Bonding Arrangements at the Si-SiO_2 and SiC-SiO_2 Interfaces and a Possible Origin of their Contrasting Properties

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(Received 15 June 1999)

We report *ab initio* calculations designed to explore the relative energetics of different interface bonding structures. We find that, for Si (001), abrupt (no suboxide layer) interfaces generally have lower energy because of the surface geometry and the softness of the Si-O-Si angle. However, two energetically degenerate phases are possible at the nominal interface layer, so that a mix of the two is the likely source of the observed suboxide and dangling bonds. In principle, these effects may be avoidable by low-temperature deposition. In contrast, the topology and geometry of SiC surfaces is not suitable for abrupt interfaces.

PACS numbers: 68.35.Ct, 68.35.Bs, 81.65.Mq, 82.65.Dp

A key component of metal-oxide-semiconductor field-effect transistors (MOSFETs) is the semiconductor-oxide interface. The predominance of Si in microelectronics is due primarily to the properties of the Si-SiO_2 interface, which can easily be made very abrupt (minimal suboxide layer) and smooth (minimal steps) with a minimal density of point defects [1]. As scaling laws are pushing the technology to ultrathin SiO_2 layers, understanding and control of the interface on the atomic scale remain open challenges. For power MOSFETs, a semiconductor with a wider band gap is preferred. SiC, whose native oxide is also SiO_2, is one of the options, but efforts to develop SiC-based MOSFETs have been thwarted by poor-quality SiC-SiO_2 interfaces.

The abruptness and smoothness of the Si-SiO_2 interface are puzzling because SiO_2 is amorphous. In addition, O has a high solubility and diffusion constant in Si. In contrast, O is not known to be an abundant impurity in SiC, and a recent calculation finds that O has very low solubility in SiC [2]. Yet, SiC interfaces are generally found to be rough for MOSFETs. Photoemission [3] has provided information on bonding arrangements at the Si-SiO_2 interface while microscopy and theory led to several interface models [4–10]. Total-energy calculations have accounted for the observed low density of interface point defects [11] and have found that, during thermal oxidation, lateral growth is preferred [10]. Yet, the mechanisms that control abruptness and smoothness remain an open issue that is critical for the ultimate control of ultrathin gate oxides.

In this Letter, we address the mechanisms that control abruptness at the Si-SiO_2 and SiC-SiO_2 interfaces. In the case of the Si (001) surface, a set of judiciously chosen *ab initio* calculations suggest that abrupt interfaces generally have lower energy. The origin of this result can be traced to the softness of the Si-O-SiO_2 angle and the particular geometry of this surface, which imposes order in the nominal interface layer (NIL). These effects make suboxide bonds energetically costly, thus setting the stage for potentially perfect interfaces, except for entropic considerations that normally introduce defects (in this case, suboxide bonds) to lower the free energy at finite temperatures, as is true of "perfect" crystals. Unfortunately, however, two distinct but energetically degenerate ordered structures are possible at the NIL. Inevitably, the NIL of real Si-SiO_2 structures is made of two types of domains. It is these domain boundaries, plus entropy effects within domains, that are the likely cause of the observed suboxide [3] and dangling bonds [12]. Thus, theory suggests that the high quality of Si-SiO_2 interfaces can be traced to processing choices, made empirically, that enable large single domains to form. It may, therefore, be possible to further suppress suboxide bonds, steps, and dangling bonds with low-temperature nonequilibrium deposition techniques that avoid entropic effects. In contrast, in the case of SiC, neither the (0001) surface of the hexagonal phase nor the (001) surface of the cubic phase offer a suitable geometry and bond lengths for abrupt models. Geometry alone suggests that suboxide bonding is inevitable.

The calculations were carried out using state-of-the-art codes based on density functional theory, the local-density approximation for exchange correlation, ultrasoft pseudopotentials, and plane waves [13]. The energy cutoff for the plane waves was set at 380 eV, as determined by extensive convergence studies. Integrations over the Brillouin zone were done using the Pack-Monkhorst scheme with two k-points in the relevant irreducible wedge. The supercells differed in size as described below. All of them had 7–9 Si layers separating the SiO_2 layers. In all cases, all the atoms and the z dimension of the supercell were allowed to relax to equilibrium values.

Though several bonding arrangements have been proposed for the Si-SiO_2 interface, comparisons of their

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relative total energies have not been possible so far. Most of the earlier work sought to match a Si substrate with a crystalline form of SiO_2. We approached the problem from a different perspective, namely, layer-by-layer deposition, leaving open the possibility that, after several layers, the film may turn out to be one of the known crystalline polymorphs. We emphasize at this point that we are describing a model construction process to obtain models whose relative total energies can be computed and compared. We will discuss the feasibility of achieving such a process in practice later in the paper.

It is well known that the (001) Si surface undergoes reconstruction by forming rows of dimers, eliminating half of the dangling bonds. Insertion of an O atom in a dimer leads to a stable configuration [6]. We investigated ordering of Si-O-Si bridges and found that rows [Fig. 1(a)] and a checkerboard pattern [Fig. 1(b)] have the same energy (the difference, 0.02 eV per Si-O-Si is smaller than the numerical error bar). The basic reason for this equality is that, in both patterns, every surface Si atom takes part in one Si-O-Si bridge and has one dangling bond. Since a Si atom cannot take part in bridges on both sides because of the bond length values, a random pattern of Si-O-Si bridges would lead to a highly defective interface. Domains separated by NIL domain boundaries or steps are the only alternative to a single pattern. We will first examine deposition of SiO_2 on each of the two distinct patterns and then examine domain boundaries.

The next step in our gedanken layer-by-layer deposition is to connect the remaining dangling bonds (one per atom) with longer bridges such as the following: (a) bridges containing one extra Si atom, namely, Si-O-Si-Si or Si-O-Si-O-Si; the first of these corresponds to suboxide bonding; (b) bridges containing two extra Si atoms, namely, Si-O-Si-O-Si-Si or Si-O-Si-O-Si-O-Si; again, the first of these corresponds to suboxide bonding.

Clearly, one can proceed with a random combination of such bridges to build an amorphous oxide [14]. In order to gain insights into energetically preferred bonding arrangements, we explored ordered structures containing only one type of long bridge at a time. We were able to form several superstructures. Each type of long bridge yields patterns that are reminiscent of bonding in different crystalline polymorphs. In addition, we inserted an additional one or two "bulk" layers within the SiO_2 film with bonding patterns reminiscent of β quartz, α cristobalite, and β tridymite. All three of them can be connected to the checkerboard pattern, but only tridymite can be connected to rows. Several of the resulting superstructures are shown in Fig. 2. We note that the ideal interface has a NIL in which all Si atoms are in the Si^{2+} oxidation state without any Si^{1+} or Si^{3+} states. In contrast, every suboxide bond,

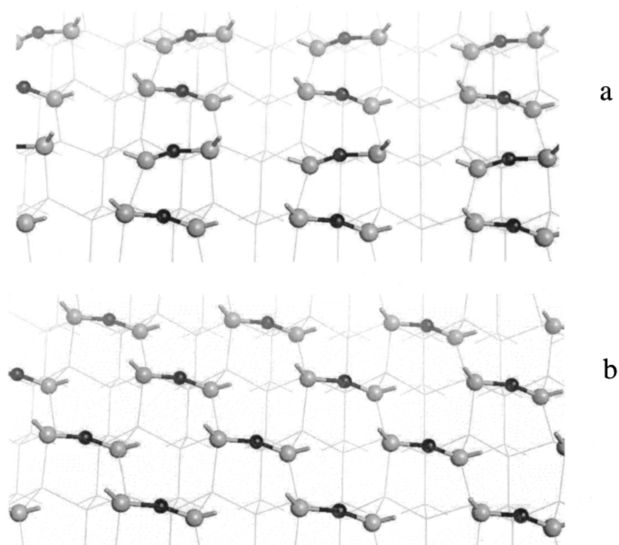

FIG. 1. Ordered structures on a Si (100) surface with half-monolayer O coverage. (a) Rows and (b) checkerboard pattern of Si-O-Si bridges. All atoms have a dangling bond.

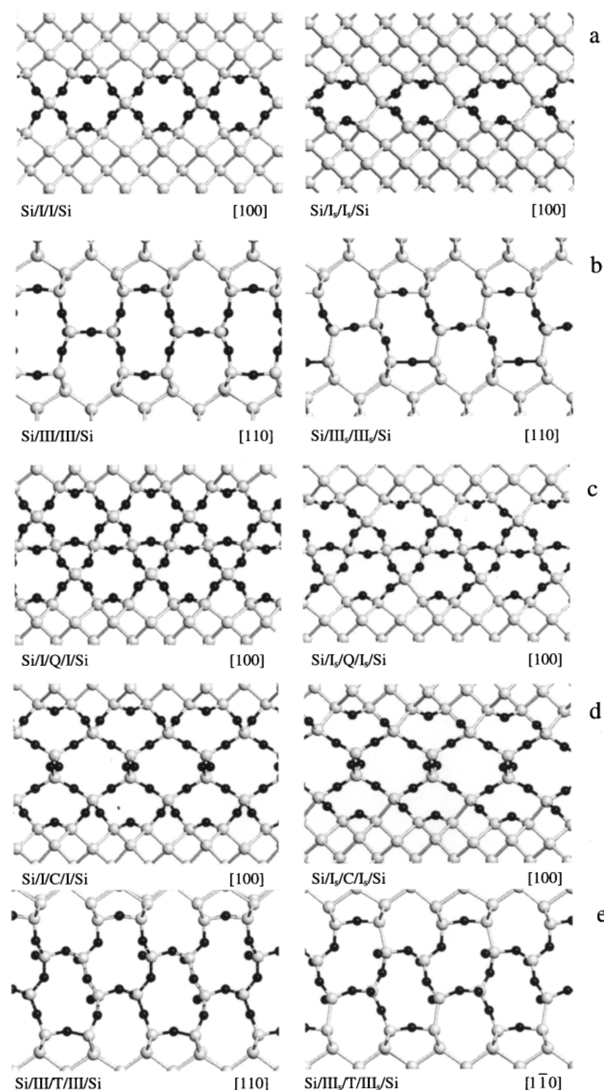

FIG. 2. Examples of Si-SiO_2-Si superstructures with one [(a), (b)] and two [(c), (d), (e)] oxide layers. The left panels are abrupt interfaces; the right panels have suboxide bonding.

TABLE I. Interface energies for studied structures. The numbers shown correspond to the sum of the two interface energies for each superstructure, normalized per 1×1 cell of the Si surface. For the structures with crystalline interlayer, the strain energy of the interlayer was subtracted as described in the text. Q stands for quartzlike bonding (the c axis of quartz lies along the [100] axis of Si). C stands for cristobalitelike bonding, and T stands for tridymitelike bonding. Interfaces I and II correspond to the checkerboard pattern of short bridges; III and IV to rows.

Superstructure		Interface energy (eV) 1 layer	2 layers	3 layers
Interfaces with suboxide layer	$Si/I_S/Q/I_S/Si$	2.1	2.2	2.0
	$Si/I_S/C/I_S/Si$		2.8	2.9
	$Si/III_S/T/III_S/Si$	2.0	2.0	1.8
Abrupt interfaces	Si/I/Q/I/S	1.3	1.4	1.4
	Si/I/C/I/Si		2.1	1.8
	Si/II/T/II/Si	1.7	1.7	1.8
	Si/III/T/III/Si	1.7	1.5	1.5
	Si/IV/T/IV/Si	1.4	1.5	1.4

as defined here, corresponds to a pair of Si^{1+} and Si^{3+} states, so that our model interfaces with 50% suboxide bonds correspond to a 1:1:1 ratio of oxidation states. This happens to be the observed ratio. We would need significantly larger supercells, beyond current capabilities, to study models with other ratios of oxidation states. Nevertheless, our calculations will be informative about the energetics and origins of suboxide bonding.

Calculation of the total energies of the superstructures described above enables us to extract and compare "interface energies." We first compute the total energy of the relaxed superstructure and then subtract $N\varepsilon + N'\varepsilon'$ where N and N' are the number of Si-Si and Si-O-Si bonds, respectively, in the superstructure, and ε and ε' are the corresponding energies per bond in perfect Si and SiO_2 crystals (β quartz, the lowest-energy form). In the cases that contain the extra SiO_2 interlayer(s), we subtracted the strain energy of the oxide, which was estimated by using suitably stressed perfect crystals (it ranges from 0.0 to 0.5 eV for one to three layers). This construction enables for the first time the extraction of the excess interface energy in different interface bonding structures.

The calculated interface energies are shown in Table I. We note that they are of the same order as those of grain boundaries [15], suggesting that these ordered interfaces are not unrealistic. Furthermore, the interface energy is always higher in all interfaces with suboxide bonding. Since the effect is true independent of whether the oxide is in compression (tridymitelike) or tension (cristobalitelike or quartzlike), we conclude that the result is quite general, though a truly amorphous structure may allow additional relaxations. There is a simple explanation for this result: Si-Si bonds cannot be bent very easily, whereas Si-O-Si bridges have a soft angle at the O atom and pivot quite freely about the O (Fig. 3). Thus, they can be both stretched and bent with minimal energy cost. For the model interfaces studied so far, the results of Table I show that insertion of O atoms in the suboxide Si-Si bonds always lowers the energy. We have, therefore, identified a mechanism that tends to make the Si-SiO_2 interface abrupt. We note further from Table I that suboxide bonding is most favored when the local SiO_2 structure is tridymitelike.

Before we consider interface domains and steps, we note from Table I that quartzlike and tridymitelike bonding are energetically preferred. Furthermore, quartzlike bonding entails tension along the c axis [parallel to the Si (100) direction], whereas tridymitelike bonding entails biaxial compression. The best choice, therefore, would be to have a checkerboard interface with a coexistence of small quartzlike and tridymitelike domains to counterbalance the overall strain. Because of the large strain in the bulk, identifiable phase domains are not likely, in favor of "intimate phase mixing," in effect amorphous bonding. Such cells can probably be constructed, but calculations would have to wait for even higher-performance computers.

We now consider the effect of interface domain boundaries and steps. The NIL atomic arrangements of domain boundaries that run parallel to the interface Si-O-Si bridges do not contribute any energy cost because every

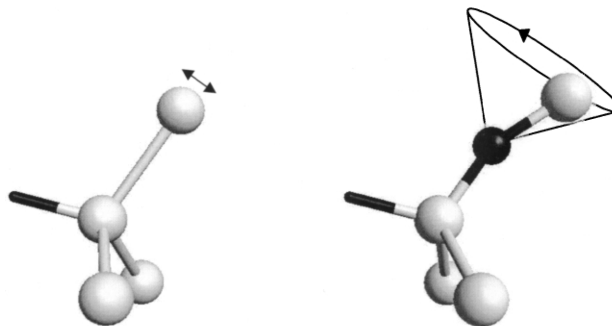

FIG. 3. Schematic illustration of the pivoting relaxation allowed by the Si-O-Si bridges. In addition, the Si-O-Si bridge can be easily stretched because the angle at the O atom is soft.

Si atom is still taking part in only one such bridge (see Fig. 1). Domain boundaries in any other direction, however, inevitably result in a ... *SLSXLSLS* ... sequence of short (S) and long (L) bridges, where X denotes a frustrated bridge (must be both S and L to satisfy both sides). If an ideal NIL is retained, such domain boundaries are lines of dangling bonds. Using stick-and-ball models, we found that reconstruction is very easy if suboxide bonds are allowed. Calculations are not feasible, but it is safe to conclude that such "suboxide intrusions" would be energetically preferred over dangling bonds. Thus, whereas we found that suboxide bonds are energetically costly within domains, they form naturally at domain boundaries. Each such suboxide bond, however, does not necessarily correspond to a pair of Si^{1+} and Si^{3+} oxidation states any more. In agreement with the theory of Ref. [11], it seems that dangling bonds are accidental defects and can potentially be suppressed by nonequilibrium deposition.

Steps require even larger calculations to assess quantitatively, but they are fundamentally suboxide intrusions. The pivoting relaxation mechanism of Fig. 3 suggests that steps are not favored, but calculations are not feasible so that no definitive conclusion can be drawn. The results of Ref. [10] regarding lateral growth are consistent with this notion.

Putting all the above considerations together, we conclude the following: The Si (001) surface imposes order at the interface layer requiring either rows or a checkerboard pattern of Si-O-Si bridges. Furthermore, the unique contrast between Si-Si and Si-O-Si bonds exerts a powerful force to keep the interface abrupt and smooth. Suboxide intrusions corresponding to the observed Si^{1+} and Si^{3+} oxidation states are most likely within domains for entropic reasons and at domain boundaries between two energetically degenerate interface structures (rows and checkerboad pattern). It appears, therefore, that a suboxide layer can, in principle, be avoided if conditions are found to grow large interface domains at low temperatures, e.g., by atomic layer epitaxy.

We close the discussion of Si by commenting briefly on the feasibility of fabricating Si-SiO_2-Si superstructures that could lead to revolutionary Si-based devices, such as single-electron transistors. Our calculations suggest that metastable ordered structures can be formed layer by layer if one starts with a checkerboard pattern of Si-O-Si bridges. Thus, a Si-SiO_2-Si superstructure may be realizable. It is a major challenge to practitioners of atomic-layer epitaxy because the structures are metastable (O would like to penetrate the Si substrate as in thermal oxidation), requiring a nonequilibrium pathway, but the rewards would be enormous.

In contrast to Si (001), in the Si-terminated cubic SiC (001) surface, the distance between dangling bonds is ~ 3 Å, so that one can easily insert an O atom between all pairs [i.e., have an O in both the "black" and "white" sites of the checkerboard pattern of Fig. 1(b)]. All dangling bonds are then saturated and growth is terminated. The same total-saturation effect is favored by geometry in the (0001) surface of hexagonal SiC and has been observed experimentally [16]. Careful examination of the hexagonal SiC (0001) surface revealed several other modes of total saturation, but no bonding arrangements that yield abrupt and smooth interfaces. Suboxide bonds seem inevitable. Such structures have been constructed, but the cells are too large for practical calculations. Visual inspection of the models suggests that elimination of the suboxide bonds is unlikely because of severe geometric constraints. We conclude that geometric consideration alone imply that suboxide bonds, either isolated or in the form of steps, are inevitable at SiC-SiO_2 interfaces.

We acknowledge useful discussions with L. C. Feldman and his group and with M. Di Ventra. This work was supported in part by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., the Office of Naval Research under Grant No. N00014-96-1-1286, a joint grant from the Advanced Research Projects Agency (MDA972-98-1-0007) and the Electrical Power Research Institute (W0806905), an Air Force Office of Scientific Research grant (F-49620-99-1-0289), and the William A. and Nancy F. McMinn endowment at Vanderbilt University.

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