

Coupled-Barrier Diffusion: The Case of Oxygen in Silicon

Madhavan Ramamoorthy and Sokrates T. Pantelides

Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37209

(Received 9 August 1995)

Oxygen migration in silicon corresponds to an apparently simple jump between neighboring bridge sites. Yet extensive theoretical calculations have so far produced conflicting results and have failed to provide a satisfactory account of the observed 2.5 eV activation energy. We report a comprehensive set of first-principles calculations that demonstrate that the seemingly simple oxygen jump is actually a complex process involving coupled barriers and can be properly described quantitatively in terms of an energy hypersurface with a “saddle ridge” and an activation energy of ~ 2.5 eV. Earlier calculations correspond to different points or lines on this hypersurface.

PACS numbers: 66.30.Jt, 31.15.Ar, 61.72.-y, 81.60.Cp

Oxygen in silicon has long been known to occupy a bridge position between neighboring Si atoms, with an Si-O-Si configuration similar to those in SiO₂ [1,2]. Its diffusion, measured to have an activation energy of 2.5 eV [3], is generally believed to consist of simple jumps between neighboring bridge positions on the (110) plane defined by the corresponding Si-Si bonds (Fig. 1). In terms of the angle θ_O defined in Fig. 1, the midpoint of the jump is at $\theta_O = 90^\circ$.

Most calculations to date [4–8] assumed such a simple adiabatic jump, with reflection symmetry about the vertical axis shown in Fig. 1. Thus, the saddle point was assumed to have the O atom at $\theta_O = 90^\circ$ and the central Si atom at $\theta_{Si} = 90^\circ$. The remaining degrees of freedom and the positions of the other Si atoms were determined by total-energy minimization. The resulting total energy, measured from the energy of the equilibrium configuration, represents the adiabatic activation energy for diffusion. Some authors [4,5] reported activation energies around 2.5 eV, while others [6–8] reported smaller values ranging from 1.2 to 2.0 eV.

In Ref. [8], Needels *et al.* found a value of 1.8 eV and attributed the discrepancy with experiment to dynamical phenomena, i.e., the neighboring Si atoms do not relax fully along the O trajectory. They reported model dynamical calculations for a “generic” nonadiabatic path in which the O atom was given an initial “kick,” i.e., an initial velocity corresponding to a kinetic energy of 2.0, 2.3, or 2.7 eV. They found that when the kick energy was < 2.5 eV, the O atom went past the saddle point but then returned to the original bridge position. When the kick was > 2.5 eV the O atom migrated to the next bridge site. They concluded that their results suggested that dynamical effects are important in O migration, but did not constitute definitive evidence.

In a recent paper, Jiang and Brown (JB) [9] sought to resolve the issue by exploring the entire migration path. They performed total-energy minimizations by stepping the oxygen atom from one bridge site to the next. They found that the total energy attains a value of only ~ 1.2 eV at $\theta_O = 90^\circ$, but then keeps rising to a maximum value

(saddle point) of ~ 2.5 eV at $\theta_O = 113^\circ$. In addition, they computed the diffusion constant and found it to agree very well with experiment over 12 decades. They concluded that the saddle point of O migration is past the midpoint of the path and that their results account for all the experimental data.

At first glance, JB’s results account nicely for the experimental data without the need to invoke dynamical effects. Nevertheless, the pronounced asymmetry of JB’s total-energy profile about $\theta_O = 90^\circ$ raises a serious question: If the global minimum of the total energy was indeed obtained at each point of the O path, the energy profile would be symmetric about $\theta_O = 90^\circ$. Clearly, JB’s minimization procedure yielded a secondary minimum for each $\theta_O > 90^\circ$, not the global minimum. The energy at the global minimum for $90^\circ + \alpha$ is by symmetry equal to that at $90^\circ - \alpha$. If an energy profile were constructed using global minima along the entire path, it would have a maximum of only 1.2 eV at $\theta_O = 90^\circ$. This value would be in poor agreement with experiment. We conclude that there is still no satisfactory account of the observed 2.5 eV

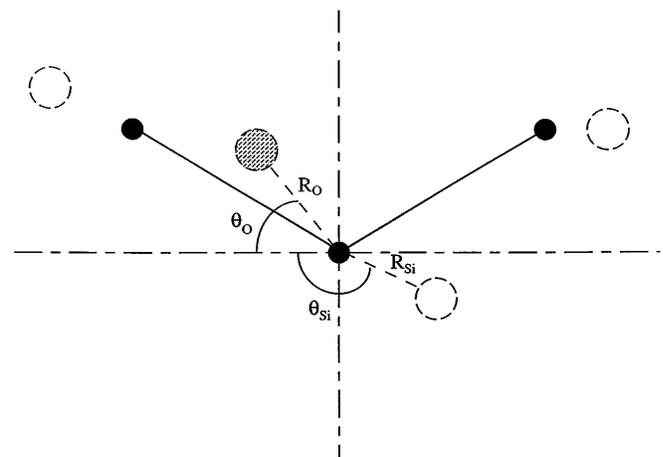


FIG. 1. The geometry of O migration in a (110) plane. The solid dots are the nominal positions of Si atoms in the perfect crystal. The open circles show the positions of the Si and O atoms in the equilibrium configuration.

activation energy, or of the mutually conflicting theoretical results published so far on oxygen diffusion in silicon.

In this paper, we report a series of first-principles total-energy calculations which show that the process of O migration is far more complex than has been recognized so far, but is still adiabatic. During the migration process, *both* the O atom and the central Si atom perform jumps and face large barriers. As a result, a quantitative description of the process requires a calculation of the total-energy hypersurface as a function of the positions of both atoms. We will show slices of this hypersurface that reveal a “saddle ridge” in multidimensional space. The migration process is adiabatic and occurs along a multiplicity of paths over this ridge with a predominant barrier of ~ 2.5 eV. Finally, we find that the results of earlier authors correspond to different points or lines on the hypersurface.

We performed calculations using density functional theory and the local-density approximation for exchange and correlation, using the form for the exchange-correlation potential given by Ceperley and Alder [10]. The ultrasoft pseudopotentials of Vanderbilt [11] were used for Si and O. These pseudopotentials have been thoroughly tested in several extensive investigations [12–14]. The calculations employed a plane wave basis set and converged results were obtained with an energy cutoff of 25 Ry. A bcc supercell with 32 Si atoms and one O atom was used. Each structure was relaxed until the force on each atom was less than 0.5 eV/Å. All calculations were first done with one special k point at $(0.5, 0.5, 0.5)$ in the irreducible Brillouin zone [15]. The key calculations were repeated with two k points at $(0.75, 0.25, 0.25)$ and $(0.25, 0.25, 0.25)$ [15]. The energy differences changed at most by about 0.2 eV, with all the qualitative results obtained with one k point being unchanged. Hence, the results with one k point were taken to be converged with respect to k -point sampling, and used in all the figures in this paper.

Our results for the equilibrium configuration of O, shown schematically in Fig. 1, are in agreement with earlier work [2]. We find a very flat minimum at $\theta_O \sim 55^\circ$. The Si-O bond length is 1.6 Å, the Si-Si length is 3.2 Å (compare with the value of 2.35 Å in bulk silicon), and the Si-O-Si bond angle is $\sim 150^\circ$. The angle θ_{Si} is also $\sim 150^\circ$. For our purposes here, the key point is that the central Si atom is well to the right of the vertical symmetry axis (see Fig. 1). As the O migrates from the left bridge position to the one on the right, the central Si needs to move from the right to the left, specifically from $\theta_{Si} \sim 150^\circ$ to $\theta_{Si} \sim 30^\circ$. We will see below that *this swing of the central Si atom controls the dynamics of the oxygen migration because the Si atom has to overcome a barrier*.

We demonstrate this key result in Fig. 2, where we plot the total energy of the system as a function of θ_{Si} when the O atom at $\theta_O = 90^\circ$ [16]. For each θ_{Si} , the total energy was minimized with respect to R_O , R_{Si} (see Fig. 1), and the positions of the other Si atoms. We

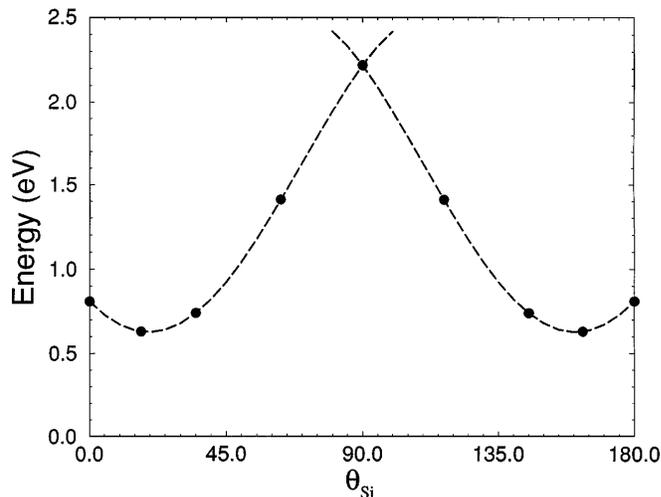


FIG. 2. The total-energy variation of the system, as a function of θ_{Si} when the O atom is at $\theta_O = 90^\circ$. The zero of the energy in this and in subsequent plots is taken as that of the equilibrium configuration.

see that it costs only 0.6 eV to place the O atom at the midpoint if the central Si atom is allowed to relax freely either to the left or to the right [17]. As we saw earlier, as the O atom moves from the left bridge position to the one on the right, the central Si atom needs to swing from the right side to the left side. Figure 2 shows that, with $\theta_O = 90^\circ$, the total barrier is 2.2 eV. This barrier corresponds to the two atoms crossing the midpoints of their respective paths at the same time. It could be argued that this configuration constitutes the saddle point, as was assumed in several previous investigations [4–8]. The total barrier of ~ 2.2 eV is indeed in good agreement with the experimental value. This simple result, however, belies an enormous complexity which we unravel below. The basis of this complexity is that the O atom and the central Si atom need not pass through the midpoints of their paths at the same time.

The above analysis makes it clear that O migration needs to be described in at least a two-dimensional space defined by θ_O and θ_{Si} because the central Si atom also must climb a barrier. This barrier, however, is not simple, but, as shown in Fig. 2, has a cusp at $\theta_{Si} = 90^\circ$, indicative of a Jahn-Teller-like instability with two symmetric total-energy manifolds. These two manifolds correspond to the central Si atom being to the left or the right of the symmetry axis, being bonded to the respective Si atom on the left or the right. For values of θ_O other than 90° , the two manifolds are not symmetric. In Fig. 3 we trace the evolution of the two total-energy manifolds for a sequence of θ_O values starting with the O atom near its equilibrium bridge position on the left of the vertical symmetry axis (bottom panel). The central Si atom is on the right side of the axis (the lower-energy manifold). As the O atom progresses along its path (higher panels in Fig. 3), the central Si atom stays in the right manifold. At $\theta_O = 90^\circ$, the two manifolds cross and the central Si atom can switch

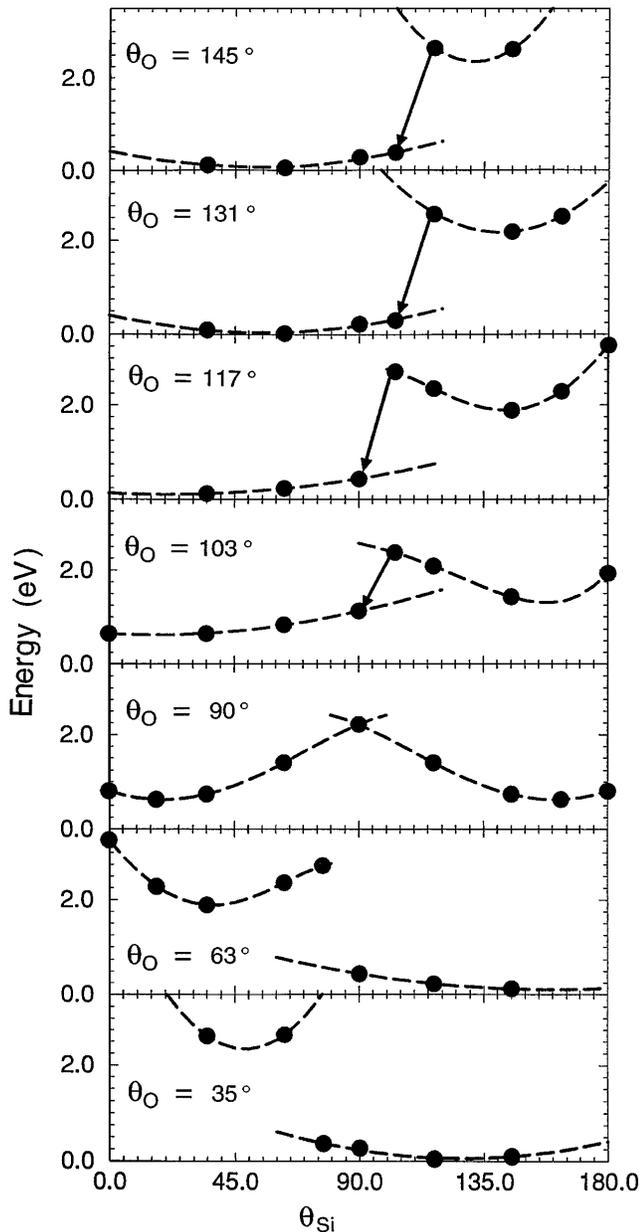


FIG. 3. A series of plots indicating the variation of the total energy as a function of θ_{Si} for several values of θ_O .

manifolds and swing over to the left of the axis, so that both the O atom and the central Si atom can head for their final destinations. The total barrier for this process is 2.2 eV.

There are additional possibilities, however. The O atom may overshoot the midpoint of its jump without the central Si atom swinging over. The relevant total-energy manifolds are shown in the upper panels of Fig. 3. The central Si atom is now in the high-energy manifold, stuck on the “wrong” side of the vertical axis. Even though the manifolds do not cross, the central Si atom is stable in the higher-energy manifold only up to a certain value of θ_{Si} , marked by the solid arrows. At those points, the calculations show that the central Si atom collapses to the lower-energy manifold, i.e., swings over to the left side of the axis. No matter how much the O atom overshoots

(i.e., any of the top four panels), the total energy needed for the central Si atom to swing over is of order 2.3–2.7 eV. In other words, the O atom and the central Si atom *need not move in concert and be at the midpoints of their respective paths at the same time*. They can move independently and still face a net barrier of ~ 2.5 eV.

The multiplicity of paths is best illustrated with a two-dimensional plot of the total energy as a function of θ_O and θ_{Si} . For clarity, we show only one of the two manifolds at each pair (θ_O, θ_{Si}) , namely, the one corresponding to coupled adiabatic migration. The surface was obtained by interpolating through a sizable number of calculated points. Note the flat regions corresponding to the two equilibrium configurations and the steep drops that correspond to the regions of the solid arrows in Fig. 3. We see that there is a “saddle ridge” with a net energy of ~ 2.5 eV over a considerable range. At the high symmetry point on the ridge ($\theta_O = 90^\circ, \theta_{Si} = 90^\circ$), the total energy is somewhat lower, ~ 2.2 eV, but this smaller value corresponds to a small fraction of all possible migration paths over the ridge (the resolution of the figure is limited by the complexity of the surface near the ridge). There are two classes of paths: those in which the O atom overshoots the midpoint of its path with the central Si atom trailing and those in which the central Si atom goes over the midpoint of its path first with the O atom trailing. Along all these paths the distance between the O atom and the central Si atom is ~ 1.7 Å. Thus, the O-Si bond acts like a pogo stick that faces a net barrier of ~ 2.5 eV no matter how it turns as it attempts to change its tilt from the left to the right.

The collapse from one manifold to the other indicated by the solid arrows in Fig. 3 (steep drops in Fig. 4) was intriguing enough to merit further investigation. The plots in Figs. 3 and 4 were constructed by picking θ_O and θ_{Si} and then letting both the O atom and the central Si atom move *radially* until the energy was minimized. It turns out that the two manifolds shown in Fig. 3 correspond to two fairly distinct regions of R_{Si} values. We explored R_{Si} values between these two regions and found that for each θ_{Si} the energy as a function of R_{Si} has two minima with a barrier that prohibits the central Si atom’s motion from one minimum to another, corresponding to a switch between the two energy manifolds. At the critical θ_{Si} value (solid arrow in Fig. 3), this barrier vanishes and the collapse occurs. The evolution of this radial barrier is also quite intriguing and will be discussed further in a longer article. In fact, a complete description of O migration requires the total energy as a function of four coordinates on the (110) plane: $(\theta_O, \theta_{Si}, R_O, R_{Si})$. Figures 3 and 4 represent slices through this hypersurface.

We now turn to examine the earlier theoretical work in light of the present work. The major point is that all earlier investigators did not recognize the important role of the central Si atom in the migration process. Nevertheless, we can map their results on Fig. 4. References [4–8] assumed that the saddle point is at $\theta_O = \theta_{Si} = 90^\circ$, shown as a dot in Fig. 4. Our value for this point lies

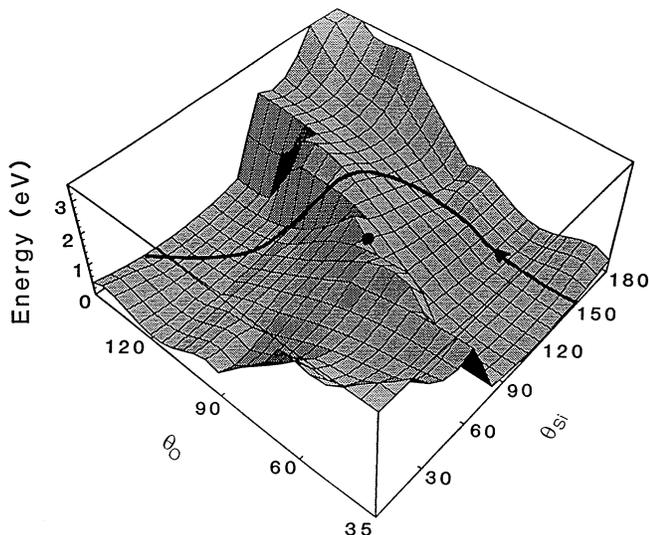


FIG. 4. The total-energy variation as a function of θ_O and θ_{Si} . The central dot and the hand-drawn path (in the direction of the arrowhead) are discussed in the text.

in the middle of the range of earlier theoretical results (1.8–2.5 eV) [18]. This spread in part reflects the fact that calculations involving oxygen are computationally extremely demanding. The important point to note is that in Fig. 4, the paths that contain the point $\theta_O = \theta_{Si} = 90^\circ$ constitute a small portion of the phase space of all paths going over the ridge. Most of the ridge is somewhat higher, ~ 2.5 eV, close to the observed activation energy.

Figure 4 also clarifies the “kick” simulations of Needels *et al.* [8] and JB’s calculations. Both calculations correspond to the path shown by the hand-drawn line in Fig. 4. Needels *et al.* gave a high kinetic energy to the O atom, whereas JB stepped the O atom gradually. In both cases, the O atom crossed the midpoint of its path before the central Si atom did. In JB’s case, the central Si atom crossed over when $\theta_O \sim 115^\circ$. In the case of Needels *et al.*, for kick energies < 2.5 eV, the O atom had to turn back because the central Si atom still faced a barrier and could not cross over. In hindsight, one should have given a kick to the central Si atom. In any case, this is not a very likely path because in reality both the O atom and the central Si atom are vibrating about their equilibrium positions, attempting to overcome their respective barriers. As the ridge has roughly a constant height over a considerable range, any point at an energy of ~ 2.5 eV may be fairly representative of the entire ridge. This might explain the good agreement obtained by JB for the diffusion constant with experiment.

Finally, Needels *et al.* [8] noticed the formation of a metastable configuration at the endpoint of the O path, when the kick was 2.7 eV. The present work shows that this configuration occurs in the right-hand manifold shown in the upper panels of Fig. 3. The metastable configuration is created *during* the migration process for all paths that do not cross $\theta_O = \theta_{Si} = 90^\circ$. Contrary to the findings of Needels *et al.* [8], this configuration

collapses to the equilibrium configuration at the end of the migration process.

In summary, we have shown that the total-energy variation during O migration is a very complex hypersurface in a multidimensional space. We have shown slices of this hypersurface along some relevant coordinates, revealing seemingly disconnected manifolds. We believe that the calculations we have done so far have captured essentially all of the very complex physics of the seemingly simple O jump in bulk Si. Our results suggest that such complexity is likely to be present whenever migration of an impurity involves bond breaking and rebonding with different host atoms.

This work was supported in part by Office of Naval Research Grant No. N00014-95-1-0906. Supercomputing time was provided by the Pittsburgh Supercomputing Center under Grant No. DMR950001P.

- [1] J. W. Corbett, R. S. Mac Donald, and G. D. Watkins, *J. Phys. Chem. Solids* **25**, 873 (1964).
- [2] E. Martinez, J. Plans, and F. Yndurain, *Phys. Rev. B* **36**, 8043 (1987).
- [3] J. C. Mikkelsen, Jr., *Appl. Phys. Lett.* **40**, 336 (1982).
- [4] L. C. Snyder and J. W. Corbett, *Mater. Res. Soc. Symp. Proc.* **59**, 207 (1986).
- [5] P. J. Kelly and R. Car, *Phys. Rev. B* **45**, 6543 (1992).
- [6] M. Saito and A. Oshiyama, *Phys. Rev. B* **38**, 10711 (1988).
- [7] A. Oshiyama and M. Saito, in *Defect Control in Semiconductors*, edited by K. Sumino (Elsevier Science Publishers, North-Holland, Amsterdam, 1990).
- [8] M. Needels, J. D. Joannopoulos, Y. Bar-Yam, S. T. Pantelides, and R. H. Wolfe, *Mater. Res. Soc. Symp. Proc.* **209**, 103 (1991).
- [9] Z. Jiang and R. A. Brown, *Phys. Rev. Lett.* **74**, 2046 (1995).
- [10] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [11] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [12] R. D. King-Smith and D. Vanderbilt, *Phys. Rev. B* **49**, 5828 (1994).
- [13] Feng Liu, S. H. Garofalini, R. D. King-Smith, and D. Vanderbilt, *Phys. Rev. B* **49**, 12528 (1994).
- [14] M. Ramamoorthy, D. Vanderbilt, and R. D. King-Smith, *Phys. Rev. B* **49**, 16721 (1994).
- [15] D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- [16] In all the calculations reported in this paper, we confined the motion of the O atom and the central Si atom to the (110) plane. Our test calculations showed that, in agreement with Ref. [9], the energy rises if either atom is allowed to go off the (110) plane.
- [17] In the symmetrical configuration $\theta_O = \theta_{Si} = 90^\circ$, O is forced to have three bonds, with each Si-O-Si bond angle about 85° . In the configurations corresponding to the minima in Fig. 2, there are only two Si-O bonds with lengths ~ 1.7 Å and the magnitude of the Si-O-Si bond angle equal to 127° , significantly closer to equilibrium values.
- [18] The value 1.2 eV of Ref. [6] was replaced by a more accurate value of 2.0 eV by the same authors in Ref. [7].