Electronic structure of the $CaF_2/Si(111)$ interface

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High-resolution core-level and Auger-electron spectroscopy, polarization-dependent near-edge x-ray absorption, and angle-resolved photoemission are used to study the electronic structure and the bonding at the CaF₂/Si(111) interface. Si core-level shifts of + 0.4 and -0.8 eV show that both Ca and F bond to Si and that the interface is atomically sharp. Interface-derived Ca and F core-level and Auger-electron shifts are found indicating layer-by-layer growth. The interface Ca 2p, 3p, 3score-level shifts are about 2 eV and the Ca 2p Auger energy shift is $\simeq 4.5$ eV. The F 1s, 2s core levels show no interface shift but a shift of 1.7-2 eV in the initial adsorption regime indicating a rearrangement of F after the completion of the first layer. The F 1s Auger electrons show an interface shift of 2.0 eV. Initial-state and relaxation contributions to the shifts are considered. In the Ca 2p and F 1s near-edge x-ray-absorption fine-structure (NEXAFS) spectra several unoccupied Caand F-derived interface states are found. The orientation of the corresponding orbitals is revealed by the polarization dependence. The oxidation state of the Ca atoms at the interface is found to be changed to 1 +. The CaF₂ valence bands start to form at 2 layers with an overall bandwidth of 3.3 eV. An occupied interface state is found at 1.2 eV. The Fermi level shifts by 0.6-0.65 eV when 2 CaF₂ layers are deposited and a new pinning position is established at the Si valence-band maximum. A bonding model for the interface is proposed.

I. INTRODUCTION

The epitaxial growth of insulators on semiconductors is an important step to achieve the long-range goal of threedimensional electronic devices. CaF₂ is currently the most promising candidate as an epitaxial insulator on silicon. It can be grown by molecular-beam epitaxy¹⁻⁸ (MBE) on silicon substrates and has a crystal structure (cubic) similar to the diamond structure of Si with a lattice mismatch of only 0.6% at room temperature. The high quality of the CaF_2 films has been established by several experimental techniques²⁻⁸ and an epitaxial growth of Si on top of CaF₂ films has been reported.³ When device dimensions shrink and become comparable to characteristic lengths such as the diffusion length or the Debye screening length, the quality of the interface becomes crucial for the performance of a device. The $CaF_2/Si(111)$ interface is an ideal test case for several reasons. (i) It can be grown epitaxially quite easily because CaF₂ evaporates as a molecule and thereby automatically solves the stoichiometry problem. (ii) The structure is simple enough for first-principles calculations. (iii) The interaction between a polar insulator with ionic bonding and a homopolar semiconductor with covalent bonding raises interesting questions about the interface bond which are not yet solved.

There are several possibilities how the $CaF_2/Si(111)$ interface may form. Figure 1 shows a tentative model⁸ of the initial adsorption of the CaF_2 molecules and the successive formation of crystalline CaF_2 . This picture is only schematic since the clean Si(111) 7×7 substrate is highly reconstructed and atomically rough, and the reconstruction is successively lifted upon CaF_2 adsorption. In the low-coverage regime we expect no simple bonding

geometry. Under certain conditions we observe a $\sqrt{3} \times \sqrt{3}$ ordering. Single CaF₂ molecules will have to rearrange when the first triple layer is formed. This implies a rebonding of the fluorine atoms. The triple layer F⁻-Ca²⁺-F⁻ is azimuthally rotated by 180° according to Rutherford backscattering data.⁴ In contrast to the SiO₂/Si interface, the CaF₂/Si(111) interface is atomically sharp. In Fig. 2 core-level shifts of the Si 2*p* levels are shown, which demonstrate the difference between these two interfaces. After subtraction of the Si 2*p*_{1/2} line (discussed, e.g., in Ref. 9), the SiO₂/Si interface shows all intermediate oxidation states with an intensity correspond-



FIG. 1. Tentative structural model for the formation of the $CaF_2/Si(111)$ interface. Layer-by-layer growth is observed. The structure of the initial CaF_2 layer is different from the structure of the interface.



FIG. 2. Characterization of interfaces by Si 2p core-level spectroscopy. (a) Diffuse interface of SiO₂/Si(100) where two layers of Si interface atoms in intermediate oxidation states are seen (only the Si $2p_{3/2}$ component is shown). (b) Sharp interface of CaF₂/Si(111) grown by MBE. A raw spectrum and a Si $2p_{3/2}$ spectrum, where the Si $2p_{1/2}$ component has been subtracted, are shown. Si atoms bond to F and to Ca at the interface as revealed by opposite core-level shifts.

ing to about two silicon layers.⁹ The CaF₂/Si(111) interface, however, exhibits an interface Si peak (-0.8 eV)that has much less intensity than the SiO₂/Si interface peaks. For CaF_2 on Si(111) a raw data spectrum and a Si $2p_{3/2}$ spectrum is shown from which the Si $2p_{1/2}$ peak has been subtracted. From the sign of the shift (towards higher binding energy) we conclude that this peak corresponds to silicon atoms interacting with fluorine. Ca interacting with Si is known to cause a shift in the opposite direction. A shoulder observed at +0.4 eV is assigned to Si atoms bonding to Ca. A quantitative evaluation of the Si 2p spectrum leads to the tentative model of the interface structure presented in Fig. 1 where Ca bonds to the outermost Si layer and F interacts with the subsurface Si layer (see Ref. 8). Such a model can be tested by other structural techniques¹⁰ which make it possible to look through an overlayer and still be sensitive to a monolayer of interface atoms.

It is of great importance to understand and control the electronic states created at the interface. For probing electron states at interfaces, one uses electrical measurements such as capacitance voltage and deep level transient spectroscopy. Direct spectroscopic techniques¹¹ are difficult to use because the signal from the interface is overwhelmed by the background from the overlayer and substrate. The main objective of this paper is to examine the electronic structure during the formation of the $CaF_2/Si(111)$ interface from a submonolayer regime up to many layers of CaF₂. Photoemission spectroscopy has earlier been used to study clean Si surfaces^{12,13} and the interaction of Ca (Ref. 14) and F (Ref. 15) with Si surfaces. Recently the initial formation of the CaF₂/Si(111) interface and of a Ca layer on Si(111) has been studied.8,16,17 Here we report on angle-resolved photoelectron spectroscopy (ARPES) of the valence-band region of $CaF_2/Si(111)$ and high-resolution spectroscopy of Si 2p, Ca 3p, Ca 3s, Ca 2p, F 2s, and F 1s core levels. Augerelectron and near-edge x-ray absorption fine-structure (NEXAFS) spectra in the Ca 2p and F 1s absorption regime are presented as well.

II. EXPERIMENTAL

The experiments were performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, New York). Two different beamlines¹⁸ were used. The angle-resolved electron distribution curves (AREDC's) and the shallow core levels (Ca 3p,2s, F 2s) were measured with a hemispherical electron analyzer with energy multidetection coupled to a 3-m toroidal grating monochromator (TGM). For the NEXAFS data, the Auger-electron and the high-resolution core-level spectra, a $\frac{6}{10}$ -m TGM and a display spectrometer was used. The Si(111) wafers (n-type, Pdoped, 5 Ω cm, oriented better than 0.5°) were cleaned by resistive heating; the cleanliness was checked with the Si 2p core level and by observing the Si(111) 7×7 surface states.¹³ CaF₂ films were grown on the clean Si(111) wafers held at a temperature of 700-750°C as measured with an infrared pyrometer. The temperature calibration is not accurate absolutely but relatively. The uncertainty is estimated to 50°C. Solid phase epitaxy (deposition at room temperature and annealing) exhibits the reordering of the interface with temperature. Figure 3 shows Si $2p_{3/2}$ core-level spectra (Si $2p_{1/2}$ subtracted) for various annealing temperatures and in the inset the Fermi level and work function shifts relative to the clean Si(111) 7×7 surface. Both SiF and SiCa core-level shifts (see also next part) are formed at the same temperature of 650-700 °C. At the same temperature E_F moves towards the Si valence-band maximum (see for an explanation in Sec. III D) and the work function is lowered compared to the clean Si surface. The reordering is completed at about 740 °C and the SiF and SiCa peaks are stable up to 800 °C where CaF₂ starts subliming. A pyrolytic boron nitrite (PBN) crucible was used as an evaporation source and the deposition rate was about one CaF_2 triple layer (3.15 Å) per minute. The growth of CaF2 was interrupted at various thicknesses and the samples were transferred into the analyzer chamber. The pressure during evaporation was in the 10^{-9} Torr range. The cleanliness of the samples were checked by core-level spectroscopy. Care had to be taken to avoid contact of hot tantalum surfaces with



FIG. 3. Si $2p_{3/2}$ core-level spectra of 2.3 layers CaF₂ deposited at room temperature on Si(111) and annealed subsequently (solid phase epitaxy). Shifts due to Ca and F bonding to Si are observed after annealing above 700 °C indicating an ordering of the layer at this temperature. The inset shows the Fermi-level shift towards the Si valence-band maximum and the lowering of the work function. Both shifts are given relative to clean Si(111) 7×7 .

CaF₂, which results in Ta incorporation into the films. We determined the thickness of the CaF₂ films by two methods: (i) from the attenuation of the Si 2*p* core levels which was observed to occur exponentially⁸ suggesting a layer-by-layer growth (escape depth of 5 Å for 20–30 eV electrons in Si⁸) and (ii) from the ratio of the peak areas of the split Ca 3*p* (2*p*) level. The splitting occurs because Ca interface atoms are in a different environment than Ca bulk atoms (for details see below and Figs. 4 and 5). A monolayer of CaF₂ is used to determine the mean-free path of electrons in CaF₂. The coverages are expressed in CaF₂ triple layers (see Fig. 1) which have a thickness of 3.15 Å.

 CaF_2 is known to be very sensitive to radiation damage.¹⁹ Care had to be taken that the samples are not too long exposed to vuv irradiation. Irradiation damage after a low dose results in a broadening of the Si core level which smears out extra structures and in a shifting of the Fermi level back to the midgap region. A metallic peak with an *s*-like dispersion is observed¹⁹ after a higher dose of vuv irradiation.

III. RESULTS AND DISCUSSION

Overview photoemission spectra of the shallow Ca 3p, Ca 3s, and F 2s core levels and the F 2p valence band for different coverages of CaF2/Si(111) are shown in Fig. 4. Figures 5(a) and 5(c) show the deeper Ca $2p_{1/2}$, $2p_{3/2}$, and F 1s core levels. At a coverage smaller than one layer we observe no splitting of the peaks. However, a dramatic change occurs if the coverage is increased between one and two layers. The F 2s and 1s peaks shift successively to higher binding energy and the Ca 2p, 3p, and 3s levels split. The shifting of the F core levels is completed when about two layers are deposited. New Ca bulk peaks emerge on the higher binding energy side beneath the existing peaks and increase in intensity with coverage. They belong to the second and third CaF₂ triple layers while the Ca peaks of the first layer are still visible. The F peaks shift and decrease in width when the coverage is increased



FIG. 4. Overview photoemission spectra of the shallow Ca 3p, F 2s, and Ca 3s core levels and the F 2p valence band for various thicknesses of CaF₂ on Si(111). After one layer is completed bulklike Ca 3p and 3s peaks appear in addition to the interface peak. The F 2s peak shifts and no separate interface peak can be detected. The photon energy for the full lines was 150 eV and for the dashed line 90 eV.



FIG. 5. (a) and (c) Photoelectron spectra of the F 1s and the Ca $2p_{3/2,1/2}$ core levels. (b) and (d) F 1s (KVV) and Ca 2p ($L_{2,3}MM$) Auger electron spectra. Spectra a and b are measured for submonolayer coverages of CaF₂ on Si(111), spectrum c for 1.5 layers and spectrum d for 4 layers.

to more than one layer. This change indicates that the fluorine has to rearrange in order to form a F-Ca-F triple layer when the first layer is completed. A possible reordering mechanism is shown in Fig. 1. The free CaF₂ molecule is probably linear according to the 16-electron rule (Walsh²⁰) although no experimental evidence is known to us (only MgF₂ and CaCl₂ are known to be linear). We find that an extra electron is added to the Ca upon adsorption on the Si(111) surface (see below), which causes the molecule to bend. After a monolayer is completed, one of the two vacuum side F atoms has to move towards the Si side in order to form the ionic CaF₂ lattice. The Ca peaks of the first, the interface layer, remain instead essentially unshifted after deposition of more CaF₂ and

the new peaks of bulk CaF_2 coexist with the interface lines. The spectra are referenced to the valence band maximum of Si which we determined by measuring the Fermi level shift for different CaF_2 thicknesses via the Si 2p core level (see Sec. III D). Table I summarizes our observed binding energies (referenced to the Si valence-band maximum) and the corresponding shifts at the interface. The binding energies of the bulk peaks agree well with previous data for a CaF_2 crystal²¹ when referenced to the CaF_2 valence-band maximum. No surface core-level shifts could be observed either for Ca or for F.

When we compare the intensity ratio of the F 2s (1s) with the Ca 3p (2p) emission we find no major differences between the submonolayer and the higher coverages (vari-

	Bulk	Interface	Initial adsorption	Interface-bulk shift
Ca 3p	28.0±0.3	26.0±0.3	26.0±0.3	2.0±0.1
Ca 3s	47.0±0.3	45.2 ± 0.3	45.2±0.3	1.8 ± 0.2
Ca $2p_{3/2}$	348.9 ± 0.6	346.8 ± 0.6	346.8 ± 0.6	2.1 ± 0.2
F 2s	31.8 ± 0.3		29.9 ± 0.3	< 0.6
F 1s	687.0±0.8		685.3±0.8	$\widetilde{\lesssim}$ 0.6
Ca 2 <i>p</i> Auger	284	≈288.5	288.5	≈4.5
F 1s Auger	649.5±0.7	651.5±0.7	652.5 ± 0.7	2.0 ± 0.2

TABLE I. Core-level binding energies (eV, relative to the Si valence-band maximum) and Augerelectron kinetic energies (eV, above the vacuum level) for CaF_2 on Si(111).

ations in the ratio of about 20-30%). An apparent lowering of the F 2s peak height in the submonolayer regime is compensated by an increase in the width to give the same area. The composition of Ca to F is therefore not considerably altered, suggesting a mainly molecular adsorption. Additional support for the existence of F at the interface comes from the intensity of the shifted interface F 1s Auger peak¹⁷ [Fig. 5(b)], consistent with about 2 layers of F. The first two F layers are both in contact with Ca¹⁺ which causes a shift of the F Auger peak. We see no evidence for Ca diffusion underneath the first Si layer as discussed by Olmstead et al.¹⁶ In this case a Si 2p core-level shift in the order of 1.0-1.35 eV would be expected as it was found for Ca on Si forming a silicide.¹⁴ Instead, we see only a shift of 0.4 eV for $CaF_2/Si(111)$ (Fig. 2).

The Si 2p level exhibits two shifted components, one at -0.8 eV due to the F-Si interaction and one at +0.4 eV attributed to a Ca-Si bond. It is now well established^{9,14,15} to interpret the Si core-level shifts in terms of charge transfer. The F atom causes a downward shift of the Si 2p levels, because it induces a positive charge on the adjacent Si whereas the Ca atom shifts the Si 2p level upwards due to its opposite electronegativity. The coexistence of shifts with either sign in the Si core levels of Fig. 2 shows that both Ca and F bond to silicon at the interface. The shift of +0.4 eV for the CaSi bond in the case of CaF_2/Si is small compared to the shift observed¹⁴ for Ca on Si (1.0-1.35 eV). Therefore, we expect only a small charge transfer from Ca to the first layer Si in our case. On the other hand, we find that the FSi shift of -0.8 eV is nearly the same as for F on Si (-1.0 to -1.1eV),¹⁵ suggesting that fluorine at the interface has received about the same charge as for F on Si. The charge could be delivered by the silicon atoms in the second layer, which are closest to the fluorine atoms in our structure model of Fig. 1. The Si atoms with -0.8 eV core-level shift can also be explained by two different interface structures side by side, one Ca-terminated, the other Fterminated.

The shifts of the F and Ca core levels are not as simple to interpret as the Si core-level shifts because they are affected by differential screening and Madelung energy effects. (The Si atoms are not much influenced by this because they are almost fully screened due to the high dielectric constant of Si. The strong screening also

reduces the Madelung energy.) For Ca and F at the interface a general lowering of the binding energies is superimposed on the chemical shifts, because there exists extra screening due to the adjacent Si atoms. One can use the observed Auger energy shifts [see Figs. 5(b) and 5(d)] to separate out the screening effects (Sec. III B). Chemical, relaxation and Madelung contributions to the core-level shifts seem to cancel in the case of fluorine because we do not see a shifted component at the interface. The width of F 1s in Fig. 5 is resolution limited. When using a higher resolution we obtain a width similar to that for the Ca 2p bulk line. Chemical and relaxation parts of the core-level shifts point in the same direction (e.g., to lower binding energy) for Ca at the interface if the Ca atom receives charge. This can explain the observed large shift of $\simeq 2$ eV. Ca at the interface is therefore not in a 2 + oxidation state as in bulk CaF2 but tends to gain contributions of 1+character. This is proven unambiguously in the NEXAFS data of Sec. III C.

B. Ca 2p and F 1s Auger energy shifts

In Figs. 5(b) and 5(d) we show F 1s (KVV) and Ca 2p $(L_{2,3}MM)$ Auger-electron spectra for two different CaF₂ coverages. Spectrum b is taken for submonolayer coverage and spectrum d for 4 layers. Together with the F 1s core level the F 1s Auger peak shifts to lower kinetic energy when increasing the coverage from 1 to more layers. Between the initial adsorption (spectrum b) and the bulk peak of the four-layer spectrum (d) an Auger energy shift of 3.0 eV occurs. In contrast to the four-layer F 1s photoemission spectrum [Fig. 5(a), spectrum d], where no interface peak can be detected, the corresponding four-layer F 1s Auger-electron spectrum shows a shoulder on the higher kinetic energy side due to the interface contribution. This shoulder becomes more pronounced in the coverage regime between 2 and 4 layers (see Ref. 17). A line fitting gives an energy separation of $\simeq 2.0$ eV between the bulk and the interface Auger peak. In the fluorine Auger spectrum we are therefore able to distinguish between the bulk and interface emission and we can apply this in the measurement of the F 1s absorption spectra (Sec. III C). The Ca 2p Auger spectrum of the 4-layer film [Fig. 5(d) spectrum d] is rather broad and cannot be separated unambiguously into bulk and interface contributions. In

the submonolayer spectrum b, three peaks can be resolved in the kinetic energy range of 280-295 eV. Superimposed on them are in the four-layer spectrum the bulk peaks which are shifted to lower kinetic energy. Comparing spectra b and d we derive an Auger-energy shift between bulk and interface of $\simeq 4.5$ eV. The smaller peak at 305eV shifts only by a smaller amount. Table I summarizes the kinetic energies (relative to the vacuum level) and shifts of the Auger peaks.

Both the core-level and the Auger energy shifts depend on initial-state and relaxation effects, but in a different manner. Knowing both shifts, we can try to distinguish between initial-state and relaxation contributions. It is known²² that the relaxation shift for the Auger electrons is about 3 times the relaxation shift for the core levels. Xe overlayers on metals exhibited this effect clearly.²³ The initial-state shift can be assumed to be the same for both processes. It is composed of short-range changes in the chemical environment (chemical effects) and of longrange changes in the Madelung energy. For F we see no interface contribution in the core-level spectra and a shift of $\simeq 2.0$ eV in the F 1s Auger spectrum. This can be explained by assuming an initial-state shift of -1 eV and a relaxation shift of +1 eV. For the core level they cancel each other and for the Auger energy the add up to 2 eV. The Ca interface core levels shift about 2 eV and the Ca 2p Auger electrons of the interface are separated by $\simeq 4.5$ eV from the bulk. In this case we obtain an initial-state shift of slightly smaller than +1 eV and a relaxation shift of slightly larger than +1 eV. The relaxation shifts for both, F and Ca, of about +1 eV demonstrate the increased screening at the interface. The initial-state shifts support the interpretation that the ionicity at the interface is reduced, because the electronegativity difference with Si is smaller than with the ionic partner. Effectively, a transfer of negative charge from the interface F to the interface Ca occurs, changing the oxidation character of Ca from 2 + to 1 + at the interface. In the submonolayer regime (initial adsorption) we observe a F 1s(2s) core-level shift of 1.7 (1.9) eV and an Auger energy shift of 3.0 eV. When we apply the same separation as above, we obtain a relaxation shift of about 0.65 (0.55) eV and an initial state shift of +1.05 (+1.35) eV. The reduced relaxation shift is in agreement with our adsorption model of Fig. 1 where F is pointing away from the surface. The opposite F initial-state shifts between the submonolayer regime and the interface could be due to different charge transfers (F sees Ca in the submonolayer regime as opposed to Si at the interface) or due to different Madelung energies for the two geometries.

It is known¹⁹ that heavy electron and x-ray irradiation of CaF_2 crystals causes F loss and induces a Ca 2p corelevel shift of 2.4 eV and an Auger energy shift of 6 eV. The irradiation dose in our core-level and Auger-electron measurements was too small in order to detect any contributions of this effect.

C. Ca 2p and F 1s NEXAFS spectra

Near-edge x-ray-absorption fine structure²⁴⁻²⁶ (NEXAFS) measurements allow one to probe the density of empty valence-band states available for excited elec-

trons. Especially when applied to an interface, unoccupied interface states can be detected.¹⁷ The dependence of the absorption upon the polarization^{17,24-26} of the exciting photons can be used to determine the orientation of the bond orbitals at the interface. The 2p subshell excitations have attracted some attention because of the strong localization of the 3d level²⁷ (the dominant final state) and the coupling of the 2p level to the final state. In this work we will focus on interface derived states. In order to discriminate interface from bulk states, we take advantage of the fact that the interface atoms exhibit shifted core level and Auger-electron energies (see above). We have measured the Ca 2p and F 1s absorption by monitoring the yield of the associated Auger electrons. For the Ca 2pa broad energy window was set comprising both the bulk and interface Auger peaks since with selective energy windows the spin-orbit intensity ratio was distorted.

In Fig. 6 three sets of Ca 2p absorption spectra are shown for 1.3, four, and seven layers CaF₂ with s and p polarization. At the Ca 2p absorption edge two prominent transitions into the empty 3d states²⁷⁻²⁹ of the Ca²⁺



FIG. 6. The absorption edge fine structure of Ca 2p measured for different thicknesses of CaF₂ films via the yield of the Ca 2p Auger electrons. The features A-E are due to transitions at the interface. Their multiplet structure shows that Ca is in a 1 + oxidation state at the interface.

ion in CaF₂ are observed which result in a sharp spinorbit split doublet F, G in bulk CaF₂. A number of smaller lines, A to E, are found with energies relative to the corresponding lines F, G of -2.4 eV (A), -1.7 eV (B), -0.9 eV (C), -1.4 eV (D), and -0.9 eV (E). These smaller lines, although somewhat smeared out, increase in intensity at 4 layers and gain much more at 1.3 layers. They can be attributed to interface transitions not only because of the attenuation with increasing film thickness but also because of the pronounced polarization dependence. Bulk CaF_2 has a cubic lattice structure which forbids, by group theory, the occurrence of polarization differences in photon absorption. The lower symmetry at either the interface or the surface can be the only reason for the observed distinction between s or p polarization. It has been investigated earlier²⁷ that the 2p absorption edges of argonlike ions have to be interpreted in an atomic picture. Dipole selection rules allow only transitions from Ca 2pinto unoccupied 3d and 4s states (plus higher lying states). The 2p-4s transitions are expected to be weak compared with the 2p-3d transitions since the 4s wave function in Ca is much more extended than the 3d wave function and has little overlap with the Ca 2p core wave function.^{27–29}

The observed multiplet structure of the 2p-3d transitions gives us a good fingerprint of the oxidation state of Ca. Neutral Ca gives rise to a triplet²⁹ with two strong lines and a 50 times weaker line, ignoring weak transitions into higher lying states which occur at higher photon energy. The two strong lines arise from the $2p_{1/2}$ and $2p_{3/2}$ core holes. For Ca^{2+} in CaF_2 we expect a similar multiplet structure because it differs from neutral Ca only by a filled 4s shell. We observe these two in our CaF_2 NEXAFS spectra except that they are much narrower (seven-layer spectrum of Fig. 6) than in neutral Ca.^{28,29} For Ca^{1+} there exists an unpaired 4s electron which creates a more complex multiplet via Coulomb and exchange interaction with the 2p core hole and the 3d electron. An estimate for this multiplet can be obtained from calculations for the isoelectronic K atom²⁹ which gives four lines for the $2p_{3/2}$ and three lines for the $2p_{1/2}$ core holes. In the 1.3-layer spectrum we observe exactly the same number of lines assuming that different transitions are excited with p and s polarization. Because p polarization contains a certain amount of the vector potential A parallel to the surface,³⁰ we see broader lines in p polarization. The polarization dependence probably originates from an orientation of the spin of the 4s electron perpendicular to the interface. In the structure model of Fig. 1, Ca is located on top of a Si surface atom and forms a bond perpendicular to the surface that orients the spin. The Ca 2p absorption data indicate, that Ca at the interface is mainly in a 1 + oxidation state, in agreement with the interpretation of the core-level spectra of Sec. III A and the Auger-electron spectra of Sec. III B.

We notice that the little peaks A-E do not vanish when the thickness is further increased beyond seven layers. This could be due to inhomogeneous layer thickness leading to thin regions transparent to the electrons from the interface or due to near surface defects (e.g., F centers). A possible initial-state configuration interaction³¹ in the bulk is conceivable but gives difficulties in explaining the observed polarization dependence. After irradiation with zero-order light, the little peaks A-E increase. This is in agreement with previous results,¹⁹ where we have found a Ca¹⁺ surface layer due to F desorption after vuv irradiation.

In Fig. 7 we show F 1s absorption spectra for seven and four layers CaF₂. Interface sensitivity could be increased in the four-layer spectra by setting the energy window at 2 eV higher kinetic energy as the bulk Auger peak, thereby sampling most of the interface Auger electrons [Fig. 5(b)]. A background spectrum is taken at a kinetic energy above the Auger peak in order to subtract the contributions of the shallow core leve photoemission peaks (Ca 3p, Ca 3s, F 2s). This spectrum is shifted down by the difference in the kinetic energy settings (Fig. 7, bottom) and subtracted from the raw data. In contrast to the 2p absorption edge of Ca, the F 1s absorption edge is mostly dominated³² by the structure of the conduction band. We observe therefore transitions into unoccupied states with F p character mixed to the Ca 4s, 3d, 4p states from which the conduction band is mainly derived.^{33,34} For the bulk sensitive partial yield spectra of the 7 layer film (Fig. 7, top), a rich



FIG. 7. The F 1s absorption spectra for four and seven layers CaF_2 on Si(111) measured via the yield of the F 1s Auger electrons. By placing the kinetic energy window at the shifted interface Auger peak [Fig. 5(b)], a better interface sensitivity could be achieved.

structure of unoccupied states is observed that is essentially independent of polarization³⁰ as expected from an optically isotropic bulk solid. In the interface sensitive spectrum of the four-layer film, we observe two prominent features (H,I) which are much less pronounced in the bulk sensitive spectrum of the same film. This spectrum has been scaled down (Fig. 7, middle) such that it represents the tail of the bulk Auger peak that falls into the interface window. The energy locations of peaks Hand I are 3.1 and 6.7 eV above the Fermi level if we neglect electron-hole interaction.³⁵ Peak I is excited mostly by the component A parallel to the surface (s polarization). The remanent of this peak in p polarization is mainly due to the residual parallel component in this polarization.³⁰ Its polarizations dependence suggest an assignment of peak I to $F 2p_{x,y}$ states of F-Ca back bonds (see Fig. 7) which are oriented essentially parallel to the interface. The polarization-independent peak H can be assigned to F_{2p} -Si 3p interface bonds tilted about 45° in our simple model. A more definitive assignment requires a calculation^{36,37} of the interface electronic structure and the transition probability.

For comparison, we have taken the analogous F 1s absorption spectra from fluorine adsorbed on a cleaved Si(111) 2×1 surface, yielding in a 1×1 surface with mainly silicon monofluoride present.¹⁵ In Fig. 8 the spectra are shown which exhibit two dominant near-edge peaks *A*,*B*, too, but with a different polarization signature. The lower peak *A* is excited by the perpendicular component of **A**, the upper peak *B* has no polarization dependence. This is exactly the opposite way as for the CaF₂/Si(111) interface. We explain the differences by assuming the top site for F on Si(111) [comparable to Cl on Si(111) (Refs. 38 and 26) and Ge(111) (Refs. 39 and 26)] and the hollow site for F at the CaF₂/Si(111) interface. Peak *A* corresponds to transitions into the perpendicular F—Si bond. The sites correspond^{36,37} to covalent and ion-



FIG. 8. The F 1s absorption edge measured for one monolayer of fluorine on a cleaved Si(111) 2×1 crystal forming a 1×1 surface with mainly silicon monofluoride present (Ref. 15). The polarization dependence of peaks A and B is opposite to peaks H and I of the CaF₂/Si(111) interface of Fig. 7.

ic bonding, respectively, and reflect the difference between adsorption of neutral F and F^{1-} in the two cases.

D. Valence-band region

The valence band of an ionic crystal is usually composed of the anion orbitals, i.e., the F 2p electrons in CaF₂. In the upper part of Fig. 9, F 2p valence-band spectra are shown for various CaF₂ thicknesses on Si(111) and for a photon energy of 36 eV. The emission angle was 20° from the surface normal. Two different regimes are observed. At submonolayer coverages we observe a $\sqrt{3} \times \sqrt{3}$ LEED pattern and in the photoemission spectra we find mainly one sharp peak (FWHM 1.1 eV) at 9.2 eV binding energy. Two smaller structures at 6.9 and 11.0 eV decrease in intensity as the coverage is increased. These two smaller peaks grow upon prolonged irradiation and can be largely reduced by heating the sample to 700 °C. For comparison we have taken a F 2p valence-band spectrum for about 1 monolayer F adsorbed on Si(111) 7×7 [dosing with 50 L XeF₂ and annealing to \simeq 400 °C (Ref. 15)], which is shown in the lower part of Fig. 9. [1 langmuir $(L) \equiv 10^{-6}$ Torr sec.] In this spectrum we see the



FIG. 9. Photoelectron spectra of the F 2p valence band showing the transition from a two-dimensional layer to a three-dimensional structure. For comparison a spectrum of one layer F on Si(111) is shown at the bottom.

same peaks at the same locations as in the submonolayer regime of CaF₂ on Si, suggesting that some of the adsorbed CaF₂ molecules dissociate after irradiation with 36 eV photons and F adsorbs on open patches of Si. The adsorbed fluorine can be heated off easily. The heavy impact of vuv irradiation has been observed also on thicker layers.¹⁹ The three fluorine derived peaks can be attributed in the same manner as for Cl on Si(111) (Ref. 38) as emission from $F(p_{x,y})$, $\sigma[F(p_z)-Si(p_z)]$ and $s[F(p_z)-Si(s)]$ states. However, in our case F is disordered and higher fluorides are present, which yields a broadening of the features.

Somewhere between one and two layers, the transition from a two-dimensional layer to a three-dimensional structure takes place and the F 2p valence band of CaF₂ develops. At 2.5 layers a broad band is seen with two peaks at 11.3 and 9.7 eV binding energy. These peaks show large intensity variations but little dispersion with k_{\parallel} when we change the angle of emission. Strong intensity variations are also observed in normal emission when the photon energy is varied. In Fig. 10 a set of AREDC's in normal emission is displayed. The photon energy



FIG. 10. Normal emission photoelectron spectra for a 2.6 layer CaF_2 film showing dramatic variations with photon energy due to three-dimensional band-structure effects.

dependence is due to the development of threedimensional bulk bands when the thickness is increased to 2.5 layers CaF₂. Observations of three-dimensional effects even in films as thin as three layers is not uncommon and are for example found⁴⁰ in Xe films three layers thick. But we do not expect to observe the full band dispersion of CaF₂ for a 2.6 layers slab, because each layer contributes only one k point to the band structure. Heaton et al.³⁵ have carried out band-structure calculations for CaF₂ and get four F 2p derived bands (from two F atoms in the CaF₂ unit cell) in the Γ -L direction with a bandwidth of 1.42 eV at Γ and 0.42 eV at the L point. Two of the bands are degenerate and in an arbitrary direction six bands form the F 2p valence band. The spectra of Fig. 10 are composed of more than two peaks and show rapid changes in the intensities of the peaks a function of photon energy rather than a dispersion. The bandwidth measured from the lowest binding energy peak at hv=28eV ($E_B = 9.54$ eV) to the highest binding energy peak at $hv = 66 \text{ eV} (E_B = 11.9 \text{ eV})$ is 2.36 eV. The overall bandwidth including half of the tails is 3.3 eV. The largest peak separation is 1.87 eV at hv = 66 eV and the smallest is 0.8 eV at hv = 30 eV. There is another possibility to account for the rapid variation of the cross section of the individual peaks as a function of photon energy. The large oscillations in the final state density, which we found in the F 1s absorption spectra (Fig. 7 of Sec. III C) could modify the transition probability.

In Fig. 11 a spectrum of a clean Si(111) 7×7 surface is



FIG. 11. Photoelectron spectra in the regime of the Si valence bands and the surface states. While the metallic Si(111) 7×7 exhibits three surface states (lower curve), the CaF₂/Si(111) interface is semimetallic and shows a broad interface state 1.1–1.2 eV below E_F due to Ca 4s—Si dangling bond interaction.

shown. It clearly exhibits the metallic character¹³ of this surface and the three surface states at 0.16, 0.9, and 1.7 eV binding energies. After evaporation of CaF2 on this surface, these states disappear and a new, broader structure at $E_B = 1.1 - 1.2$ eV appears. This structure gets weaker when the film thickness grows, suggesting that the associated state is located at the interface. This interface state exhibits no dispersion with k_{\perp} and a small downward dispersion with k_{\parallel} near the zone boundary. In this region the interface peak gains intensity because it enters the band gap. A similar peak has been predicted⁴¹ for Na on Si(111). The Na 3s electron couples in this case to the Si dangling bond surface states resulting in a pair of bonding and antibonding bands. At the Fermi level the density of states tails off towards zero which shows that the $CaF_2/Si(111)$ interface is not metallic although it could be semimetallic. The pinning position of the Fermi level changes when we deposit CaF₂. At the clean Si(111) 7×7 surface E_F is found⁴² to be pinned $\simeq 0.63$ eV above the valence-band maximum. After evaporation of CaF₂ we see a shift of the Si 2p bulk core level towards lower binding energy relative to E_F indicating a new Fermi level position (relative to the Si valence band) at the interface. In Fig. 12 this shift is plotted versus the CaF₂ coverage. The Fermi level shifts successively towards the Si valenceband maximum and beyond 2 layers a new pinning position about 0.55-0.65 eV below the old one is established. This is at the Si valence-band maximum. The full amount of this shift can only be found if CaF₂ is evaporated on a sample held at least at 700-750 °C. At about two layers the interface seems to be accomplished. Upon vuv irradiation¹⁹ the Fermi level shifts back up, probably because F is lost at the interface which leaves extra electrons that can fill up the holes in the valence band.

A self-consistent picture of the electronic structure of the interface arises from our core-level shifts, the changed Fermi-level pinning position and the interface state at $E_B = 1.2$ eV. This is schematically drawn in Fig. 13. The band lineup between the Si valence and conduction band and the CaF_2 bands at the interface is determined by the position of the F 2p valence band of CaF₂ in our spectra of Fig. 9 and 10. We find the onset⁴³ of the F 2p peak \simeq 8.8 eV below the Si valence-band maximum. When the band gap of CaF₂ of 12.1 eV (Ref. 35) and of Si (1.1 eV) is taken into account, we find that the conduction-band minimum of CaF_2 is aligned $\simeq 2.2$ eV above the conduction-band minimum of Si. The Si atoms at the interface (first layer) are nearly neutral if we judge from the relatively small Si core-level shift of +0.4 eV. Therefore the Si 3p dangling bond orbital is still mainly half filled and can interact with the 4s electron of the interface Ca^{1+} by forming a pair of bonding-antibonding states. We identify the bonding state as the broad peak 1.2 eV below E_F in the upper spectrum of Fig. 11. We tried to resolve the corresponding antibonding state of the Si-Ca interac-tion in the Si 2p absorption edge.¹² But the spectra showed only a weak increase of an existing feature in the clean Si 2p absorption spectra at $\simeq 1.7$ eV. It could be that the Si 3p character of the dangling bond state prevents us from seeing the transition due to the dipole selection rules (p to p is forbidden). The transition to dangling bond orbitals is very weak for clean Si surfaces.¹² There are several models that can account for the transfer of negative charge to Ca at the interface. If we assign the Si atoms with -0.8 eV core-level shift to second layer Si, they are the ones which provide the extra Ca 4s electron



FIG. 12. Shift of the Fermi level towards the valence-band maximum as a function of CaF_2 coverage relative to clean Si(111) 7×7. The shift was determined by the kinetic energy position of the Si 2p core-level peaks. In clean Si(111) 7×7 the Fermi level is pinned $\simeq 0.63$ eV above the valence-band maximum (Ref. 42).



FIG. 13. Band lineup and energy diagram of the $CaF_2/Si(111)$ interface. A bonding model is proposed where Ca changes its oxidation state to 1 + and forms a bond that involves the Ca 4s and the Si dangling electrons.

with the interface F as intermediate. In order to accomplish a charge transfer from second layer Si to interface Ca, the Fermi level has to be placed near the Si valenceband maximum, which is already bulklike for secondlayer silicon atoms. This agrees with our observation. The Si atoms with -0.8 eV core-level shift can also be explained by assuming two different interface structures side by side, one Ca-terminated (e.g., models 1,4 in Ref. 8), the other F-terminated (models 3,6). For the Ca-terminated portion one would have a transfer of negative charge from interface F (Ref. 44) to interface Ca. For the Fterminated portion it is difficult to explain where the negative charge from the surface Si goes.

IV. CONCLUSIONS

From the interface core-level shifts of all partners of the interface (Si, Ca, and F) strong support for a microscopic model (see Figs. 1 and 13) of the interface is given in which Ca sits on top of the Si atoms in the first layer and interacts with the Si dangling bonds. Auger electron, Si 2p core level, and polarization dependent F 1s NEXAFS spectra show that F is present at the interface. The electronic structure of the interface is mainly characterized by a transfer of negative charge to the interface Ca, resulting in Ca¹⁺ character at the interface. This is inferred from the interface core level shifts and from the Ca 2p NEXAFS spectra. An occupied interface state 1.2 eV below the Fermi level suggests the formation of a Ca 4s—Si 3p (dangling bond orbital) bond. The electronic structure at the interface is drastically different from bulk CaF₂ with the band gap shrinking from 12.1 eV to an estimated 3 eV for the bonding-antibonding interface splitting. In fact, the interface is semimetallic because the Fermi level is pinned close to the valence band maximum of Si. The observation of such strong changes in the band structure of an interface layer opens the door for fabricating novel materials.

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- ¹R. F. C. Farrow, P. W. Sullivan, G. M. Williams, G. R. Jones, and C. Cameron, J. Vac. Sci. Technol. **19**, 415 (1981); T. P. Smith III, Julia M. Phillips, W. M. Augustyniak, and P. J. Stiles, Appl. Phys. Lett. **45**, 907 (1984); T. Asano, Y. Kuriyama, and H. Ishiwara, Electron. Lett. **21**, 386 (1985).
- ²L. G. Schowalter, R. W. Falthauer, R. P. Goehner, L. G. Turner, R. W. DeBlois, S. Hasimoto, J.-L. Peng, W. M. Gibson, and J. P. Krusius, J. Appl. Phys. 58, 302 (1985).
- ³H. Ishiwara and T. Asano, Appl. Phys. Lett. 40, 66 (1982); Thin Solid Films 93, 143 (1982); J. Appl. Phys. 55, 3566 (1984); R. W. Falthauer, N. Lewis, L. J. Schowalter, and E. L. Hall, J. Vac. Sci. Technol. B 3, 736 (1985); Masayoshi Sasaki and Hiroshi Onda, J. Appl. Phys. 59, 3104 (1986).
- ⁴T. Asano and H. Ishiwara, Appl. Phys. Lett. 42, 517 (1983).
- ⁵G. M. Gibson and J. M. Phillips, Appl. Phys. Lett. **43**, 828 (1983).
- ⁶W. Fathauer and L. J. Schowalter, Appl. Phys. Lett. **45**, 519 (1984).
- ⁷For an overview of recent work, see L. J. Schowalter and R. W. Fathauer, J. Vac. Sci. Technol. A **4**, 1026 (1986).
- ⁸F. J. Himpsel, F. U. Hillebrecht, G. Hughes, J. L. Jordan, U. O. Karlsson, F. R. McFeely, J. F. Morar, and D.Rieger, Appl. Phys. Lett. 48, 596 (1986).
- ⁹G. Hollinger and F. J. Himpsel, Appl. Phys. Lett. 44, 93 (1984).
- ¹⁰E. J. van Loenen, J. W. M. Frenken, J. F. van der Veen, and S. Valeri, Phys. Rev. Lett. **54**, 827 (1985); F. A. Ponce, G. B. Anderson, M. A. O'Keefe, and L. Schowalter, J. Vac. Sci. Technol. B **4**, 1121 (1986).
- ¹¹P. E. Schmid, P. S. Ho, Föll, and G. W. Rubloff, J. Vac. Sci. Technol. 18, 937 (1981); J. E. Houston, C. H. F. Peden, Peter J. Feibelmann, and D. R. Hamann, Phys. Rev. Lett. 56, 375 (1986).

- ¹²F. J. Himpsel, P. Heimann, T. C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).
- ¹³F. J. Himpsel, D. E. Eastman, P. Heimann, B. Reihl, C. W. White, and D. M. Zehner, Phys. Rev. B 24, 1120 (1981); D. M. Zehner, C. W. White, P. Heimann, B. Reihl, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B 24, 4875 (1981); T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, Solid State Commun. 39, 1001 (1981); R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flodström, Phys. Rev. B 31, 3805 (1985).
- ¹⁴A. Franciosi, J. H. Weaver, and D. T. Peterson, Phys. Rev. B 31, 3606 (1985).
- ¹⁵J. F. Morar, F. R. McFeely, N. D. Shinn, G. Landgren, and F. J. Himpsel, Appl. Phys. Lett. **45**, 174 (1984); F. R. McFeely, J. F. Morar, N. D. Shinn, G. Landgren, and F. J. Himpsel, Phys. Rev. B **30**, 764 (1984).
- ¹⁶Marjorie A. Olmstead, R. I. G. Uhrberg, R. D. Bringans, and R. Z. Bachrach, J. Vac. Sci. Technol. B 4, 1123 (1986).
- ¹⁷F. J. Himpsel, U. O. Karlsson, J. F. Morar, D. Rieger, and J. A. Yarmoff, Phys. Rev. Lett. **56**, 1497 (1986).
- ¹⁸B. Tonner, Nucl. Instrum. Methods **195**, 17 (1980); F. R. McFeely (unpublished); F. J. Himpsel, Y. Jugnet, D. E. Eastman, J. J. Donelon, D. Grimm, G. Landgren, A. Marx, J. F. Morar, C. Oden, R. A. Pollak, J. Schneir, and C. A. Crider, Nucl. Instrum. Methods Phys. Res. **222**, 107 (1984); D. E. Eastman, J. J. Donelon, N. L. Hien, and F. J. Himpsel, Nucl. Instrum. Methods **172**, 327 (1980).
- ¹⁹U. O. Karlsson, F. J. Himpsel, J. F. Morar, F. R. McFeely, D. Rieger, and J. A. Yarmoff, Phys. Rev. Lett. 57, 1247 (1986); C. L. Strecker, W. E. Moddeman, and J. T. Grant, J. Appl. Phys. 52, 6921 (1981).
- ²⁰A. D. Walsh, J. Chem. Soc. (London) 1953, 2266 (1953).
- ²¹R. T. Poole, J. Szajman, R. C. G. Leckey, J. G. Jenkin, and J.

Liesegang, Phys. Rev. B 12, 5872 (1975).

- ²²G. Hohlneicher, H. Plum, and H. J. Freund, J. Electr. Spectrosc. Relat. Phenom. **37**, 209 (1985); C. D. Wagner, Farad. Discuss. Chem. Soc. **60**, 291 (1975).
- ²³G. Kaindl, T. C. Chiang, D. E. Eastman, and F. J. Himpsel, Phys. Rev. Lett. 45, 1808 (1980).
- ²⁴J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler, and S. Brennan, Phys. Rev. Lett. **47**, 381 (1981); J. Stöhr and R. Jaeger, Phys. Rev. B **26**, 4111 (1982).
- ²⁵D. Norman, J. Stöhr, R. Jaeger, R. J. Durham, and J. B. Pendry, Phys. Rev. Lett. **51**, 2052 (1983).
- ²⁶P. H. Citrin, J. E. Rowe, and P. Eisenberger, Phys. Rev. B 28, 2299 (1983).
- ²⁷A. A. Maiste, R. E. Ruus, and M. A. Elango, Zh. Eksp. Teor. Fiz. **79**, 1671 (1980) [Sov. Phys.—JETP **52**, 844 (1980)].
- ²⁸For Ca metal, see: J. Barth, F. Gerken, and C. Kunz, Phys. Rev. B 28, 3608 (1983); J. Zaanen, G. A. Sawatzky, J. Fink, W. Speier, and J. C. Fuggle, *ibid.* 32, 4905 (1985).
- ²⁹M. W. D. Mansfield, Proc. R. Soc. London, Ser. A 346, 555 (1975); 348, 143 (1975).
- ³⁰For s polarization the light was incident normal to the sample; for p polarization the sample was turned around so that the light was incident 60° from the sample normal with A in the plane of incidence. Electrons were collected in a 85° (full angle) cone which was centered around the sample normal for p polarization and 60° off normal for s polarization.
- ³¹D. A. Shirley, J. Phys. (Paris) Colloq. 39, C4-35 (1978).
- ³²T. M. Zimkina and A. S. Vinogradov, J. Phys. Colloq. 32, C4-278 (1971).

- ³³J. P. Albert, G. Jouanin, and C. Gout, Phys. Rev. B 16, 4619 (1977).
- ³⁴Richard A. Heaton and Chun C. Lin, Phys. Rev. B 22, 3629 (1980).
- ³⁵The electron-hole interaction is 0.9 eV for the F 2p valence exciton [see G. W. Rubloff, Phys. Rev. B 5, 662 (1972)]. Increased screening will reduce the electron-hole interaction at the interface.
- ³⁶See, e.g., M. Schlüter and Marvin L. Cohen, Phys. Rev. B 17, 716 (1978).
- ³⁷M. Seel and P. S. Bagus, Phys. Rev. B 28, 2023 (1983).
- ³⁸R. D. Schnell, D. Rieger, A. Bogen, F. J. Himpsel, K. Wandelt, and W. Steinmann, Phys. Rev. B 32, 8057 (1985).
- ³⁹R. D. Schnell, F. J. Himpsel, A. Bogen, D. Rieger, and W. Steinmann, Phys. Rev. B 32, 8052 (1985).
- ⁴⁰T. Mandel, G. Kaindl, M. Domke, W. Fischer, and D. W. Schneider, Phys. Rev. Lett. 55, 1638 (1985).
- ⁴¹J. E. Northrup, J. Vac. Sci. Technol. A **4**, 1404 (1986).
- ⁴²F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B 28, 7018 (1983).
- ⁴³The onset was determined by taking an energy of 0.2 eV (resolution of the spectrometer and the monochromator) below the onset of the valence bands of Fig. 10.
- ⁴⁴An alternative model for the charge transfer is conceivable where the F layer next to the interface is missing and donates its electrons to the Ca interface layer, but it is very difficult to make such a model consistent with our core-level and Augerelectron results.