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Oxygen-induced broken-bond defect in silicon

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The electronic and geometric structure of a recently proposed oxygen-related defect in silicon is studied using a precise *ab initio* quantum-molecular-dynamics method based on local-density-functional theory, nonlocal pseudopotentials, and the supercell approximation. This defect is a metastable configuration of interstitial oxygen in Si (Si:O_i), and it is closely related to a vacancy-interstitial pair. This defect has a relatively low formation energy despite the presence of a silicon broken bond. A simple and straightforward procedure is used to identify the static barrier for the formation of an intimate vacancy-interstitial pair in silicon and the static barrier for the recombination of the broken bond in metastable Si:O_i. The similarities in geometric configurations for both cases are explored to introduce a mechanism for the creation of intimate vacancy-interstitial-like defects in silicon.

I. INTRODUCTION

In pure crystalline silicon, broken bonds can be created by native defects such as vacancies or interstitials. These broken bonds are very reactive and they usually trap carriers. Although it is very difficult to measure the formation energy of native defects directly, it is believed[1] that the creation of this kind of center is energetically very costly.

From diffusion experiments, a related quantity, the activation energy for self-diffusion, Q, can be obtained. This quantity, Q, is equal to the sum of the relevant defect's formation and migration energies. In silicon, Q is in the range from 3.5 to 5 eV. Unfortunately, these measurements do not directly identify the native defect mediating the self-diffusion process. Alternatively, Dannefaer, Mascher, and Kerr[2] report positron annihilation experiments from which they extract a vacancy formation energy of 3.6±0.2 eV. The most successful method for isolated vacancy production is radiation damage[3] at cryogenic temperatures. The damage process is induced by high-energy electrons (1–3 MeV) at 4 K. The primary process is the formation of a Frenkel pair (vacancy-interstitial) as the recoiling silicon atom is dislodged into a nearby interstitial site.

Theoretically, the formation energies for the isolated vacancy and self-interstitial have been calculated from first principles. Total-energy pseudopotential calculations based on Green's function[4] and supercell techniques[5] exhibit very good agreement. These calculations show that the isolated vacancy and interstitial have comparable formation energies, both on the order of 4 eV. It is interesting to note, however, that the energetics of the intimate vacancy-interstitial (V-I) pair have not yet been explored. It is one of the goals of this paper to show that the intimate Frenkel pair is *not* a stable defect in pure silicon.

In undoped silicon, the presence of an impurity could induce or stimulate the formation of silicon broken bonds. In such a case, dangling bonds could be created with a rather low formation energy. In the present work, we intend to study a recently proposed interstitial oxygen defect in silicon. Based on our results, we discuss the possibility of having oxygen as an actuator for broken-bond formation in silicon.

Oxygen is one of the most studied impurities in crystalline silicon due to the following facts: (i) In device-quality Czochralski silicon samples, oxygen is present in concentrations as high as 10^{18} cm^{-3}, and (ii) oxygen can give rise to several different types of defects. In the interstitial position (its stable configuration), oxygen atoms form a bent-bridge bond between two silicon atoms giving rise to Si-O-Si chains similar to those found in SiO_2. After annealing, O atoms can segregate into electrically active complexes called thermal donors (TD). The exact atomic configuration of these TD defects is not yet completely understood. After irradiating the sample, oxygen can be found as an off-center substitutional impurity in silicon, the so-called A center.

In recent years, advances in *ab initio* computational procedures[6–9] have allowed oxygen-related centers in semiconductors to be studied in a very reliable fashion. The application of such an approach to the migration barrier of interstitial oxygen in Si, by Needels *et al.*[10] lead to a variety of new predictions. The authors obtain a value of 1.8±0.1 eV for the adiabatic (static) barrier and propose that dynamical effects could play an important role in the process. From dynamical simulations, they have verified that the oxygen atom could move faster than the adjacent silicon atoms can relax. A dynamical migration barrier in the range 2.3–2.7 eV is then obtained, in good agreement with the experiment. Furthermore, they propose a metastable configuration for interstitial O in silicon. In this configuration, the O—Si bonds are ~5% longer than in the bridge (stable) configuration, the bond angle is reduced and, even more interestingly, a silicon broken bond is present. The authors have called attention to the similarities between the metastable configuration and a *V-I* pair in pure silicon. A striking aspect of the defect is its very low formation energy (only 1.2 eV) as compared to the formation energy (~8 eV) of a *V-I* pair in silicon.

In the present work, we use a straightforward procedure to obtain the adiabatic barrier of a general defect defects and apply this procedure to investigate the existence of a barrier to create an intimate *V-I* pair in Si. We also study the electronic structure of the Si:O_i defect and determine the adiabatic energy barrier for the reconstruction of the broken bonds in the metastable Si:O_i. All calculations were performed within a quantum-molecular-dynamics approach, based on local-density-functional, pseudopotential, and supercell approximations.

II. RESULTS AND ANALYSIS

In this section we present the results of our calculations on the vacancy-interstitial pair in silicon and on the metastable Si:O_i defect. We begin with a brief description of the technical details of our calculations.

Our calculations were performed within density-functional theory.[11] The exchange-correlation functional was approximated as a local-density functional with Ceperly-Alder parametrization[12] of the Perdew-Zunger[13] form. We have employed separable norm-conserving nonlocal pseudopotentials[14] which were created using the technique of Rappe *et al.*[8] and 32-atom bcc supercells to deal with the defects in the context of Bloch's theorem. The cutoff energy for the plane-waves basis set was 40 Ry in the case of Si:O_i and 12 Ry for the native defect. In all calculations, the *k*-point summations were restricted to the Γ point. Relaxation of the electronic and nuclear coordinates was performed using the modified Car-Parrinello molecular-dynamics[9] algorithm of Payne, Needels, and Joannopoulos.[7]

To determine the lowest barrier path for an atom *X* to move from a point *A* to *B* we use the following very simple and fairly general procedure. A vector **v** is drawn from *A* to *B* and normal planes crossed by **v** are defined by $a\mathbf{v}$ ($0 \leq a \leq 1$). Given a value of *a*, the forces on *X* are projected onto the $a\mathbf{v}$ plane, so that *X* is constrained to relax in that plane while all other atoms relax without restriction. By repeating this procedure for several distinct values of *a*, one obtains the desired energy barrier path. This technique was used to identify the lowest energy barrier for both, the intimate vacancy-interstitial pair in Si, and the dangling-bond reconstruction in metastable Si:O_i. An illustration of this procedure is shown in Fig. 1.

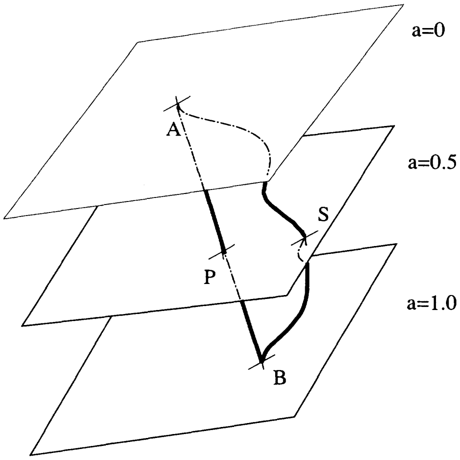

FIG. 1. Illustration of the procedure to determine the lowest barrier path that an atom *X* has to overcome to move from *A* to *B*. The vector *AB* defines the family of normal planes crossed by *X* during its movement. Each plane is characterized by the scalar *a* and cases where $a=0$, 0.5, and 1.0 are schematically presented. The lowest energy barrier path crosses the $a=0.5$ plane at *S* while the vector *AB* crosses the same plane at *P*.

A. Intimate vacancy-interstitial pair in silicon

To create an intimate vacancy-interstitial pair in pure crystalline silicon, an atom (Si*) must be displaced along the [111] direction. Thus, **v** is the vector parallel to [111] whose length is exactly a Si—Si bond length. Consequently, $a=0$ corresponds to the plane that contains the normal Si* position and $a=1$ corresponds to the plane where the tetrahedral (T_d) interstitial lies. In order to determine the adiabatic barrier to create the *V-I* pair, a series of first-principles total-energy calculations were performed. The procedure allows every atom to relax (including Si*), therefore the adiabatic barrier can be obtained.

The energy variation (ΔE) due to the presence of Si* in the plane $a\mathbf{v}$ was computed and it is presented in Fig. 2.

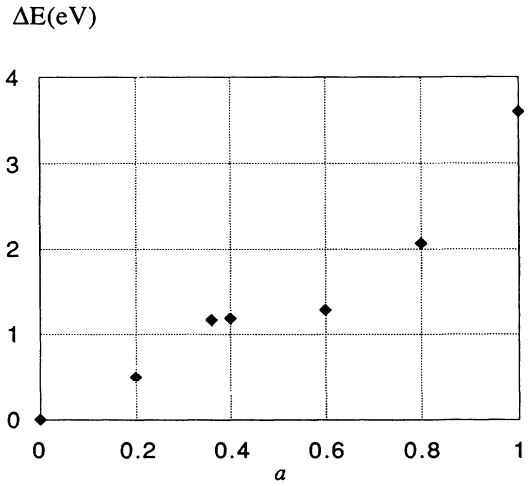

FIG. 2. Energy variation of pure silicon as a function of the displacement of a Si atom from its normal site ($a=0$) towards the tetrahedral interstitial site ($a=1$) corresponding to the creation of an intimate Frenkel pair.

The most striking features in this figure are (i) there is no barrier for the recombination of the intimate pair *V-I*, so this is *not* a stable defect in silicon, and (ii) when Si* is located in the region of space where $0.3 < a < 0.5$ the energy changes very slowly.

Our calculations do not predict the existence of an energy barrier, thus a vacancy and an interstitial *cannot* co-exist if they are separated by only one bond length. The energy behavior in the region of space where $0.3 < a < 0.5$ can be easily understood from geometrical considerations. When $a \sim 0.4$, Si* and its three nearest neighbors lie almost in the same plane. These neighbors form an equilateral triangle with Si* at its center so that the forces these atoms exert on Si* tend to cancel out. The next-nearest neighbors are more than 3 Å away and do not interact very strongly with Si*. This simple geometrical reasoning clearly explains why the energy varies slowly in the region of space where $0.3 < a < 0.5$.

Finally we note that, due to the energy behavior in the region of space where $0.3 < a < 0.5$, even a small perturbation, caused by the presence of an impurity for example, might introduce a barrier. In such a case, a defect similar to the *V-I* pair would be stable. This provides a very intriguing possible mechanism for the creation of intimate vacancy-interstitial-like defects in silicon. We believe that this is the case for the Si:O_i metastable defect in silicon.

B. Metastable Si:O_i

In the metastable configuration of Si:O_i, one of the silicon atoms (Si**) is displaced from its stable position by 0.56 Å. Such a displacement towards the T_d-interstitial position leads to the formation of broken bonds and makes the geometry of this defect closely related to a vacancy-interstitial pair in pure silicon.

From our first-principles calculations of Si:O_i, we have confirmed the existence of dangling bonds in the proposed metastable defect. The forces on the atoms were quantum mechanically calculated and complete relaxation of the system was performed. All forces were less than 0.12 eV/Å. Figure 3 schematically displays the geometry of the stable [Fig. 3(a)] and the metastable [Fig. 3(b)] Si:O_i defects.

Figure 4 exhibits a contour plot of the total valence charge density of the metastable Si:O_i in the plane defined by the oxygen and its nearest neighbors. Due to the large range of charge-density values involved, logarithmic spacing between contour curves was chosen. The presence of oxygen leads to strong charge rearrangement in its proximity. In that plane, the atomic structure of silicon consists of a series of zigzag chains. The oxygen atom (black triangle) interrupts the normal sequence of a zigzag chain and acts as a bridge between two silicon atoms (Si—O—Si). One of the silicon atoms in this bridge is displaced towards the T_d interstitial so that immediately after the bridge, this zigzag chain is broken as reflected in the electronic charge density.

Figure 5 displays the charge density associated with the highest filled band in the same plane as above. As before a logarithmic scaling was used in this contour plot. Here the localized character of the new broken-bond defect can be observed. It is interesting to notice that the electrons in this band are localized on the silicon atom that is a member of the Si—O—Si bridge with very little density at the other dangling-bond site.

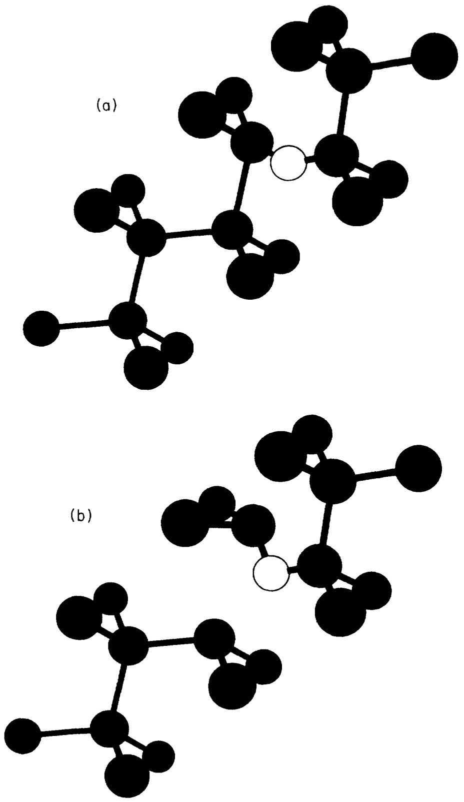

FIG. 3. Atomic configuration of Si:O_i defects in silicon. (a) Stable, (b) metastable. The gray circles are silicon atoms and the open circle is the oxygen.

In order to determine the adiabatic barrier for the reformation of the broken Si—Si bond, a series of total-

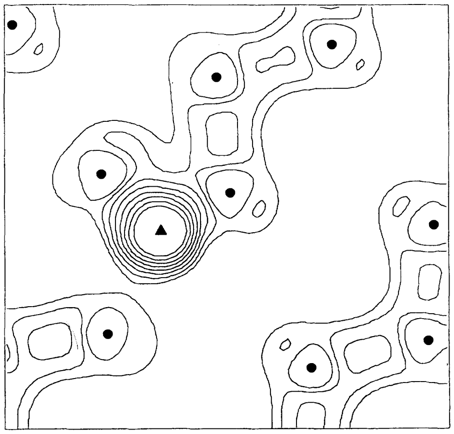

FIG. 4. Contour plot of the total valence charge density of metastable Si:O_i in the plane defined by oxygen and its nearest neighbors. A logarithmic spacing was chosen so that the lowest contour corresponds to 0.21 electrons $Å^{-3}$ and each additional contour represents a factor 1.6 higher in density. The oxygen atom is represented as a black triangle and the silicon atoms as black circles.

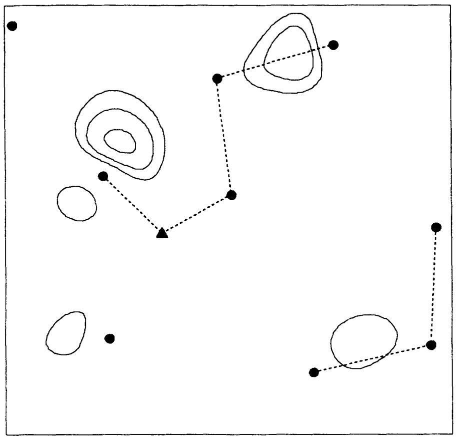

FIG. 5. Contour plot of the charge density of the highest filled band of metastable Si:O_i in the plane defined by the oxygen atom and its nearest neighbors. A logarithmic spacing was chosen so that the lowest contour corresponds to 0.02 electrons Å^{-3} and each higher contour represents a factor 2.0 higher in density. The oxygen atom is represented as a black triangle and the silicon atoms as black circles.

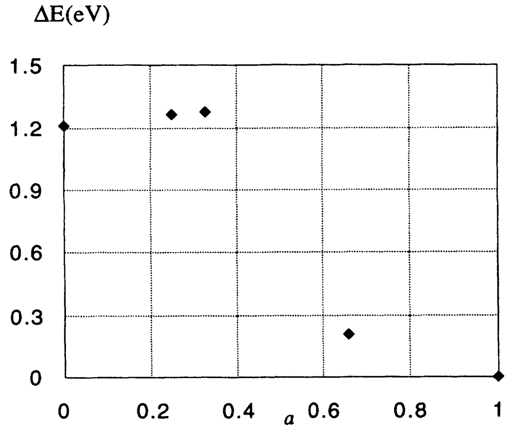

FIG. 6. Energy barrier calculation of Si:O_i as a function of the displacement of a Si atom from its site in the metastable configuration ($a = 0$) towards its site in the stable one ($a = 1$).

energy calculations was performed. The same procedure introduced before was applied again. Vector **v** is now redefined, it connects the displaced silicon atom (Si**) from its position in the metastable configuration to its position in the stable configuration. The new vector **v** has a magnitude of 0.56 Å and its direction is nearly parallel to $[\bar{1}\bar{1}1]$. Here, $a = 0$ denotes the metastable configuration and $a = 1$ corresponds to the stable configuration; alternatively $a = 0$ is related to the presence of dangling bonds and $a = 1$ with no dangling bonds. The results of the total-energy calculations as a function of $a\mathbf{v}$, where a ranges between 0 and 1 are shown in Fig. 6. A value of 0.08 eV was found to be the static activation energy for the recombination of dangling bonds. The height and the shape of the barrier can be understood if we compare these results with those of Fig. 2. In Fig. 6, when $a \sim 0.25$, Si** and its three silicon nearest neighbors lie almost in the same plane. These neighbors, analogously with the *V-I* defect, form an equilateral triangle with Si** in its center. As before, the total force these atoms apply on Si** is almost zero. The presence of the oxygen atom disturbs the system generating the small barrier.

Our results indicate that oxygen can behave as an actuator to the formation of dangling bonds in silicon. Because of the low recombination barrier this is only possible at very low temperatures. An experiment that could characterize the defect and test our predictions would be highly desirable. Unfortunately it does not seem to be an easy task to accomplish. The small recombination barrier and the fact that the stable configuration of Si:O_i is not electrically active conspire to make detection of the defect very difficult.

III. FINAL REMARKS

In this paper we have shown that the intimate Frenkel pair is not a stable defect in silicon. From the analysis of the energetics of this system, we have proposed a mechanism to create vacancy-interstitial-like defects in Si. We have also studied the dangling-bond character of a metastable defect induced by oxygen in silicon. We have determined the static barrier (0.08 eV) for broken-bond reconstruction in this defect. Furthermore, we have interpreted this result by comparing it to the *V-I* pair in Si and shown that this defect is a probable example of the proposed mechanism. By the same mechanism, it is likely that other elements can behave as actuators to the formation of broken bonds or alternatively, other impurities in silicon may show metastability or bistability due to this mechanism. Finally, at very low temperature, our results indicate that it could be easier to create silicon broken bonds in silicon samples that contain oxygen as opposed to pure ones.

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