Photoemission study of bonding at the CaF_2-on-Si(111) interface

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The bonding at the interface between calcium fluoride and the silicon (111) surface has been studied with surface-sensitive core-level photoemission spectroscopy. The interface is found to consist of predominately Si—Ca bonds, with a dissociation of the CaF_2 molecule at the interface resulting in depletion of fluorine atoms. When the interface is grown at temperatures below the optimal epitaxial growth temperatures, there is both more fluorine and more disorder at the interface. This affects the valence-band offset between the two materials, which ranges between about 7.3 and 8.3 eV. When the interface is annealed at 700—800 °C, the CaF_2 film reevaporates until a 3×1 reconstruction is obtained on which there is calcium but no fluorine. The bonding at this surface is similar to that at the CaF_2-on-Si(111) interface.

I. INTRODUCTION

The epitaxial growth of calcium fluoride on silicon is important both technologically and as a prototypical system for the study of semiconductor-insulator interfaces. The high degree of lattice matching between the fluorite-structure CaF_2 and diamond-structure Si crystals allows the growth of high-quality crystalline epilayers, both of CaF_2 on Si[1,2] and of epitaxial silicon grown on these structures.[3–5] A number of studies have addressed the crystalline quality of these epilayers on the scale of ≥ 20 nm with ion channeling and Rutherford backscattering (RBS) (e.g., Refs. 1, 3, 4, 6, and 7), reflection high-energy electron diffraction (RHEED),[7,8] and electron microscopy.[2,5,7,8] There is much less information, however, relating to the microscopic structure of the CaF_2-on-Si(111) interface,[9–13] which is still an open question. In this paper, we report surface-sensitive core-level photoemission results which lead us to propose a model for the interface which involves predominately Si—Ca bonds, and in which there is a depletion of flourine from the interface. Such a model is depicted in Fig. 1.

The potential technological applications of the CaF_2-on-Si interface are wide ranging and rapidly developing. The crystalline Si/CaF_2/Si system is of importance for three-dimensional circuits, and multilayer systems including epitaxial silicides in combination with Si and CaF_2 have been demonstrated.[14,15] Calcium fluoride is also under study as an insulating (band gap approximately equal to 12.1 eV), low-permittivity ($\varepsilon \simeq 7$) buffer between silicon and gallium arsenide,[16] and could prove to be important for GaAs-on-Si technology. In addition, CaF_2 layers on Si substrates can be patterned on a nanometer scale by electron-beam lithography in a 100-keV electron microscope,[17] or on a micrometer scale with a 3-keV Auger microprobe and subsequent development in water.[18]

In addition to its technological importance, the interface between CaF_2 and Si is of interest as a prototype for study of the bonding between polar and nonpolar materials. Over a range of a few Å, the character of the bonding must change from the ionic Ca—F bonds in the insulator to the covalent Si—Si bonds in the semiconductor. The relative alignment of electronic bands across such an interface is expected to be a function not only of the average bulk potentials, but also of the interface dipole.[19,20] This dipole should be affected by the relative numbers of Si—Ca and Si—F bonds, as well as the ionic or covalent character of these bonds. The stoichiometry at the interface also should play a role in determining the band alignment. Comparison of the chemical state of the interface atoms with that of a Si(111) surface terminated by fluorine[21] or calcium[22,11] via the various core-level bind-

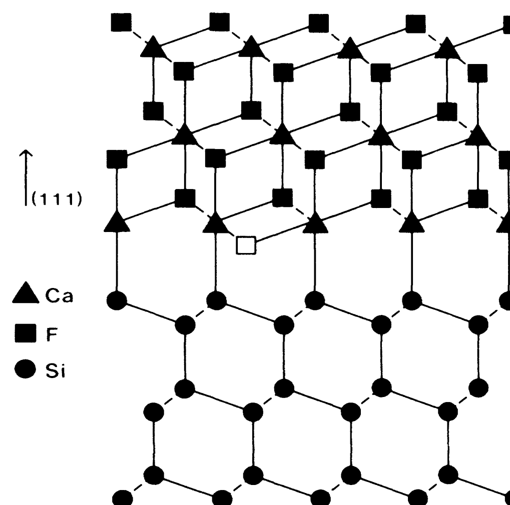

FIG. 1. Model for the CaF_2-on-Si(111) interface showing Si—Ca bonds and removal of one layer of F from the interface. Incomplete reaction may leave some F atoms in the site indicated by the empty box. The Si—Ca bond length is taken to be larger than the Si—Si or Ca—F bond length, corresponding to the longer length in calcium silicide structures (3.0—3.2 Å). The "type-B" epitaxy is incorporated to agree with RBS and electron microscopy measurements on thicker films.

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ing energies of Si, Ca, and F allows determination of the character of the interface bonds.

The crystalline quality of epitaxial calcium fluoride films on silicon substrates as determined by Rutherford backscattering measurements is a strong function of the substrate temperature, with the optimum temperature being in the range of 600—800 °C for Si(111) and 500—600 °C for Si(100).[1] In addition to the narrower range of epitaxial growth temperatures, the surface morphology of CaF_2 films on Si(100) is inferior to that for Si(111).[2,7] This has been attributed to the higher surface free energy of the polar CaF_2(100) crystal face compared to the (111) face.[2,7] The Si(111) surface was thus chosen as the substrate for these studies of the initial stages of interface formation between CaF_2 and Si.

When solid calcium fluoride is heated to temperatures above about 1100 °C, it sublimates as a molecule, and stoichiometric films can therefore easily be grown on Si substrates in ultrahigh vacuum. Since these molecules are stable against dissociation in the gas phase ($\Delta H_{\text{diss}} \sim 8.9$ eV/molecule),[23] it has generally been assumed that the molecule remains intact at the interface.[9] The Si(111) surface, however, may serve as a catalyst for this dissociation reaction. If the CaF_2-on-Si(111) interface is not reconstructed, the unpaired electron on each surface Si atom, in combination with the even number of electrons in the CaF_2 molecule, would result in an odd number of electrons in each interface unit cell. This should lead to a metallic interface with a density of interface states of $\sim 8\times 10^{14}$ cm^{-3} (one per interface silicon atom). Experimentally, however, interface state densities in the Si energy gap of less than 10^{-3} per interface atom have been observed after rapid thermal anneal (1100 °C for 20—30 sec) of the interface.[24] This implies either that the CaF_2 molecule is dissociated by losing a fluorine atom, or that the interface is reconstructed in such a way that the extra electrons can pair within the interface unit cell. The absence of extra diffraction spots in RHEED observations of the growing films,[7,8] the value of the ion backscattering yield,[1,3,4,6,7] as well as transmission electron microscopy results,[13] indicate that the interface is not strongly reconstructed parallel to the interface. However, our results presented below indicate that it is possible to dissociate the CaF_2 molecule at the CaF_2-on-Si(111) interface at temperatures of 700—800 °C.[11,12] This means that a model for the interface in which the CaF_2 molecule has lost a fluorine atom is plausible, and may explain the absence of a metallic interface.

We have performed surface-sensitive core-level photoemission measurements of the initial stages of CaF_2 growth on Si(111). We find a well-ordered interface for growth at 700 °C with predominately Si—Ca bonds, and limited interaction of Si and F. In contrast, growth at 500 °C results in a less well-ordered interface, with evidence of more Si—F bonds in addition to the Si—Ca bonds which are in the majority. Electron bombardment of this interface with 3-keV electrons results in silicon and calcium core levels which are closer to those for 700 °C growth. Electron bombardment is known to remove fluorine from the CaF_2 film.[25] Annealing of the CaF_2-on-Si(111) interface at 750—800 °C also results in a reevaporation of the CaF_2 film, and at coverages below about one monolayer, a sequence of reconstructions $2\times 1 \rightarrow 5\times 1 \rightarrow 3\times 1 \rightarrow 7\times 7$ is observed, with progressively smaller amounts of fluorine at the interface. The "3×1" surface contains no fluorine and a fraction of a monolayer of calcium. Further annealing of this structure returns the clean Si(111)7×7 reconstruction.

II. EXPERIMENTAL CONSIDERATIONS

In the performance of these experiments, calcium fluoride was thermally evaporated from a boron nitride crucible onto clean Si(111)7×7 surfaces. The p-type (boron doped, 10 Ω cm) samples were held at either 500 °C or 700 °C during the deposition by passing a direct current through them. The rate of growth of the CaF_2 films was approximately two molecular layers (6—7 Å) per minute for the 700 °C deposition, and somewhat higher for the 500 °C deposition due to less reevaporation of the film at the lower deposition temperature. The Si(111)7×7 surfaces used as substrates were cleaned by repeated cycles of ion bombardment (500-eV Ar^+ ions) and annealing (800—850 °C), with the cleanliness determined from the Si $2p$ core-level line shape. The photoemission spectra were obtained at the Stanford Synchrotron Radiation Laboratory. Care was taken not to expose the CaF_2 films to either the low-energy electron diffraction (LEED) or the Auger electron beams unless it was desired to remove fluorine from the film. Brief LEED exposures ($\lesssim 1$ μA, ~ 70 eV) had no significant effect at room temperature, while extended exposures at higher temperatures aided in the decomposition of the film.

To understand the role of fluorine at the interface, thin films of CaF_2 were purposefully irradiated with a high-energy electron beam to remove fluorine from the film. The electron bombardment of the thin CaF_2 films was performed with a 5-μA, 3-keV beam, with an exposure of 30 sec at each of 25 points with 0.4-mm spacing over a 1.6×1.6-mm^2 square. The film was almost completely removed at the center of the irradiated region, and milder effects which are discussed below were observed near to this region.

III. EXPERIMENTAL RESULTS

To investigate the bonding at the CaF_2-on-Si(111) interface we have measured the photoemission spectra of the Si $2p$, Ca $3p$, F $2s$, and F $2p$ electronic states for CaF_2 films grown at two different substrate temperatures, as well as after annealing or electron bombardment of these films. The core-level binding energies are indicative of the chemical environment of the atoms, and give information on the type of bonding in which they are involved. For example, Ca atoms in bulk CaF_2 are surrounded by eight F atoms and are in a Ca^{2+} state. If the CaF_2-on-Si(111) interface involves Ca—Si bonds, then the interface Ca atoms will retain more electrons than their counterparts in the bulk, leading to a smaller binding energy for the Ca $3p$ state. In the case of Si, a bond with the strongly electronegative F atoms will remove electrons from the Si, leading to an increase in the Si $2p$ binding energy; the

converse is true for a Si—Ca bond.

The angle-integrated photoemission from the shallow Ca and F core levels and the Si and CaF_2 valence bands is shown in Fig. 2 for four cases. The top spectrum is for a thick (≥ 50 Å) film of CaF_2 grown on a 500 °C Si(111) substrate. The next spectrum is from a thin (~ 11 Å) film where the Si(111) substrate was held at 700 °C during the deposition. This thin film was then annealed at ~ 750 °C for about 20 min while watching the LEED pattern in one section of the sample. The spectrum in Fig. 2(c) was taken from a different part of the sample (4 mm away) which displayed a 5×1 LEED pattern (briefly examined), while the lower spectrum [2(d)] was from a region which had been exposed to the electron beam and displayed a 3×1 LEED pattern. It should be noted that electron bombardment is not necessary to obtain the 3×1 pattern.[11] Spectra 2(b)—2(d) are aligned relative to the Si valence-band maximum, as determined from the Si $2p$ bulk contribution. Since no Si reference could be derived for spectrum 2(a), it was aligned relative to 2(b) using the Ca $3p$ peak position for comparison. It is likely, however, that the offsets between the CaF_2 and Si bands were different in the two cases, as will be discussed more fully below.

The uppermost spectrum in Fig. 2, taken from a thick film of CaF_2, shows the bulk emission for CaF_2. The large peak at low binding energy is due to emission from the valence band of CaF_2, derived from F $2p$ states. The double-peaked structure is expected from band-structure calculations[26] and is characteristic of bulk alkali halides. The inelastic scattering background is very small until ~ 11 eV below the top of the CaF_2 valence band, where an onset in the inelastic scattering intensity is observed. Reflectivity measurements indicate the energy for exciton formation in CaF_2 to be 11.2 eV,[27] which is consistent with exciton formation as the primary loss mechanism for inelastically scattered photoelectrons. The peaks of binding energies of 15—20 eV below the CaF_2 valence band are derived from the F $2s$ and Ca $3p$ states, as indicted in the figure. The Ca $3p$ peak is slightly asymmetric, which is expected from band-structure calculations[28] showing a slight broadening of this shallow core-level into a band.

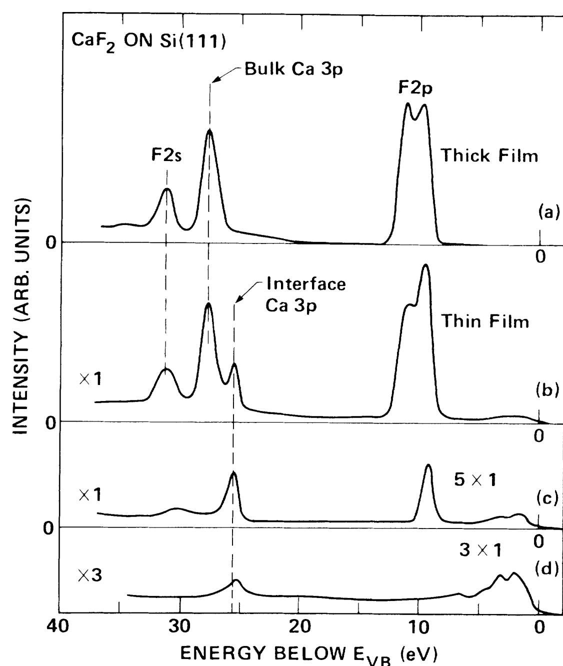

FIG. 2. Photoemission from shallow core levels for (a) thick CaF_2 film on Si(111) ($T_{dep}=500$ °C, $d \geq 50$ Å, $h\nu=130$ eV); (b) thin CaF_2 film on Si(111) ($T_{dep}=700$ °C, $d\sim 11$ Å, $h\nu=135$ eV); (c) 5×1 structure obtained upon annealing film in (b) ($h\nu=135$ eV); (d) 3×1 structure obtained upon annealing film in (b) ($h\nu=135$ eV). Spectra (b), (c), and (d) are aligned relative to the Si valence-band maximum E_{VB}.

The second spectrum in Fig. 2 is from a thin CaF_2 film grown on a 700 °C Si(111)7×7 substrate. A crystal thickness monitor near the sample indicated a growth of about 10 Å of CaF_2. This film is sufficiently thin so that emission from the silicon substrate can be observed, and silicon valence-band emission can be seen at low binding energies. Even though the CaF_2 film contains only a few molecular layers, the band structure can be seen to be well developed. The F $2p$ level is broadened into the CaF_2 valence band similarly to the bulk spectrum. The increase in inelastic scattering 11 eV below the CaF_2 valence band is another indication that the insulating bulk-band structure of the CaF_2 is present. The valence-band offset between the CaF_2 film and the Si(111) substrate is ~ 8.3 eV in this case of the 700 °C growth. A range of valence-band offsets between ~ 7.3 and ~ 7.7 eV was observed for 500 °C growth. It is difficult to determine an accurate value for the band offset due to uncertainty in locating the top of the two valence bands. A more accurate number is the difference in energy between the bulk Si $2p$ and Ca $3p$ states. This difference was 70.9 eV for the 700 °C film, and ranged between 71.5 and 71.9 eV for the 500 °C films.

The Ca $3p$ peak for this film shows two components [Fig. 2 spectrum (b)]. The larger peak at a binding energy of 27.9 eV relative to the Si valence-band maximum corresponds to Ca atoms in a bulklike environment; the peak at a binding energy of 25.6 eV is due to Ca atoms at the CaF_2-on-Si(111) interface. The F $2s$ peak for the film is very similar to the bulk peak. The Ca $3p$ interface component is 20% of the total Ca $3p$ emission. With an effective electron escape depth of 12 Å, typical of alkali fluorides at 100-eV kinetic energy,[29] this implies that there are ~ 2.5 bulklike Ca atoms per interface Ca atom. This average film thickness of 11 Å is consistent with the crystal monitor reading.

After annealing to the 5×1 structure, there is roughly a monolayer each of Ca and F on the surface. The F $2p$ emission forms a narrow, atomic-like peak instead of the broad CaF_2 valence band [Fig. 2 spectrum (c)]. The predominant Ca $3p$ emission is at the same energy as the interface peak in spectrum 2(b). The ratio of the F $2p$ to Ca $3p$ areas in spectrum 2(c) is only about half that for the thin film spectrum [2(b)], implying approximately equal numbers of Ca and F atoms in the 5×1 structure. The additional emission at higher binding energy than the interface Ca is at an energy between that of the bulk Ca $3p$ and F $2s$ states, making its origin difficult to assign.

From the ratio of the F 2s to the F 2p emission in spectra 2(a) and 2(b), only about 30% of the emission at higher binding energy than the main peak is due to the F 2s (assuming constant cross sections). If this is the case, then the F to Ca atomic ratio is 0.9; if only the main peak is assigned to the Ca 3p emission, the F 2p—Ca 3p area ratio implies an F to Ca atomic ratio of 1.25.

In the 3×1 structure there is no fluorine on the surface, as evidenced by the absence of F 2p or F 2s emission in spectrum 2(d). The ratio of the photoemission cross section for F 2p to that for Si 3p (valence band) at a photon energy of 135 eV is 12:1,[30] which makes this a sensitive test. Other data (not shown) at a photon energy of 21.2 eV, where this ratio is 28:1,[30] confirm the absence of fluorine in this structure. Comparison of the Ca 3p intensity with that of the interface peak in 2(b) (corrected for the 11 Å attenuation) leads to a Ca coverage of ~0.1 monolayers (ML) in the 3×1 structure. This may mean that the true symmetry is 3×3 with $\frac{1}{9}$ ML Ca rather than the 3×1 symmetry which requires at least $\frac{1}{3}$ ML of Ca. The central spot in the LEED pattern which would distinguish a 3×3 structure from a three-domain 3×1 pattern was, however, never observed. The 3×1 surface is discussed in more detail in Ref. 11.

In addition to the information contained in the Ca and F emission, information about the Si bonding environment at the CaF_2-on-Si(111) interface can also be obtained from the Si 2p core level. The Si 2p components shifted in energy from the bulk peak will be due to emission from the CaF_2-on-Si(111) interface. As mentioned above, we expect bonding to Ca to shift the Si 2p to lower binding energy, and bonding to F to shift it to higher binding energy.

The Si 2p emission for the same film as that for spectrum 2(b) ($d\sim11$ Å, $T_{dep}=700\,°C$) is shown in Fig. 3. The upper two curves are data taken under bulk and surface sensitive conditions, respectively. The lower curve is the $2p_{3/2}$ component of the surface-sensitive spectrum after a quadratic background subtraction (dashed line in central spectrum). The $2p_{3/2}$ component was extracted using a $2p_{3/2}$-$2p_{1/2}$ spin-orbit splitting of 0.600 eV and the statistical intensity ratio of 2:1. In addition to the bulk Si component, at least two chemically shifted components are present in the data. Using the top curve to fix the bulk Si $2p_{3/2}$ peak position at 99.01 eV below the Fermi level E_F, the data were fitted to four components as is shown in the figure. The curves are a convolution of a Lorentzian [full width at half maximum (FWHM) is 0.075 eV] with a Gaussian (FWHM is 0.35 eV). The bulk contribution accounts for 61% of the total intensity. A component with 29% of the total is shifted by 0.36 eV to lower binding energy from the bulk peak. The remaining ~10% of the intensity lies in one or two small peaks shifted to higher binding energy from the main peak. The fit shown in Fig. 3 contains 6% of the intensity in a peak shifted by 0.44 eV and 3.5% in a peak shifted by 0.83 eV. If the fit is forced to contain only a single peak shifted to higher binding energy, the fitted width of the peaks increases (to Gaussian FWHM of 0.38 eV), and 7% of the total is shifted by 0.57 eV to higher binding energy from the bulk peak. The spectrum is consistent with Si—Ca bonds at the interface, with a small portion of the interface containing F atoms in a layer between the Ca and Si atoms. This will be discussed in Sec. IV.

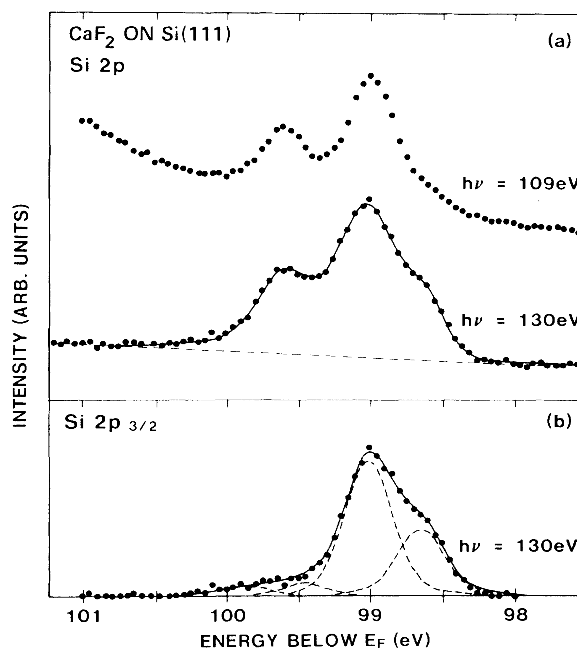

FIG. 3. Silicon 2p core-level spectrum for thin CaF_2 film on Si(111) ($T_{dep}=700\,°C$, $d\sim11$ Å). (a) Bulk-sensitive ($h\nu=109$ eV) and surface-sensitive ($h\nu=130$ eV) spectra. Zeros of intensity are offset to avoid overlapping of curves, and magnitudes are scaled arbitrarily. (b) Si $2p_{3/2}$ component obtained from surface-sensitive spectrum in (a) after subtraction of quadratic background (dashed line). Solid lines in both cases indicate the sum of the fitted components (see text).

The Si 2p spectrum for CaF_2 films grown at 500 °C [Fig. 4(b)] is broader than that for the 700 °C film [Fig. 4(a)]. These spectra were taken on films of comparable

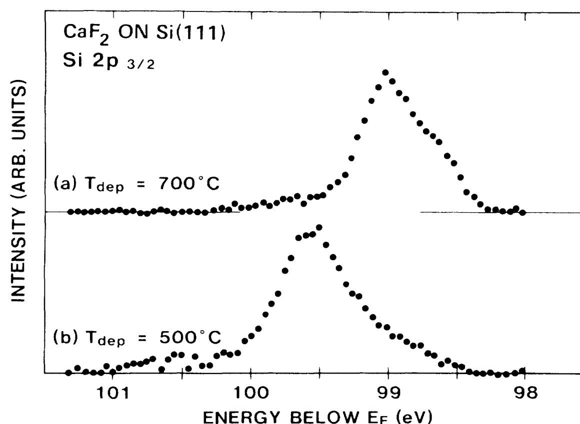

FIG. 4. Si $2p_{3/2}$ components for (a) thin CaF_2 film on Si(111) with $T_{dep}=700\,°C$ ($h\nu=130$ eV); (b) Similar film with $T_{dep}=500\,°C$ ($h\nu=135$ eV). Spectra are aligned relative to the Fermi level.

thickness and are aligned relative to the Fermi level E_F. The Si $2p$ peak for the $T_{dep}=500\,°C$ film cannot be deconvolved unambiguously, although in comparison with the film deposited at higher temperature, we see there are more shifted components, and less intensity in a bulklike peak, indicting a less abrupt interface. When the $T_{dep}=500\,°C$ film was irradiated with 3-keV electrons, the Si $2p$ spectrum became more similar in shape to that for the $T_{dep}=700\,°C$ film than the original 500 °C film. The change in shape upon electron bombardment is to decrease the higher binding-energy components and to increase the height of the lowest binding-energy component. Since electron bombardment is known to remove fluorine from the film, one major difference between the two deposition temperatures is likely the amount of fluorine at the interface.

The effect of electron bombardment on the Ca and F states for the $T_{dep}=500\,°C$ film is shown in Fig. 5. Again we see that electron bombardment leads to an interface which is close to those grown at $T_{dep}=700\,°C$. The interface Ca $3p$ peak for the as-grown $T_{dep}=500\,°C$ film [Fig. 5(b)] is not as well resolved as for the $T_{dep}=700\,°C$ film [Fig. 5(a)]. Its energy is closer to that for bulk CaF_2 and it contains a smaller fraction of the total intensity when compared to that for the $T_{dep}=700\,°C$ film. Upon electron bombardment of the $T_{dep}=500\,°C$ film, however, the spectrum changed to that shown in Fig. 5(c). The interface Ca $3p$ peak is now more similar to that for the $T_{dep}=700\,°C$ film. The position of the bulk CaF_2 bands relative to the Fermi level is also near to the value for the $T_{dep}=700\,°C$ film, shifting by ~ 0.5 eV after electron bombardment. A smaller shift in the opposite direction was observed for the Si $2p$ core level, so that the total band offset between the Si and CaF_2 bands was increased by ~ 0.6 eV upon irradiation. Spectrum 5(c) was taken from a point near the edge of the electron irradiated region. Towards the center of this region, the greater electron dose removed $>90\%$ of the fluorine, and the Ca peak (reduced less in intensity) broadened toward lower binding energy, indicative of Ca—Ca bonds in addition to Ca—Si and Ca—F bonds.

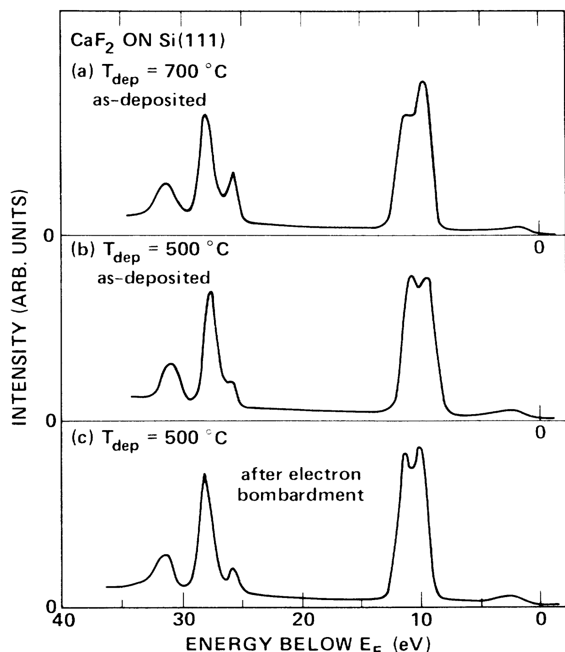

FIG. 5. Shallow core-level spectra for thin CaF_2 films grown on Si(111) ($h\nu=135$ eV). (a) $T_{dep}=700\,°C$. Same as Fig. 2(b); (b) $T_{dep}=500\,°C$ film as deposited; (c) $T_{dep}=500\,°C$ film after electron bombardment. Spectra are aligned relative to the Fermi level.

IV. DISCUSSION

The Ca $3p$ state in bulk CaF_2 has a binding energy 2.3 eV higher than that at the well-ordered CaF_2-on-Si(111) interface. This implies that the bonding environment at the interface is very different from bulk CaF_2, where each Ca^{2+} ion is surrounded by eight F^- ions, having transferred $\frac{1}{4}$ electron to each F. The environment of the Ca atoms nearest the CaF_2 surface, on the other hand, appears to be similar to that in the bulk. A shifted peak due to surface Ca atoms would have been observed for the thick CaF_2 film [Fig. 2 spectrum (a)] as well as for the thin film [Fig. 2 spectrum (b)]. The similarity of the bulk and surface Ca $3p$ binding energies arises because the lowest energy CaF_2(111) surface is presumably fluorine terminated, as shown in Fig. 1. If the CaF_2 were terminated similarly at the interface, with a layer of F atoms between the Ca atoms and the Si substrate, then the interface Ca atoms would have a very similar environment to those in the surface trilayer. The different core-level binding energies, however, indicate that this is not the case.

Dissociation of the CaF_2 molecule at the CaF_2-on-Si(111) interface, on the other hand, would lead to a Ca bonding environment quite different from that of bulk CaF_2. If the F layer between the Ca and Si atoms were missing, as shown in Fig. 1, the four fluorine atoms above the interface Ca would each take $\frac{1}{4}$ electron, and the remaining Ca valence electron would be available for bonding with the silicon substrate. This geometry would be expected to have a similar Ca $3p$ binding energy to that of a Si—Ca—F entity. The 5×1 structure obtained upon annealing the thin films has approximately equal numbers of Ca and F atoms, and shows no evidence in the Si $2p$ core level of isolated Si—F bonds (which would have a binding energy shift of 1.1 eV to higher energy from the bulk[21]). The main species on that surface is thus likely Si—Ca—F, so that the similarity in binding energies of the Ca $3p$ states at the interface and for the 5×1 structure supports a model such as that shown in Fig. 1 in which F is depleted from the interface. It should be noted that the Ca $3p$ binding energy for the 3×1 surface is also at a similar energy, again indicative of a covalent Si—Ca bond. In this case, it is possible that the isolated Ca atoms could go below the outermost Si layer.[11]

The model for the interface shown in Fig. 1 is also consistent with the photoemission results for the Si $2p$ state. The expected fractional intensities for the bulk and interface components can be inferred from those of the well-ordered Si(111):As 1×1 system, where the ideal Si(111) surface is terminated by As atoms replacing Si in the top half of the outermost double layer.[31] When measured

under similar experimental conditions (photon energy, collection geometry, etc,), the Si atoms bonded to arsenic (lower half of the outermost double layer) contributed 40% of the total Si $2p$ intensity, which corresponds to an effective electron mean free path of 3.4 Å. For CaF_2 on Si(111), the same mean free path would result in fractions of 33%, 27%, and 40% for the emission from the first, second, and remaining Si layers, respectively.

While we expect the predicted intensity fractions to be accurate to only about $\pm 10\%$, the observed bulk contribution of 61% to the Si $2p$ spectrum in Fig. 3 implies that a substantial fraction of the second-layer silicon atoms are in a bulklike environment. The component shifted by 0.36 eV to higher binding energy (29%) is consistent with all or most of the surface Si layer being bonded to Ca. The magnitude of this binding energy shift is $\sim \frac{1}{3}-\frac{1}{4}$ of that reported for films of calcium silicide (1.1—1.4 eV, increasing with coverage[22]), and is also consistent with this picture. At the CaF_2-on-Si(111) interface, only $\frac{1}{4}$ of the Si—Si bonds have been replaced by Si—Ca bonds, while in the silicide, the Si atoms are surrounded by Ca. The remaining Si $2p$ intensity, shifted to higher binding energy from the bulk contribution, is presumably due to Si which is interacting with F, and appears to arise from $\sim 10\%$ of the top double layer of the Si(111) substrate.

We discuss three possibilities for these Si—F bonds at the interface.

(i) A likely candidate is the incomplete dissociation of the CaF_2 layer at the interface, leaving a fraction of a monolayer of fluorine. The site which these F atoms would occupy in the bulk CaF_2 lattice is the "hollow" site above the fourth-layer Si atoms (see open box in Fig. 1). Calculations by Seel and Bagus[32] for isolated F atoms in this site show a very low barrier for penetration between the first and second Si layers. They calculate Si $2p$ binding energy shifts of 0.3—0.6 eV to higher energy from bulk Si, depending on the location of the F atom. The multiple components shifted to higher energy would be consistent with the first and second layer Si atoms bonding partially with this F atom. The removal of interface states upon annealing of CaF_2 films is also consistent with this explanation, since the F atoms trapped at the interface could diffuse into the silicon when thermally activated. The larger fraction of the Si $2p$ core-level intensity shifted to higher binding energy for the interfaces grown at 500 °C is also accounted for, since the dissociation of the molecule would be less complete at the lower deposition temperature. This is also consistent with the result in Fig. 5(b), where a larger fraction of the Ca atoms are in more bulklike environments for the $T_{\rm dep}=500\,^{\circ}\mathrm{C}$ films than for those deposited at a higher temperature. The electron bombardment could aid in removal of the interfacial fluorine, leading to the similarity in the Ca $3p$ interface binding energy between the bombarded $T_{\rm dep}=500\,^{\circ}\mathrm{C}$ film and the $T_{\rm dep}=700\,^{\circ}\mathrm{C}$ film.

(ii) The higher binding-energy components of the Si $2p$ core level could also arise from a different type of interface structure over a small fraction of the interface. The existence of two types of interface is shown by recent transmission electron microscopy results,[13] which show most of the interface having a structure where interface Ca atoms occupy the next Si lattice site, and a small fraction of the interface consistent with a structure where F atoms are in this position. The Si—F bonds in this structure could lead to the component shifted by ~ 0.8 eV to higher binding energy from the bulk Si $2p$ component. While a small contribution in the present work, a larger component at the same energy was observed in results from another group,[9] and different growth conditions could lead to different fraction of the interface in the two configurations. This could also be true of the degree of dissociation of the CaF_2 molecule at the interface.

(iii) A third possibility is that a fraction of the interface contains a stacking fault in the top double layer of the Si substrate, so that the interface F layer is directly above the second Si layer, instead of in the hollow above the fourth layer. This was suggested by Himpsel *et al.*[9] to explain the large component shifted by 0.8 eV to higher binding energy from the bulk in their results. Since the original Si(111)7×7 surface likely contains a stacking fault over half of each unit cell,[33] such a structure is plausible. However, if the interface fluorine layer is present over the entire interface, as suggested by Himpsel *et al.*[9] it is difficult to explain the binding energy of the Ca $3p$ state, which is similar in the two sets of experimental results.

The actual interface may well contain a combination of the factors described above. Both the electron microscopy results, and the variability among different photoemission results, indicate that more than one structure can coexist at the CaF_2-on-Si(111) interface. The uniformity of the interface may depend, for example, on the cleanliness and defect structure of the initial substrate, and the growth rate of the CaF_2 film, both of which could affect the degree of dissociation of the CaF_2 molecule. The strain and misfit dislocations induced in the film during cooling from the growth temperature to room temperature will also be different among different experimental conditions.

The dissociation of the CaF_2 molecule at the CaF_2-on-Si(111) interface is likely driven by the removal of metallic states from the Si band gap. The "as-grown" interface has a fairly high density of interface states which pin the Fermi level, but these are largely removed by a subsequent high temperature anneal.[24] This is consistent with small amounts of F at the interface (each F atom would contribute an interface state) which are removed during the annealing process. This is also consistent with the broader Si $2p$ spectrum obtained for the 500 °C growth. Valence-band photoemission spectra for these low-temperature growth samples were not of sufficient sensitivity to observe the expected metallic states. A second interface geometry which involves Si—F bonds could also give rise to states which pin the Fermi level, and high-temperature anneals could also account for the transformation to the Si—Ca interfacial arrangement. Further work which combines the various techniques and treatments is necessary to resolve these questions.

The variation of the band offset with growth conditions is also important. The CaF_2 band gap is estimated to be ~ 12.1 eV,[27] and the Si band gap is ~ 1.1 eV. Thus the 7.3—8.3 eV valence-band offset observed with this work implies a conduction-band offset of 2.7—3.7 eV. The band offset has previously been reported as 7.0 eV (Ref.

11) and 8.5 eV,[10] which represents an even wider variation in the offset (some of which may result from differences in the means of determining the offset in terms of experimental parameters). An uncontrolled variation of this magnitude (1.0—1.5 eV) could be very detrimental to the operation of a device, especially if electrons are the majority carriers. The source of this variation can be attributed to varying amounts of F at the interface, which could have an effect on the interface dipole. The offset in the $T_{dep}=500\,^{\circ}C$ film increased upon electron bombardment by about 0.6 eV (see Fig. 5), supporting this argument. Different geometries are also candidates for variation in the band offset and Fermi-level pinning position.

The depletion of fluorine atoms at the CaF_2-on-Si(111) interface in the equilibrium structure has important implications for the subsequent growth of Si on top of CaF_2. The stable termination of the CaF_2 lattice is a complete F—Ca—F trilayer, as indicated by the absence of a surface shift for the Ca core levels in addition to various stability arguments. If the stable, nonmetallic interface requires the removal of the surface fluorine layer, this may explain the difficulty in obtaining high-quality Si overlayers. The Si(111)7$\times$7 substrate may provide catalytic centers for the dissociation of the CaF_2 molecule which are not present when growing Si on a CaF_2 substrate; also, the large internal energy of the sublimed CaF_2 molecules ($T\sim1100$—$1300\,^{\circ}C$) is not available for breaking the Ca—F bond when the CaF_2 molecules are bound in a CaF_2 crystal. The enhanced reactivity of the hot Si atoms, however, may enable dissociation of the outer layer of CaF_2. Recent results by Karlsson *et al.*[34] have shown that F atoms may be removed from the surfaces of thin CaF_2 films by irradiation with 36-eV photons (approximately equal to the F 2*s* excitation energy). It would be interesting to see if Si growth on CaF_2 substrates is aided by the removal of this top F layer.

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