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Mechanism for hydrogen-enhanced oxygen diffusion in silicon

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Oxygen diffuses in silicon with an activation energy of 2.53–2.56 eV. In hydrogenated samples, this activation energy is found to decrease to 1.6–2.0 eV. In this paper, a microscopic mechanism for hydrogen-enhanced oxygen diffusion in *p*-doped silicon is proposed. A path for joint diffusion of O and H is obtained from an *ab initio* molecular-dynamics simulation in which the O atom is ''kicked'' away from its equilibrium position with a given initial kinetic energy. After reaching a maximum potential energy of 1.46 eV above the ground state, the system relaxes to a metastable state on which a Si-Si bond is broken and the H atom saturates one of the dangling bonds. With an extra 0.16 eV, the Si-H bond is broken and the system relaxes to an equivalent ground-state configuration. Therefore, the migration pathway is an intriguing two-step mechanism. This path represents a 0.54-eV reduction in the static barrier when compared with the diffusion of isolated O in Si, in excellent agreement with experiments. This mechanism elucidates the role played by the H atom in the process: it not only serves to ''open up'' a Si-Si bond to be attacked by the oxygen, but it also helps in reducing the energy of an important intermediate state in the diffusion pathway. [S0163-1829(99)03607-3]

Being the predominant impurity in Czochralski-grown silicon, oxygen has been extensively studied since the early years of semiconductor research.[1] In particular, the diffusion of oxygen in silicon is extremely important from a technological point of view, since it governs both the formation of electric-active oxygen complexes (''thermal donors'')[2,3] and the precipitation of SiO_2 in silicon.[1] The ground-state configuration of a single oxygen in silicon is a bent bond-center (BC) interstitial (O_i). Diffusion of O_i in silicon occurs by jumps between neighboring BC sites with a measured activation energy of 2.53–2.56 eV.[4] It has been observed, however, that oxygen diffusion in hydrogenated silicon occurs with a much lower activation energy, 1.6–2.0 eV.[5–7]

The microscopic mechanism responsible for this enhancement of oxygen diffusion in the presence of hydrogen is still controversial. There are a few theoretical proposals in the literature. Based on Hartree-Fock cluster calculations, Estreicher[8] has proposed that the diffusion process would initiate with H in a metastable tetrahedral (T) site, which would then assist an oxygen jump to a neighboring bond center with an activation energy of 1.25 eV. During the process, the H atom itself would become trapped in a stable BC configuration. This model assumes that H diffusion in silicon is an out-of-equilibrium process on which the hydrogen atoms jump between adjacent T sites, without actually visiting the BC ground state. This view is not supported by either *ab initio*[9] or tight-binding[10] molecular-dynamics (MD) simulations of hydrogen diffusion. Another proposal is due to Jones *et al.*,[11] based on local-density-functional (LDF) cluster calculations. In disagreement with Estreicher, they find the antibonding (AB) site opposite to the Si-O-Si unit to be the ground state for H in the presence of O (as opposed to the BC site). They propose a mechanism for migration on which the Si-H backbond becomes stronger as the O jumps from one BC position to another, therefore lowering the saddle-point energy to 1.4 eV. Recently, Ramamoorthy and Pantelides[12] have investigated the relative stability of several $O+H$ configurations in silicon at different charge states. They find the BC configuration to be stable for the positive and neutral charge states, while the AB is stable for the negative configuration. Based on a procedure in which the atoms that drive the diffusion are moved in small steps and the others are allowed to fully relax, a joint migration pathway is proposed for the neutral BC structure in which the oxygen and hydrogen jump together to adjacent BC configurations, with an activation energy of 1.2 eV.

In this work, we perform *ab initio* total-energy calculations and MD simulations to investigate the mechanism for H-enhanced O diffusion in Si. Our calculations are based on the pseudopotential, local-density functional and supercell approximations. We use the Rappe *et al.* optimized pseudopotentials,[13] which allow converged calculations for

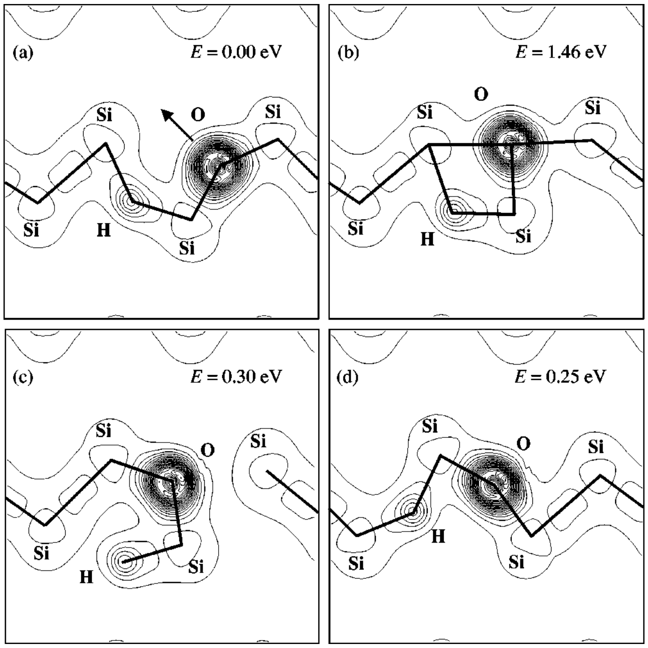

FIG. 1. Geometries and electronic densities of four configurations of the O+H pair in silicon, on the (110) plane, which contains both impurities. Atomic positions are represented by the vertices formed on the thick lines. Contours run from 0.25 to 6.25 electrons/Å^3. (a) Initial ground-state configuration, with BC O and H. The arrow indicates the direction of the initial ''kick'' on the oxygen. (b) ''Saddle-point'' configuration, defined as the configuration with maximum potential energy (1.46 eV above the ground state) during the MD simulation. (c) Metastable state with 0.30 eV, with H-saturated Si-Si broken bond. (d) Final ''ground-state'' configuration, with BC O and H. A true ground state can be obtained by rotations of H and O along the Si-Si axes.

oxygen-containing systems with a plane-wave cutoff of only 40 Ry. A cubic supercell with 64 Si, 1 O, and 1 H is adopted, allowing atomic relaxation of up to the third-nearest neighbors of both O and H. Γ point is used for k-point sampling in most of the calculations. Electronic minimizations are performed using the conjugate-gradients technique.[14] We focus our calculations on the H^+ charge state, for it is the dominant state for isolated hydrogen in *p*-doped silicon.[15,16]

Initially, we search for the ground state of the O+H system in silicon. We find the configuration with both atoms at adjacent BC sites to be lower in energy by 0.22 eV when compared with the metastable AB configuration. In Fig. 1(a) we show our calculated ground-state geometry and electronic density, and in Table I some calculated bond lengths and bond angles are presented.

We then proceed to investigate the migration pathway. We seek for a pathway that represents a joint diffusion of the O+H complex, i.e., in which the final configuration is equivalent to the initial ground-state configuration, except by a translation of both atoms in the jump direction. A rigorous calculation of the saddle point for the joint migration is a formidable task, due to the many degrees of freedom involved in the problem. Moreover, it has been shown[9,17] that the diffusion pathway of light impurities in silicon can be very much influenced by the *dynamics* of the diffusion jump, rather than being simply the minimum-energy adiabatic path. For these reasons, we try a dynamical approach: we ''kick'' the O atom in a perpendicular direction to the Si-(O)-Si axis [indicated by the arrow in Fig. 1(a)] with a 2.0 eV kinetic energy and then let the system evolve in a MD simulation. We define our calculated energy barrier as the energy of a ''saddle point'' given by the configuration of *maximum potential energy* along the trajectory. If our guess to this initial kick is good enough so that it mimics the actual movement of the O atom just before a migration jump, the other atoms will respond to it in a way to generate a pathway hopefully similar to the lowest-energy path. It is important to emphasize that the energy barrier calculated by this procedure *will be an upper bound* to the true minimum barrier for diffusion.[18]

TABLE I. Some bond lengths and bond angles of the ground- and metastable-state configurations of O+H in Si, shown in Figs. 1(a) and 1(c), respectively. Si_c denotes the central Si atom, which is initially bonded to both O and H.

Ground state		Metastable state	
Si-O	1.629 Å	Si-O	1.669 Å
Si_c-O	1.582 Å	Si_c-O	1.630 Å
Si_c-H	1.586 Å	Si_c-H	1.567 Å
Si-H	1.645 Å		
Si-O-Si_c	142.7°	Si-O-Si_c	117.4°
O-Si_c-H	100.6°	O-Si_c-H	98.0°
Si_c-H-Si	132.2°		

The MD simulations are performed using the Verlet algorithm with a 10^{-3}-ps time step. As a result of the simulation, we observe that the O atom jumps over a barrier of 1.46 eV. The ''saddle-point'' configuration is shown in Fig. 1(b). After the O atom overcomes the barrier and the potential energy starts to increase again, the MD simulation is stopped and the system is relaxed to a new minimum-energy configuration. Surprisingly, this configuration is not equivalent to the initial ground state, but rather a metastable state. This state is shown in Fig. 1(c). Instead of jumping to the next BC position, the H atom remains bonded to the central Si atom. Moreover, the Si-Si bond on which the O was centered initially is not reformed. Therefore, the dynamics of the diffusion jump produces a broken-bond defect in Si. This configuration has an energy of only 0.30 eV above the ground state. Interestingly, this type of defect has been proposed to be produced by the diffusion jump of a single O atom in silicon, but in that case it has an energy of 1.2 eV above the respective ground state.[17,19] Here, the H atom plays an important role in saturating one of the Si dangling bonds, and therefore, greatly reduces the energy of this state. The other Si dangling bond remains and it produces a gap state that is empty in the positive charge state. Some geometrical parameters related to this metastable state are also listed in Table I.

In order to complete the joint diffusion jump, the Si-H bond has to be broken so that the H goes to the BC position and the Si-Si bond reforms. We calculate the activation energy for this process by performing constrained total-energy calculations on which the Si-H distance is kept fixed at several values between two extreme limits: an initial situation where the Si-H distance is small and there is a bond between the two atoms and a final situation where the distance is large and the bond is broken. As a result of these calculations, we find an extra activation energy of just 0.16 eV (0.46 eV above the ground state) to bring the system to a final configuration with H and O at adjacent BC sites, shown in Fig. 1(d). This configuration is not exactly equivalent to the ground state (in fact, it has an energy of 0.25 eV above it), but the true ground state can be trivially obtained by rotations of the O and H atoms by 180° around their respective Si-Si axes, which are expected to cost very little energy.

Therefore, we conclude that H-enhanced O diffusion in *p*-doped silicon occurs in a very interesting two-step mechanism. The initial step consists of a jump of the O atom between two adjacent BC configurations and the simultaneous formation of an intermediate metastable state corresponding to a H-saturated Si-Si broken-bond defect. In the second step, this defect is annealed and the H jumps to the stable BC configuration. It is important to emphasize that the occurrence of the metastable state is directly related to the dynamics of the diffusion jump: Ramamoorthy and Pantelides[12] apparently did not find this state, despite the similarity of the total-energy methods employed, probably because of the adiabatic ''step-by-step'' procedure used. It should be interesting to try an experimental detection of this metastable state, but this should be a difficult task due to its small annealing energy barrier. An overall energy barrier of *at most* 1.46 eV for the combined process is obtained. This is somewhat smaller than the experimental values of 1.6–2.0 eV, but this discrepancy can be explained by dynamical effects that should produce deviations from predictions based on a static saddle-point calculation.[17] Since we calculate our energy barrier not as the initial kinetic energy, but as the maximum potential energy along the trajectory, we do not probe these dynamical effects. However, our result can be directly compared to the saddle-point energy of a single oxygen jump, given by the total energy of the well-known ''ylid'' configuration with threefold coordinated O, which we calculate to be 2.0 eV above its respective BC ground state. Therefore, the presence of hydrogen is responsible for at least a 0.54-eV reduction in the saddle-point energy, in excellent agreement with experiments. It is now clear the fundamental role played by H during the diffusion process: it serves both to ''open up'' a Si-Si bond on which the O atom will jump into and, more importantly, to decrease the energy of an important intermediate state during the diffusion jump by saturating a Si broken bond. This behavior is quite typical of hydrogen in semiconductors; therefore, we believe that hydrogen may behave in similar ways in assisting diffusion jumps of other impurities in semiconductors.

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[18] In fact, a trajectory generated by this molecular dynamics would approach the minimum energy trajectory if the diffusing atom had a mass much greater than the mass of the host atoms, so that the latter would respond almost instantaneously to the movement of the diffuser. In our case, we have the opposite situation: the O mass is smaller than the Si mass. Because of this mass diference, the oxygen loses its kinetic energy very rapidly to the lattice, an undesirable effect that can be prevented by giving back the available kinetic energy to the O atom. We have used this artifact once during the dynamics.

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