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Initial stages of growth and formation of CaF_2 nanostructures on Si (001)

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Introduction

Stimulated by a number of potential applications [1], growth of fluorite (CaF_2) on Si(111) has been extensively studied [2]. Only a few attempts have been undertaken, however, to investigate the initial stages of CaF_2 growth on a technologically important Si(001) surface [3, 4], where anisotropic CaF_2 growth accompanied by the formation of the quasi-one-dimensional islands was observed using TEM and STM techniques. Such islands with nanometer scale width could be attractive for nanolithography. In this work we studied the initial stages of the fluorite growth and the formation of nanometer-scale islands on Si(001) using electron diffraction (RHEED and LEED), atomic force microscopy (AFM), ultraviolet photoemission spectroscopy (UPS) and metastable atom deexcitation spectroscopy (MDS).

1. Experimental

Calcium fluoride nanostructures have been grown in the UHV conditions by evaporation of CaF_2 small pieces in an amorphous carbon crucible onto a thermally cleaned at 1250°C Si(001) surface. The temperature of the substrate during the fluorite deposition was in 400−750°C range, the deposition rate was 2–3 nm/min. Electron energies in RHEED and LEED measurements were 15 keV and 70 eV respectively. The surface morphology of the CaF_2/Si(001) structures was measured *ex-situ* in the tapping mode of a P4-SPM atomic force microscope produced by NT-MDT (Zelenograd, Russia). The typical lateral resolution of the AFM measurements was 10–20 nm, depending on the sharpness of the cantilever tip. In the UPS experiments a He windowless differentially pumped discharge lamp emitting He I (21.2 eV) photons and a hemispherical electron analyzer have been used. In the MDS a differentially pumped discharge nozzle-skimmer source was used.

2. Results and discussion

Before the fluorite deposition, electron diffraction patterns clearly showed 2×1 and 1×2 domains (see for example inset in Fig. 1). Atomic force microscopy showed 100–200 nm width terraces separated by steps of 1 to 8 monolayers (ML) height (Fig. 1). Depositing a few CaF_2 monolayers (typically 1–6 ML) at this surface, we found that the surface morphology drastically changed with the temperature of the Si(001) substrate.

After the growth at 450°C, an array of more or less uniformly distributed CaF_2 islands with characteristic size of 10–20 nm (Fig. 2(a)) could be seen on the surface. The islands were 3–8 nm in height and most of them were elongated in the $[110]$ or $[1\bar{1}0]$ directions. The transmission spots on the RHEED patterns taken along these directions (inset in Fig. 2(a)) showed that the lattice orientation in the silicon substrate coincided with that of the fluorite islands. It is noteworthy that during the CaF_2 growth the Si(001) 2×1 superstructure

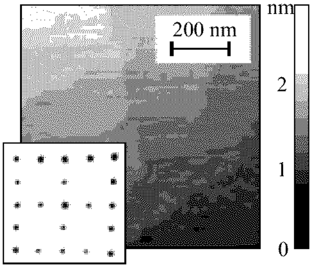

Fig. 1. AFM topography image of Si(001) substrate before CaF_2 deposition. Inset — LEED pattern of the surface taken at 70 eV.

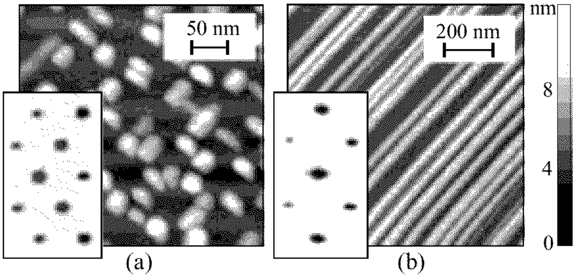

Fig. 2. AFM topography images after deposition of one CaF_2 monolayer at 450°C (a) and 6 ML at 650°C. Insets — corresponding RHEED patterns.

disappeared gradually: it could be distinguished in the pattern even after 2–3 ML of CaF_2 were deposited.

Increasing the deposition temperature above 700°C, a different type of nanostructures was obtained. The fluorite forms an array of very narrow parallel stripes of several microns length (Fig. 2(b)), running along either the [110] or $[1\bar{1}0]$ directions, depending on which direction was closer to the surface steps on Si. At intermediate temperature, however, structures with two perpendicular arrays could be observed. The width of the stripes was 15–20 nm, measured by AFM, and their height was 3–8 nm. Since the earlier stages of deposition, the RHEED pattern taken with the e-beam perpendicular to the stripes (inset in Fig. 2(b)) showed distinct transmission spots which were different from the low-temperature case (see inset in Fig. 2(a)). The pattern indicated that CaF_2 [110] axis was normal to the substrate plane while the CaF_2 $[1\bar{1}0]$ axis coincided with Si $[1\bar{1}0]$. The RHEED pattern taken with the e-beam parallel to the stripes showed the 3×1 reconstruction, reported earlier [5] for CaF_2 growth on the Si(110) surface. This fact was another evidence for the unusual (110) orientation of the CaF_2 lattice.

A detailed analysis of the RHEED pattern evolution during the high-temperature growth has shown that the stripes form after the deposition of a single CaF_2 monolayer. Unlike thicker structures, the first CaF_2 monolayer covered the substrate uniformly, acting as a wetting layer (Fig. 3). During the formation of the wetting layer the surface remained flat. However, a drastic change of the surface step pattern took place. Instead of the ill-defined shape of the step edges on the initial silicon surface, the step edges of the wetting layer were aligned along the [110] or $[1\bar{1}0]$ directions. During the wetting layer formation, in the direction where the stripes were expected to develop at higher CaF_2 coverage, one could observe a 3×1 superstructure in the RHEED pattern (inset in Fig. 3).

MDS and Photoemission measurements with He I photons allowed us to monitor the formation of new bonds at the interface. Figure 4 (curves a and b) shows that the intensity of the Si surface state peak after the deposition at low temperature (450°C) practically has not change, indicating that the most part of the surface keeps the silicon superstructure. This correlates with the observation of the Si(001) 2×1 superstructure in the RHEED patterns even after the deposition of 2–3 ML of CaF_2. These findings allowed us to conclude that the area between the CaF_2 dots (see Fig. 2(a)) was bare silicon surface. However, after the deposition of one CaF_2 monolayer at high temperature (700°C) the silicon surface state peak disappeared (Fig. 4(c)). This correlates with the formation of the wetting layer uniformly covering the silicon surface. It is believed that the wetting layer results from the

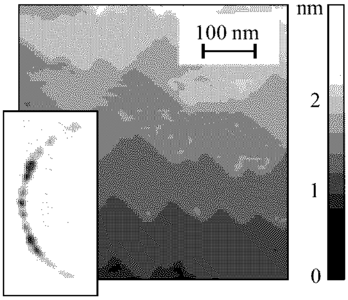

Fig. 3. AFM topography image of the wetting layer formed after fluorite deposition at 750°C. Inset — RHEED pattern.

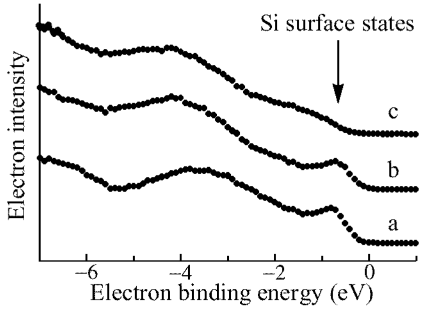

Fig. 4. Ultraviolet photoemission spectra in Si valence band region: (a) bare Si(001) 2 × 1 surface; the same surface covered with 1 ML of CaF_2: (b) at 450°C; (c) at 700°C.

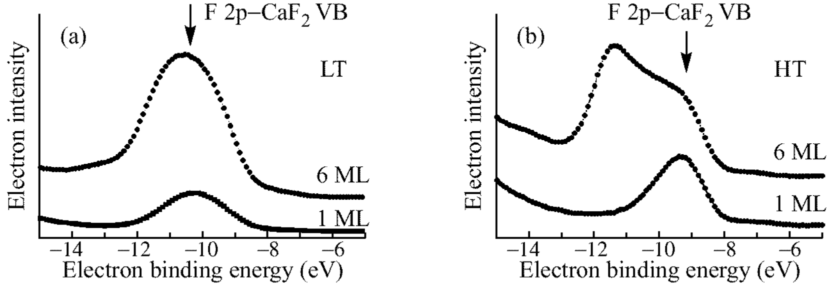

Fig. 5. Ultraviolet photoemission spectra in CaF_2 valence band region after CaF_2 deposition at 450°C (a) and 700°C (b).

chemical reaction at the interface with the creation of strong chemical bonds and change in calcium ion charge, somewhat similar to what is observed in CaF_2/Si(111) [2].

Also from MDS measurements it was evident that a part of the substrate remained unreacted when deposition occured at low temperature, since contributions from Auger neutralization [6] from clean Si were observed on the experimental spectrum. On the other hand, after the completion of 1 ML at high temperature, MDS showed the formation of a distinct low binding energy band that could be associated to the Ca 4*s* states. In this case no contributions from the substrate were observed.

UPS spectra at increasing CaF_2 coverage (Fig. 5) were drastically different for low-temperature and high-temperature growths. At low temperature deposition (Fig. 5(a)) the position of F2*p* line was almost independent on the CaF_2 coverage: this could be explained in terms of the 3D growth mode observed in RHEED from the initial stages of deposition. The slight shift to the higher binding electron energy and the broadening of the peak could be associated to an increase of the average size of the CaF_2 dots.

As was mentioned above, at high temperatures and submonolayer coverage, the formation of reacted fluoride wetting layer took place. The considerable shift (~1 eV) to the lower binding energies of the fluorine peak (Fig. 5(b), lower curve) could be associated to the different from the bulk fluorine environment in this layer. Drastic transformations of the photoemission spectra at larger coverage and high deposition temperature (Fig. 5(b), upper curve) could be naturally related with the formation of a bulk-like valence band in the fluoride stripes observed in RHEED and AFM (see Fig. 2(b)). A similar effect was observed in the CaF_2/Si(111) system after the deposition of a CaF_2 layer as thin as 2.5 ML.

One of the puzzling phenomena observed in our experiments was the formation of the single array of the parallel fluorite stripes on the initially two-domain 2 × 1 and 1 × 2 surface. The well-pronounced two-fold anisotropy of the RHEED patterns taken from the wetting layer provided a strong evidence for the transformation of the surface symmetry from four- to two-fold during the formation of the wetting layer. We found that several CaF_2 MLs deposited on the wetting layer at low temperature resulted in the formation of the stripes rather than dots. The RHEED pattern taken in the azimuth across these stripes obtained at low temperature showed that the CaF_2 lattice was oriented in the same way as in the high-temperature stripes, i.e. with the CaF_2 axis normal to the substrate. This was an additional evidence of the key role played by the wetting layer in the formation of the fluoride stripes.

Another attractive issue was clarifying the driving forces for the formation of so narrow and long fluorite stripes. Taking into account that in the fluorite structure (111)-surface has the minimum energy [1], one could expect that both CaF_2 islands and stripes were formed by (111) facets. Though the resolution of the AFM was not sufficient to confirm this, in the RHEED patterns, at certain diffraction conditions, inclined streaks expected for such facets were clearly seen. From the RHEED data one could conclude that a good lattice matching existed only along the stripes, but across the stripes a mismatch as high as 45% was expected. This is one of the possible reasons for the observed growth anisotropy. Another probable reason of the long fluorite stripes formation could be due to the diffusion anisotropy of the CaF_2 molecules on the surface of the wetting layer. One more reason of the anisotropy in CaF_2 growth could be related to the fact that the ends of the stripes are formed by the vertical (111) facets. The molecules, which attach the stripes in the base of these facets, form a larger number of bonds than the molecules at the base of the inclined facets. This would also favor the preferential growth along the stripes.

Acknowledgements

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