Structure and Energetics of the Si-SiO$_2$ Interface

Yuhai Tu and J. Tersoff
IBM Research Division, T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 7 September 1999)

Using a Monte Carlo approach, we identify low-energy structures for the (001)-oriented Si-SiO$_2$ interface. The optimal interface structure found consists of an ordered array of Si-O-Si "bridges," with low strain energy. This structure explains several puzzling experimental observations.

PACS numbers: 68.35.Ct, 82.65.Dp

Silicon has long been synonymous with semiconductor technology. This unique role is due largely to the remarkable properties of the Si-SiO$_2$ interface, especially the (001)-oriented interface used in most devices [1]. Although Si is crystalline and the oxide is amorphous, the interface is essentially perfect, with an extremely low density of dangling bonds or other electrically active defects. With the continual decrease of device size, the nanoscale structure of the silicon/oxide interface becomes more and more important. Yet despite its essential role, the atomic structure of this interface is still unclear.

Experiments offer many clues to the interface structure, but their interpretation remains controversial because of the complexities inherent in studying disordered materials. Proposed models range from a graded interface [2,3] to a sharp interface [4,5] and even to a crystalline oxide layer at the interface [6]. Most theoretical studies have involved guessing candidate structures [7,8], sometimes even using hand-built models [4,9]. More recently, there have been attempts to obtain an unbiased structure using unconstrained molecular dynamics [10] and Monte Carlo (MC) studies [11]. However, because of kinetic limitations these studies have not attempted to identify the equilibrium structure.

Here we employ a novel approach in which the Si-SiO$_2$ system is modeled as a continuous network of bonds connecting the atoms, and the thermodynamic ensemble of possible network topologies is explored via MC sampling. The basic method has been described elsewhere [12] in a simpler context.

Our approach samples only defect-free configurations, in which Si and O have four and two bonds, respectively, and there are no O-O bonds. Because of this restriction, the energy may be reasonably approximated by a simple model:

$$E_{\{r\}} = \frac{1}{2}\sum_i k_b(b_i - b_0)^2 + \frac{1}{2}\sum_{i,j} k_\theta(\cos\theta_{ij} - \cos\theta_0)^2 + U\,. \quad (1)$$

The first two terms represent the cost of bond-length and bond-angle distortions, respectively; we call these the "strain energy." The term U represents a "suboxide penalty," the chemical energy cost of any suboxide, based on recent *ab initio* calculations [13]. Here $\{\mathbf{r}\}$ is the set of atom positions, $E_{\{r\}}$ is the total energy for a given network topology and given $\{\mathbf{r}\}$, i represents the ith bond, with b_i as its length, and θ_{ij} is the angle between bonds i and j to a common atom. The material parameters depend implicitly on the type of atom, where b_0 is the preferred bond length, θ_0 is the preferred bond angle, and k_θ and k_b are "spring constants." We take $k_{b,\text{Si-Si}} = 9.08\ \text{eV}/\text{Å}^2$, $k_{\theta,\text{Si-Si-Si}} = 3.58$ eV, $b_{0,\text{Si-Si}} = 2.35$ Å, $\cos(\theta_{0,\text{Si}}) = -1/3$, $k_{b,\text{Si-O}} = 27.0$ eV, $b_{0,\text{Si-O}} = 1.6$ Å, $k_{\theta,\text{O-Si-O}} = 4.32$ eV, $k_{\theta,\text{Si-O-Si}} = 0.75$ eV, and $\cos(\theta_{0,\text{O}}) = -1$. For Si-Si-O bonds we set the spring constant to be the geometric mean $k_{\theta,\text{Si-Si-O}} = (k_{\theta,\text{Si-Si-Si}}k_{\theta,\text{O-Si-O}})^{1/2}$. (There is an additional term in the energy which simply enforces the restriction of two and four neighbors for O and Si, respectively [12].)

In order to focus on the role of network structure, we treat the energy as a function solely of bond *topology*, minimizing $E_{\{r\}}$ with respect to the geometrical coordinates $\{\mathbf{r}\}$. Thus for a given network topology

$$E = \min_{\{\mathbf{r}\}} E_{\{r\}}\,. \quad (2)$$

The structure of the system is allowed to evolve toward thermodynamic equilibrium through Monte Carlo bond-switching moves [12,14]. (We adapt the original move to preclude O-O bonds.) At each step a random trial bond-switch is accepted with probability $\max(1, e^{-\Delta E/k_BT})$ where ΔE is the energy increase, guaranteeing that the system will evolve toward thermodynamic equilibrium. This approach gives a fairly accurate description of the structure of both amorphous Si [12,14] and amorphous SiO$_2$. Specifically, the average bond length and bond angles are in agreement with experiment, and the elastic constants are accurate to better than 20%.

Our model for the energy is rather simple compared with the more accurate *ab initio* methods used in some recent studies [7,10,11]. Our approach should nevertheless be reasonably accurate for the defect-free structures considered here. More important, this approach allows the large-scale MC sampling necessary for the system to move toward thermodynamic equilibrium, which is not feasible with *ab initio* methods. It also allows us to determine the actual interface energy, using thermodynamic averaging. More accurate methods are not at present able to determine

0031-9007/00/84(19)/4393(4)$15.00 © 2000 The American Physical Society

the interface energy, even for a given interface structure, because it is impractical to average over the statistical ensemble of configurations of the amorphous oxide.

We begin with a convenient though unphysical structure, a perfect interface between crystalline Si and highly strained α crystobalite. We use 10 layers of Si, and SiO_2 containing an equal number of Si atoms, periodically repeated in the interface-normal (z) direction. In the other two dimensions, we use cells with 2×2 and 4×4 periodicity, for a total of 160 and 640 atoms, respectively. To correctly describe the real physical system, the cell size is constrained to match Si(001) in two directions, while the period normal to the interface is allowed to vary to maintain zero stress in that direction.

We first perform MC bond switching within the oxide at a relatively high temperature, allowing it to amorphize and relax the large strain by viscous flow. We then perform unconstrained MC switching of the entire system, allowing it to equilibrate at a temperature of 887 °C ($k_B T = 0.1$ eV) for up to 300 000 MC steps.

We have carried out 10 independent MC simulations for a 2×2 cell. The resulting interface structures are shown in Fig. 1. The key structural element is an oxygen bridge between each pair of Si atoms terminating the Si crystal. This eliminates half the bonds from the Si side, correcting the mismatch between the bond densities in the two very different materials. This structure allows each atom to maintain its preferred coordination, with essentially no additional distortion of the bond angles or bond length beyond that already present due to the amorphous nature of the oxide. Bridge bonds have appeared in several previous models of the Si-SiO_2 interface [6,7,9,11]. However, it has apparently not been previously recognized that these are the key elements minimizing the interface energy.

All of these simulations gave fully bridge-bonded structures. However, two distinct arrangements are possible within our 2×2 periodicity, and both occur in the simulations. We refer to these as the "stripe" and "check" phases, respectively, and they are compared in Fig. 1.

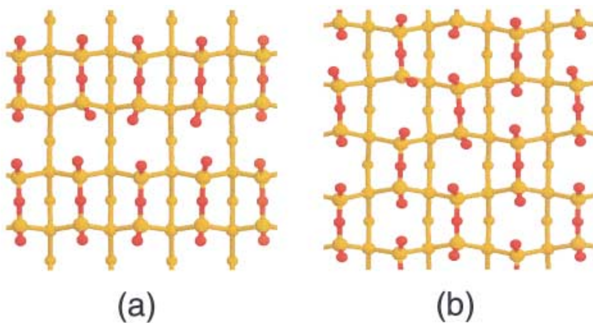

FIG. 1 (color). Plan view illustrating two Si-SiO_2 interface structures. The last three layers of Si are shown in gold, with atoms farther from the interface shown smaller. The first layer of O is shown in red. (a) Stripe phase, having (2×1) symmetry. (b) Check phase, having $c(2 \times 2)$ symmetry.

Similar runs with a 4×4 cell also give bridge-bonded structures. The key role of the bridge bonds is illustrated in Fig. 2, where the strain energy of the system and the number of bridge bonds at the interface are plotted against MC "time" for a typical 4×4 simulation. There is a clear drop in energy each time a new bridge bond is formed.

For the 4×4 cell, the system typically becomes "stuck" in a metastable state with incomplete (of order 75%) bridge bonding, due to antiphase or stripe/check boundaries. Nevertheless, the energy is consistently lower in structures with more complete bridge bonding. If we prepare the system in a fully bridge-bonded structure before annealing, the bridge bonds are conserved (up to $k_B T = 0.15$ eV), and the resulting structures have lower energy than those with partial bridge bond coverage. Thus it seems clear that, with sufficient annealing, the 4×4 cell would always reach the ideal stripe structure. A side view of this structure is shown in Fig. 3a.

Past work, both experimental and theoretical, has focused primarily on the suboxide content of the interface, as revealed by the Si charge-state statistics. However, our simulations suggest that this is relatively peripheral to the network structure and energy. This is best understood by defining a "canonical" interface structure, in which the ideally bridge-bonded Si (whether stripe or check) is connected to the SiO_2 through a single layer of Si^{+2}. It is this canonical structure that is shown in Figs. 1 and 3. It is then possible to alter the charge-state statistics without changing the underlying network topology by replacing a Si-Si bond with Si-O-Si or vice versa. For example, inserting an oxygen into the first Si-Si bond at the interface converts a Si^{+2} and a Si^0 into a Si^{+3} and a Si^{+1}.

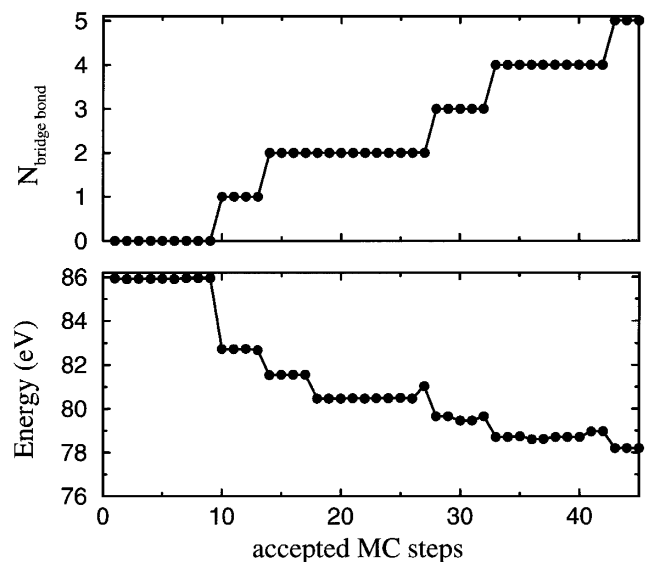

FIG. 2. "Strain energy" E, and number of interfacial bridge bonds, versus number of accepted Monte Carlo steps. The decrease in the energy each time a bridge bond forms illustrates their crucial role in giving a low interface energy.

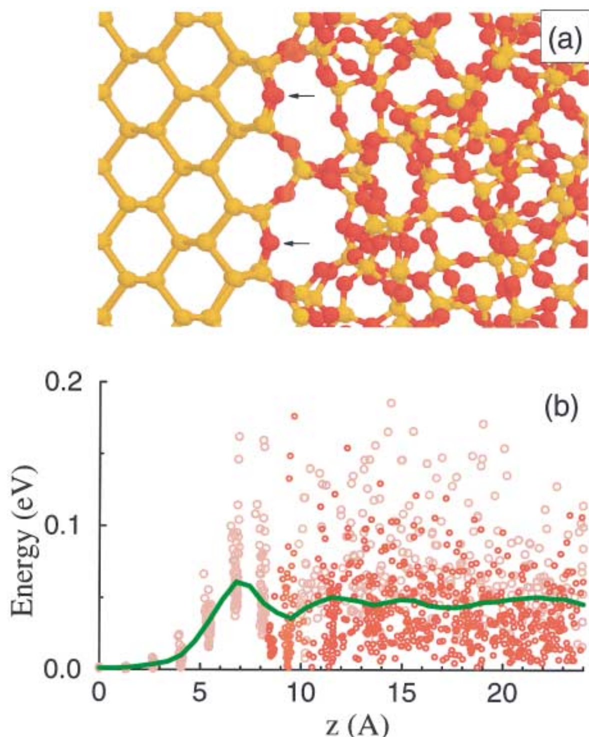

FIG. 3 (color). (a) Side view of canonical interface, for 4×4 cell of stripe phase, in [110] projection. The Si and O atoms are represented by gold and red spheres, respectively. Each arrow points to a row of oxygen atoms that form the bridges at the interface. Notice the substantial voids above each bridge bond. (b) Energy of each atom versus its z coordinate. Red circles represent oxygen atoms and gold circles represent silicon atoms. The green line is the local energy per atom, averaged over 20 configurations (and over a z range of $\sim$1 Å for smoothness).

We have repeated our calculations with and without the suboxide energy U [13] in Eq. (1), and also using a somewhat different energy function [15]. In all cases we find the same basic structure. However, the number of atoms in different charge states varies substantially, depending on the specific model used. Simulations without the suboxide penalty give a monolayer of Si^{+2} plus (very roughly) another half-monolayer each of Si^{+1} and Si^{+3}. Including the suboxide penalty reduces the total amount of suboxide by roughly half a monolayer. In all cases the overwhelming majority of the interfacial dimers are Si-O-Si bridge bonds, although at any given time a very small fraction are Si-Si dimers.

Perhaps the most interesting point is that the energy of all these structures is *higher* than that of the canonical interface, by an amount of order $k_B T$ per interface atom. We conclude that the canonical structure is the ground state of the interface. We believe that the ground state is ordered in the stripe phase, although we cannot rule out check or other more complex arrangements of bridge bonds. Any additional suboxide appears to be driven entirely by entropy rather than energy. (We also cannot rule out possible structures having different atomic coordinations, O-O bonds, or other defects.)

Beside the structure, the most important property of the interface is its energy (or at finite T, its free energy). The interface energy can be calculated by subtracting the bulk energy of the amorphous oxide and crystalline Si (obtained in independent calculations) from the total energy. In all cases the energy is averaged over roughly 10 000 MC steps after the system reaches equilibrium. If we constrain the interface to have the canonical structure (no extra suboxide), the calculated interface strain energy for the stripe phase is 6.8 ± 1.3 meV/Å^2 (0.10 eV per 1×1 cell), reflecting the nearly ideal match between the bridge-bonded Si(001) and the amorphous oxide. For the check phase, we find a similar (but slightly higher) energy of 9.5 ± 1.9 meV/Å^2 (0.14 eV per 1×1 cell). The total interface energy includes in addition the suboxide penalty for a monolayer of Si^{+2} (0.51 eV per 1×1 cell according to Ref. [13]). As described above, unrestricted equilibration gives additional suboxide, and an interface energy of order $k_B T$ higher than this.

We can gain further insight into the energetics by decomposing the total energy of the system into individual atomic contributions. This decomposition is not unique, but a natural choice is to divide the bond-stretching energy in Eq. (1) equally between the two atoms. Half of the bond-angle energy is assigned to the vertex atom, and one quarter to each of the other atoms. In Fig. 3b, the strain energy of each atom is plotted versus its z coordinate, for a 4×4 cell in the stripe-phase canonical structure, after equilibration for 300 000 MC steps. A striking feature is that the main contribution to the interface energy comes from local distortions inside the crystalline Si. The energy within the oxide is rather uniform, even right up to the interface.

There has been considerable interest in the possibility of a crystalline interfacial oxide [6,16]. We can form an interface between Si(001) and tridymite (0001) which resembles the stripe phase above, but the tridymite is under considerable strain (about 7% in one direction and 13% in the other). The properties of this interface are summarized in Fig. 4. The interface energy is actually much higher than that for amorphous SiO_2, about 29 meV/Å^2 (0.43 eV per 1×1 cell). Thus there appears to be no interfacial driving force for formation of a crystalline oxide.

Yet several experiments have suggested the presence of a crystalline oxide layer roughly 5 Å thick at the interface, based on electron microscopy [6] and x-ray diffraction [16]. These results have remained an outstanding puzzle, but they are immediately explained by our structure.

Electron microscopy suggested a 5 Å layer of tridymite at the interface [6]. Comparison of Figs. 3a and 4a shows that the structure of the Si-tridymite interface is indistinguishable from the more realistic crystal-amorphous interface, in a region several angstroms thick at the interface. Thus our proposed interface structure is entirely consistent with the electron microscopy results. However, it is best

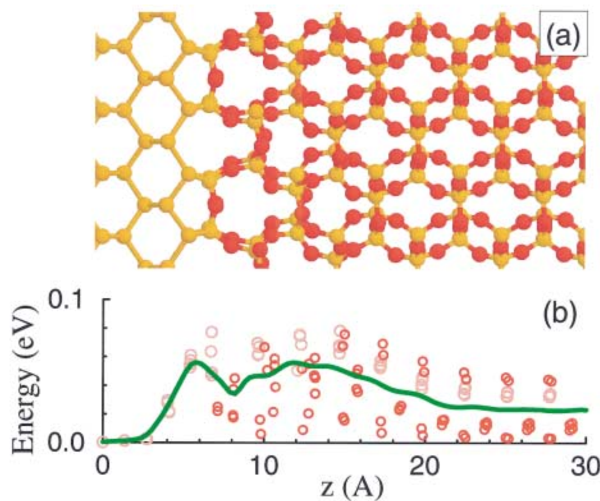

FIG. 4 (color). Interface between Si and tridymite, as in Fig. 3, to illustrate similarity of interface regions.

viewed as an ordered *interface* structure, without reference to any crystalline bulk phase.

X-ray diffraction experiments show an ordered 2×1 structure at the interface, with a thickness of under 6 Å and a domain size comparable to the step spacing [16]. The stripe phase exactly satisfies these characteristics. It has an overall 2×1 periodicity. Moreover, every interface step causes a 90° rotation from 2×1 to 1×2, so the step spacing sets an upper bound on the domain size. The presence of random small atomic displacements (associated with the amorphous oxide and disordered suboxide) explains the inability of Ref. [16] to determine precise atomic positions from the diffraction data.

Most experiments, however, have not noted any evidence of order. In analogy with layer-by-layer growth of crystals, it is likely that oxidation creates alternating up and down steps at the interface, as well as domain boundaries or antiphase boundaries. (This is compatible with angstrom-level interface smoothness.) The density of steps and boundaries depends on the oxidation kinetics (and the smoothness of the initial Si), and a very high density would preclude observation of order in either diffraction or electron microscopy.

Prior models of the interface have generally focused on the measurement and explanation of charge-state statistics [2,3,7,11,17]. However, the interpretation is surprisingly subtle [17]. There appears to be some consensus that the primary connection between Si and SiO_2 occurs via Si^{+2} [3,17], with some additional suboxide near the interface; and our model is consistent with this picture. Since the precise amount of suboxide is somewhat sensitive to the choice of potential, we cannot address this issue quantitatively. Moreover, a high density of interface steps and other defects could significantly affect the charge-state statistics. But we emphasize that, whatever the amount and type of suboxide, the ordered, bridge-bonded network structure remains the same.

In conclusion, we have identified a simple ordered structure for the Si-SiO_2 interface. This structure is free of dangling bonds or other coordination defects. It has low strain energy, and appears to reconcile the various puzzling experimental observations. The computational method focuses on a more complete exploration of the thermodynamic ensemble, even when this requires significant approximations in treating the energetics. It is our hope that this approach will open the door to a new class of computation studies of disordered systems.

[1] L. C. Feldman, E. P. Gusev, and E. Garfunkel, in *Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices,* edited by E. Garfunkel, E. Gusev, and A. Vul' (Kluwer Academic Publishers, Boston, 1998), pp. 1–24, and references therein.

[2] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).

[3] P. J. Grunthaner, M. H. Hecht, and N. M. Johnson, J. Appl. Phys. **61**, 629 (1987).

[4] S. T. Pantelides and M. Long, *The Physics of SiO_2 and its Interfaces* (Pergamon, New York, 1978).

[5] D. A. Luh, T. Miller, and T. C. Chiang, Phys. Rev. Lett. **79**, 3014 (1997).

[6] A. Ourmazd, D. W. Taylor, J. A. Rentschler, and J. Bevk, Phys. Rev. Lett. **59**, 213 (1987).

[7] A. Pasquarello, M. S. Hybertsen, and R. Car, Appl. Phys. Lett. **68**, 625 (1996).

[8] R. Buczko, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. **84**, 943 (2000).

[9] I. Ohdomari, H. Akatsu, Y. Yamakoshi, and K. Kishimoto, J. Non-Cryst. Solids **89**, 239 (1987).

[10] A. Pasquarello, M. S. Hybertsen, and R. Car, Nature (London) **396**, 58 (1998).

[11] K. O. Ng and D. Vanderbilt, Phys. Rev. B **59**, 10 132 (1999).

[12] Y. Tu, J. Tersoff, G. Grinstein, and D. Vanderbilt, Phys. Rev. Lett. **81**, 4899 (1998).

[13] D. R. Hamann (unpublished), (private communication). The extra cost of the suboxide is captured by including energies of 0.47, 0.51, and 0.24 eV for each Si^{+1}, Si^{+2}, and Si^{+3}, respectively. The variation of other parameters with oxidation state is less important, and can be omitted here.

[14] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).

[15] R. B. Laughlin and J. D. Joannopoulos, Phys. Rev. B **17**, 2790 (1978).

[16] G. Renaud *et al.,* Appl. Phys. Lett. **58**, 1044 (1991).

[17] M. M. Banaszak Holl, S. Lee, and F. R. McFeely, Appl. Phys. Lett. **65**, 1097 (1994).