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Interstitial O in Si and its interactions with H

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Interactions between interstitial H and interstitial O in crystalline silicon have been studied at the approximate *ab initio* (parameter-free) Hartree-Fock level in three clusters containing 5, 26, and 35 host atoms, respectively. The key results are (1) no configurations with significant O—H bonding are energetically favorable and (2) the activation energy for diffusion of interstitial O is considerably lower when H is present than when it is not. It is estimated that H enhances the diffusivity of interstitial O by several orders of magnitude. The results provide insights into the interpretation of the recently observed enhancement by atomic hydrogen of the rate of formation of thermal donors in silicon.

I. INTRODUCTION

Oxygen is one of the most studied impurities in crystalline silicon. It is found in concentrations of the order of 10^{18} cm^{-3} in Czochralski (CZ) -grown samples. As an interstitial impurity, O forms a bent-bridged bond between two Si host atoms.[1] The Si—O stretching vibration has been identified as the famous 9-μm ir absorption band,[1-4] and interstitial O (O_i) is nearly free to rotate around the $\langle 111 \rangle$ axis.[2] The Si—O bond length and Si—O—Si bond angle are estimated[2,4] to be about 1.6 Å and 160°, respectively. Stress-induced dichroism experiments[3] led to an activation energy of 2.56 eV for O_i diffusion, with preexponential factor $D_0 = 0.23$ cm^2/s. Very similar numbers have been obtained by other groups.[5-8] The equilibrium configuration of O_i has been calculated at various levels of Hartree-Fock (HF) theory.

Geometry optimizations were first performed[9] in a small cluster (OSi_5H_{12}) at the *ab initio* HF level with a split-valence (3-21G) basis set. In this cluster, the central Si atom is surrounded by four SiH_3 groups. The inclusion of O_i results in a bent Si—O—Si bond. Because of the small size of this cluster, the two Si nearest neighbors (NN) to O_i are unequally displaced: One of them relaxes against three Si NN's by 0.43 Å, the other against three H saturators by 0.26 Å. The calculated Si—O bond lengths are 1.588 and 1.598 Å, respectively. The transition point for O_i diffusion, assumed to be a "split-$\langle 100 \rangle$" (also called "ylid") configuration, was calculated[9] to be only 2.84 eV above the equilibrium structure. This barrier drops to 2.39 eV when corrections for electron correlation are included up to MP3 (third-order Møller-Plesset perturbation expansion). These values for the activation energy of O_i are remarkably close to the experimental value[3] of 2.56 eV.

Other calculations[10] at the HF level, with a minimal basis set, have been performed for O_i in Si_8H_{18}. This cluster is symmetric around the center of a Si—Si bond. Each of the central Si atoms is connected to three SiH_3 groups. The calculated geometry is the one expected, with an optimized Si—O bond length of 1.62 Å, and a Si—O—Si bond angle of 162°. The Mulliken charge on the O atom is -0.89, the positive charge being equally distributed on the two Si NN's. This leads to a rather large dipole moment for the defect. Finally, Snyder *et al.*[11] studied the potential-energy surface (PES) for up to four O interstitials in a much larger cluster ($Si_{47}H_{60}$) with the semiempirical MINDO/3 (modified intermediate neglect of differential overlap) method and a very carefully selected parametrization. Even though the optimized Si—O—Si bond was linear, the calculated barrier for diffusion of O_i via the "ylid" configuration was only 2.49 eV, i.e., slightly lower than the experimental one.

The activation energy of isolated O_i is much too high to explain the rate of formation of oxygen-related thermal donors (TD's).[12,13] There are at least nine distinct double donors[13] which form sequentially during heating. The initial formation rate is proportional to the fourth power of the O_i concentration, and the kinetics implies an activation energy of only 1.7 eV (Refs. 14–17). This led to a number of suggestions,[12,13] one of which being that oxygen *dimers*, rather than O_i alone, are the fast diffusing species responsible for TD formation. Assuming that dimers are formed, Snyder *et al.*[11] have calculated that at least two configurations involving a pair of oxygen interstitials bound to the lattice can be stable: a C_{2v} di-interstitial, and a four-membered structure combining two O and two Si atoms. The activation energy for the latter configuration was shown to be less than 1.36 eV at the MINDO/3 level. This led to an estimated[11] diffusivity for the dimer at 450 °C some 10^8 times larger than that of O_i. However, the rate of TD formation still is limited by the rate at which individual O_i's can diffuse and form dimers (for a discussion, see Ref. 13).

The formation kinetics of TD's depends upon the history of the sample. In particular, the presence of some impurities enhances the rate at which TD's are generated. For example, transition metals enhance O_i diffusion[18] and TD formation.[19] However, it has recently been observed[20-23] that atomic hydrogen dramatically enhances the rate of TD formation over conventional furnace anneals by factors of 6 (at 400 °C) up to 400 (at 300 °C). The observed correlation[22] between the enhanced rate of TD

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production and the rate of loss of O_i's is the first direct evidence that the rate of TD formation is controlled by the rate of diffusion of O_i. The results[23] show that H—which is known[24] to diffuse rapidly in Si at 400 °C—somehow acts as a catalyst of the O_i-to-TD reaction. For this to be true, one needs to assume that interstitial H undergoes a long-ranged attraction towards O_i, and ends up being in its immediate neighborhood. This assumption is supported by results of muon-spin rotation (μSR) and positron blocking (from muon decay) experiments in float-zone (FZ) and CZ silicon.[25-27] In FZ samples, and for a wide range of dopant concentration, three signals are observed: μ^+ (which could be a bare muon or a negatively charged muonium atom, Mu^-, and is not paramagnetic), Mu (believed to be at or close to the tetrahedral interstitial site), and Mu* (bond-centered muonium: see, e.g., Refs. 28–30). The latter two signals correspond to paramagnetic species. The formation probabilities of μ^+, Mu, and Mu* are about 7%, 60%, and 35%, respectively (these are average values: see Ref. 27, p. 109, for error bars and details). However, in CZ samples, the μ^+ and Mu signals *completely disappear*, while Mu* remains unaffected. Blocking patterns[25] indicate that the trapped Mu is located at *T* sites "presumably neighboring" O_i. Finally, several ir absorption peaks (2191, 2123, and 1894 cm^{-1}) corresponding to Si—H stretching vibrations have been observed to be oxygen related.[31] This also suggests that H is very near O_i in *c*-Si. A long-ranged attractive interaction between H (and/or H^+) and O_i could be the result of the significant strain induced by O_i in the lattice, and/or to the large dipole moment of the Si-O-Si defect. In the former case, H might be attracted to any locally distorted regions of the crystal, such as bond-centered H or H-passivated dopants. As a result, the concentration of isolated interstitial H would be very low in all but the purest undoped samples.

In the present contribution, the interactions between O_i and a single H interstitial are studied. It is assumed that H is in the immediate neighborhood of O_i. Various O—H bonded configurations are considered, and the barriers for O_i diffusion with and without H calculated. In the following section, the details of the calculation are given. Section III contains the results and their implications are discussed in Sec. IV.

II. DETAILS OF THE CALCULATION

Most of the calculations were performed with the method of partial retention of diatomic differential overlap[32,33] (PRDDO) in two clusters: $Si_{26}H_{30}$ and $Si_{35}H_{36}$. PRDDO is an approximate *ab initio* HF method which calculates (or approximates) all of the two-electron integrals with the exception of those of the form $(\chi_i,\chi_j|\chi_k,\chi_l)$ when the orthogonalized atomic orbitals χ_i, χ_j, χ_k, and χ_l are on *different* centers. Because PRDDO uses Löwdin-orthogonalized orbitals, these four-center, two-electron integrals are very small and therefore neglected. This reduces the N^4 problem to an N^3 one (N is the total number of orbitals) and introduces small and *systematic* errors relative to *ab initio* calculations. These errors are corrected[32-34] at the Fock matrix level. Thus PRDDO reproduces consistently and accurately the results of minimal basis set *ab initio* HF calculations at a fraction of the cost *without* introducing semiempirical parameters. The method has been extensively tested.[35] Because PRDDO uses Slater orbitals rather than linear combinations of Gaussians, the tails (and cusps) of the orbitals are quite realistic, and the geometries optimized at the PRDDO level usually are closer to experimental values than all but the most sophisticated *ab initio* HF calculations.

Even though the minima of a PES usually are accurately described, the relative energies of transition points may be overestimated.[36] There are several reasons for this. First, PRDDO is a minimal basis set method. The use of split-valence or polarized basis sets to describe transition states is desirable. Second, while exchange is fully accounted for, electron correlation is not included, except for the antisymmetry of the wave function. The effects of correlation often are more important for transition states, where bonds generally are longer and weaker, than for equilibrium configurations. In the case of O_i alone, the calculations were performed using a closed-shell restricted HF (RHF) wave function. The results involving O_i and H in the same cluster were obtained with an unrestricted open-shell HF (UHF) wave function.

The clusters chosen are large enough to allow lattice relaxations to be included while minimizing the number of displaced host atoms which are connected to a surface H saturator. In the calculations involving the transition point of O_i in $Si_{26}H_{30}$, only one of the Si atoms relaxed is connected to a surface saturator, and this relaxation does not greatly affect the host-saturator bond length. The cluster $Si_{35}H_{36}$ is centered at a Si atom site and contains five host atom shells. The smaller cluster, $Si_{26}H_{30}$, is a fraction of the former one. Several calculations at the *ab initio* HF and PRDDO levels were performed in Si_5H_{12}. However, this cluster is too small to provide insights into the situation under consideration here (O-H interactions).

III. O and O-H INTERACTIONS

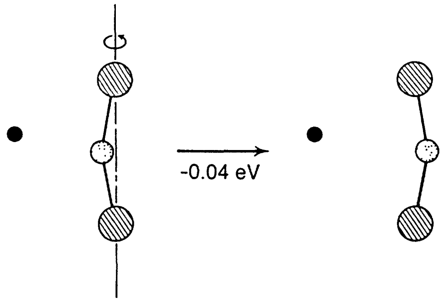
A. Interstitial O

The equilibrium geometry of an O_i calculated with PRDDO is similar to that obtained by other groups.[9,10] O_i forms a bent-bridged bond between two Si host atoms. The calculated O—Si bond length and Si—O—Si bond angles are 1.566 Å and 163.8°, respectively. This corresponds to a relaxation of the Si—Si bond by almost 32%. This is slightly less than the relaxation required to accommodate[28] bond-centered hydrogen (39%), which forms a straight-bridged bond. As noted by other groups,[10] the Mulliken charges are about -0.81 on O_i and $+0.42$ on the two Si NN's. While bond-centered H forms a three-center two-electron bond, O_i forms a three-center three-electron bond by capturing some of the electron density from the six Si NN's to Si second NN bonds.

The transition point between two adjacent (bent) bond-centered (BC) sites for O_i is assumed to correspond to a ylid configuration with C_{2v} symmetry.[9,11,13] At this site, O and one Si atom lie along the $\langle 001 \rangle$ direction and are each threefold coordinated as shown in Fig. 1(a). The positions of all six atoms nearest to the center of the complex (O, Si, and their Si NN's) were optimized. At the PRDDO level, the difference in energy between this transition point and the equilibrium configuration is 4.09 eV. As discussed above, PRDDO *should* overestimate the barrier height in the present case for the following reasons: (1) it is a minimal basis set method (see Ref. 36 for a discussion and examples of basis size effects on potential-energy barriers), (2) electron correlation tends to lower the energy of transition states more than that of ground states (this is documented[9] in the case of O_i), (3) it cannot be ruled out that the true transition state corresponds to a geometry with symmetry lower than the one considered here, and (4) the electronic configuration of the transition state can only be approximately described by a RHF wave function (the electrons are paired in doubly occupied molecular orbitals, which restricts the configurations available). A better description would be provided with a restricted open-shell HF wave function with several open shells. Such wave functions are not yet available in PRDDO. Therefore the PRDDO barrier should be too large in this particular case. However, with the PRDDO geometries in the cluster OSi_5H_{12}, *ab initio* HF calculations with a split-valence (6-31G) basis set predict a barrier of 2.48 eV, in close agreement with experiment as well as the activation energy reported in Ref. 9.

B. Activation energy with H

We now assume that interstitial H is in the immediate neighborhood of O_i. This assumption is based on a variety of (indirect) experimental information[20–23,25–27,31] as discussed in Sec. I. If H is placed at various T sites nearest to the bent Si—O—Si bond, O_i rotates around the ⟨111⟩ axis to a configuration where O points away from H. The maximum rotation by 180° monotonically lowers the energy by 0.04 eV:



From this configuration, if the positions of H, O, and the two Si NN's to O are optimized, H moves by 0.24 Å towards the BC site as shown in Fig. 2(a). This configuration is a local minimum of the PES and defines the zero of the energy in this paper ($E = E_0$). Then, O_i is displaced towards another nearest bond-centered site in the {110} plane as shown in Fig. 2. At each intermediate step, the coordinates of H and all the Si atoms shown in Fig. 2 were optimized. The search for a transition point was therefore restricted to the {110} plane. The new transition point is shown in Figs. 1(b) and 2(b). The O atom is very close to the C site, and H essentially forms a single bond with the Si atom nearest to O. This transition point is only 1.25 eV above E_0. As can be seen in Figs. 1(b) and 2(b), O is twofold coordinated and the nearest Si atom is fourfold coordinated (to two Si atoms not shown in the figure, to O, and to H). This contrasts with the ylid transition point for O without H [Fig. 1(a)], where O and the nearest Si atom each are threefold coordinated. Figure 2(c) shows the final configuration with O_i at another equilibrium site and H very close to the BC site. The energy is $E_0 - 0.66$ eV. During the entire process, no O—H bond is formed.

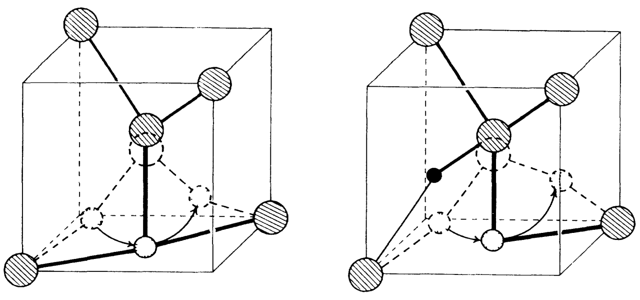
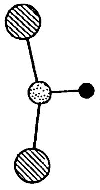

(a) (b)

FIG. 1. Qualitative comparison between the transition points for O_i diffusion without H (a) and with H (b). The shaded circles are host Si atoms, the dotted circle is O, and the solid circle is H. The thickness of the bonds is proportional to the amount of overlap between two atoms. The curved arrows show the path of O_i from one equilibrium site to the next. In order to simplify the figure, only the central Si atom is shown displaced. A quantitative representation of the transition point in (b) is discussed in the text and shown in Fig. 2(b).

It should be emphasized that the 1.25 eV barrier is an upper limit to the true barrier height. Even though a UHF wave function was used (the spatial orbitals for each spin direction are independent), this is a minimal basis set calculation with no corrections for electron correlation. Both large basis sets and electron correlation corrections tend to lower potential-energy barriers. Finally, the search for the transition point was limited to the {110} plane. However, the calculated energy difference between configurations 2(a) and 2(c) is much more reliable since it results from the comparison of two *minima* of the PES rather than of a minimum and a saddle point. In any case, an upper limit of 1.25 eV to the activation energy for O_i diffusion in the presence of H is lower by a factor of 2 than even the *experimental* value[3] of the activation energy for O_i alone (2.56 eV).

C. Other configurations

Two other configurations combining O and H have been investigated. First, the threefold-coordinated interstitial O



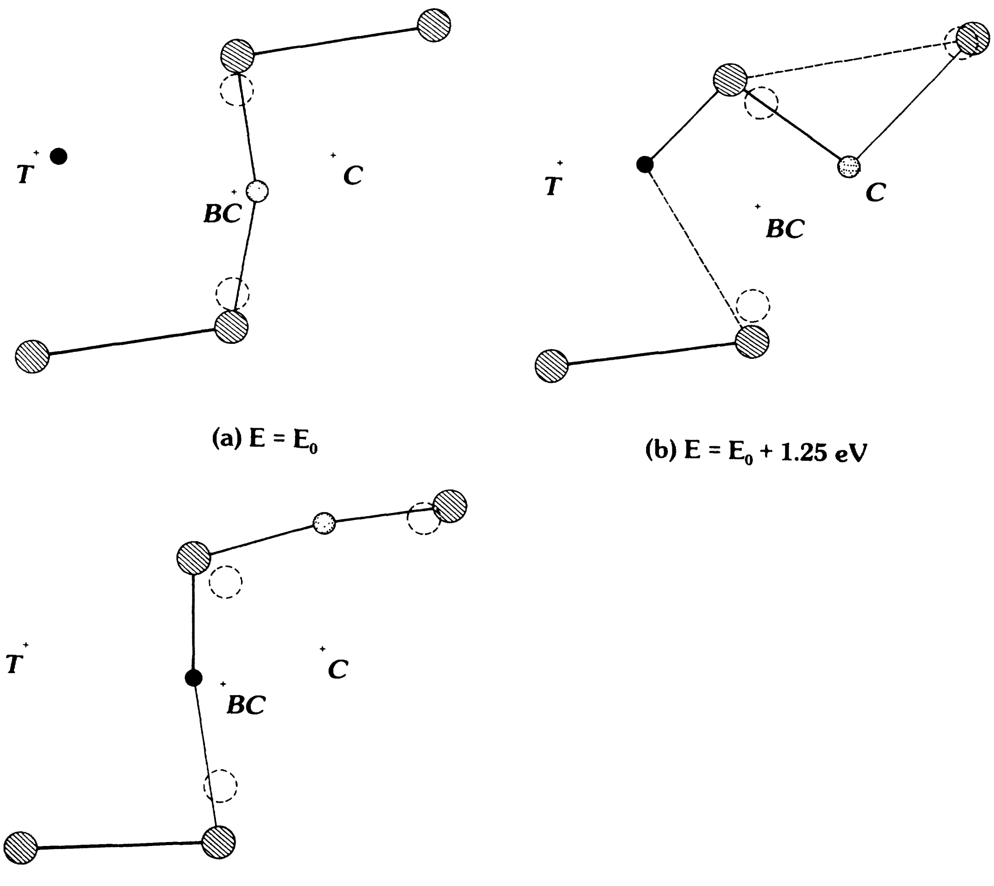
is not a stationary point of the PES. In a favorable geometry, the energy is some 5 eV above E_0. If H is allowed to move, it is repelled from O and the energy decreases rapidly as H moves away towards the nearest T site.

The geometry was also optimized for various positions of an interstitial OH molecule close to the T site in the perfect lattice. The lowest-energy configuration corresponds to OH lying along a $\langle 111 \rangle$ axis, with bond length O—H$=0.983$ Å, where O is about 0.11 Å from the T site and H is close to the hexagonal interstitial site. However, the energy is 2.78 eV *above* E_0, i.e., 3.44 eV above the configuration in Fig. 2(c). Hence, the formation of OH pairs as an intermediate step for H-enhanced motion of O_i is not energetically favorable.

IV. SUMMARY AND DISCUSSION

Upper limits for the activation energies for O_i diffusion with and without the presence of interstitial H have been determined. Most calculations were performed at the all-electron, parameter-free, approximate *ab initio* HF level (PRDDO) in two clusters containing 26 and 35 host atoms, respectively. The surface dangling bonds are saturated with H atoms.[36] The two most important results of these calculations are as follows.

First, the presence of interstitial H lowers the barrier for O_i diffusion to less than 1.25 eV. The final configuration, where H and O both are at nearly ideal



(a) $E = E_0$

(b) $E = E_0 + 1.25$ eV

(c) $E = E_0 - 0.66$ eV

FIG. 2. Geometries calculated in the $\{110\}$ plane at the PRDDO level for H near O_i in c-Si. The shaded circles are host Si atoms, the dotted circle is O, and the solid circle is H. The open dashed circles show the positions of the host atoms in the perfect lattice. The thickness of the lines increases with the amount of covalent bonding between two atoms. Three interstitial sites are indicated by crosses: the tetrahedral (T), bond-centered (BC), and C sites. (a) is a local minimum of the PES (with energy E_0). Hydrogen is off the T site by 0.24 Å and O_i is almost at its normal interstitial site. (b) shows the transition point for O between two adjacent interstitial sites. Hydrogen is primarily bound to one Si atom, and O is twofold coordinated. This configuration is 1.25 eV above E_0. Finally, (c) shows a minimum of the PES with both O_i and H near their normal stable configurations in c-Si. The energy is 0.66 eV below E_0. Hydrogen still forms a stronger bond with one of its two NN's.

bond-centered sites, corresponds to an energy 0.66 eV *lower* than the initial one (H near the T site and bond-centered O). In the case of interstitial H in an otherwise perfect Si crystal, PRDDO calculations[28] predict that H at the T site must overcome a 2.0 eV barrier to get to the (stable) bond-centered site. The presence of O_i therefore makes it easier for H to get to the BC site, while the presence of H makes it easier for O_i to diffuse. This is because the new transition point [Figs. 1(b) or 2(b)] is very different from that of the $T \rightarrow$BC transition for H alone (Ref. 28) and of the BC$\rightarrow$BC transition for O alone [Fig. 1(a)].

Second, there are no configurations involving covalent bonding between O and H that are energetically favorable. In Si, O is more likely to form bonds with the host than with H. This appears reasonable in view of the fact that the O—Si bond strength is greater than the O—H one. For example,[37] in diatomic molecules, the bond strengths are 8.29 eV for SiO and 4.43 eV for OH, and in $HOSi(CH_3)_3$ and $HSi(CH_3)_3$, the O—Si and H—Si bond strengths are 5.55 and 3.92 eV, respectively. Therefore, the assumption[9] that an intermediate OH species is involved in the enhancement by H of the rate of TD formation is not supported by the present calculations. It should be noted that a recent calculation[38] reported the possibility of O-H pairing in the O-vacancy complex (A, center[39,40]). In this configuration, however, O forms longer and weaker bonds with Si than O_i does.

An estimate of the diffusivity of O_i induced by H has been proposed by Seager:[41] The rate of arrival of H interstitials at an O_i site is

$$R_{\mathrm{H}} = 4\pi r_c N_{\mathrm{H}} D_{\mathrm{H}} \ (\mathrm{s}^{-1}) , \tag{1}$$

where r_c is the capture radius of H by O_i, N_{H} the concentration of H, and D_{H} the diffusivity of interstitial H. Assuming that O_i performs a jump every time H is in its neighborhood, the resulting induced diffusivity of O_i is given by

$$D_{\mathrm{O}} = R_{\mathrm{H}} \frac{d^2}{6} = 4\pi r_c N_{\mathrm{H}} D_{\mathrm{H}} \frac{d^2}{6} \ (\mathrm{cm}^2/\mathrm{s}) , \tag{2}$$

where d is the net displacement of O_i (calculated here to be 2.07 Å) and 6 is a geometrical factor for interstitials diffusing in the diamond lattice. Assuming a capture radius $r_c = 5$ Å and $N_{\mathrm{H}} = 10^{15}$ cm^{-3} (see Refs. 42 and 43), we get $D_{\mathrm{O}} = 4.5 \times 10^{-8} D_{\mathrm{H}}$. A variety of values for the diffusivity of H at the temperatures relevant in the present study have been reported in the literature (for a recent review, see Ref. 24). However, the use of extrapolations to low temperatures of the high-temperature diffusivity of Van Wieringen and Warmoltz[44] is strongly supported by a number of recent studies.[43,45,46] I will therefore use $D_{\mathrm{H}} = 9.4 \times 10^{-3} \exp(-0.48/kT)$ cm^2/s. At 400 °C, $D_{\mathrm{H}} = 2.4 \times 10^{-6}$, and $D_{\mathrm{O}} = 1.1 \times 10^{-13}$ cm^2/s. Without the presence of H, the diffusivity of O_i is given by[3] $0.23 \exp(-2.56/kT)$. This is 1.6×10^{-20} at the same temperature. Thus the net enhancement of the diffusivity of O_i due to H is of the order of 6.8×10^6 at 400 °C. At 300 °C, the enhancement is 3.5×10^9. Such an enhancement of the diffusivity could directly contribute to TD formation. But it is likely that the immediate consequence is an enhancement in the formation rate of oxygen *dimers* if this formation is energetically favorable. Two configurations involving a pair of O interstitials bound to the lattice have been proposed as the fast diffusing species responsible for TD formation with an activation energy of 1.7 eV (see Refs. 9 and 11). In this case, H would only indirectly enhance TD formation.

Finally, the results of the present calculations are consistent with μSR and positron blocking experiments[25–27] which show that both μ^+ and Mu species disappear from the spectrum in the presence of O_i while the bond-centered species, Mu*, remains. However, detailed experimental data regarding the microscopic mechanisms involved in the H-enhanced formation rate of TD's and O-H interactions still are missing. The model proposed here is (qualitatively) consistent with the limited experimental information available, but is not necessarily unique. Further studies are needed to confirm (or replace) this model.

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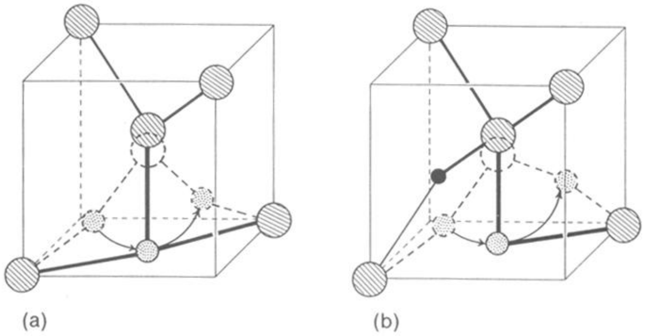
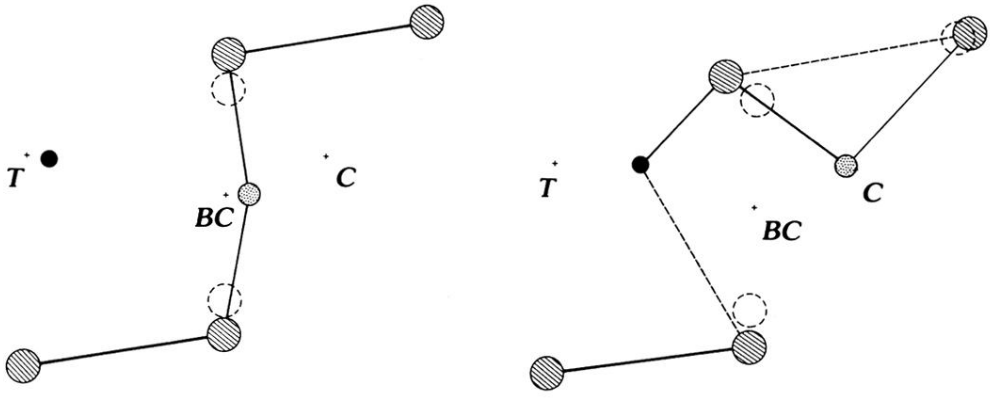
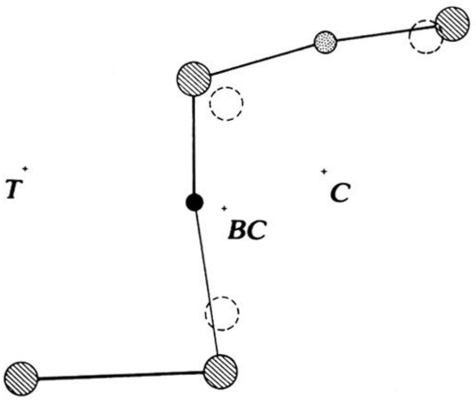


FIG. 1. Qualitative comparison between the transition points for O_i diffusion without H (a) and with H (b). The shaded circles are host Si atoms, the dotted circle is O, and the solid circle is H. The thickness of the bonds is proportional to the amount of overlap between two atoms. The curved arrows show the path of O_i from one equilibrium site to the next. In order to simplify the figure, only the central Si atom is shown displaced. A quantitative representation of the transition point in (b) is discussed in the text and shown in Fig. 2(b).



(a) $E = E_0$

(b) $E = E_0 + 1.25$ eV



(c) $E = E_0 - 0.66$ eV

FIG. 2. Geometries calculated in the $\{110\}$ plane at the PRDDO level for H near O_i in c-Si. The shaded circles are host Si atoms, the dotted circle is O, and the solid circle is H. The open dashed circles show the positions of the host atoms in the perfect lattice. The thickness of the lines increases with the amount of covalent bonding between two atoms. Three interstitial sites are indicated by crosses: the tetrahedral (T), bond-centered (BC), and C sites. (a) is a local minimum of the PES (with energy E_0). Hydrogen is off the T site by 0.24 Å and O_i is almost at its normal interstitial site. (b) shows the transition point for O between two adjacent interstitial sites. Hydrogen is primarily bound to one Si atom, and O is twofold coordinated. This configuration is 1.25 eV above E_0. Finally, (c) shows a minimum of the PES with both O_i and H near their normal stable configurations in c-Si. The energy is 0.66 eV below E_0. Hydrogen still forms a stronger bond with one of its two NN's.