Electronic Properties of the Si/SiO_2 Interface from First Principles

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Unoccupied oxygen p-projected densities of states, calculated from first principles in a model Si/SiO_2 interface, are found to reproduce trends in recent atomic resolution electron energy-loss spectra [D. A. Muller *et al.,* Nature (London) **399**, 758 (1999)]. The shape of the unoccupied states and the magnitude of the local energy gap are explicitly related to the number of O second neighbors of a given oxygen atom. The calculated local energy gaps of the oxide become considerably smaller within 0.5 nm of the interface, suggesting that the electronic properties do not change abruptly at the interface.

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Active element density in integrated circuits has doubled roughly every 18 months for the last 30 years, a progression embodied in Moore's law. The smallest but crucial controlling feature of these circuits is a thin, insulating silica (a-SiO_2) layer, the gate oxide, the thickness of which is rapidly nearing scales comparable to atomic bond lengths. Industrial gate oxides are currently about 8–10 oxygen atoms (2.0–2.7 nm) thick, and nanotransistors can be made with gate oxides in which atoms at interfaces comprise 40% of the layer, i.e., less than 5 O atoms (1.3 nm) thick [1]. By examining the electronic properties of ultrathin (<1.5 nm) a-SiO_2 gate oxides with electron energy-loss spectroscopy (EELS), Muller *et al.* [2] recently predicted that at least 0.8 nm of silica is necessary to maintain the required bulk electrical properties. These predictions arise in part from significant measured differences in the oxygen K edge spectra near and at the Si/SiO_2 interface, indicating a reduced local energy (or excitation) gap [3] for the oxide near the interface. The importance of such large departures from bulk structural properties cannot be overemphasized, as they will necessarily lead to changing dielectric and conductance behavior. A device with such a thin oxide layer will no longer function as intended, and new technology will be required for the scaling implicit in Moore's law to continue.

In this Letter we extend the results of Ref. [2] by closely examining the electronic structure of a model Si/SiO_2 interface [4] using density functional theory within the local density approximation (LDA) [5]. After establishing agreement between calculated unoccupied oxygen local densities of states and O K EELS spectra, we find that they are both quite sensitive to second neighbor arrangements; the physical width of the interface as measured with core-level photoemission spectroscopy (PES), in contrast, has been found to be sensitive to smaller length scales (just *nearest* neighbors) in previous first-principles studies [4]. Thus while the structure may change discontinuously at the interface, we find that its associated electronic properties will change over distances comparable to those between oxygen *second neighbors.*

Empirically there is evidence for both graded [6,7] and abrupt [8] Si/SiO_2 interfaces, and crystalline silica has even been observed at the interface [9]. In sorting out the various possibilities presented by experiment, the primary criterion for many theoretical models [4,10–13] has been consistency with core-level PES. Any first-principles model of the Si/SiO_2 interface must accommodate the twofold reduction in Si bond density while continuing to impose long-range order on the oxide (as required by periodic boundary conditions). As we wish to understand EELS measurements, which probe local electronic properties [2], the loss of long-range disorder is acceptable. Here we implement existing structural models from the work of Pasquarello, Hybertsen, and Car [4] whose starting point is a supercell consisting of seven layers of β-tridymite bonded to ten layers of Si-(001), the extremities being saturated by H atoms [14]. In what follows, we use two fully relaxed modifications of the β-tridymite near the interface calculated in Ref. [4]: the first (model III) introduces a Si-Si bond oriented perpendicular to the interface (by eliminating an oxygen); the second (model IV) adds an extra O atom between an Si atom at the interface to the bulk Si substrate. Both modifications result in a locally disordered suboxide region (roughly 1.5 monolayers) at the interface that naturally accommodates the bond density mismatch, in addition to saturating any residual dangling bonds present after attaching the tridymite [15]; the graded suboxide region is also consistent with the partial oxidation states (Si^{+3}, Si^{+2}, and Si^{+1}), as it has been used to calculate $2p$ core-level shifts that agree with those observed using PES [4].

The electronic charge density from the atomic positions determined in Ref. [4] is obtained from the Vienna *ab initio* Simulations Package (VASP) [16], which utilizes a plane wave basis set. Ultrasoft pseudopotentials are used for O and H; a norm-conserving pseudopotential is used for Si [17]. The charge density is initially converged self-consistently at the Γ point; non-self-consistent calculations are then performed to generate the electronic structure. To examine the variation in electronic properties over the

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interface and compare with the EELS measurements, we partition the single-particle density of states (DOS) by position both in the supercell and in the atomic species, and project out states of unique angular momentum (unoccupied p states for comparison with EELS K edges, s and d states for EELS L edges). The resulting *local* density of single-particle states (LDOS) $g_{i,l}(E)$ is calculated by using 12 **k** points in the Brillouin zone and broadened with a Gaussian whose full width at half maximum is 0.7 eV to match the EELS energy resolution of Ref. [2]. The features are converged with this mesh, agreeing well with an 81 **k**-point calculation.

Because the calculated single-particle DOS ignores collective excitations of the system (which cannot be ruled out *a priori* in experiments), we initially compare our first-principles calculations of bulk α-quartz with EELS measurements [2] of the K and L edges of a-SiO$_2$. As can be seen in Fig. 1, the calculated Si s- and d-projected unoccupied densities of states (UDOS) of α-quartz differ appreciably from the measured Si L edge of bulk silica because of a pronounced core-hole exciton; the replacement of a single Si with a phosphorus atom in the unit cell can be used to mimic this core hole [18], and the corresponding calculations result in combined phosphorus s- and d-projected UDOS in better agreement with the measured Si L edge. The calculated p-projected UDOS of an O atom (O p-UDOS) already corresponds quite well to the observed oxygen K edge of silica, indicating that the O K edge is not particularly affected by the exciton at this energy resolution. Of additional interest is the fact that the intrinsic long-range disorder of the oxide does not appear to have any measurable effect on it either, a demonstration of the strong dependence of the electronic structure on the local bonding environment [19].

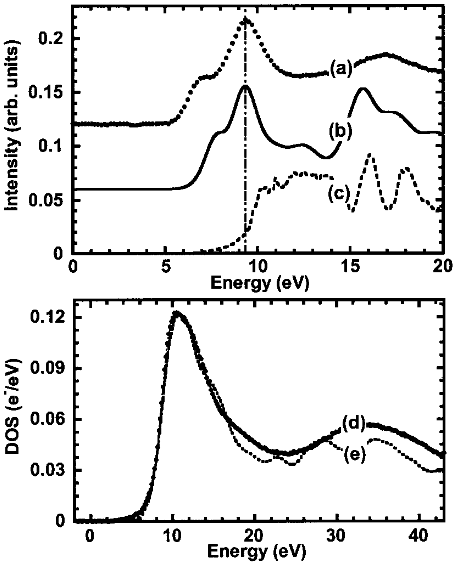

FIG. 1. EELS resolves electronic dipole transitions from the core states of a particular atom to *unoccupied* final states; it is therefore comparable to the site-specific LDOS. Many-body effects, however, can limit the comparison in some cases and in fact the measured Si $L_{2,3}$ edge (a) exhibits a strong exciton, which can be well modeled by replacing a silicon in the α-quartz unit cell by a phosphorus atom (b); it does not resemble the ground state calculation of the unoccupied Si s- and d-DOS (c). In contrast, the vertically scaled unoccupied O p-DOS (d) does resemble the measured O K edge (e) without modification of the cell.

Since the O p-UDOS can be directly compared with experiment, we calculate it for oxygen atoms both near and away from the interface, and the results for model III appear in Fig. 2. The calculated band gaps for bulk Si and β-tridymite are 0.5 and 6.5 eV, respectively; these are underestimated by the LDA as is well known [20], the empirical gaps being 1.17 eV for Si and 8.9 eV for a-SiO$_2$. About 8 Å from the interface in the supercell, all oxygens are coordinated as in the bulk, and the O p-UDOS in Fig. 2 reproduces the measured O K edge of amorphous silica. Near the Si/SiO$_2$ interface, however, the calculated UDOS is radically different from its bulk counterpart: The onset of the unoccupied states is reduced by 3 eV, implying a reduced local energy gap [21]; the sharp peak is absent at the interface; instead, the UDOS is relatively flat. These changes agree remarkably well with those previously observed by experiment [2] in the O K edge (Fig. 2).

To understand the changes in electronic structure, it is important to note that neither the edge onset of O p-UDOS nor its shape diminish abruptly at the interface. As Fig. 3 attests, the local energy gap of the oxide is close to that of bulk Si ~3 Å from the interface, finally reaching that of bulk SiO$_2$ after 5 Å: From this we can conclude that the electronic properties of oxide layers within 5 Å of the interface *are not* those of bulk silica. The p-DOS of the oxygen labeled 4b in Fig. 3 exhibits a gap nearly that of bulk

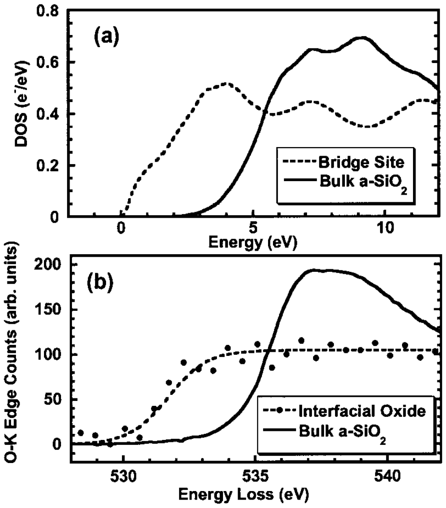

FIG. 2. Theory and experiment compared: (a) unoccupied O p-DOS calculated for an oxygen atom at the bridge site and in the bulk of the model supercell agree well with (b) the intensity profiles of O K edges measured with EELS [2].

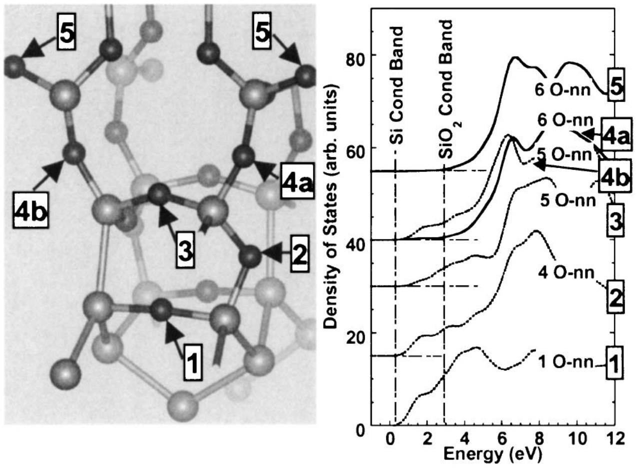

FIG. 3. The calculated O p-UDOS are shown as a function of position from the interface for model III of Ref. [5]. The number of oxygen nearest neighbors dictates both the shape and the local energy gap of the O p-UDOS. Note that the gap changes as the number of O nns drops from six to five. The changes in the offset of the occupied states are similar to the changes shown here in the unoccupied DOS, in qualitative agreement with the bulk cluster calculations.

Si. Calculations of an atomically abrupt model interface by Kaneta and Yamasaki [22] recently showed a similarly changing local electronic structure over a distance of 4 Å into the oxide. These calculations agree both with the data presented here and the EELS data, an indication that the reduction in the local energy gap is largely insensitive to the concentration of different oxidation states of Si.

Both the diminishing peak associated with and the reduced onset of the unoccupied states of the O p-DOS at a given O atom near the interface are, however, dependent on its surrounding *oxygen* neighbors. In the bulk, each oxygen sits at the corner of a tetrahedron, bridging two Si (each 1.6 Å away) at the center of neighboring tetrahedra. In addition to two Si nearest neighbors (nns), every oxygen has six O nns (these are strictly second neighbors) at a distance of roughly 2.7 Å. To understand the importance of the O nns, consider the p-UDOS of two oxygens equidistant from the interface (4a and 4b) in Fig. 3: They have different oxygen coordination (4a having 6 and 4b having 5 O nns) and, crucially, *different energy gaps.* As the number of O nns decreases, the spectra become noticeably different, culminating in the relatively flat behavior of the O p-UDOS right at the interface. Thus in the simplest approximation we expect electronic properties to change over a distance into the oxide comparable with the average O-O distance, or roughly 3 Å. With the importance of the role of the O nns now identified, an abrupt change in local energy gap at the interface *cannot* be expected.

The importance of the number of oxygen neighbors to the local energy gap is quantitatively illustrated by the use of the fourth moment $\mu_{O,p}^{(4)}$ of the *total* (both occupied and unoccupied) O p-DOS. The moments of the DOS bring out the general features of its shape, and, in particular, a low value of the normalized fourth moment of the O p-DOS $[\mu_{O,p}^{(4)}/(\mu_{O,p}^{(2)})^2]$ can indicate a large local energy gap [23]. A more robust definition involves the kurtosis parameter s defined in Fig. 4, which is quantitatively related to the local energy gap in the same manner but accounts for the larger intensity of the occupied DOS through the third moment or *skewness.* Figure 4 displays quite convincingly a strong correlation between the number of O nns and s (i.e., increasing states in the energy gap). This correlation is expected by Cyrot-Lackmann's moments theorem [24], which explicitly connects $\mu_{O,p}^{(4)}$ to the second neighbor arrangements (i.e., O-Si-O vs O-Si-Si) through all paths of length 4 that start and finish on the same site. Consequently we would expect the kurtosis parameters for any relaxed Si/SiO$_2$ interface to collapse on the line shown in Fig. 4. The decreasing intensity of the O K edge fine structure with the number of O nns has been noted before [25]; the relation made here between the O K edge and the O p-UDOS in the vicinity of the conduction band edge allows conclusions to be drawn about evolution of the states in the gap with changes in the second neighbor oxygen coordination. Since the oxygen density must drop near the interface, the diminishing intensity of the p-UDOS peak (and the K edge in the EELS data [2]) can be understood as characteristic of the absence of coordination of oxygen *by other oxygen atoms.*

Since the fourth moment can also be approximately connected to changes in the cohesive energy through a bond-order formalism [26], there is yet a further consequence of the importance of second neighbor arrangements. Empirical potentials used to describe an Si/SiO$_2$ interface must have significant three-body interactions involving O-Si-O triplets to correctly capture the contributions of the O nns arrangements and O-Si-O bond angles to the O

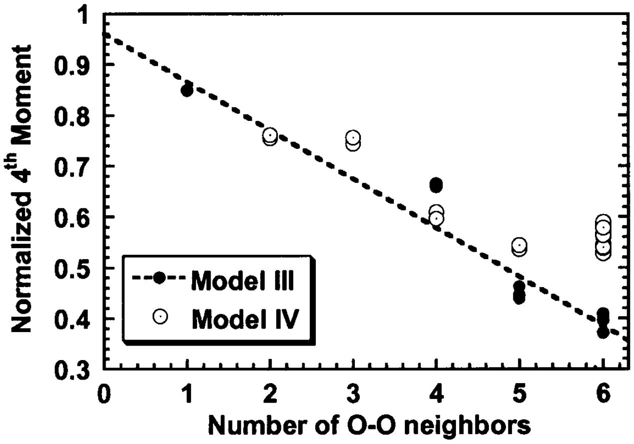

FIG. 4. The kurtosis parameter $s = [\mu_{O,p}^{(4)}\mu_{O,p}^{(2)} - (\mu_{O,p}^{(2)})^3 - (\mu_{O,p}^{(3)})^2]/(\mu_{O,p}^{(2)})^3$ of $g_{O,p}(E)$ plotted as a function of oxygen nearest neighbors for models III and IV of Ref. [5]. As $\mu_{O,p}^{(4)}$ is dependent on the local energy gap, this illustrates the correlation between the number of oxygen nearest neighbors and the gap, following Cyrot-Lackmann's moments theorem [24].

sites: Simple ionic models of the oxide will not reproduce these features. Finally, the sensitivity of the electronic properties of the interface to second neighbor arrangements clearly has important consequences for the practical functionality of gate oxides presently approaching these dimensions: Two-thirds of a 1.5 nm gate oxide will be expected to exhibit a *very different* local energy gap from that of bulk silica. Since the energy gap of the oxide dictates its dielectric properties (specifically its ability to screen out Si-induced interface states), this is of extreme technological import. The changing dielectric constant will also affect the accuracy of ellipsometric measurements of the oxide thickness (which underestimate the chemical thickness [2] by about 0.5 nm).

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