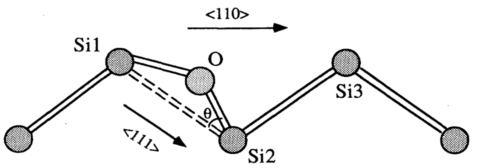

FIG. 1. Schematic diagram showing the constraint angle θ and its relationship to the two silicon atoms (Si1 and Si2) that are bonded to the oxygen atom. The constraint of constant θ does not confine the oxygen atom to the (110) plane.

The parameters are fitted to the structure, vibrational frequency, and formation energy of an oxygen interstitial in silicon. Details of the construction and parameter fitting process for this composite interatomic potential are published in [16], where the potential is also used to study the structural, energetic, and vibrational properties of interstitial-oxygen and vacancy-oxygen clusters, yielding results in good agreement with available experiments on vacancy-oxygen structure. For instance, our calculations [16] predicted that an oxygen atom bonds to a vacancy (V) by forming a Si-O-Si cluster in a (110) plane with two silicon atoms neighboring the vacant site; the V-O cluster has a Si-O-Si angle of 168° and a binding energy of 1.5 eV. Only the form of the potential is described in this Letter; the parameters for the potential and their values are listed in Table I of [16].

The total potential energy of the system is given by

$$E(\{\mathbf{r}_i\}) = \sum_i e_i(q_i) + \sum_{i<j}[\nu_2(i,j) + \phi_{ij}] \sum_{i<j<k} \nu_3(i,j,k)\,, \tag{1}$$

where $\{\mathbf{r}_i\}$ represents the positions of the particles, (i,j,k) are taken over all atoms, and the energy is measured in units of $\varepsilon = 50$ kcal/mol and distances are in units of $\sigma = 2.0951$ Å, as used in the SW potential for silicon [19]. The term ϕ_{ij} in Eq. (1) has the same form as the van Beest potential [20]

$$\phi_{ij} = q_i q_j / r_{ij} + A_{ij}\exp(-b_{ij} r_{ij}) - c_{ij}/r_{ij}^6\,, \tag{2}$$

where q_i is the effective charge on atom i, r_{ij} is the distance between ith and jth atoms, and (A_{ij}, b_{ij}, c_{ij}) are parameters that depend upon the species of interacting atoms. The effective charge on each atom is defined as

$$q_i = \begin{cases} \sum\limits_{j\subset \mathrm{O}} q_o H(r_{ji})\,, & \text{if } i \subset \mathrm{Si}\,, \\ -\sum\limits_{j\subset \mathrm{Si}} q_o H(r_{ji})\,, & \text{if } i \subset \mathrm{O}\,, \end{cases} \tag{3}$$

where $r_{ji} = |\mathbf{r}_j - \mathbf{r}_i|$, q_o is a constant, and the charge-transfer function $H(r)$ is

$$H(r) = \begin{cases} 1, & \text{if } r < r_o\,, \\ \frac{1}{2} + \frac{1}{2}\cos\left(\pi \dfrac{r - r_o}{r_s - r_o}\right), & \text{if } r_0 \le r \le r_s\,, \\ 0, & \text{if } r < r_s\,, \end{cases} \tag{4}$$

with the parameters r_s and r_o. The remaining portion of the two-body term in Eq. (1) is written in a modified form of the corresponding term from the SW potential as

$$\nu_2(i,j) = \begin{cases} g_{ij} f_2(r_{ij}), & \text{if } i \subset \mathrm{Si} \text{ and } j \subset \mathrm{Si}\,, \\ 0, & \text{otherwise}\,, \end{cases} \tag{5}$$

where $f_2(r_{ij})$ is defined exactly as in the SW potential:

$$f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r - a)^{-1}], & \text{if } r < a\,, \\ 0, & \text{if } r \ge a\,, \end{cases} \tag{6}$$

and the constants (A, B, p, q, a) have the same values as in the SW potential. The constant $\{g_{ij}\}$ in Eq. (5) is a charge-dependent bond-softening function,

$$g_{ij} = \begin{cases} \exp\left(\dfrac{1}{q_s}\right)\exp\left[\dfrac{1}{q_i + q_j - q_s}\right], & \text{if } q_i + q_j < q_s\,, \\ 0, & \text{if } q_i + q_j \ge q_s\,, \end{cases} \tag{7}$$

which decreases monotonically from 1 to 0 as the sum of the charges $(q_i + q_j)$ increases from 0 to the cutoff value of q_s. The three-body term has the form

$$\nu_3(i,j,k) = \begin{cases} g_{ij} g_{ik} h(r_{ij}, r_{ik}, \theta_{jik}) + g_{ji} g_{jk} h(r_{ji}, r_{jk}, \theta_{ikj}) + g_{ki} g_{kj} h(r_{ki}, r_{kj}, \theta_{ikj})\,, & \text{if } i,j,k \subset \mathrm{Si}\,, \\ 0\,, & \text{otherwise}\,, \end{cases} \tag{8}$$

where the function $h(r_{ij}, r_{ik}, \theta_{jik})$ is the same as in the SW potential:

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} A\exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}]\left(\cos\theta_{jik} + \frac{1}{3}\right)^2, & \text{if } r_{ij} < a \text{ and } r_{ik} < a\,, \\ 0\,, & \text{otherwise}\,, \end{cases} \tag{9}$$

where θ_{jik} is the angle between $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$, and the constants (λ, γ) have the same values as those in the SW potential.

The ionization energy $e_i(q_i)$ is modeled for each atom by

$$e_i(q_i) = \begin{cases} e_0 \exp[-1/(q_i - q_{\mathrm{Si}}^0)], & \text{if } q_i > q_{\mathrm{Si}}^0, \\ 0, & \text{otherwise}, \end{cases} \tag{10}$$

for silicon atoms ($i \subset$ Si), and

$$e_i(q_i) = \begin{cases} e_0 \exp\left(\dfrac{1}{q_i - q_{\mathrm{O}}^0}\right), & \text{if } q_i < q_{\mathrm{O}}^0\,, \\ 0\,, & \text{otherwise}, \end{cases} \tag{11}$$

for oxygen atoms ($i \subset O$). In these forms, the constants q_{O}^{0} and q_{Si}^{0} are fixed at the values of the charge on the oxygen and silicon atoms, respectively, as given by the van Beest potential for silica.

The diffusion constant is given from jump rate theory [17,18] as an Arrhenius expression

$$D = D_0 \exp(-\Delta E/k_B T), \qquad (12)$$

where ΔE is the diffusion energy barrier, and the prefactor D_0 is determined by

$$D_0 = 2d/gl^2\nu \qquad (13)$$

with d the dimensionally of space, l the elementary jump length, and g the number of equivalent diffusion paths [17]. Since each bond-center site has six nearest neighbors and sixfold degeneracy [3,17,21], $g = 36$. The attempt frequency ν in Eq. (13) is given by [18]

$$\nu = \prod_{i=1}^{3N} \nu_i^e \Big/ \prod_{i=1}^{3N-1} \nu_i^s , \qquad (14)$$

where $\{\nu_i^e\}$ are frequencies of the N-atom system in the equilibrium state and $\{\nu_i^s\}$ are $3N - 1$ frequencies of the system at the saddle point configuration along the diffusion path.

The diffusion path and the energetic barrier are calculated from a series of energy minimization calculations which are performed with the constraint of a constant cone angle θ, as shown in Fig. 1. This constraint allows the oxygen atom to move out of the (110) plane; molecular dynamics simulations reported in [16] predicted an equilibrium value $\theta = 3.5^\circ$ at 297 K, which decreases to 0° as the temperature tends to zero. A cell of 216 silicon atoms with periodic boundary conditions is used to calculate the energy of the constrained system for a given value of θ. The constraint is implemented using the augmented Lagrangian method [22]with the generalized energy function

$$E_c(\{\mathbf{r}_i\}, \lambda) = E(\{\mathbf{r}_i\}) + \lambda g(\mathbf{r}_{20}, \mathbf{r}_{21}) + \tfrac{1}{2} w g^2(\mathbf{r}_{20}, \mathbf{r}_{21}) \qquad (15)$$

minimized by the steepest descent method with w chosen to satisfy the error criteria that the deviation from the desired value of the angle is less than 0.1° and the total contribution of the last two terms in Eq. (15) is $< 2.0 \times 10^{-5}$; the value $w = 1000$ satisfied these conditions. In Eq. (15), λ is the Lagrangian multiplier,

$$g(\mathbf{r}_{20}, \mathbf{r}_{21}) = \mathbf{r}_{20} \bullet \mathbf{r}_{21}/r_{20} r_{21} - \cos\theta \qquad (16)$$

is the constraint function, where $\mathbf{r}_{20}$ is the vector from Si2 to O and $\mathbf{r}_{21}$ is the vector form Si2 to Si1 (see Fig. 1). The value of θ is increased gradually from 0°, and the converged configuration for each θ is used as the initial configuration for the steepest-descent minimization at the next larger value of θ.

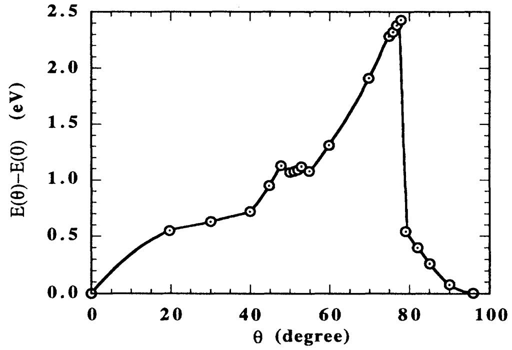

FIG. 2. The computed energy of the system as a function of θ. The saddle point configuration occurs at $\theta = 78^\circ$.

The computed energy is shown in Fig. 2 as a function of θ. The saddle point configuration is predicted to occur at $\theta = 78^\circ$ and corresponds to an energy barrier of $\Delta E = 2.43$ eV. The diffusing oxygen atom reaches the top of energy barrier at a point beyond the midpoint between the two bond-center sites, which corresponds to $\theta = 55^\circ$. The configurations of the oxygen atoms are shown in Fig. 3 for several values of θ. The diffusion path is primarily in the (110) plane. As the oxygen atom moves from the original equilibrium site, one of the Si-O bonds is stretched, but is not broken until the oxygen moves through the saddle point at $\theta = 78^\circ$. Beyond the saddle point, the stretched bond is broken and a new Si-O bond is formed with a silicon atom in the other ⟨111⟩ direction, thus forming a new bridging configuration

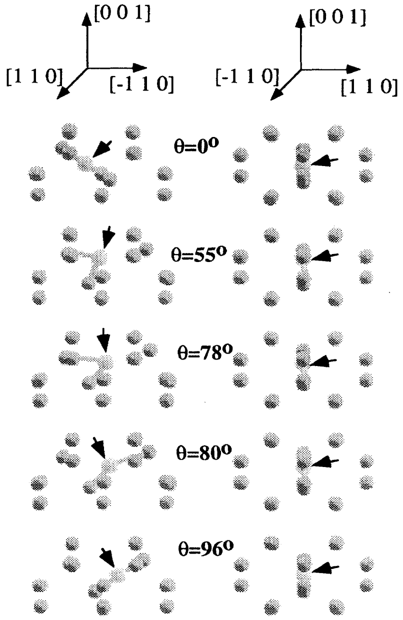

FIG. 3. The configuration of the oxygen and neighboring silicon atoms are shown for $\theta = 0^\circ$, 55°, 78°, 80°, and 96°, respectively, as viewed at the [110] and [−110] directions. The pictures in the right column correspond to the side view of those in the left column, and show that the oxygen atom (in lighter grey and pointed to by an arrow) is in the (110) plane.

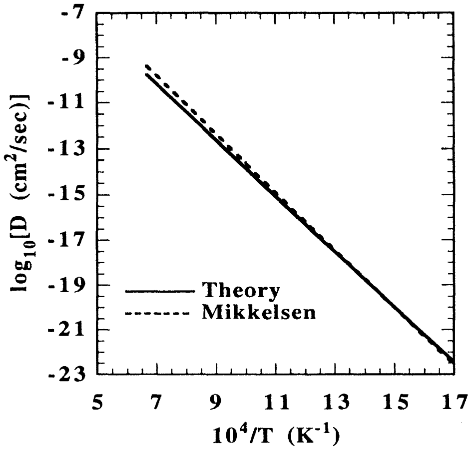

FIG. 4. Comparison of the calculated expression for the oxygen diffusivity with Mikkelsen's best fit to the data [10].

for the oxygen. In the diffusion process, only the three silicon atoms involved in the O-Si bonds are significantly displaced from their lattice positions.

The frequencies ν_i^e and ν_i^s are calculated by direct diagonalization of the Hessian matrix of the system at the equilibrium and saddle point configurations. The Hessian is calculated using a centered finite difference method with a step size in the coordinate positions of 3×10^{-4} in the SW units. The jump frequency is computed as $\nu = 11.5$ THz, which is of the typical order of magnitude of attempt frequencies for interstitial impurities [17,23]. In the equilibrium state, the distance between two nearest-neighbor bond-center sites is $l = 1.91$ Å. Using Eqs. (12) and (13), the diffusion constant is predicted as

$$D = 0.025 \exp(-2.43 \text{ eV}/k_B T) \text{ cm}^2/\text{sec}, \qquad (17)$$

which is plotted in Fig. 4 together with the experimental fit of Mikkelsen [10], $D = 0.13 \times \exp(-2.53 \text{ eV}/k_B T) \text{ cm}^2/\text{sec}$. The agreement is excellent although the prefactors and energy barriers are different. The difference is well within range of experimental error in the data. Indeed, Newman, Tucker, and Livingston [9] reported an Arrhenius fit of the form $D = 0.02 \exp(-2.42 \text{ eV}/k_B T) \text{ cm}^2/\text{sec}$ to data from an experiment relating to the kinetics of oxygen precipitation. Their expression is virtually the same as ours.

In summary, we have presented a theoretical calculation of oxygen diffusion in silicon crystal using an empirical potential constructed to describe the complicated charge-transfer and bond-formation process between silicon and oxygen atoms. We found the oxygen jumps from a bond-center site to another bond-center site along a path in the (110) plane. Contradictory to current belief, the saddle point configuration is not predicted to be exactly at the midpoint between these sites, because the oxygen atom has to break a Si-O bond before it is able to form a new bridging configuration with the other silicon atom. The diffusion coefficient predicted using this saddle point configuration and jump rate theory is in excellent agreement with experiments. Our calculations demonstrate that it is possible to model accurately intrinsically quantum processes using classical potential by introducing components which effectively capture the main features of the processes. In the specific case of oxygen in silicon, the main features are charge transfer and bond formations which are described, respectively, by the charge-transfer function and the bond-softening function in our potential.

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[1] W. Zulehner and D. Huber, in *Crystals: Growth, Properties and Application,* edited by J. Grabmaier (Springer, New York, 1982), Vol. 8.
[2] R. A. Brown, AIChE J. **34**, 881 (1988); T. A. Kinney and R. A. Brown, J. Crystal Growth **132**, 551 (1993).
[3] J. W. Corbett, R. S. McDonald, and G. D. Watkins, J. Phys. Chem. Solids **25**, 873 (1964).
[4] J. C. Mikkelsen, Jr., Appl. Phys. Lett. **40**, 336 (1982).
[5] S. T. Lee and D. Nichols, Appl. Phys. Lett. **47**, 1001 (1985).
[6] J. Gass, H. H. Muller, H. Stussi, and S. Schweitzer, J. Appl. Phys. **51**, 2030 (1980).
[7] Y. Itoh and T. Nozaki, Jpn. J. Appl. Phys. **24**, 279 (1985).
[8] M. Stavola, J. R. Patel, L. C. Kimerling, and P. E. Freeland, Appl. Phys. Lett. **42**, 73 (1983).
[9] R. C. Newman, J. H. Tucker, and F. M. Livingston, J. Phys. C **16**, L151 (1983).
[10] J. C. Mikkelsen, Jr., Mater. Res. Soc. Symp. Proc. **59**, 19 (1986).
[11] M. Needels, J. D. Joannopoulos, Y. Bar-Yam, S. T. Pantelides, and R. H. Wolfe, Mater. Res. Soc. Symp. Proc. **209**, 103 (1991).
[12] A. Oshiyama and M. Saito, in *Defect Control in Semconductors,* edited by K. Sumino (Elsevier Science Publishers, North-Holland, 1990).
[13] M. Saito and A. Oshiyama, Phys. Rev. B **38**, 10711 (1988).
[14] L. C. Snyder and J. W. Corbett, Mater. Res. Soc. Symp. Proc. **59**, 207 (1986); **104**, 179 (1988).
[15] P. J. Kelly, Mater. Sci. Forum **38-41**, 269 (1989).
[16] Z. Jiang and R. A. Brown, Chem. Eng. Sci. **49**, 2991 (1994).
[17] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949); K. Weiser, Phys. Rev. **126**, 1427 (1962).
[18] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957); J. H. Harding, Rep. Prog. Phys. **53**, 1403 (1990).
[19] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[20] B. W. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).
[21] C. Haas, J. Phys. Chem. Solids **15**, 108 (1960).
[22] D. M. Greig, *Optimisation* (Longman, London, 1980).
[23] V. Milman, M. C. Payne, V. Heine, R. J. Needs, J. S. Lin, and M. H. Lee, Phys. Rev. Lett. **70**, 2928 (1993).