"Ab Initio" Studies of Hydrogen-Enhanced Oxygen Diffusion in Silicon

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A novel 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 "kick" simulation. The migration pathway consists of a two-step mechanism, with a maximum energy of 1.46 eV. 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.

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 migration energy of 2.53-2.56 eV [4]. Theoretical calculations [6, 7] have been performed within the framework of transition state theory (TST) [5], in which the migration energy is expressed as the energy difference between two static configurations: the ground-state and the saddle-point. For the case of O_i, the saddle-point is the well-known "ylid" configuration, with a three-fold coordinated oxygen. These *ab-initio* pseudopotential, local-density-functional, supercell calculations give migration energies in the range of 1.8-2.2 eV. Several mechanisms have been proposed to explain this discrepancy with

respect to experimental results [6, 7, 8].

It has been observed that oxygen diffusion in hydrogenated silicon occurs with a much lower activation energy, 1.6-2.0 eV [9, 10, 11]. 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 [12] 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* [13] or tight-binding [?] molecular-dynamics (MD) simulations of hydrogen diffusion. Another proposal is due to Jones *et al*[15], based on local-density-functional (LDF) cluster calculations. In disagreement with Estreicher, they find the anti-bonding (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 [16] 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. A joint migration pathway is proposed for the neutral BC structure on 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 molecular dynamics (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 [17], which allow converged calculations for 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 3rd-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 [18]. We focus our calculations on the H^+ charge state, for it is the dominant state for isolated hydrogen in p-doped silicon [19, 20].

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 which represents a joint diffusion of the O+H complex, i.e., on 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.

Therefore, we try a dynamical approach: The O atom is "kicked" in a direction perpendicular to the Si-(O)-Si axis (indicated by the arrow in Fig. 1(a)) with a 2.0 eV kinetic energy and then we 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 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 [21].

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 allowed to 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 initially centered 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 generated in the diffusi! on jump of a single O atom in silicon, but in that case it had an energy of 1.2 eV above the respective ground state [6, 22]. 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 which is empty in the positive charge state. The electronic density associated to this state is shown in Fig. 2. Some geometrical parameters related to this metastable state are also listed in Table I.
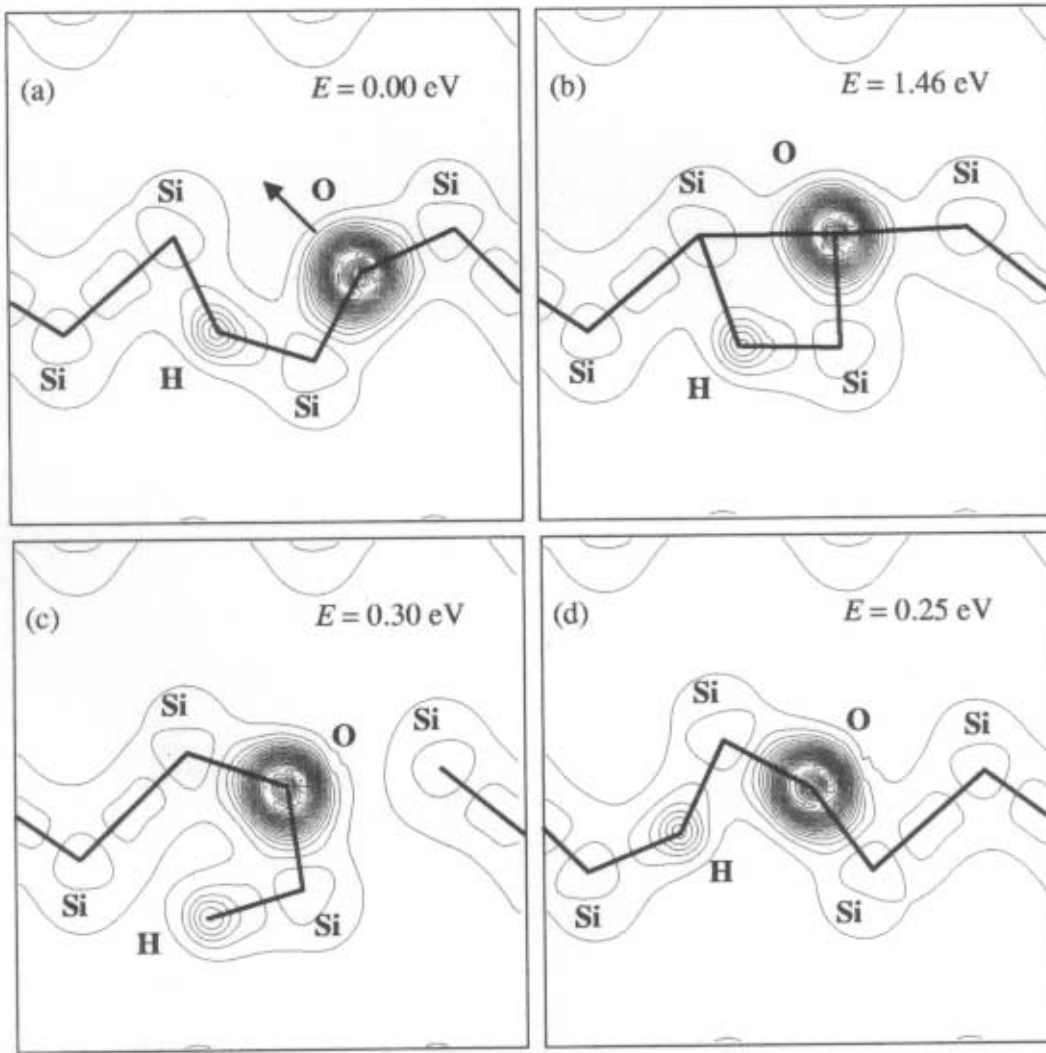
Figure 1. Geometries and electronic densities of four configurations of the O+H pair in silicon, on the (110) plane which contains both impurities. Atomic positions are represented by the vertices formed the thick lines. Contours run from 0.25 to 6.25 electrons/Å^3. (a) Initial ground-state configuration, 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.

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

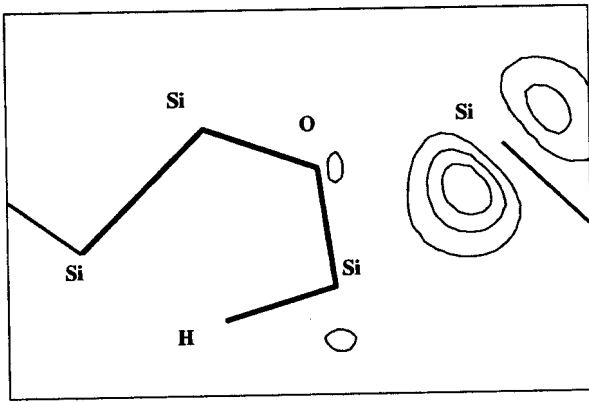| Ground state		Metastable state	
Si-O	1.629 Å	Si-O	1.669 Å
Si_c-O	1.582 Å	Si_c-O	1.630 Å
Si_c-H	1.586 Å	Si_c-H	1.567 Å
Si-H	1.645 Å		
Si-O-Si_c	142.7°	Si-O-Si_c	117.4°
O-Si_c-H	100.6°	O-Si_c-H	98.0°
Si_c-H-Si	132.2°		

Figure 2. Electronic density for the empty gap state at the metastable configuration. Contours run from 0.02 to 0.10 electrons/Å^3.

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: a 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 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. This discrepancy is similar to the case of isolated oxygen. Therefore, our barrier should be compared to the total energy of the "ylid" configuration. We calculate this energy to be 2.0 eV above its respective BC ground state, consistent w! ith previous *ab initio* calculations [6, 7]. 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.

Acknowledgments

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