Mechanism of Epitaxial Growth of Monolayer CaF on Si(111)-(7×7)

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Using scanning tunneling microscopy, the epitaxial growth of a monolayer of CaF on the Si(111)-(7×7) surface has been studied. We observe how the Si atoms of the 7×7 structure rearrange into a bulklike structure and find that four excess Si atoms per 7×7 unit cell are produced in the transition to the bulklike structure. These excess Si atoms seem to remain in the epitaxial CaF layer, creating defects.

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The epitaxial growth of calcium fluoride (CaF_2) on silicon (Si) substrates has attracted much attention because of its potential for the construction of microelectronic and optoelectronic devices [1]. This is because CaF_2 is an excellent insulator with a small lattice mismatch (0.6%) to Si and can be congruently deposited from a thermal evaporation source.

In the case of the Si(111)-(7×7) substrate [2-6], when CaF_2 is deposited onto it at temperatures appropriate for epitaxial growth, the substrate is first covered with a monolayer of CaF rather than CaF_2 [2], and then a film of CaF_2 grows on this monolayer [5]. The formation of the initial CaF layer causes the rearrangement of substrate Si atoms from the 7×7 structure to a bulklike structure [2-4]; the quality of the CaF_2/Si(111) interface is determined in this initial stage. If we want to control the structure of this interface to make it as well ordered as possible on the atomic scale, the following problem arises. The density of Si atoms in the 7×7 structure is different from that in the bulklike structure [7], so that the created CaF_2/Si(111) interface may be disrupted because of the inevitable existence of excess Si atoms.

In this paper, we report scanning tunneling microscope (STM) observations which show that the excess Si atoms remain in the CaF layer making defects. This result emphasizes an important factor to be considered in the structural control of heteroepitaxial interfaces on the atomic scale, namely, the commensuration of the number of substrate atoms before and after interface formation. In order to reach this conclusion, it has been essential to understand how the Si atoms in the 7×7 structure are rearranged into the bulklike structure during the formation of the CaF/Si(111) interface. This has been revealed by analyzing the positions of Si atoms at the CaF/Si(111) interface relative to those of the remaining Si(111)-(7×7) structure, using the STM.

Si(111) substrates (P doped *n* type) were cleaned in ultrahigh vacuum (UHV) better than 3×10^{-8} Pa by repeated flash heating at 1250°C to obtain a clean 7×7 surface structure. Controlled amounts of CaF_2 were deposited onto the substrate at a temperature of 600°C using a temperature-controlled shuttered Knudsen cell with a pyrolitic boron nitride crucible in UHV better than 3×10^{-7} Pa. At this substrate temperature, the 7×7 structure directly changes to the 1×1 structure when CaF_2 is deposited, in contrast to higher temperatures at which other intermediate structures (3×1, 3×2, and 4×1) appear [5,8]. STM images were obtained using a commercial STM operated in UHV (Omicron UHV-STM) with an electrochemically sharpened tungsten tip.

Figure 1(a) shows an STM image of the Si(111) surface partly covered with the monolayer of CaF grown at 600°C. This image (230×480 nm^2) is composed of several overlapping images of a smaller area (150×150 nm^2), all of which were recorded at a sample bias (V_s) of +1.5 V and a tunneling current (I_t) of 20 pA. The region covered with the monolayer of CaF is observed as darker islands in this empty-state image, although the islands have many bright spots due to structural defects discussed later. If we magnify a part of the CaF island which is free from such bright spots, a regular array of protrusions is observed as shown in Fig. 1(b), which was obtained at a larger I_t of 500 pA for better image contrast. The array of these protrusions has a unit cell indicated by a rhombus in Fig. 1(b), and this unit cell coincides with that of the ideal Si(111)-(1×1) surface. Namely, the CaF layer has a 1×1 structure, in agreement with previous studies for a full monolayer of CaF [2-4,8]. The regions between the CaF islands in Fig. 1(a) retain the Si(111)-(7×7) structure, as shown in Fig. 1(c) on a magnified scale. In the lower part of Fig. 1(a), a Si double-layer step is observed, and a region on the lower terrace adjacent to the step is covered with the CaF layer. This CaF layer has an additional structure consisting of bright lines running along $\langle 01\bar{1}\rangle$, which has been discussed in a previous study [8]. This structure, however, is not dominant in any STM images observed in the present study.

According to the structural analysis of the CaF layer, F atoms are most protruded, forming the topmost layer. The tilted F-Ca bond lies in the $\langle 11\bar{2}\rangle$ azimuth of the Si(111) substrate, and the Ca atom is situated just above

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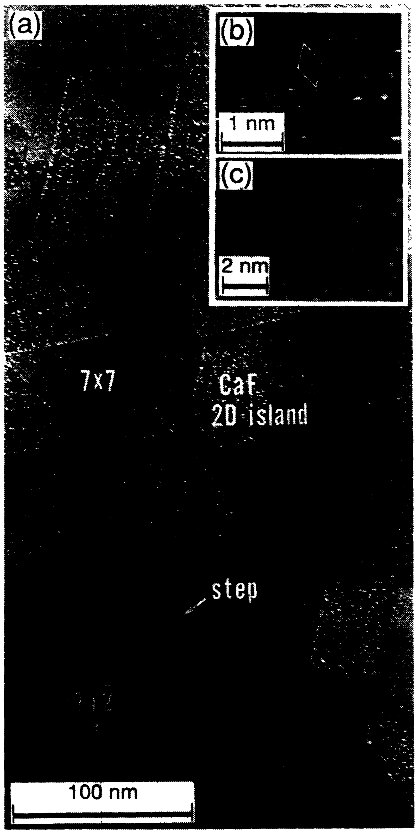

FIG. 1. (a) An empty-state STM image of a Si(111)-(7×7) surface partly covered with a monolayer of CaF. The CaF and remaining Si(111)-(7×7) regions are magnified in (b) and (c).

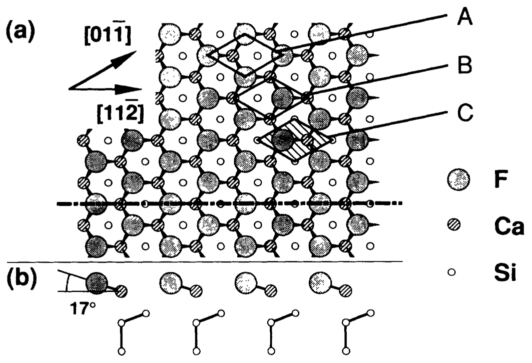

FIG. 2. Top (a) and side (b) views of the CaF/Si(111) structure.

the second-layer Si atom of the Si(111) substrate [2,3], as shown in Fig. 2. The unit cell drawn in Fig. 1(b), in which the four corners are occupied by the empty-state protrusions, may correspond to unit cell *A*, *B*, or *C* shown in Fig. 2(a), depending on the electronic structure of the layer. Unit cell *A* whose corners are occupied by F atoms seems unlikely, because the F atoms are negatively ionized with a closed shell structure [9–11] and therefore should not make the empty-state protrusions. So, the unit cell drawn in Fig. 1(b) probably corresponds to either unit cell *B* or unit cell *C* in Fig. 2(a). Below, we show how STM images can be used to distinguish between these two possibilities.

Figure 3(a) shows an STM image near the boundary between a CaF island (right) and the remaining Si(111)-(7×7) structure (left); this image was taken at $V_s = +1.5$ V and $I_t = 500$ pA. Although the CaF region appears to be lower than the Si(111)-(7×7) region in this empty-state image, this is an artifact due to a large difference in electronic state between the two regions. In fact, the CaF region appears to be higher than the Si(111)-(7×7) region in a filled-state image (see Fig. 5 discussed later). For this reason, it is practically impossible to know the relative heights of the two regions from STM topography itself. Yet such information is essential in understanding how the Si atoms of the 7×7 structure are rearranged into the bulklike structure during the growth of the CaF layer. In the following, we describe a way to estimate the relative heights, which is similar to that used previously [12].

In Fig. 3(b), the large and small filled circles indicate the protrusions in the Si(111)-(7×7) region and in the CaF region in Fig. 3(a), respectively. Since the protrusions in the Si(111)-(7×7) region correspond to the outermost Si adatoms, we can readily determine the lateral positions of subsurface Si atoms in the Si(111)-(7×7) region, as indicated by open circles in Fig. 3(b).

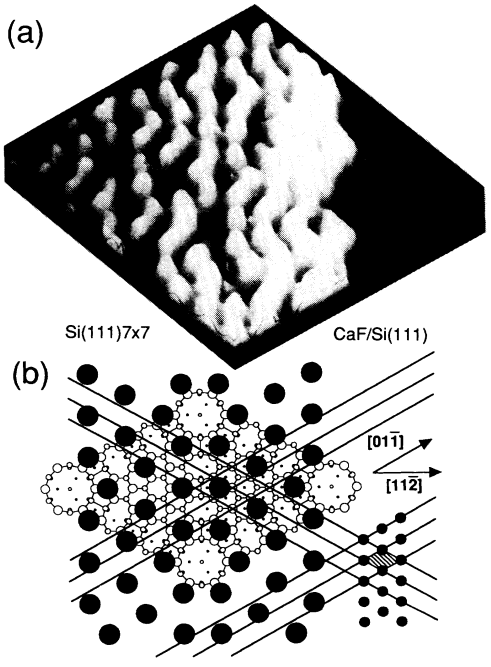

FIG. 3. (a) An empty-state STM image near the boundary between the CaF region and the remaining Si(111)-(7×7) region. The positions of protrusions observed in (a) are shown in (b).

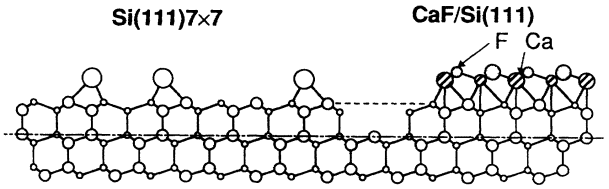

FIG. 4. Atomic arrangement near the boundary between the CaF region and the remaining Si(111)-(7×7) region in side view.

The solid lines in Fig. 3(b) show the 1×1 lattice whose lattice points are occupied by the second layer Si atoms in the unfaulted region of the Si(111)-(7×7) structure. If we extend this lattice toward the CaF region, its lattice points coincide with the protrusions in the CaF region, as seen in Fig. 3(b). The result indicates that the unit cell shown by a hatched rhombus in the CaF region in Fig. 3(b), which is the same as that drawn in Fig. 1(b), corresponds to unit cell C rather than unit cell B in Fig. 2(a). This is illustrated in Fig. 4 in side view. The reason why we can exclude unit cell B in Fig. 2(a) is that if this were the case, five substrate Si layers would have to be removed during the creation of the CaF layer in order to explain Fig. 3(b), which is unrealistic.

If we look at Fig. 4, the third Si layer in the CaF region and the fourth Si layer in the Si(111)-(7×7) region are common, as shown by a dash-dotted line, and there is no difference in Si atom arrangement below this layer for the two regions. In other words, the Si atoms in the first and second Si layers in the CaF region have been supplied from the first, second, and third Si layers of the original 7×7 structure. The number of Si atoms in the former two Si layers is 98 per 7×7 unit cell (49 in each of the two layers), while that in the latter three Si layers is 102 per 7×7 unit cell (12, 42, and 48 in the first, second, and third layers, respectively [7]). There must therefore be four excess Si atoms per 7×7 unit cell after the creation of the CaF/Si(111) interface. Where do these excess Si atoms go?

One possibility is that the excess Si atoms are swept out of the growing CaF region. If this were the case, the excess Si atoms should be found somewhere on the remaining Si(111)-(7×7) region, just outside the lateral growth front of the CaF region or at other distant places. Such Si atoms are, however, never observed. In fact, the ordered arrangement of Si atoms in the remaining Si(111)-(7×7) region is continuous up to the lateral growth front of the CaF region, and any other structures attributable to such excess Si atoms, such as those seen during Si epitaxy on Si [13], are not observed in the Si(111)-(7×7) region. Another possibility is that the excess Si atoms migrate to naturally existing Si double-layer steps and are trapped there. However, as we see in Fig. 1, the growth of the CaF layer starts preferentially from the Si double-layer step on the lower terrace. Therefore, if the excess Si atoms were trapped at the step, they should be piled on such a CaF layer adjacent to the step, since the excess Si atoms are created continuously during the growth of the CaF region. However, the 1×1 structure of such a CaF layer is continuous up to the edge of the step. A further possibility is that the additional structure on such a CaF layer mentioned earlier, which is observed as bright lines in the lower part of Fig. 1(a), is due to the excess Si atoms. However, even if each of the bright lines consists of closely arranged Si atoms, the number of such Si atoms is only about 8% of the excess Si atoms. Thus we must conclude that most of the excess Si atoms exist somewhere in the CaF region itself, presumably as defects.

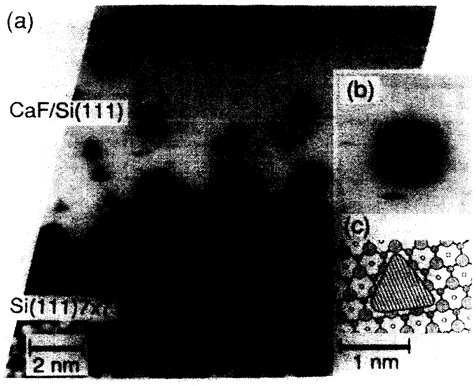

FIG. 5. (a) A filled-state STM image near the boundary between the CaF region and the remaining Si(111)-(7×7) region. The smallest dark spot (elemental defect) observed in the CaF region in (a) is magnified in (b) and its position, shape, and orientation are shown in (c).

We argue that the many bright spots in the CaF islands in Fig. 1(a) are most probably due to such defects. The number of the bright spots agrees with that of the excess Si atoms as follows. The bright spots observed in empty-state images such as Fig. 1(a) become dark in filled-state images as shown in Fig. 5(a), which was obtained at $V_s = -1.5$ V and $I_t = 500$ pA. Although the dark spots have different sizes, about 60% of them have the smallest common size, suggesting that the smallest dark spots correspond to an elemental defect and larger ones to their complexes. The smallest dark spot has a triangular shape as reproduced in Fig. 5(b) on a magnified scale. The size, position, and orientation of the triangle are shown in Fig. 5(c) together with the structure of this CaF layer drawn in Fig. 2(a). Although the structure of the elemental defect has not been clarified yet, it should contain one or three Si atoms judging from the size, shape, position, and orientation of the smallest dark spot. Two or four Si atoms cannot make a triangular defect and five, six, or more Si atoms cannot make such a small defect. We can therefore estimate the total number of Si atoms in the defects to be in the range 5×10^{13} to 9×10^{13} per cm^2 depending on whether the number of Si atoms in the elemental defect is one or three; the reason why the latter estimate is not 3 times the former is that the effective area of a defect does not increase linearly with increasing number of atoms involved. In comparison, the number of excess Si atoms is 6.4×10^{13} per cm^2, based on the assumption of four excess atoms per 7×7 unit cell.

The close agreement of these two numbers and the fact that no extra Si atoms are observed at any other places suggest that most of the excess Si atoms remain in the CaF layer, forming the defects there. In other words, the excess Si atoms created in the CaF region cannot migrate to the Si(111)-(7×7) region, over the boundary.

To summarize, we have studied how Si atoms are rearranged from the 7×7 structure to a bulklike structure during growth of a monolayer of CaF using the STM. From this study, we have found that four excess Si atoms per 7×7 unit cell are produced in the transition to a bulklike Si arrangement and that these excess Si atoms seem to remain in the CaF layer, creating defects.

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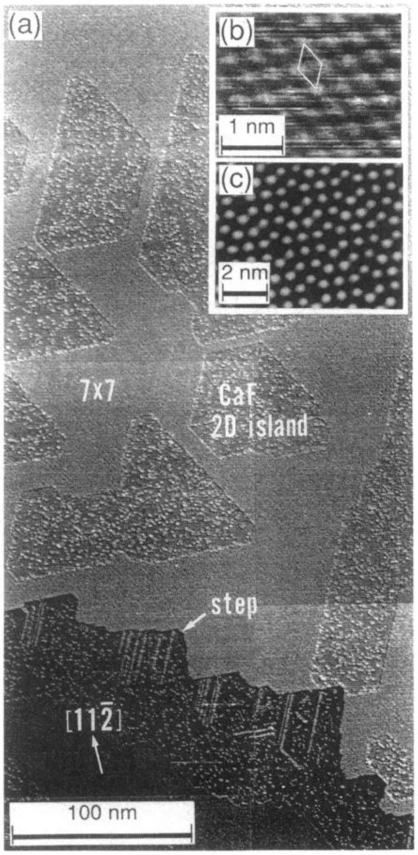

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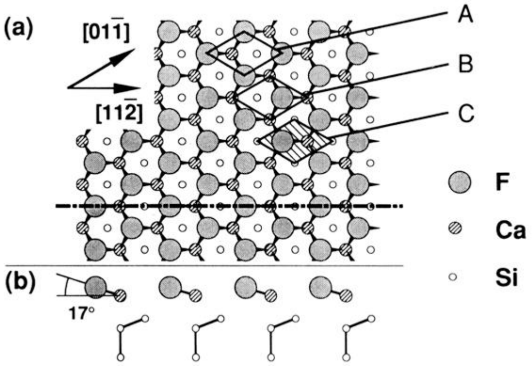
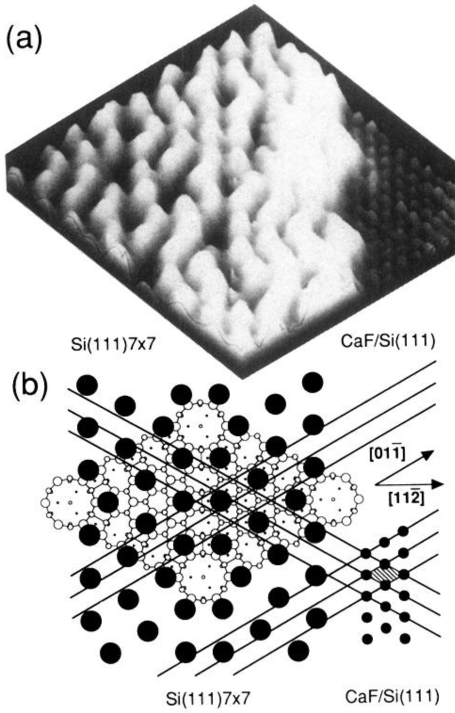


FIG. 2. Top (a) and side (b) views of the CaF/Si(111) structure.



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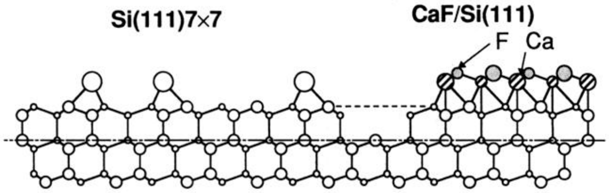

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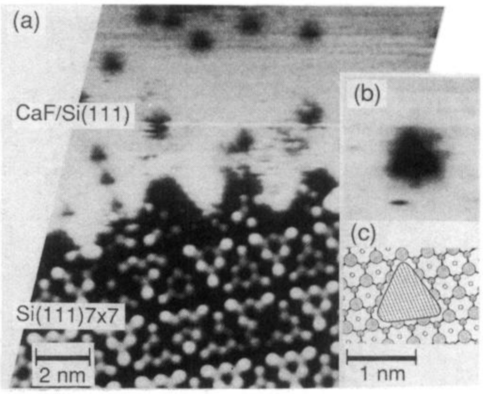

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