Determination of Interface States for CaF_2/Si(111) from Near-Edge X-Ray-Absorption Measurements

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The technique of polarization-dependent near-edge x-ray absorption is applid to an interface by taking advantage of core-level and Auger energy shifts for interface atoms. For epitaxial CaF_2/Si(111) several unoccupied Ca- and F-derived interface states are found. The orientation of the corresponding orbitals is determined from the polarization dependence. The Ca atoms at the interface are found to be in the 1+ oxidation state.

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Interfaces play an increasingly important role in science and technology. The performance of electronic devices is limited by the quality of the interfaces when the device dimensions become smaller than one of the characteristic lengths such as the diffusion length or the Debye screening length. Structural techniques[1] have been developed which make it possible to look through an overlayer and still be sensitive to a monolayer of interface atoms. For probing electronic states at interfaces, one uses electrical methods which essentially detect the response of an electronic device to interface states. Among the common methods are capacitance-voltage and deep-level transient spectroscopy. Direct spectroscopic techniques[2] are difficult if not impossible to use because the signal from the interface is overwhelmed by the background from the overlayer and the substrate.

We are applying, for the first time, the technique of polarization-dependent near-edge x-ray absorption[3,4] to an interface and demonstrate that unoccupied interface states can be detected. In order to discriminate interface from bulk states, we take advantage of the fact that interface atoms see a chemical environment different from the bulk and, therefore, exhibit shifted core-level and Auger-electron energies (see Fig. 1). From the polarization dependence, the orientation of the bond orbitals at the interface is obtained and, thus, the bond direction. With use of a structural model these orbitals can be assigned to interface bonds and back bonds. Thereby one obtains a microscopic picture of the electronic structure at the interface, e.g., the Fermi-level pinning. Such understanding will be very helpful in the ability to control interface properties in a systematic fashion.

The CaF_2/Si(111) interface is an ideal test case since it exhibits epitaxial growth.[5,6] One can expect a simple structure which is amenable to first-principles calculations. This interface also has technological potential[5] for fabrication of three-dimensional integrated circuits and ultrathin gate insulators. CaF_2 films were grown on Si(111) wafers (*n*-type, P-doped, 5 Ω cm, oriented better than 0.5°) by molecular-beam epitaxy at a substrate temperature of 750 °C with a rate of one triple layer (3.15 Å) per minute. Layer-by-layer growth is observed for substrates with good 7×7 reconstruction (established by LEED and photoelectron spectroscopy of surface states and surface core levels[7]). A single CaF_2 layer exhibits Ca and F core levels shifted towards lower binding energy by about 2 eV. With increasing thickness, bulklike Ca and F core levels

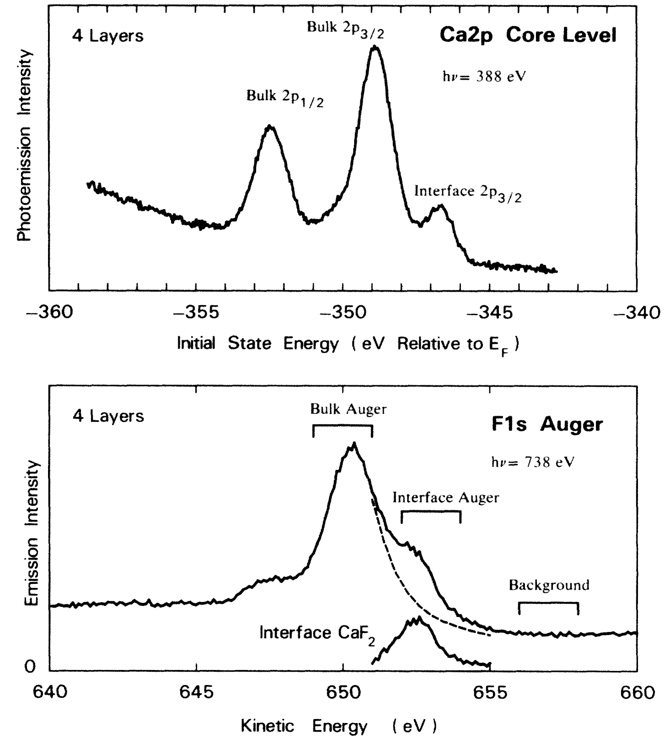

FIG. 1. Photoelectron spectra from epitaxial CaF_2/Si(111) showing shifted core-level and Auger energies of interface atoms. The dashed spectrum is obtained from a thicker film (seven layers) where the interface contribution is strongly attenuated by the overlayer. The difference (bottom) gives the interface Auger spectrum. Brackets denote the energy windows chosen for the partial yield spectra in Fig. 3.

emerge. The shifted F core level disappears when two layers are completed but a shifted Ca core level remains at the interface (2.0–2.5-eV shift; see Fig. 1). We conclude that the F atoms undergo rebonding when going from the chemisorption regime to the formation of an interface. Therefore, a film several layers thick (typically four to seven) is used to probe a realistic interface. The thickness is determined from the interface-to-bulk intensity ratio of the Ca $2p$ core level with an escape depth[6] of 5 Å.

Transitions from a core level into unoccupied interface states are detected near the Ca $2p$ and F $1s$ absorption edges via the yield of Auger electrons (Figs. 2 and 3). The F $1s$ (Fig. 1) and the Ca $2p$ Auger peaks are both found to be shifted[9] at the interface by 2 and 4 eV towards higher kinetic energy, respectively. At the Ca $2p$ edge (Fig. 2), one observes prominent transitions into the $3d$ states[10,11] of the Ca^{2+} ion which result in a sharp spin-orbit–split doublet F,G in bulk CaF_2. A number of extra lines (A to E) are observed which are assigned to interface transitions because they are attenuated with increasing film thickness. The energies relative to the corresponding bulk line are -2.4 eV (A), -1.7 eV (B), -0.9 eV (C), -1.4 eV (F), and -0.9 eV (E). There is a pronounced polarization dependence[12] indicating the lower symmetry at the interface as opposed to the isotropic bulk. In particular, structure E appears to be absent in s polarization, i.e., it is excited by the component of the electric field **E** perpendicular to the surface only. For a close examination of the Ca $2p$ absorption edge it is useful to start from an atomic picture.[10,11] Dipole selection rules allow transitions from Ca $2p$ into unoccupied $3d$ and $4s$ states (plus higher-lying states). The $2p$-to-$4s$ transitions are expected to be weak compared with the $2p$-to-$3d$ transitions since the $4s$ wave function is much more extended than the $3d$ wave function in Ca and has little overlap with the $2p$ core wave function.[10,11] The multiplet structure of the $2p$-to-$3d$ transition gives us a fingerprint of the oxidation state of Ca at the interface. Neutral Ca gives rise to a triplet[11] with two strong lines and a 50-times weaker line. For Ca^{2+} in CaF_2 we expect a similar multiplet structure since it differs from neutral Ca only by the filled $4s$ shell. This is observed except that the lines are much narrower in our bulk CaF_2 spectra than in neutral Ca. For Ca^{1+} there exists an unpaired $4s$ electron which

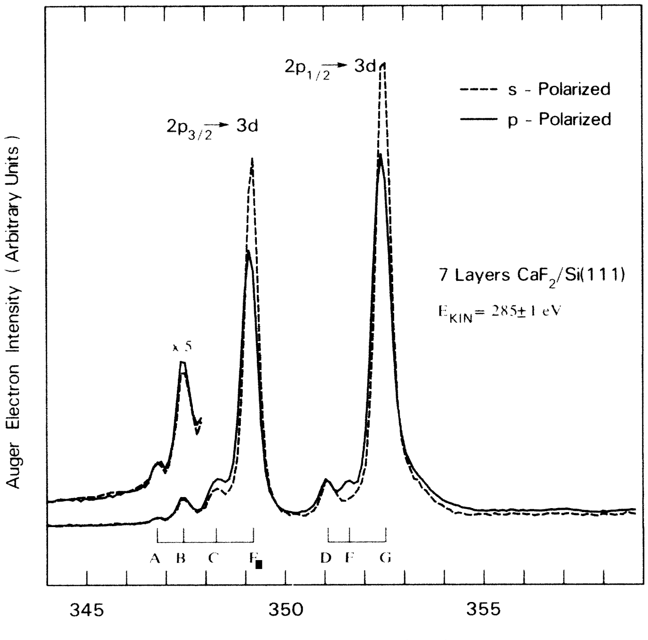

FIG. 2. The Ca $2p$ absorption edge measured via the yield of Ca $2p$ Auger electrons. Several interface-related structures A to E are seen which can be assigned to Ca^{1+} at the interface.

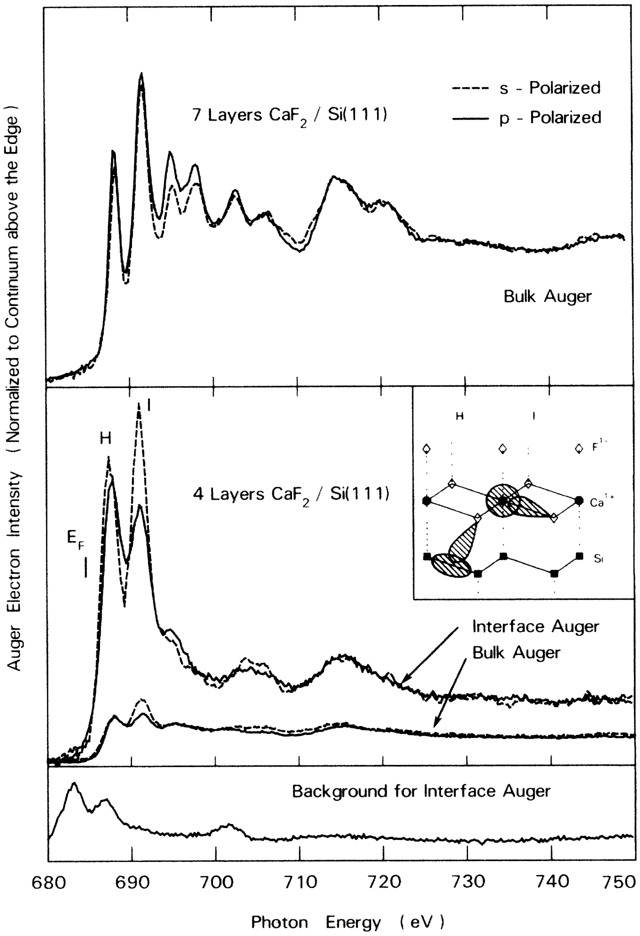

FIG. 3. The F $1s$ absorption edge measured via the yield of F $1s$ Auger electrons. Interface sensitivity is achieved (Ref. 8) by our placing the kinetic-energy window at the shifted interface Auger peak (see Fig. 1). Peaks H and I correspond to transitions into orbitals of interface and backbonds, respectively (see inset).

creates a more complex multiplet structure via Coulomb and exchange interaction with the $2p$ hole and the $3d$ electron. An estimate for this multiplet can be obtained from calculations for the isoelectronic K atom[11] which give four lines for the $2p_{3/2}$ and three lines for the $2p_{1/2}$ core holes. We observe the same number of interface features assuming that two of them are hidden under the bulk peaks. In fact, peaks F and G do not disappear in the submonolayer regime as one would expect from a pure bulk feature. The polarization dependence probably originates from an orientation of the spin of the $4s$ electron perpendicular to the interface. In a structural model proposed previously[6] (Fig. 3 inset) the Ca is located on top of a Si surface atom and forms a bond perpendicular to the surface that orients the spin.

A self-consistent picture of the electronic structure at the interface arises from our core-level data (Fig. 4). The Si atoms at the interface are nearly neutral if we judge from the relatively small Si $2p$ core-level shift[6] of $+0.4$ eV. Therefore, one has a half-filled dangling-bond orbital which can interact with the $4s$ electron of the interface Ca^{1+} by forming a pair of bonding-antibonding states. We see the occupied bonding state in photoemission at 1.2 eV below the valence-band edge. A similar type of bonding has been predicted[13] for Na on Si(111). The extra electron is provided to the interface calcium by silicon atoms in the layers underneath the surface. This can be inferred from the large core-level shift of -0.8 eV observed for the Si atoms in the second layer.[6] In order to make possible a charge transfer from bulk Si to the interface one has to place the Fermi level at the valence-band maximum of Si (or just below). Indeed, this is observed by use of the Si $2p$ level for measuring[14] the band bending change relative to Si(111)7×7.

At the F $1s$ absorption edge[8] one observes transitions into states with F $2p$ character (Fig. 3). Since the F $1s$ interface core level is not shifted[9] we use the shift of the F $1s$ Auger line (Fig. 1) to select interface transitions. Yield spectra are taken with the energy window set at the interface and bulk Auger-electron energies, respectively (brackets in Fig. 1). In addition, a background spectrum is taken at a kinetic energy above the Auger peak in order to subtract the contribution of shallow core-level photoemission peaks (Ca $3p$, Ca $3s$, F $2s$). This spectrum is shifted down by the difference in the kinetic-energy settings and subtracted from the raw data. For the bulk-sensitive partial yield spectrum of a thick film (Fig. 3, top), a rich structure of unoccupied states is observed that is essentially independent[12] of the polarization as expected from an optically isotropic bulk solid. In the interface-sensitive spectrum of a thinner film, we observe two prominent features (H,I) that are much less pronounced in the bulk-sensitive spectrum of the same film.[15] The energy locations of states H and I are 3.1 and 6.7 eV above the Fermi level if we neglect electron-hole interaction.[16] Peak I is excited mostly by the component of **E** parallel to the surface. The remnant of this peak in p polarization is mainly due to the residual parallel component which corresponds to about $\frac{1}{3}$ of the intensity for our geometry.[12] Its polarization dependence suggests an assignment of peak I to F $2p_{x,y}$ states of F-Ca back bonds (Fig. 4 inset). The polarization-independent peak H is assigned to F $2p$–Si $3p$ interface bonds which are tilted by about 45° in our simple model. A definitive assignment requires a calculation[17] of the electronic structure and of the transition probability.

For comparison, we have taken analogous F $1s$ spectra from F/Si(111)1×1. They exhibit two dominant near-edge peaks, too, but with a different polarization signature. The lower peak is excited by the perpendicular component of **E**; the upper peak has little polarization dependence. These observations can be explained by our assuming the top site for F on Si(111) and the hollow site for F at the $\mathrm{CaF_2}$/Si(111) interface. The two sites correspond[17] to covalent and ionic bonding, respectively, and reflect the difference between adsorption of neutral F and F^- in the two cases.

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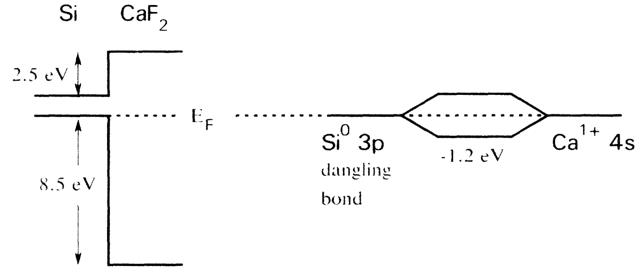

FIG. 4. Energy diagram of the $\mathrm{CaF_2}$ interface and model for the bonding obtained from core-level and valence-band photoemission.

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