

Structure of the Si(111)-CaF₂ Interface

R. M. Tromp and M. C. Reuter

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

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The structure of the Si(111)-CaF₂ interface has been determined with medium-energy ion scattering. Ca bonds to the Si substrate in a geometric arrangement virtually identical to CaSi₂. Half of the F atoms at the interface are missing; there is no F-Si bonding and the interface is charge neutral. The structure we find has not been considered previously and provides a natural explanation for the results of published photoemission studies.

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The Si(111)-CaF₂ interface has received extensive attention in the last few years. CaF₂ is an excellent insulator with a lattice constant (5.46 Å) almost identical to that of Si (5.43 Å), allowing epitaxial growth on Si. NiSi₂ and CoSi₂ have the same crystal structure and can also be grown epitaxially on Si. Therefore, CaF₂ appears to be the insulator of choice for three-dimensional, fully epitaxial devices on Si. A detailed knowledge of the structures of these diamond/CaF₂ interfaces is critical for our understanding of their interface electronic properties.

Most studies to date have focused on the electronic and chemical nature of the interface. Evidence was found for Ca-Si interface bonding in high-resolution core-level studies,^{1,2} leading to several proposed structural models. High-resolution transmission electron microscopy has been used to obtain lattice images of the interface region.^{3,4} Batstone, Phillips, and Hunke, using such transmission electron microscopy data, expressed their preference for one interface model, although a systematic interface structure determination was not performed (only on-top bonding sites were considered).⁴

The questions we address in this Letter are the following: (1) What is the ratio Ca:F in the first Ca-F layer that adsorbs on the Si(111) substrate? (2) Which species bonds to the Si substrate? (3) What is the detailed interface geometry? These crucial questions have remained unresolved in previous studies and are answered here for the first time. We arrive at an interface structure that has not been considered previously. We present detailed atomic coordinates, which should make realistic theoretical studies of the electronic nature of the interface possible.

The growth conditions of CaF₂ on Si(111) were optimized by monitoring the interface formation *in situ* with x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and medium-energy ion scattering.⁵ Si(111) samples were cleaned in UHV by very mild sputtering and annealing, routinely resulting in the (7×7) surface structure. CaF₂ was grown at a rate of 1-2 monolayers (ML) per minute (1 ML = 7.83 × 10¹⁴ atoms/cm²) by exposing the sample at 770 °C to CaF₂

molecules evaporated from a Knudsen cell. We obtained high-quality epitaxial films with a well defined and reproducible interface structure. Our photoemission results are comparable to published data.^{1,2} Growth at significantly lower temperatures resulted in irreproducible and ill-defined interfaces. CaF₂ is extremely sensitive to ionizing radiation. All experiments were performed at sufficiently low ion doses to prevent decomposition of the CaF₂ overlayers.

Figure 1 shows an energy spectrum of 200-keV He⁺ ions scattered from a Si(111) surface covered with 1 ML of CaF₂. [All scattering experiments have been done in the (110) plane shown in the inset.] Backscattering peaks due to Ca, Si, and F are indicated. Using standard calibration procedures for the scattering intensities,⁵ we obtain Ca and F coverages of 1.05 ± 0.06 ML and 1.0 ± 0.1 ML, respectively. (The Ca peak is larger than the F peak because the scattering cross section is proportional to the square of the atomic number.) Thus, the first layer of Ca-F contains equal amounts of Ca and F, indicating the loss of 1 ML of F upon adsorption of the first Ca-F layer. We assume that the lost F desorbs into the vacuum.

Secondly we ask which species bonds to the Si. If Ca forms the topmost layer, then ions scattering from Ca

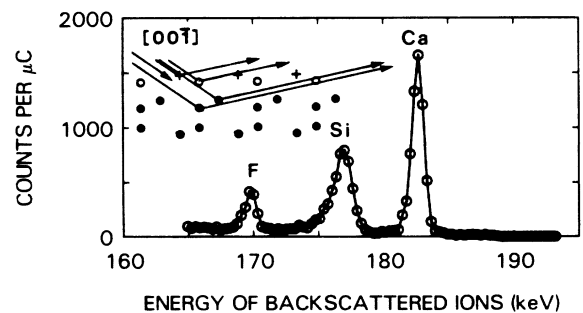


FIG. 1. Energy spectrum of 200-keV He⁺ ions scattered from a Si(111) surface covered with one monolayer of Ca-F. The scattering geometry is shown in the inset. Solid dots are Si atoms, open circles are Ca atoms, and pluses are F atoms.

can reach the vacuum in any direction. However, if F forms the topmost layer, then ions scattered by Ca will be blocked by F along the Ca-F internuclear direction. Figure 2 shows the Ca scattering intensity as a function of scattering angle (the incoming beam direction is shown in the inset). A distinct blocking minimum is observed at a scattering angle of 45.2° . Thus, F forms the topmost layer. The two possible threefold adsorption sites of F on top of the layer are labeled A and B in the inset of Fig. 2. Two-atom blocking calculations for these sites are shown by the solid lines. (In these and all subsequent calculations we used the Moliere scattering potential.⁵) The depth and angular position of the calculated minima have been fitted to the experiment. The minimum calculated for the A site is clearly too broad. Good agreement is found for the B site. By simple goniometry we determine the Ca-F interlayer spacing to be 0.78 ± 0.03 Å, yielding a Ca-F bond length of 2.35 ± 0.01 Å. F forms the topmost layer, with Ca bonding to the Si substrate.

Upon adsorption of 1 ML of Ca-F on the Si(111) substrate we observe a sharp and strong (1×1) low-energy electron diffraction (LEED) pattern. Within a (1×1) unit cell there are only three high-symmetry sites for adsorption of Ca: the T site (Ca on top of the first layer Si atom), the H_3 site (Ca in the threefold hollow site), and the T_4 site (Ca on the threefold site on top of a second layer Si atom).

To distinguish between these adsorption sites we have studied the blocking of Si by Ca in the geometry shown in the inset of Fig. 3. The Si scattering intensity is plot-

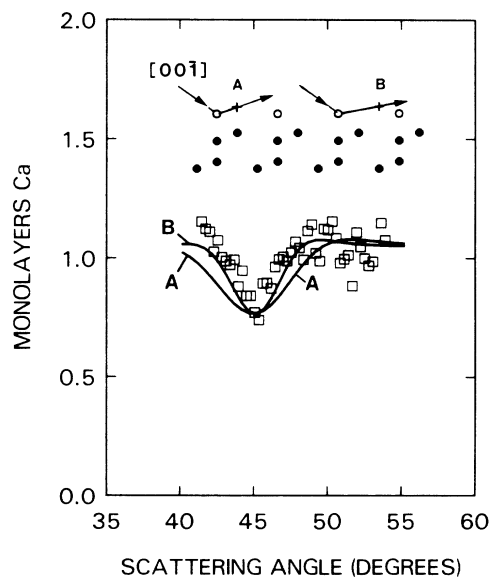


FIG. 2. The number of Ca monolayers visible to ion beam and detector as a function of scattering angle. Inset: scattering geometry and the two possible threefold F adsorption sites (A and B). Also shown are calculations for the A and B sites.

ted as function of scattering angle. Wherever ions scattered by Si are blocked by other Si, Ca, or F atoms, blocking minima will occur. The blocking minima at 54.7° and at smaller scattering angles are due to overlapping Si-Si, Si-Ca, and Si-F blocking. At scattering angles above 60° we only expect Si-Ca and Si-F blocking, with Si-Ca blocking occurring at the largest scattering angle. The broad blocking minimum at 63° is due to Si-Ca blocking. With use of simple goniometry the Si-Ca bond lengths can be calculated for the T , H_3 , and T_4 geometries.⁶ These bond lengths are 3.42 Å (T site), 2.57 Å (H_3 site), and 3.05 Å (T_4 site). The Si-Ca bond length in CaSi_2 is 3.03–3.06 Å,⁷ almost identical to the value found here for the T_4 site. The bond lengths calculated for the H_3 and T sites differ by more than 10% from this value, which seems chemically unreasonable. We therefore tentatively conclude that Ca adsorbs on the T_4 site and use this in our further analysis. The Ca-Si interlayer spacing found for the T_4 geometry is 2.1 ± 0.1 Å. The solid line in Fig. 3 is a two-atom blocking calculation for this T_4 geometry.

In order to determine the Si-Ca interlayer spacing and a possible relaxation of the outermost Si-Si double layer with high accuracy we have measured Si surface blocking minima in the geometry shown in Fig. 4(a). Again, the Si scattering intensity is shown as a function of scattering angle. Calculated Si surface blocking minima (varying the Si-Ca interlayer spacing between 2.0 and 2.3 Å and the relaxation of the outermost Si-Si double layer between 0- and 0.3-Å expansion) were compared with the experimental results by calculating the normalized χ^2 function: $\chi^2 = (N - m)^{-1} \sum (y_i^c - y_i^m)^2 / \sigma_i^2$. N is the number of data points, m the number of fitting parameters, y_i^c are the calculated and y_i^m the measured data points, and σ_i are the statistical error bars on the experi-

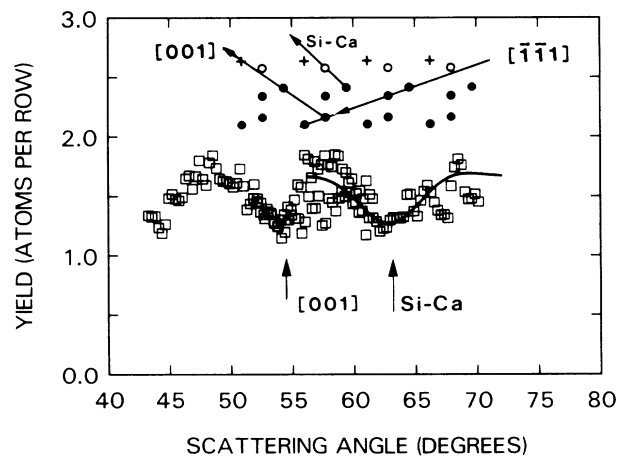


FIG. 3. Si scattering intensity as a function of scattering angle. The scattering geometry is shown in the inset. Arrows indicate the [001] Si-Si blocking direction and the Si-Ca blocking direction discussed in the text.

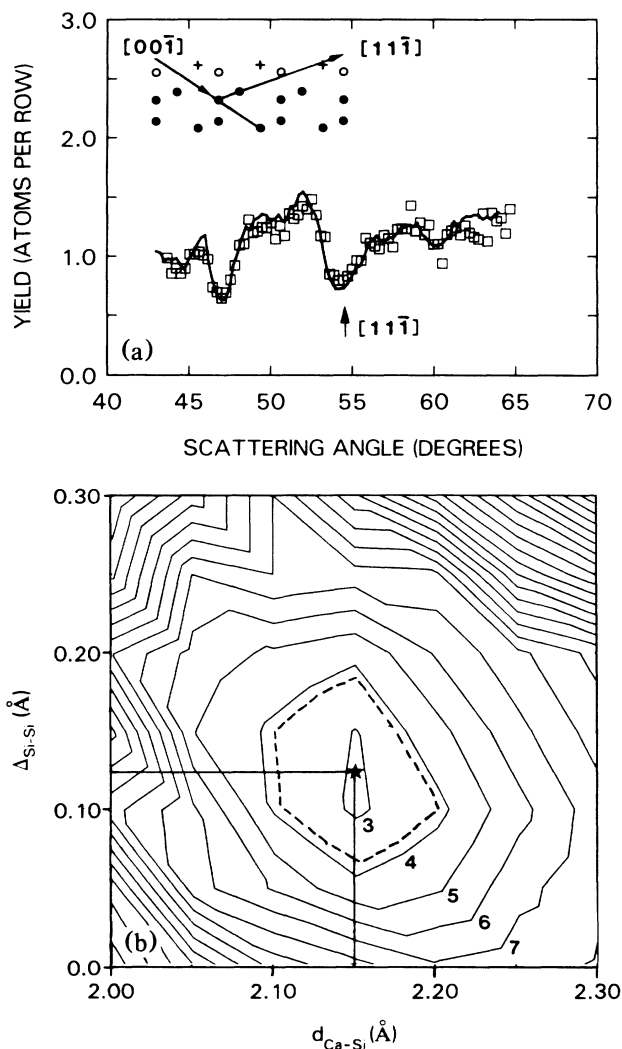


FIG. 4. (a) Si scattering intensity vs scattering angle for the geometry shown in the inset. (b) Contour plots of χ^2 (see text) vs Ca-Si interlayer spacing ($d_{\text{Ca-Si}}$) and expansion of the outer Si-Si double layer ($\Delta_{\text{Si-Si}}$). The blocking curve for the best-fit parameters (star) is shown by the solid line in (a).

mental points. w reflects the uncertainty in the absolute calibration of the experiment and was allowed to vary between 0.95 and 1.05 to minimize the value of χ^2 , and Σ indicates summation over $i=1-N$. Contours of constant χ^2 are shown in Fig. 4(b). A well-defined minimum is found for a Si-Ca spacing ($d_{\text{Ca-Si}}$) of 2.15 ± 0.05 Å and an expansion of the outermost Si-Si double layer ($\Delta_{\text{Si-Si}}$) of 0.125 ± 0.06 Å. [The error bars are determined by the dashed contour in Fig. 4(b) indicating an increase of 1 in χ^2 over the best-fit value of 2.8.] The solid line in Fig. 4(a) was calculated with these parameters. The vibration amplitude of the Si atoms in the outer Si double layer was taken to be 0.09 Å (bulk value 0.078 Å) and a value of 0.13 Å was used for the Ca and F atoms. Changing these values degrades

the quality of the fit, but the minimum in the contour plot shown in Fig. 4(b) does not move. We have also calculated surface blocking minima for the T and H_3 geometries and tried to optimize the interlayer spacings. For these geometries, however, we do not obtain satisfactory agreement with the data. This allows us to conclude definitively that Ca adsorbs on the T_4 site (as shown in the insets).

The bond length between Ca and first layer Si is 3.09 ± 0.03 Å and between Ca and second layer Si is 3.06 ± 0.06 Å. In bulk CaSi_2 layers of Ca are separated by double layers of Si.⁷ Alternating double layers of Si have Ca atoms occupying H_3 and T_4 sites, respectively. Each Ca atom is surrounded by seven first-neighbor Si atoms. In the T_4 site the Si-Ca bond lengths are 3.03 (to the first layer) and 3.06 Å (to the second layer). These values are virtually identical to the values we find for the Si-Ca-F interface. Without expansion of the outer Si-Si double layer the Ca atoms would be too close to the second-layer Si atoms. The Si-Si bond length in the outer double layer is 2.40 ± 0.03 Å, close to the value in CaSi_2 (2.45 Å).

With Ca bonding to Si and one terminating F layer the interface is charge neutral. Upon adsorption of the next layer of CaF_2 the chemical environment of Si does not change, nor would the chemical environment of the interface Ca layer change very much. However, the F atoms would bond to Ca in the next CaF_2 layer, which has charge state 2^+ , unlike the interface Ca, which has charge state 1^+ .^{1,2} Hence, the interface Si and Ca core levels are not expected to change much upon adsorption of the second layer, whereas one expects the F core level to shift to larger binding energies. This is exactly what is observed experimentally.^{1,2} No satisfactory explanation for this shift of the F core level has been proposed in previous studies.

It is interesting to compare with the epitaxial Si(111)/ NiSi_2 and Si(111)/ CoSi_2 interfaces, which show an abrupt transition from the CaF_2 structure to the diamond structure, maintaining MX_2 stoichiometry up to the very interface.^{8,9} In contrast, the Si(111)/ CaF_2 transition is not abrupt, but is mediated by a CaSi_2 -type layer which is deficient in F. This unique interface structure fulfills the requirement of charge neutrality and is facilitated by the occurrence of Si double layers in both Si(111) and CaSi_2 , with almost identical lattice constants. Adsorption on the T_4 site rather than the H_3 site (which occur equally in CaSi_2) results in optimum coordination of the interfacial Ca atoms.

One might ask whether the one-monolayer system described above is typical of the bulk Si- CaF_2 interface. We have adsorbed an additional layer of CaF_2 on top of the first layer and measured surface blocking minima in the same geometry as used in Fig. 4. The results are consistent with the model derived for 1 ML. More experiments will be needed to fully determine the stoichiometry and interlayer relaxations in this two-layer

system. As explained above, the lack of change in the Si and Ca interface core levels provides additional evidence for the stability of this interface upon further CaF₂ adsorption. Finally we note that we have obtained high-quality cross-section transmission electron microscopy images of the Si-CaF₂ interface.¹⁰ We have compared these experimental images with simulated images using the geometry described above, and also using the geometry preferred by Batstone, Phillips, and Hunke.⁴ The geometry determined in this study gives superior agreement with the experimental images.

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