Energetics and diffusion of hydrogen in SiO$_2$

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(Received 16 August 1999; revised manuscript received 18 October 1999)

We explore the energetics and migration of neutral hydrogen in SiO$_2$ using ab initio density-functional calculations. From static minimizations ($T=0$), we have calculated the formation energy and the adiabatic potential-energy surface of hydrogen in bulk SiO$_2$. Using our $T=0$ results, we employ classical transition state theory to derive the temperature dependent diffusivity: $D(T)=(8.1\times10^{-3}$ cm$^2$/sec)exp($-0.2$ eV/K$T$). This result is in good agreement with our molecular-dynamic simulations at $T=600$ K, and agrees reasonably with recent experiments.

Due to its scientific and technological importance, hydrogen in silicon dioxide (SiO$_2$) has garnered much interest in the literature.$^{1-15}$ In ubiquitous metal-oxide-semiconductor (MOS) transistors, hydrogen is used primarily to passivate interfacial defects that occur because of the lattice mismatch between SiO$_2$ and Si. From hydrogen-deuterium isotope experiments (Ref. 12), it has recently been shown that hot electron degradation in MOS devices is due in large part to the depassivation of atomic hydrogen at interface. Moreover, interface degradation is argued (Refs. 5 and 6) to be limited by hydrogen diffusion away from the interface into bulk SiO$_2$. In Ref. 14, observed thermal desorption was proposed to occur by neutral, atomic hydrogen diffusing into bulk SiO$_2$. In Ref. 10, diffusion of atomic hydrogen through SiO$_2$ to the Si-Si$_2$ interface was shown to generate interfacial electrical traps. In the bulk SiO$_2$ of MOS devices, atomic hydrogen was also implicated in leakage currents (Refs. 3 and 6) and in anomalous positive charge buildup (Ref. 11). The diffusion of neutral, atomic hydrogen is implicated in these disparate phenomena. Despite several experimental studies$^{7-14}$ and recent theoretical calculations,$^{1-4}$ a consistent atomistic picture of neutral hydrogen in SiO$_2$ has not fully emerged. In this study, we employ $ab$ initio simulations based on density-functional theory to provide reliable information regarding the energetics and migration of neutral hydrogen in SiO$_2$.

For our total-energy and molecular-dynamics calculations, we employ the Vienna ab initio simulation programs.$^{16,17}$ These calculations are based on density-functional theory within the local-density approximation (LDA).$^{18}$ Core electrons are implicitly treated by way of ultrasoft Vanderbilt-type pseudopotentials$^{19}$ provided by Kresse and Hafner.$^{20}$ The eigenfunctions are expanded on a plane-wave basis. As a test calculation, we compare theoretical properties of H$_2$ in the gas phase to experiment. We have found converged properties of H$_2$ using 30 Ry for the plane-wave basis cutoff energy, an empty box with sides of 14 Å and a $\Gamma$ point for the Brillouin-zone integration. Our result for the bond length is 0.765 Å, exactly the value found by Dickson and Becke,$^{21}$ whose LDA method is free of any errors due to pseudopotentials or periodic supercells. Also, our binding-energy result is 2.32 eV, which is within 0.01 eV of the previous high-quality LDA, pseudopotential result of Van de Walle,$^{22}$ and is less than 0.1 eV higher than experimental values.$^{23}$ Based on these results and tests reported in Ref. 22, we estimate a numerical uncertainty of 0.1 eV for the absolute energetics, noting that the numerical uncertainty for relative energetics for similar configurations should be smaller.

For our studies of H in SiO$_2$, we employ a nearly cubic supercell based on $\alpha$-crystobalite with $a=\sqrt{2}a_{prim} =7.0327$ Å and $c=c_{prim}=6.9389$ Å, where $a_{prim}$ and $c_{prim}$ are the theoretical lattice constants of the primitive unit cell as determined from calculations using 36 Ry for the basis-set cutoff. Note that our lattice constants are within 1% of previous LDA and experimental results.$^{24}$ There are eight SiO$_2$ units in the supercell. With calculations of point defects, it is important to test that defects are not interacting strongly with their periodic image. A measure of this interaction is the dispersion of the localized defect level. Using a $3\times3\times3$ k-point grid, we find the dispersion of the hydrogen-related defect level is at most $\pm 0.06$ eV for H at its minimum. We also investigated the effect of k-point sampling on total energies. The energy difference between using the $\Gamma$ point and the L point is 0.2 eV, whereas the difference between the L point and a $3\times3\times3$ grid is 0.01 eV. For all reported calculations, we use the L point for our k-point sampling. Finally, spin polarization is included and found to be important.

Global minimum: We have explored the total-energy surface for neutral hydrogen in our supercell. For these calculations, we use $E_c=30$ Ry, and all atoms are allowed to relax until the forces on each atom are less than 0.001 eV/Å. Although the total energy of the local minima is converged at a higher force tolerance, we use the lower tolerance to allow us to reliably calculate the low H frequencies using a force-matrix diagonalization scheme. For the force-matrix calculation, we displace the hydrogen by 0.02 Å in the x, y, and z directions, keeping all other atoms fixed. This frozen phonon approach is reasonable because the hydrogen atom is much lighter than the oxygen and silicon atoms.

In agreement with Ref. 1, we find that neutral hydrogen has a local minimum in an open void. Figure 1 shows the atomic picture for H at two equivalent local minima with the middle H at the saddle point for migration between these local minima. The minimum-energy location would be near the tetrahedral interstitial site in the corresponding c-Si lattice. At this local minimum, little interaction occurs between
the hydrogen and the lattice. Oxygen atoms are closest, and these are far away. The O-H distances are over 2.2 Å compared to 1.0 Å, the O-H bond length in water. The vibrational frequencies for neutral hydrogen at its minimum are at and below the vibrational peaks in amorphous SiO2. The frequencies are calculated to be 460, 320, and 220 cm⁻¹, which gives a zero-point energy of 0.06 eV. The formation energy for hydrogen at its minimum is 0.06 eV, only modestly more favorable than for hydrogen in free space. The relaxation energy, the energy gained by allowing atoms to relax around the H atom fixed at its minimum, is very small; 0.02 eV. The effect of spin polarization is significant as in the case of neutral hydrogen in a vacuum. We find that 0.6 eV is gained by including spin polarization. As in Ref. 1, we find a H-related defect level deep in the SiO2 band gap.

Migration barrier: We have explored the total-energy surface in order to determine the barrier for the hydrogen to migrate between local minima. As above, we have used $E_r = 30$ Ry for the basis-set cutoff energy. In order to represent the total-energy surface of hydrogen in $\alpha$-crystobalite, we have calculated over 100 data points with H fixed on a three-dimensional grid between two minima. Given the small relaxation energies for H at its minimum, we have concentrated on the unrelaxed total-energy surface, i.e., the neighboring atoms around the hydrogen are fixed in their crystalline positions.

Figure 2(a) shows a plane including two isoenergetic minima and the saddle point between them. Data here have been taken at a 0.5-Å spacing, and have been fit with a third-order polynomial interpolation function. The minima are positioned at opposing corners. Given that the zero-point energy is 0.06 eV, there is a large volume of nearly 1 Å³ which the hydrogen will occupy even at $T=0$ K. The results in Fig. 2(a) suggest a broad, low-energy migration path with the migration barrier being less than 0.3 eV. In Fig. 1 the middle hydrogen atom is at the saddle point which occurs in a region near the hexagonal interstitial site in the corresponding $c$-Si lattice. Figure 2(b) shows the same plane in a region close to the saddle point. The data here are taken at a spacing of 0.1 Å. We find one of our data points nearly coincides with the saddle point determined from Fig. 2(b). Indeed, the forces on H at this point are small, <0.1 eV/Å. The minimal barrier for migration is estimated to be 0.22 eV. In the estimated saddle position, the H atom is still far from other atoms; over 2.0 Å separates the H atom from its nearest oxygen neighbors. These nearby oxygens are positioned along the horizontal line from the middle H atom in Fig. 1(a). Allowing neighbors to relax for H at both the minimum and our saddle point indicates that the migration barrier is lowered, but only by 0.02 eV. Although we only show one plane of data, we have examined the forces and energies for H in regions perpendicular to this plane. These results confirm the picture presented in Fig. 2. Our calculations indicate that neutral hydrogen can easily migrate through SiO2 with
energy with the result derived for neutral hydrogen in crystalline silicon. We find the formation energy for H in SiO₂ is −0.06 eV compared to the value of −1.05 eV reported in Ref. 22 for H in c-Si. Therefore, we expect hydrogen to favor c-Si over SiO₂. In Refs. 4 and 26, it was noted that the measured activation energy of 2.56 eV for Si-H desorption at the Si-SiO₂ interface was consistent with the desorbed H atom entering bulk Si; in addition, it was suggested that a higher barrier would be needed for H to enter SiO₂. From the present results, we indeed find an additional 1.0 eV would be needed for neutral, atomic hydrogen to enter SiO₂ from c-Si. These results suggest a revision of the physical chemistry of H and defects at the Si-SiO₂ interface, with H in Si playing a more important role.

From our calculated migration path for neutral hydrogen in crystalline SiO₂, we can estimate the diffusivity of hydrogen. There are a number of theoretical methods one can employ to extract a diffusivity from our calculation of the total-energy surface. Bloch et al. recently employed a rate theory formalism to rigorously derive the temperature-dependent diffusivity of H⁺ in Si.25 Such a calculation is beyond the scope of the present study. Instead, we employ an approximate expression based on classical transition state theory:

\[ D(T) = l^2 \nu \exp \left( \frac{-E_a}{kT} \right) \]  

where \( l \) is the hopping distance between minima, \( \nu \) is the attempt frequency, \( E_a \) is the activation barrier, and \( kT \) is the Boltzmann constant times the temperature. We derive the above free parameters from our density-functional calculations. As indicated in Fig. 2(a), \( l \sim 3 \) Å; as estimated from our MD simulation and force-matrix calculation, \( \nu \sim 330 \text{ cm}^{-1} \) or \( 10^{13} \text{ sec}^{-1} \); and from Fig. 2(b), \( E_a \sim 0.2 \text{ eV} \). Using these values, we find the diffusivity at \( T = 600 \text{ K} \) is \( (1.5 \times 10^{-4} \text{ cm}^2/\text{sec}) \) which is within the range estimated from our MD simulation \( [(1–4) \times 10^{-4} \text{ cm}^2/\text{sec}] \). Although both our diffusivity estimates employ severe approximations, the agreement between the two results encourages confidence that the approximations are reasonable.

Several experiments have investigated the migration of hydrogen in SiO₂. However, we are aware of no experiments for H in α-cristobalite, and most studies investigate hydrogen in amorphous SiO₂. Nevertheless, α-cristobalite is fairly isotropic (see Fig. 1), and is one of the most stable SiO₂ polymorphs. Therefore, we expect our results should be a good starting point for understanding H in amorphous SiO₂. For oxides grown thermally on Si, we expect α-cristobalite to be particularly relevant. For amorphous SiO₂ thermally grown on c-Si, the oxide grows by the insertion of oxygen into Si-Si bonds at the moving Si-SO₂ interface. Over 10 Å from the interface, the thermally grown oxide is dense and well relaxed.

The experimentally derived activation energy barriers have a large spread from 0.05 to 0.9 eV (see Ref. 2, and references therein). The large spread may be due to the uncertainty of the hydrogen charge state being observed or, in some cases, there is controversy over whether neutral atomic H or \( H_2 \) are involved in the observed processes.13-15 More recent experiments for neutral, atomic hydrogen appear to agree on a value between 0.05 and 0.2 eV.7-10 Specifically, in dense oxides the activation energy is observed to be be-
between 0.1 and 0.2 eV \(^{7-10}\) whereas in open silica channels the barrier is found to be lower, 0.05 eV.\(^{8}\) Cartier \textit{et al.}\(^{10}\) injected neutral atomic hydrogen into SiO\(_2\) thermally grown on Si. The activated behavior observed in the generation of electrical traps at the Si-SiO\(_2\) interface is attributed to the diffusion of atomic hydrogen (and/or deuterium) through the oxide. The activation energy is measured to be 0.20 eV, precisely the value determined by the present calculations. The range of activation energies are in general agreement with our calculated activation barrier. The values below 0.2 eV are expected for more open, lower-density oxides. Higher values found in the literature may be due to mistakes in assigning the H charge state or errors in correlating observed kinetics to atomistic processes.

In only a few studies have the diffusivity for H been experimentally derived. Specifically, in wet fused silica,\(^{7,9}\) the diffusivity of neutral H is estimated at \((10^{-2} \text{ cm}^2/\text{sec})\exp(-0.17\pm0.02 \text{ eV/kT})\) compared to our value of \((8.1\times10^{-3} \text{ cm}^2/\text{sec})\exp(-0.2 \text{ eV/kT})\). Given the uncertainties in both experiment and theory, the agreement is fair; the theoretical activation energy is larger, which for the temperatures of interest in part compensates for the larger theoretical prefactor. More definitive comparisons and analysis could be made if experiments were available on \(\alpha\)-cristobalite. Both of these results appear to contradict the empirical MD simulations of Ref. 2. Their ambitious MD simulations extend for several hundred picoseconds, and one reported estimate for the H diffusivity in amorphous silicon is \(10^{-10} \text{ cm}^2/\text{sec}\) for \(T=800\) K. Both our present theoretical and recent experimental estimates\(^{7,9}\) are several orders of magnitude higher \((10^{-4} \text{ and } 10^{-5} \text{ cm}^2/\text{sec}, \text{ respectively})\). One explanation for the discrepancy may be due to the manner in which the empirical potentials in Ref. 2 were fit. That is, the parameters of a six-term Morse potential were fit to situations when H forms strong bonds with either oxygen or silicon atoms. Such a fitting may tend to overestimate the bonding interactions, which our present \textit{ab initio} calculations find to be very weak.

In conclusion, we have performed \textit{ab initio} density-functional calculations for neutral hydrogen in a supercell based on \(\alpha\)-cristobalite. We find the lowest-energy configuration involves H in an open interstitial over 2 Å from its nearest neighbor. The formation energy of H at its minimum is found to be only modestly more favorable than H in free space, and significantly less favorable than H in c-Si. From our force-matrix calculations, we find H frequencies between 200 and 500 \(\text{ cm}^{-1}\). We have surveyed the potential energy of H in SiO\(_2\). We find the adiabatic barrier for migration is 0.2 eV, in agreement with experiments for H in oxides thermally grown on Si. From both our potential energy survey and our \(T=600\) K MD simulations, we conclude that H interacts only weakly with the defect-free SiO\(_2\) lattice. From our potential-energy surface, we calculate the diffusivity for H in SiO\(_2\) to be \((8.1\times10^{-3} \text{ cm}^2/\text{sec})\exp(-0.2 \text{ eV/kT})\) which nicely agrees with the range derived from our \(T=600\) K MD simulation and is in fair agreement with results derived from experiments on wet fused silica.

I gratefully acknowledge stimulating interactions and collaborations with R. Martin, K. Hess, M. Staedele, L. F. Register, and C. G. Van de Walle. I also would like to acknowledge funding from the DOE (Grant No. DEFG02-96-ER45439), NSF (through DesCanES) and ONR (MURI Grant No. N00014-98-1-0604). Calculations were performed on SGI-ORIGIN2000 machines at NCSA in Urbana, IL.

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