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Reference

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Si $2p$ Core-Level Shifts at the Si(001)-SiO_2 Interface: A First-Principles Study

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Using a first-principles approach, we calculate core-level shifts at the Si(001)-SiO_2 interface. By fully relaxing interfaces between Si and tridymite, a crystalline form of SiO_2, we obtain interface models with good local structural properties and with no electronic states in the Si gap. Calculated values of Si $2p$ core-level shifts agree well with data from photoemission experiments and show a linear dependence on the number of nearest-neighbor oxygen atoms. Core-hole relaxation accounts for ~50% of the total shifts, in good agreement with Auger experiments.

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Precise knowledge of the microscopic structure of the Si(001)-SiO_2 interface could lead to an improvement of the quality of metal-oxide-semiconductor devices and is therefore highly desirable. However, despite the use of many experimental techniques [1], the detailed atomic structure of this interface remains to date essentially unknown. The intrinsic difficulty lies in the fact that the bond pattern at this interface connects a perfectly ordered crystal to a fully disordered amorphous phase.

Core-level (Si $2p$) photoelectron spectroscopy (PES) has been one of the principal tools for investigation, providing valuable yet indirect information on the structure at this interface [2–4]. PES experiments indicate the presence of a transition region with intermediate-oxidation states of Si. Three partial oxidation states of Si are observed and all appear to be present in significant amounts. The various suboxide peaks are attributed to Si atoms with a different number of nearest-neighbor O atoms. This empirical assumption based on a charge-transfer model is generally accepted and has been heavily relied upon in the construction of structural models. However, this simple picture has been challenged by a very recent experiment [5], which suggests that second nearest-neighbor effects might be important. These considerations motivate interface models which do not contain all the possible oxidation states [6]. Additional uncertainty has been generated by recent calculations which seem to indicate that unequal shifts are obtained with different interface models [7,8].

The purpose of this work is to determine how the core-level shifts at the Si(001)-SiO_2 interface relate to the underlying microscopic structure. Since the actual structure is unknown, a prerequisite to this study is an interface model with supposedly good electronic and structural properties. We have adopted a model based on an interface between two periodic structures, Si and tridymite [9]. Although the long-range disorder is not taken into account, this model is sufficient for our purpose, since the electronic properties in which we are interested mainly reflect the local microstructure. The presence of an intralayer of tridymite has first been proposed [9] to account for a metastable interface structure observed by x-ray scattering [10] and transmission electron microscopy [9]. Although this interpretation has been controversial [11], we adopt this model rather than previously reported models based on beta-crystobalite [12,13] because it is a likely candidate for a structure without unsaturated dangling bonds. This property is suggested by measurements of the interface trap densities [14] which show that not more than one electronic state in the fundamental gap of Si is found for every 10^4 interface atoms.

The structure has been fully relaxed using density functional theory in the local density approximation (DF-LDA) to describe the electronic structure. Bond lengths and angles similar to those of other SiO_2 structures and the absence of electronic states in the fundamental Si gap suggest that our relaxed model gives a good representation of the local structural and electronic properties. The calculated Si $2p$ core-level shifts at the interface show a linear dependence on nearest-neighbor O atoms, and negligible dependence on the charge state of more distant atoms, confirming the validity of the simple charge-transfer model. Our values for the shifts are in very good agreement with PES experiments [4]. To achieve this agreement it has been crucial to include core-hole relaxation effects, which are found to account for about 50% of the total shift, in accord with estimates from Auger experiments [15,16].

The atomic positions of our initial structure are obtained by attaching tridymite [17] to bulk terminated Si(001). The c axis of tridymite is aligned to the Si [110] direction, and the tridymite [100] direction is taken parallel to the Si $[1\bar{1}0]$ direction. In order to match the two periodic structures, the tridymite is compressed by 12% and 7% along its [100] and [001] directions, respectively. In this geometry the oxide is built up by alternating planes of O atoms and Si-O chains parallel to the interface. One of the dangling bonds of every Si atom at the bulk termination is saturated by forming a bond to the oxide, whereas the other one can be saturated either by dimerization or by the formation of O bridges [9]. We have studied two different models: a first one in which we have allowed for

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the formation of dimers, and a second one in which we have replaced the dimers by O bridges.

In our calculations the atomic coordinates have been relaxed to minimize the total energy using the Car-Parrinello method [18], which provides the electronic structure as well as the forces that act on the ions. Only valence electrons are explicitly considered using pseudopotentials (PP's) to account for the core-valence interactions. A norm-conserving PP is used for Si [19], whereas the O atoms are described by an ultrasoft Vanderbilt PP [20]. The electronic states were expanded on a plane-wave basis set. Exchange and correlation were included using Perdew and Zunger's interpolation formulas [21]. A description of the method is given in Ref. [22].

In order to achieve good convergence in the electronic properties, we have used a plane-wave cutoff of 16 Ry for the wave functions and of 150 Ry for the augmented electron density. In this way, the experimental bond length for molecules such as SiO_2 and SiO could be reproduced to within 1%. Our system contains a 2×2 interface unit of side $L = 7.65$ Å (based on the theoretical equilibrium lattice constant of Si). The dimension of the cell in the direction orthogonal to the interface is 31.7 Å containing 14 layers of Si (18 Å) and seven monolayers of oxide (9 Å), the extremities being saturated with hydrogen atoms. Hence, our system contains 68 Si, 28 O, and 12 H atoms. In the case of O bridges, two additional O atoms are introduced. In the minimization process, all the atoms of the oxide as well as the first six Si layers are allowed to relax. The Brillouin zone (BZ) of our simulation cell is sampled using only the Γ point.

At the end of the relaxation process the Si atoms have formed a dimer bond under the first layer of oxide chains, as shown in Fig. 1(a). The relaxed structure with O bridges is shown in Fig. 1(b). In both relaxed models, the Si-O bond distance is found to be rather constant, about 1.62 ± 0.02 Å, and the O-Si-O bond angle distribution is peaked at the tetrahedral angle. Most of the stress seems to be relieved by the rather flat distribution of the Si-O-Si angle, which ranges from 110° to 170°. The ranges of these values are characteristic of the different crystalline structures as well as of the amorphous phase of SiO_2 (see, e.g., Ref. [23]).

By analyzing the electronic wave functions, we find that the highest occupied state as well as the lowest unoccupied state are both Si related and do not present any significant weight at the interface. Despite our modest k-point sampling, we are able to conclude that there are no states in the fundamental gap of Si. Indeed, shallow interface states would be predominantly associated to band extremities near Γ and the X point of the Si BZ, both of which are folded back onto the Γ point of our simulation cell. Deep localized states would be well described by our sampling as well. The interface state closest to the gap has been found in the case of the dimerized interface at ~ 1 eV below the Si valence band edge. Its charge density shows that this state is mainly localized in the back-

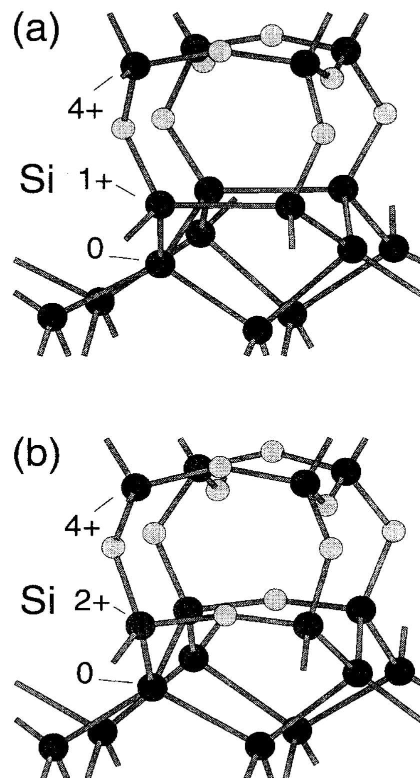

FIG. 1. Models showing the relaxed positions of our interface structures: (a) dimer case, (b) oxygen bridge case. The Si partial oxidation states are indicated.

bonds of the Si atoms forming the dimers. This is in good agreement with calculations of the reconstructed Si(001) surface, in which a similar state is found in the same energy range [24].

Recent calculations for a series of molecules have shown that DF-LDA core-level shifts differ by less than 0.5 eV from the corresponding experimental values [25]. Since we do not treat the Si $2p$ state explicitly, we calculate the relative shifts in first-order perturbation theory [26]. We evaluate the expectation value of the atomic $2p$ orbital on the local self-consistent potential. We do not consider splitting nor spin-orbit hybridization of the $2p$ level induced by the crystal field [7,26].

To gain insight, we first calculate the core-level shifts for some appropriately designed test molecules. We take as a reference the core level of the central Si atom in the tetrahedral molecule $Si(SiH_3)_4$. The Si-Si bond length is taken as in bulk Si, and a Coulomb potential is used for H [27]. In order to study the different oxidation states, we then consider the molecules $SiO_n(SiH_3)_4$, where O atoms have been inserted in n of the Si-Si bonds (with n varying between 1 and 4). The $n = 1$ case is shown in the inset of Fig. 2. The Si-O bond length and the Si-O-Si bond angle are fixed to 1.6 Å and 180°, respectively. The calculated shifts, given in Fig. 2, show a linear dependence on the oxidation state n, but underestimate by about 50% the experimental values for the interface [2–4].

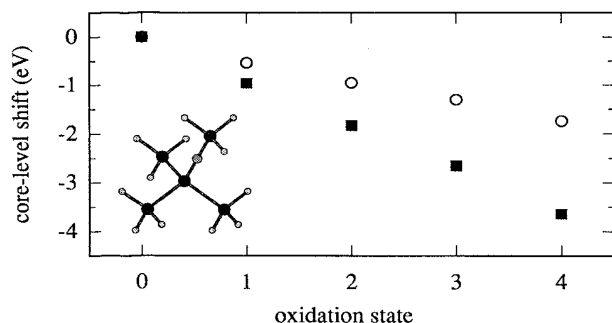

FIG. 2. Si $2p$ core-level shifts of central Si in the $SiO_n(SiH_3)_4$ test molecules as a function of oxidation state (number n of nearest-neighbor O atoms), with (filled squares) and without (circles) final state effects. The case $n = 1$ is shown in the inset.

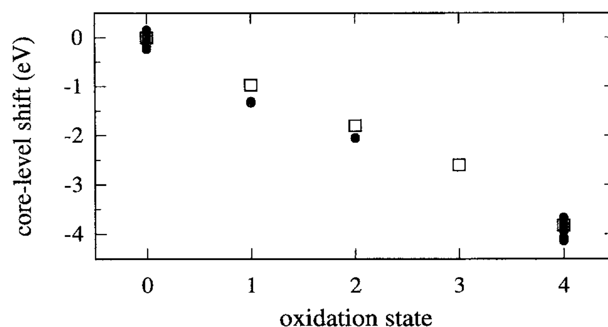

FIG. 4. Si $2p$ core-level shifts at the Si(001)-SiO_2 interface as a function of oxidation state: models (disks) and experiment (open squares) [4].

Following the procedure of Ref. [28] to include final state effects, we have generated a Si PP with a screened $2p$ hole [29]. When core-hole relaxation effects are accounted for, the values of the shifts approximately double as reported in Fig. 2. These results agree very well with Auger parameter measurements in SiO_2, from which a core-hole relaxation energy of 2.0 eV is derived [15,16]. Such large contributions due to core-hole relaxation are rather unexpected when compared to the case of the isolated Si atom, where final state effects account only for 10%–20% of the total shift. The enhancement of the final state effects can be understood as caused by a reduced valence screening in oxidized Si atoms.

In Fig. 3 we give the Si $2p$ core-level shifts for our model interface structures. The shifts are plotted as a function of the position of the Si atoms along the direction orthogonal to the interface planes. Core-hole relaxation effects have been accounted for by rescaling initial-state shifts according to the results for the test molecules. We have taken as a reference value the shift of atoms in the Si slab sufficiently distant from the interface, but far enough from the hydrogen terminated surface (at $z = 0$). The two interface models show essentially the same shifts, except for the interface Si atoms, which are differently coordinated by oxygen in the two structures. In Fig. 4 the same shifts are displayed as a function of

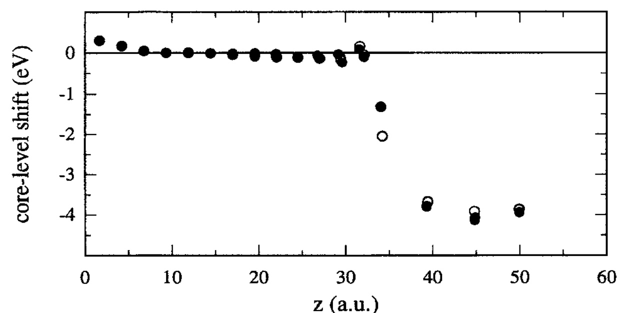

FIG. 3. Si $2p$ core-level shifts at the Si(001)-SiO_2 interface along the z direction, orthogonal to the interface plane, for the dimer case (disks) and the oxygen bridge case (circles).

the number of nearest-neighbor oxygen atoms, showing a linear relationship. The $n = 1$ and $n = 2$ oxidation states correspond to interface Si atoms forming dimers and O bridges, respectively (see Fig. 1). The oxidation state $n = 3$ is not present in our models. We find very good agreement between calculated shifts and experimental data [4], also shown in Fig. 4. All the $n = 4$ shifts fall relatively close to each other in spite of the wide Si-O-Si bond angle distribution in our models. This shows that the Si $2p$ core-level shift is rather insensitive to the Si-O-Si bond angle, contrary to an early proposal [30]. Our results show that the $n = 4$ shift is rather constant for distances very close to the interface, in accord with the experimental results of Ref. [16] which attribute the experimentally observed increase of the shifts as a function of oxide thickness to charging effects [16,31].

Our results strongly support the traditional picture, in which the shifts are mainly determined by nearest-neighbor oxygen atoms. Second nearest-neighbor effects do not appear to be important at this interface. For instance, in the case of the interface with O bridges [see Fig. 1(b)], the Si atom closest to the $n = 2$ interface atom is in a $n = 0$ state and its shift is negligibly small (see Fig. 3), at variance with the suggestions in Refs. [5,6]. The same conclusion is reached in the test molecules when the shift of Si atoms with no oxygen nearest neighbors are considered: for the $n = 1$, 2, and 3 cases, this shift is always smaller than 0.15 eV. Similarly, our results show that a description based on local electronegativity concepts [32] does not apply. This description predicts a significant change of the $n = 0$ and $n = 4$ shifts in the vicinity of the interface, in contrast to the rather constant shifts we find. In a recent experiment in which the PES spectrum was monitored during a monolayer by monolayer oxidation of Si(111), the $n = 1$ and $n = 3$ suboxide peak intensities were found to oscillate in antiphase [33]. Given the orientation of the substrate and assuming a nearest-neighbor picture, a straightforward interpretation of these observations is provided.

The quantitative agreement between the shifts for the test molecules and the interface models suggests that

interface dipoles do not contribute significantly to the core-level shifts. This is confirmed by experiments in which a difference of 0.20 eV is measured between the $n = 4$ shift for Si(001)- and Si(111)-SiO_2 interfaces [32,34]. On the basis of simple arguments which consider bond density and orientation, the contribution to the shift due to dipoles at the (111) interface is expected to be twice as large as at the (100) one. Therefore, these experiments bound the possible dipole contribution to the shift of the $n = 4$ core level relative to the substrate.

Finally, we would like to stress the importance of the choice of the models. When models are used in which all the bonds are saturated and the tetrahedral structure of the oxide is preserved, the calculated shifts are found to be in quantitative agreement with experiment. We believe that the varying values for the shifts calculated in Refs. [7] and [8] should be attributed to the presence of dangling bonds rather than to the different model structures.

In conclusion, we have shown that Si $2p$ core-level shifts at the Si(001)-SiO_2 depend linearly on nearest-neighbor oxygen atoms. Second nearest-neighbor effects turn out to be negligibly small. Therefore, a correct interpretation of photoemission spectra requires that all Si oxidation states be present at the interface.

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