Diffusion and dissociation mechanisms of vacancy-oxygen complex in silicon

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We are examining diffusion mechanisms of the vacancy-oxygen complex (VO) in bulk Si using *ab initio* calculations based on a 64-atom supercell. We found two atomic mechanisms involved in the VO diffusion; one is caused by migration of an interstitial oxygen atom, another by migration of a vacancy. The energy barrier of the mechanism due to an oxygen migration is 2.02 eV, and that caused by a vacancy migration is 1.98 eV. These energy barriers are close to the experimental activation energy of 2.0 eV required for the dissociation and diffusion of VO. The derived activation energies of the two mechanisms suggest that these mechanisms plausibly occur simultaneously. In addition, we clarify that the dissociation energy of VO, 1.85 eV, is lower than the diffusion energy of VO. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1897433]

Major impurities in silicon grown by the Czochralski technique are the oxygen atoms that distribute over an entire silicon ingot at a concentration of about 10^{18} cm^{-3}. Among them, interstitial oxygen atoms are known as sinks for migrating vacancies to form the vacancy-oxygen complex (VO), so-called A centers.[1] Since VO is a precursor to the $V_X O_Y$ complex, which causes a leakage current of the *p-n* junction,[2,3] the formation and dissociation mechanisms of VO have to be clarified in order to develop a fabrication process of *p-n* junctions with low leakage current. However, little attention has been paid to the formation and dissociation mechanisms of VO at an atomic level.

The point symmetry group of VO is C_{2v}, where the oxygen atom attaches to the dangling bonds across the silicon vacancy. The electrical properties of VO have been measured with deep-level transient spectroscopy (DLTS), from which the ionization level $(-/0)$ of VO has been derived as $E_c - 0.17$ eV.[4] From experimental evidence it has been reported that the dissociation and diffusion energies of VO are 2.0 eV,[5] and the reorientation energy of VO is 0.38 eV.[4]

The aim of this work is to clarify atomic diffusion mechanisms of VO by using *ab initio* total energy calculations.

Details of the calculation are as follows. We performed *ab initio* total energy calculations within the generalized gradient approximation to derive the exchange-correlation energy. The Vanderbilt ultrasoft pseudopotentials were used for silicon and oxygen atoms,[6] and the total energies of the defects were calculated using periodically repeated supercells containing 64 silicon lattice sites with a lattice constant of 10.8 Å. The energy cutoff for the plane-wave expansion used in the calculations was 300 eV. We performed Brillouin zone sampling with a $2 \times 2 \times 2$ Monkhorst Pack **k**-point mesh for the supercell.[7] Atomic positions were allowed to relax fully until all residual forces became smaller than 0.05 eV/Å. We then performed the synchronous-transit method[8] with a conjugate gradient technique to find the microscopic transition states and activation energies. In transition-state searches, the
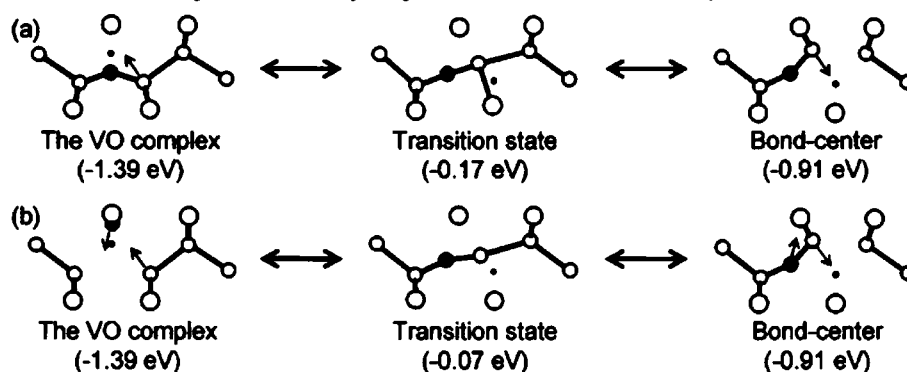
atoms were relaxed until their residual forces had converged to less than 0.15 eV/Å.

VO used in this work has a Si–O length of 1.68 Å and a Si–O–Si angle of 146°. The calculated total energy of the C_{3v}-symmetric VO complex with a trivalently bonded oxygen is 0.40 eV higher than that of the C_{2v}-symmetric structure in a neutral charge state. This energy difference of 0.40 eV agrees well with the experimental reorientation energy, 0.38 eV, of VO.[4] Such a result supports the idea that the reorientation of VO takes place via the C_{3v}-symmetric structure.

We calculate the total energies of several microscopic structures, including a vacancy and an interstitial oxygen, in order to elucidate the formation and dissociation of VO. The formation energy of an infinitely separated vacancy from an interstitial oxygen is defined as *zero energy*. The binding energy of VO is defined by $E_b(\text{VO}) = E(\text{Si}_{63}) + E(\text{Si}_{64}\text{O}) - E(\text{Si}_{63}\text{O}) - E(\text{Si}_{64})$, where $E(\text{Si}_{63})$ is the total energy of a 63-atom supercell including a vacancy, $E(\text{Si}_{64}\text{O})$ is that of a 65-atom supercell with an interstitial oxygen, and $E(\text{Si}_{63}\text{O})$ is that of a 64-atom supercell with VO. The calculated binding energy of a vacancy and an interstitial oxygen is 1.39 eV. This is close to the calculated binding energies reported, 1.4 eV,[9] 1.57 eV,[10] and 1.7 eV.[11] The interstitial oxygen occupies a bridging position between neighboring Si atoms to form a Si–O–Si bonding structure, which traps the vacancy. In this letter, the atomic configuration in which a vacancy is the nearest neighbor to Si–O–Si is called a "bond-center" structure, as shown in Fig. 1. The formation energy of the bond-center structure is −0.91 eV. Structural changes from the bond-center structure to VO occur via one of the five transition states shown in Fig. 1 due to the symmetry of the bond-center structure. Paths (a) and (b) are structural changes involving a vacancy migration, while paths (c), (d), and (e) are those caused by an interstitial oxygen migration. The formation energies of the transition states in paths (a), (b), (c), (d), and (e) are −0.17, −0.07, +0.77, +0.73, and +0.63 eV, respectively, and the bond-center structure is an intermediate state for VO diffusion. The separated vacancy and oxygen recombine at a position different to the original VO complex via one of the reverse reactions illustrated in

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Structural changes caused by migration of a silicon vacancy

(a)

The VO complex (-1.39 eV)   ⟷   Transition state (-0.17 eV)   ⟷   Bond-center (-0.91 eV)

(b)

The VO complex (-1.39 eV)   ⟷   Transition state (-0.07 eV)   ⟷   Bond-center (-0.91 eV)

Structural changes caused by migration of an interstitial oxygen

(c)

The VO complex (-1.39 eV)   ⟷   Transition state (+0.77 eV)   ⟷   Bond-center (-0.91 eV)

(d)

The VO complex (-1.39 eV)   ⟷   Transition state (+0.73 eV)   ⟷   Bond-center (-0.91 eV)

(e)

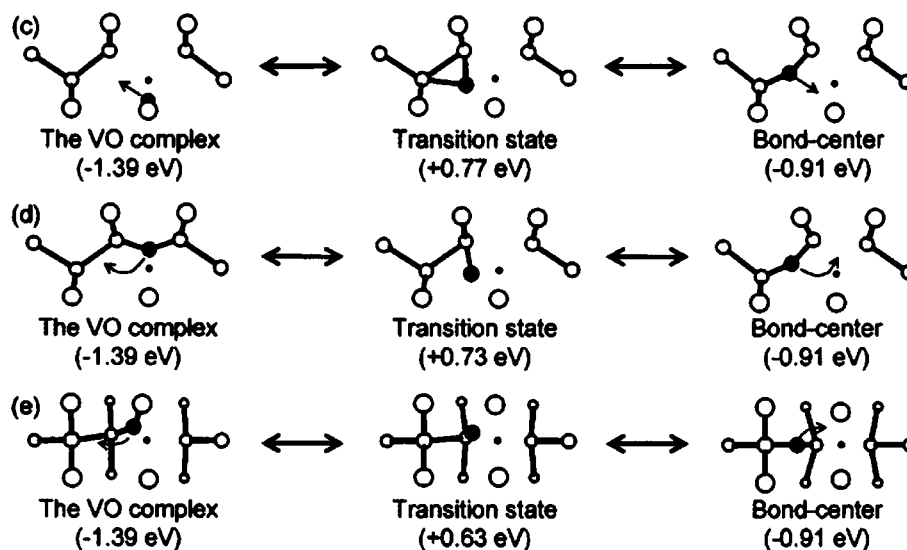The VO complex (-1.39 eV)   ⟷   Transition state (+0.63 eV)   ⟷   Bond-center (-0.91 eV)

FIG. 1. Structural changes in the reaction of $V+O_i \leftrightarrow VO$. (a)–(d) are shown projected to a [110] plane of silicon. (e) is shown in a section of a [100] projection. Silicon, oxygen, and vacancy are represented as white, black circles, and black dot, respectively.

Fig. 1. Comparison of the formation energies has revealed that paths (a) and (b), associated with a vacancy migration, are most probable for the formation and dissociation of VO; however, a vacancy migration gives rise to the reorientation

(a) -1.39 eV   (b) -0.91 eV

[110] [1$\bar{1}$0] [001]

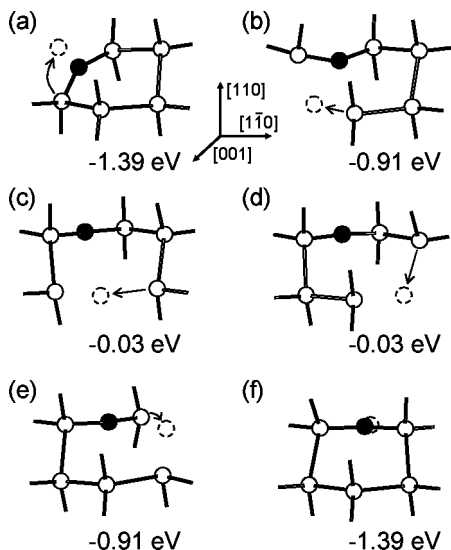(c) -0.03 eV   (d) -0.03 eV

(e) -0.91 eV   (f) -1.39 eV

FIG. 2. Diffusion steps of VO caused by migration of a vacancy along a six-member ring. Silicon, oxygen, and vacancy are represented as white, black, and dashed circles, respectively.

of VO without diffusion in bulk Si. Note that a combination of two different types of structural change involving both vacancy and interstitial oxygen migrations causes diffusion of VO. The lowest activation energy of the structural change caused by an interstitial oxygen migration, via path (e), is 2.02 eV, which agrees well with the experimental dissociation energy of VO measured with DLTS.[5] This agreement suggests that a structural change due to the path (e) involves in VO diffusion in bulk Si.

In addition to the VO diffusion via structural change shown earlier, we found a diffusion mechanism of VO with a vacancy migration along a six-member ring as shown in Fig. 2. First, VO transforms to the bond-center structure [Figs. 2(a)→2(b)], after which a vacancy migrates on each Si site

E (eV)

+0.59
+0.46   +0.46
-0.17   Fig. 2(c) -0.03   Fig. 2(d) -0.03   -0.17
Fig. 2(b) -0.91   1.98   Fig. 2(e) -0.91
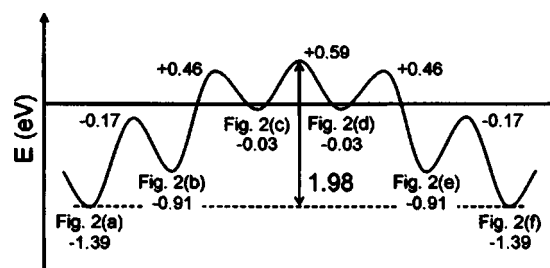Fig. 2(a) -1.39   Fig. 2(f) -1.39

FIG. 3. Formation energy diagram for VO diffusion caused by migration of a vacancy along a six-member ring.

step by step along a six-member ring and becomes the nearest neighbor to a Si–O–Si structure again [Figs. 2(b)→2(c)→2(d)→2(e)]. Finally, the bond-center structure newly forms VO after the vacancy jumps into the Si site nearest to the oxygen [Figs. 2(e)→2(f)]. By repeating these structural changes, VO diffuses without an oxygen migration. Figure 3 shows the formation energy diagrams along with the structural changes based on this mechanism. A vacancy migration via Figs. 2(a)→2(b) has the same probability as one via Figs. 2(f)→2(e). The two structures shown as Figs. 2(c)→2(d) are structurally the same, and their formation energy is 1.36 eV higher than that of VO. The energies associated with these changes have a peak of 1.98 eV through the transition states shown as Figs. 2(c)→2(d). The activation energy of VO diffusion caused by a vacancy migration along a six-member ring is 1.98 eV.

Finally, we point out that up to now, a diffusion of VO has been confused with a dissociation.[5,12,13] Since a dissociation of VO has a much higher probability of occurring than a diffusion, once a VO vacancy separates from the oxygen, the VO complex generally dissociates unless the vacancy again comes close to the oxygen: a vacancy is prone to move out of the six-member ring with the remaining oxygen atom, as shown in Figs. 2(c)→2(d). This is because the activation energy required for a vacancy to migrate to the outside of a six-member ring (0.45 eV) is lower than that for migrating along a six-member ring (0.62 eV), which means that the dissociation energy of VO is lower than the diffusion energy. The calculated dissociation energy of 1.85 eV is very close to the dissociation energy of 1.86 eV obtained from the IR measurement.[12]

In summary, *ab initio* total energy calculation clarified that VO diffuses via two mechanisms: either an interstitial oxygen migration or a vacancy migration. In the oxygen-migration mechanism, for VO diffusion in bulk Si, a vacancy of VO separates from the oxygen and forms an atomic structure where the vacancy is adjacent to a Si–O–Si bond. Subsequently, the vacancy and the oxygen are recombined at a position different to that in the original VO complex, thus completing an atomic step diffusion of VO. The activation energy involved in this structural change is 2.02 eV. In the mechanism that operates due to a vacancy migration along a six-member ring, an activation energy of 1.98 eV is involved. The two activation energies agree well with the experimental energy of 2.0 eV. The existence of two activation energies also suggests that two mechanisms occur in a parallel fashion at a similar rate. In addition, we clarified that the dissociation energy of VO is lower than the diffusion energy.

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