CaF_2/Si heteroepitaxy: Importance of stoichiometry, interface bonding, and lattice mismatch

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With use of x-ray standing waves in UHV and synchrotron radiation, the early stages of growth of CaF_2 on Si(111) were investigated. A new and subtle arrangement of the Si(111)/CaF_2 interface emerges from this study. For deposition at high substrate temperatures, the first monolayer of CaF_2 dissociates, and CaF is formed at the surface with Ca in the T_4 *and* H_3 sites. At lower temperature, a larger fraction of the CaF_2 remains undissociated, and a third Ca site sevenfold F coordinated in addition to H_3T_4 sites is consistent with the standing-wave experiments. These results have a direct bearing on the interfacial electronic behavior and its dependence on deposition conditions.

The growth of good-quality heteroepitaxial films has become a highly developed art.[1] However, in most systems the various factors which influence the growth are not really understood and successful growth is often accomplished by following recipes developed by trial and error. Considerations are frequently limited to easily accessible facts such as lattice mismatch between substrate and film material.[2,3] While a good lattice match is certainly an important criterion for good epitaxy, it is not sufficient and other factors are often involved. Of particular importance are the chemical and structural properties of the interface and an understanding of the processes under which the interface is formed. For instance, bond strengths at the interface will determine how much mismatch strain can be accommodated without forming discontinuous island growth. But it is not only the epitaxial, crystalline quality which must be considered. Interface stoichiometry and structure also determine the electronic properties of the heteroepitaxial system.[4-6]

As an example of a closely-lattice-matched heteroepitaxial system,[2] we have studied the location of Ca atoms during the early stages of growth of CaF_2 on Si(111) (with a lattice mismatch of only 0.6%), using x-ray standing waves to determine their position and registration to the Si substrate. In the growth of this two-component system on Si, we must also consider the stoichiometry of the interface structure. Using the standing-wave results and crystal-symmetry arguments, we show that the interface stoichiometry and structure is critically dependent on substrate temperature and no unique interface site for Ca exists for coverages in the monolayer range and higher. At least three distinct sites for Ca atoms are proposed, whose relative population depends critically on the substrate deposition temperature.

The experiments were performed in an ultrahigh-vacuum (UHV) system (base pressure 1×10^{-10} Torr) equipped with separate chambers for growth, low-energy electron diffraction (LEED), and Auger-electron spectroscopy (AES) (all chambers were accessed by a transfer arm; the specimen always remained in vacuum). A highly stable manipulator stage in the x-ray chamber made possible high-resolution x-ray standing-wave measurements. Well-oriented (111) crystals of silicon were chemically cleaned using the Shiraki etch.[7] Sharp (7×7) LEED patterns were observed following heating of the silicon substrates to 850–900 °C. CaF_2 was evaporated from a cleaned and out-gassed effusion cell on Si(111)-(7×7) substrates, held at the desired temperature. Films, deposited on substrates held at temperatures from $\sim$450 to $\sim$770 °C, with deposition rates from $\sim$0.02 to 0.2 monolayer (ML) s^{-1} (1 ML$=7.84\times10^{14}$ cm^{-2}) and various coverages from $\sim$0.1 to 10 ML, were studied. The samples were then transferred to the UHV x-ray chamber for the standing-wave measurements. It is well known that CaF_2 is sensitive to particle beams; therefore LEED and AES measurements were made only after completion of the x-ray experiments. A (1×1) LEED pattern was observed, and both Ca and F signals were observed by AES. Because of the decomposition of the CaF_2 layer, AES does not provide a reliable measure of film stoichiometry. However, Tromp and Reuter,[8] using low ion doses and medium-energy ion scattering (MEIS), have shown that for a substrate temperature of 770 °C and $\sim$1 ML coverage the film composition is CaF with 1 ML each of Ca and F. From their estimate 1±0.1 ML F is lost during deposition on the hot Si substrate and presumably desorbs into vacuum.

The x-ray standing-wave technique is an interferometric method for locating the position of a particular atomic species with respect to substrate Miller planes. The technique has been described previously.[9] The angular dependent fluorescence yield Y_F (of Ca in our case) which comprises the result of an x-ray standing-wave measurement is given by

$$Y_F=1+R+2\sqrt{R}\,F^{hkl}\cos(\nu-2\pi P^{hkl}) , \tag{1}$$

where R is the (hkl) substrate reflectivity and ν is the phase between the two plane waves which form the interference field. The quantities F^{hkl} and P^{hkl} are called coherent fraction and coherent position, respectively, and contain the information on the location of the atoms under consideration. Alternatively, the position of each *in-*

dividual atom (i) of the N (Ca) adsorbate atoms, normal to the (hkl) diffraction plane, can be described by P_i^{hkl}. The angular dependent fluorescence yield is then given by the sum over the positions P_i^{hkl},

$$Y_F = 1 + R + 2\sqrt{R} \sum_{i=1}^{N} \cos(\nu - 2\pi P_i^{hkl}) . \quad (2)$$

Equations (1) and (2) are identically equal. If all of the adsorbate atoms reside at the same position normal to the (hkl) plane, F^{hkl} in Eq. (1) will be close to unity and P^{hkl} gives this position directly. If more than one position P_i^{hkl} is occupied by the adsorbate, F^{hkl} will be significantly smaller than unity, and P^{hkl} does not necessarily define a unique adsorption site.

The reflectivity and Ca fluorescence yield for 0.6 ML CaF deposited on Si(111)-(7×7) held at 770 °C are shown in Fig. 1. With a high coherent fraction of $F^{111}=0.82$, the (111) measurement [Fig. 1(a)] establishes the Ca position *normal* to the surface at $P^{111}=0.87$, i.e., $0.87d_{[111]}=2.73$ Å ($d_{[111]}=3.14$ Å) above the surface diffraction plane, or at 2.34 Å above the top half of the (unrelaxed) Si(111) surface double layer as shown in the inset in Fig. 1(a). The result of the (220) measurement, which probes the *lateral registration* of Ca, is shown in Fig. 1(b). In this case, the position parameter is $P^{220}=0.48$, almost in the middle of the (220) planes [inset, Fig. 1(b)]. The low coherent fraction $F^{220}=0.32$ implies that the average in-plane Ca resides in different crystal lattices sites, and the intersecting P^{111} and P^{220} position values in Fig. 2 do not define a unique position.

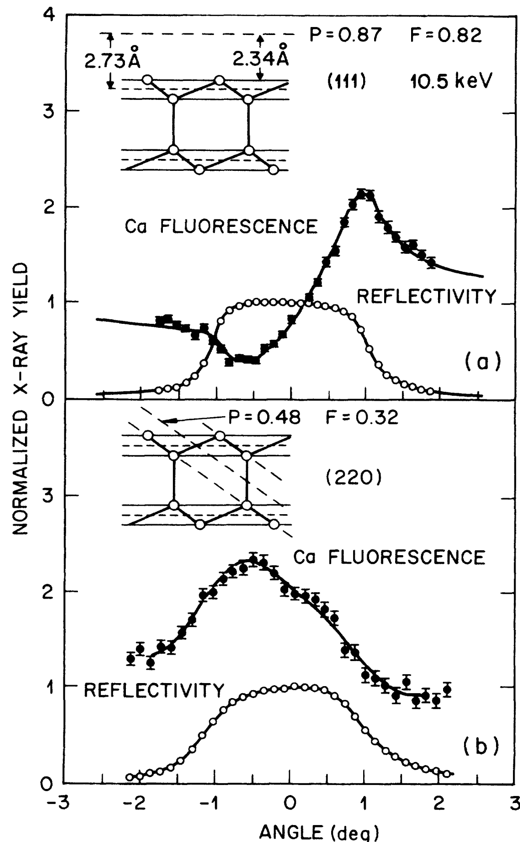

FIG. 1. Reflectivity and Ca $K\alpha$ fluorescence for ~1 ML CaF_2 on Si(111): (a) (111) reflection showing vertical position of Ca. The angular width of the reflectivity to ~5″. (b) (220) reflection showing registry of Ca atoms to the substrate crystal.

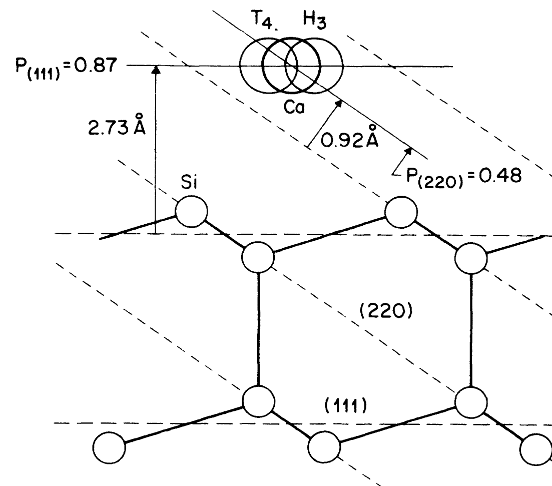

FIG. 2. Schematic showing the measured averaged location of Ca atoms above the bulk extrapolated crystal surface plane between the H_3 and T_4 sites. The average position shown is made up of 50% Ca in H_3 and 50% in T_4 sites.

The x-ray standing-wave results impose strong constraints on possible lattice sites. Any crystal-lattice sites for Ca must lie at the same vertical displacement (2.34 Å) normal to the surface because of the high coherent fraction obtained for the (111) reflection. Furthermore, the particular choice of sites must be compatible with the measured P^{220} and F^{220} values. At the silicon surface, two high-symmetry adsorption sites T_4 and H_3 (Fig. 2) fulfill these conditions. For equal numbers of Ca atoms populating these two sites, we obtain $P^{220}=0.50$ and $F^{220}=0.50$ from Eq. (2), in reasonable agreement with the measured values.

The position value $P^{111}=0.87$ was confirmed by measurements on two other films deposited at 770 °C with coverages ≲1 ML. With Ca in either H_3 or T_4 sites, and for an unrelaxed Si(111) surface, this position value leads to a Si—Ca bond length of 3.22 Å, in reasonable agreement with bond lengths in $CaSi_2$ (3.03–3.25 Å).[10] If the Si(111) surface planes are relaxed outwards, as suggested by Tromp and Reuter,[8] our measured bond length corresponds to a value somewhat smaller than 3.22 Å. Thus at high deposition temperatures (~770 °C) a large fraction of the Ca atoms are arranged on the Si(111) surface in two positions (H_3 and T_4).

To study the influence of substrate temperature on the interface structure, we have deposited 0.3 ML of CaF_2 on Si(111) substrates held at 670 °C. The standing-wave values for the measurement gave $P^{111}=0.99$ and $F^{111}=0.66$, and $P^{220}=0.47$ and $F^{220}=0.37$. The combined (111) and (220) results yield an average apparent T_4 site for the Ca atoms, as indicated in Fig. 2. However, in

this position Ca cannot be bonded directly to the Si(111) surface since with $P^{111}=0.99$ the Ca—Si bond would be 3.53 Å, which is much too large. We have indicated earlier that the CaF_2 molecule dissociates and F desorbs from the surface at high temperatures due to the catalytic action of the hot silicon substrate. At low temperature we expect less dissociation, resulting in a larger fraction of F—Si bonds at the interface. A configuration where the Ca atoms occupy the sevenfold-coordinated site above the F/Si interface, Fig. 3(a) is consistent with our result. If all Ca atoms were in this site, and the Si—F bond length equals the Si—Si bond length, the position value P^{111} should be 1.125 and $F^{111}=1.0$. The lower value observed experimentally indicates that even at this temperatuer some dissociation of CaF_2 has occurred and about half the Ca atoms are located directly above the silicon surface in H_3 and T_4 sites as discussed earlier, Figs. 3(b) and 3(c). This distribution can account directly for the coherent fractions and positions observed for the (111) and (220) measurements.

Since the interface is type B,[11] Ca in the sevenfold position can relax into the T_4 site directly below it if dissociation occurs and F atoms are lost. It is reasonable to expect that even at higher substrate temperature (770 °C) dissociation of CaF_2 is not complete and a small fraction of Ca atoms are present in the sevenfold-coordinated site, Fig. 3(a). Ca atoms at this third lattice location can account for the 18% incoherent fraction observed for the high-temperature preparation ($P^{111}=0.87$, $F^{111}=0.82$). Thus for low-temperature deposition ($\sim$670 °C) CaF_2 does not fully dissociate and a substantial fraction of Ca is located in a third site, sevenfold coordinated, with F most probably atop the (111) silicon dangling bonds.

There are currently two quite different structural models proposed for the Si/CaF_2 interface. Batstone *et al.*[12]—from transmission-electron-microscopy observations of the interface—have proposed an atop site (see Ref. 13) for Ca. More recently, Tromp and Reuter[8] have concluded from MEIS studies that a unique T_4 site accounts for the ion-scattering results. We disagree with both of the proposed models; the interfacial Ca positions are much more complex. Our conclusions are that the Ca-atom position at the interface is a strong function of the substrate temperature and interface stochiometry.

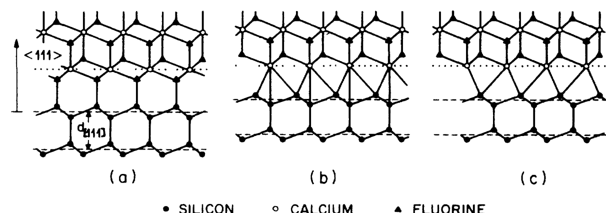

FIG. 3. Schematic showing the interface between Si and CaF_2: (a) F atoms at the interface with Ca in a sevenfold site, (b) Ca atoms at the interface T_4 site, and (c) Ca atoms at an H_3 interface site.

The importance of the substrate temperature has also been pointed out previously.[5,8] At high temperatures Ca atoms are located at the Si(111) surface occupying both the H_3 and T_4 sites. At lower temperatures more Si—F bonds to the Si(111) surface are present with sevenfold-coordinated Ca in addition to the H_3 and T_4 sites for Ca. The occurrence of three distinct sites in such a well-lattice-matched system emphasizes the important role that chemistry and interface bonding plays in heteroepitaxial growth. Our model involving F dissociation is consistent with the near-edge x-ray-absorption experiments of Himpsel *et al.*[4] and the photoemission studies of Olmstead *et al.*,[5] where these authors find that Si—Ca bonds predominate at high temperatures, while at lower temperatures more F is incorporated and produces a greater amount of disorder.

Since they are both populated, H_3 and T_4 sites must represent a low-energy configuration with little or no differences in energy for Ca occupation. For instance, for $CaSi_2$ both H_3 and T_4 sites are occupied by Ca layers, and total-energy calculations for $CaSi_2$ (Ref 14) show that the difference in energy between these sites is negligible ($\sim$0.01 eV), with bonding predominantly between the Ca and the Si dangling bonds only, rather than between individual Ca-Si atoms. Similar considerations might apply to CaF at the Si interface, and one would expect Ca atoms to occupy both H_3 and T_4 interface sites.

Of the factors that have been considered–(1) chemical bonding, (2) chemical reaction at the interface, and (3) crystal lattice matching—the first two obviously play a critical role in the CaF_2/Si interface structure. It is, furthermore, important to realize that the system Si(111)/CaF_2 is not perfectly lattice matched. The bulk lattice constant of CaF_2 is 0.6% larger at room temperature and more than 2% larger at $T>700$ °C. Thus the dislocation formation energy will eventually be exceeded by strain energy caused by the lattice mismatch. For epitaxial systems this leads to the formation of interfacial dislocations. For the Si(111)/CaF_2 system, interfacial misfit dislocations can occur very naturally. Since Ca atoms occupy two adsorption sites, T_4 and H_3, that are very similar in binding energy, slip by $\frac{1}{6}\langle 211\rangle$ can shift the film from the one to the other site, leading very naturally to relief in strain energy and the formation of dislocations. Thus at the very early stages of high-temperature growth two phases in the H_3 and T_4 configurations predominate, separated by phase or domain boundaries.

Another mechanism for strain relief and switching between $T_4 \leftrightarrow H_3$ is linked to substrate surface steps.[15] For a CaF_2-type film on Si(111) with B-type orientation it is not possible to cross a surface step without introducing a misfit dislocation (or switching from H_3 to T_4 in the case of CaF_2). This intrinsic source of strain relief is most likely the underlying reason that CaF_2 prefers to grow in a B-type orientation.

The effect of mismatch strain can also result in deviations from the ideal coherent fractions, since the lattice-mismatch energy will force the Ca out of its ideal position, leading to some distribution around the mean posi-

tion, and thus will reduce the coherent fraction. Finally, from our observations we predict that growth at temperatures higher than 770 °C should lead to a higher coherent fraction with Ca exclusively in H_3 and T_4 sites.

In summary, heteroepitaxial growth of CaF_2 on Si(111) is more complex than has been previously proposed. At high temperature F is easily dissociated and the interface consists mainly, though not exclusively, of Ca—Si bonds with Ca in both the H_3 and T_4 sites. At lower temperatures less F is desorbed and, in addition to the H_3 and T_4 sites, there is a third site for Ca, which is sevenfold coordinated and located in the top half of the CaF_2 double plane at the interface. These observations have a direct bearing on the electronic properties and surface states at the interface, which have been known to depend on deposition conditions.

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