BONDING AT SILICON/INSULATOR INTERFACES

F.J. HIMPSEL, T.F. HEINZ, A.B. McLEAN and E. PALANGE

IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598, USA

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Various techniques for the spectroscopy of interfaces are discussed such as core level spectroscopy, near-edge absorption, and optical second harmonic generation. The CaF$_2$/Si(111) interface serves as a model for determining electronic states at an interface. A pair of interface states is found, one occupied, the other empty. They represent the bonding (antibonding) combinations of the orbitals that hold the interface together. The interface layer exhibits new properties, e.g., more than twice the band gap of bulk Si. The bonding at complex interfaces, such as SiO$_2$/Si, can also be analyzed using the simple relation between core level shift and oxidation state. Only models with an extended interface are compatible with the observed distribution of intermediate oxidation states.

1. Introduction

The physics of interfaces is much less explored than the physics of surfaces. One reason for this lag is the difficulty in obtaining a clean signal from the interface. Usually one finds a large background from the substrate and the overlayer. In surface physics one can suppress the substrate signal by choosing a technique with a very short probing depth (e.g. scanning tunneling spectroscopy or atom scattering). However, such probes do not penetrate overlayers. The key problem of interface physics, i.e., to penetrate an overlayer and still be sensitive to a monolayer at the interface, can be solved in various ways. For example, in ion scattering the ions may channel through a crystalline overlayer and then encounter displaced atoms at the interface. Core levels are shifted in energy at the interface due to the different chemical environment. They can be used to tag interface atoms, either by measuring directly core level binding energies or by looking for transitions from interface core levels into unoccupied valence states in the near-edge X-ray absorption fine structure (NEXAFS). Optical methods have good penetration and can be made sensitive to the interface by taking advantage of dipole selection rules. For example, frequency doubling (or second harmonic generation, SHG) occurs only in the absence of inversion symmetry. We will demonstrate the application of these methods for determining the bonding and the two-dimensional electronic structure of interfaces.

Insulator/silicon interfaces are prime examples for this purpose since they exhibit large differences in bonding across the interface, e.g. from covalent to ionic. As a consequence, the properties of the interface layer are found to be quite different from those of either silicon or insulator. For example, the band gap of the interface layer in CaF$_2$/Si(111) is twice as large as that of Si (and 5 times smaller than that of CaF$_2$), indicating some intermediate type of bonding. Such strong modification of materials at an interface suggests that new types of materials can be engineered at interfaces and in superlattices.

2. Bonding across the interface
2.1. SiO$_2$/Si(100)

The SiO$_2$/Si interface has been the subject of intense study because of its dominant role in silicon technology. The structure of this interface has been elusive despite many efforts to come up
At a photon energy of 130 eV, the escape depth of photoelectrons [3] from the Si 2p core level has a minimum of about 3 Å in Si, compared with about 15 Å in conventional XPS. The short escape depth makes it easy to detect a monolayer of Si atoms at the interface.

A coarse look at the distribution of oxidation states (fig. 1) gives two qualitative results about the structure of the interface. (i) The interface is not ideal, as evidenced by the coexistence of all three intermediate-oxidation states Si$^{1+}$, Si$^{2+}$, Si$^{3+}$. With a truncated bulk structure, one would obtain only Si$^{2+}$ for Si(100) and Si$^{1+}$ or Si$^{3+}$ for Si(111) by bonding oxygen to the broken bonds. (ii) However, there is a remnant of the crystallographic dependence expected from a truncated bulk structure, as Si(111) exhibits less Si$^{2+}$ than Si(100). Can these findings be made consistent? In order to come up with sensible models we have to consider the possible driving forces for the interface structure. A critical boundary condition is the density mismatch between SiO$_2$ and Si. The SiO$_2$ lattice has a density of Si atoms that is 2.2 times lower than that in Si. Consequently, a SiO$_2$ surface has only half as many open bonds as a Si surface. In the following, we will discuss how this difference can be accommodated for the SiO$_2$/Si(100) interface.

The truncated bulk structure can be connected to an amorphous SiO$_2$ network as shown by Pantelides and Long [4]. Such a model has a full monolayer of Si atoms in the 2+ oxidation state. An epitaxial model by Herman et al. [5] has the density difference between SiO$_2$ and Si built in. This model uses a diamond-like structure of SiO$_2$ similar to α-cristobalite, with oxygen atoms inserted into Si–Si bonds. The bond-length ratio between Si–O–Si and Si–Si is close to $\sqrt{2}$. Therefore, an epitaxial ($\sqrt{2} \times \sqrt{2}$)R45° structure can be constructed on Si(100). In this case, the bond density across the interface changes by a factor of 2, i.e. only half of the atoms at the Si(100) surface are connected to oxygen in SiO$_2$. To absorb the remaining broken bonds one has to introduce impurities such as H, F, and OH at the interface. The distribution of oxidation states expected at such interfaces is 0.5–1.0 monolayer of Si$^{2+}$ and 0.5–0.0 monolayer of Si$^{3+}$. Thereby, Si atoms
bonding to hydrogen are counted as Si$^0$. An alternative way to take care of the density mismatch has been proposed recently by Ourmazd et al. [6]. Only one of the two broken bonds of the Si surface atoms is connected to SiO$_2$. The other is presumed to pair up with a neighboring Si atom in a 2×1 structure, like on the clean Si(100) surface. This configuration matches tridymite, another crystalline modification of SiO$_2$, where oxygens are inserted into the Si–Si bonds of the hexagonal diamond structure. The interface consists of a full monolayer of Si$^{1+}$ for this model. A third possibility to fix the bond density mismatch has been proposed by Ohdomari et al. [7]. The Si(100) surface is terminated by Si(111) facets with one broken bond per atom, resulting in about a monolayer of Si$^{1+}$ at the interface. All these atomically abrupt interface models give only Si$^{2+}$ and Si$^{1+}$ as intermediate-oxidation states. In order to explain the observed Si$^{3+}$ peak, we have to resort to extended-interface models.

Extended-interface models explain not only the Si$^{3+}$ peak, they also provide a solution to the density mismatch problem. Strain energy calculations by Ohdomari et al. [8] show that a properly graded SiO$_2$/Si(100) interface has significantly lower strain energy than an abrupt one. A specific model has been proposed [8] based on strain-energy minimization. There are similar structures [3] which agree equally as well with the data. A peculiar feature common to these models is the occurrence of Si$^{3+}$ protrusions into the SiO$_2$ layer.

2.2. CaF$_2$/Si(111)

Calcium fluoride is a simple insulator that is lattice matched with silicon to a high degree (0.6% lattice mismatch at room temperature, 2% at the growth temperature). This property makes CaF$_2$ a prime candidate for silicon-on-insulator technology, which is a prerequisite for achieving the long-range goal of three-dimensional device structures. For pure interface sciences, CaF$_2$/Si(111) is also well suited, since it exhibits an atomically-abrupt and well-ordered interface.

Very direct information about the bonding at the CaF$_2$/Si(111) interface can be extracted from the core-level spectra [9–11], like for SiO$_2$/Si. Our aim is to determine whether Ca of F bonds to Si at the interface. This can be decided from the sign of the Si core-level shift. Ca transfers electrons to Si and, therefore, causes a negative electrostatic potential at the Si atom that drives the Si core level up in energy. F does the reverse and causes a downward shift, like oxygen in fig. 1. Looking at the Si 2p core level spectrum for CaF$_2$/Si(111) in fig. 2 on finds predominantly Si–Ca bonding with an interface core level at 0.4 eV above the bulk line. There is a smaller contribution from Si–F bonds below the bulk line. It can be suppressed by
using well-oriented Si(111) substrates and by annealing the CaF$_2$ film close to the desorption point. Such an annealing does also improve the electrical quality of the interface (see ref. [12]). In the following, we will concentrate on this Ca-terminated interface structure. Further corroboration for Ca–Si bonds comes from the Ca and F core level spectra in fig. 2. Whereas Ca exhibits a shifted interface core level, F does not. Note that the Ca as well as the Si core levels are shifted upwards at the interface, indicating negative charge on both of them. This charge is provided by removing a layer of F$^-$ ions at the interface as neutral F$^0$, leaving a layer of electrons behind (see ref. [10]). These electrons stay mainly with the Ca atoms at the interface, converting them from Ca$^{2+}$ to Ca$^{+}$. Only a fraction of an electron spills over to the Si (we estimate about 0.2 e by comparing the Si 2p core-level shift of 0.4 eV for Si–Ca with the shift of 1.1 eV for Si–F, with a charge transfer of 0.6 e for Si–F according to Pauling [1,13]).

The change in oxidation state from Ca$^{2+}$ to Ca$^{+}$ at the interface can independently be inferred from near-edge X-ray absorption fine structure (NEXAFS) data (see ref. [14]). Basically the Ca 2p → Ca 3d absorption edge has atomic character. Its multiplet structure contains information about the presence of an unpaired 4s electron, which is present in Ca$^{+}$.

3. Electronic interface states

3.1. Band gap of the interface

Beyond looking at the atomic structure of an interface, it is interesting to determine the electronic structure, e.g., the bond orbitals that connect the overlayer with the substrate. For the Ca-terminated CaF$_2$/Si(111) interface such a picture has emerged from various photoelectron spectroscopy experiments (see fig. 3 and ref. [14]). A key feature of this interface is a change in oxidation state of the Ca atoms from 2$^+$ to 1$^+$. Ca$^{+}$ has an unpaired outer 4s electron, which pairs up with the Si dangling bond electron to form the interface bond. The bonding and antibonding combinations of these orbitals form the valence band and conduction band of a semiconducting interface band structure. As shown in fig. 3 the band gap of the interface layer is 2.4 eV, compared with 12 eV in bulk CaF$_2$ and 1.1 eV in Si. The gap between the bonding and antibonding interface states is detected by the onset of optical second harmonic generation (figs. 3 and 4 and ref. [15]). This technique picks up a signal from the interface without any background from the bulk.

Fig. 3. Model for the electronic structure of the calcium-terminated CaF$_2$/Si(111) interface. The interface band structure is formed by bonding (antibonding) combinations of the Si 3p dangling bond orbital and the Ca 4s orbital of Ca$^{+}$ [14]. The band gap shrinks from 12 eV for bulk CaF$_2$ to 2.4 eV for the interface layer. The Ca is located at the hollow site (bottom) according to ion scattering [20].

Fig. 4. Optical second harmonic intensity versus incident photon energy $h\nu$ for CaF$_2$/Si(111) (circles; from ref. [15]). The onset of interband transitions at the interface at $h\nu = 2.4$ eV is modelled by the square of the second-order susceptibility (full line) with a step-like imaginary part (dot-dashed).
since second harmonic generation is dipole-forbidden in bulk Si and CaF$_2$ by inversion symmetry. When adding the interface band gap of 2.4 eV to the valence band maximum of the interface (0.8 eV below the valence band maximum of Si, see section 3.2 and ref. [16]), we find that the conduction band minimum of the interface lies just above the conduction band minimum of bulk Si: This leaves the Si band gap free of intrinsic interface states.

3.2. Band dispersion of interface states

The proper description of interface states is in terms of two-dimensional $E(k_{\parallel})$ band dispersions, where $k_{\parallel}$ is the reduced wavevector parallel to the interface (fig. 5). Such band dispersions have been used extensively to describe surface states [17,18]. The CaF$_2$/Si(111) interface makes it possible to determine the band dispersion of an interface state using angle-resolved photoemission (fig. 5 and ref. [16]). The band dispersion is in qualitative agreement with a first principles band calculation [19] for the isoelectronic Na/Si(111) monolayer system. The geometry (Na in the open hollow site) is similar to a recent structure determination [20] of a monolayer of CaF$_2$ on Si(111) using ion scattering (Ca in the filled hollow site). From the Na/Si(111) calculation and from our general bonding arguments one expects an unoccupied band, which represents the antibonding counterpart to the occupied band seen in photoemission. The minimum of this band is predicted to be at $\Gamma$. The optical transition across the band gap observed with optical second harmonic generation at 2.4 eV has been placed as a data point in fig. 5.

The results presented in fig. 5 allow us to make some predictions about the nature of the interfacial bonding between the covalent Si(111) surface and the ionic CaF$_2$ overlayer. Firstly, the energy position of the interface state below the valence band maximum determines the energy gained by interfacial bonding. Taking the average over all $k_{\parallel}$ (or using angle-integrated photoemission spectra) we find about 1.4 eV for the interface bond energy. The Si and Ca bond energies add up since they each contribute one electron to the band. However, other energies will have to be subtracted (e.g. the energy cost of removing a F layer) for evaluating the total interfacial energy. The width of the interface state reflects the residual interaction with bulk states of the Si substrate (hatched in fig. 5). We estimate about 0.7 eV FWHM for the width of the state at $\Gamma$. At K and M the interface state becomes narrower (0.5 FWHM) since it splits off from the bulk bands. The amount of dispersion (~0.6 eV along $\Gamma$-M, 0.8 eV along $\Gamma$-K) determines the lateral interaction between the orbitals that hold the interface together.

In summary, it is shown that techniques are available for obtaining a microscopic picture of the bonding at interfaces. This extra knowledge will make it easier to modify surfaces and interfaces for the purpose of achieving better growth or improved electrical properties.

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References


[16] A.B. McLean and F.J. Himples, Phys. Rev. B 39 (1989) 1457. Note that the position of the valence band maximum at the interface varies from $-0.8$ to $-1.2$ eV depending on whether the spectrum is resolved into two peaks or not.


