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Structural and photoemission studies of SrF_2 adsorption on Si(001)

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Abstract. The growth modes of SrF_2 on Si(001) are investigated by AFM and ultraviolet photoemission. Two growth regimes are identified according to the substrate temperature during deposition, resulting in flat and ordered fluoride layers or in nano-patterned films with characteristic triangular islands. The flat layer growth obtained at high temperature is accompanied by molecular dissociation at the interface.

1. INTRODUCTION

The study of the growth of insulators on semiconductors is an attractive field both for fundamental research and technological applications. In particular, the formation of interfaces between different materials and the Si(001) surface, which is the most relevant for technological applications, usually results in three-dimensional (3D) structures whose morphology, crystal structure and size critically depend on the suitable choice of the growth parameters (substrate temperature, substrate orientation, deposition method, etc.) The final growth mode and film morphology can thus be tailored through the knowledge and control of the growth parameters, with the possibility to tune the film quality and properties.

We recently investigated the growth mode of CaF_2 on Si(001) by molecular beam epitaxy (MBE) at different substrate temperatures during deposition [1-4]. It was found that at low coverage and at low temperature of deposition, i.e. below T = 600°C, rectangular shaped CaF_2 nanoscale islands develop, leaving the main part of the surface of Si unreacted. These fluoride islands are uniformly distributed over the surface and grow with their [001] axis aligned with the [001] axis of the substrate.

At deposition temperatures above 600 - 650°C, CaF_2 molecules adsorbed at the surface dissociate, reacting and bonding to the silicon substrate atoms. This generates a wetting layer covering uniformly the surface. The dissociative reaction appears to terminate at 1 ML of coverage. After this stage elongated islands (stripes) develop on top of the wetting layer running along either the [110] or $[1\,\bar{1}\,0]$ substrate directions. It was found that in this case the fluoride islands grow with their [110] axis aligned parallel to the [001] axis of the substrate.

The physical properties of strontium fluoride (SrF_2) are in many respects similar to those of CaF_2: both materials have the same fluorite-type crystal structure and show good insulating properties

typical of wide band-gap materials. Epitaxial layers and nanostructures of strontium and calcium fluorides are interesting for basic studies of low dimensional effects and, doped with rare-earth ions, are quite attractive for applications in optoelectronics. Strontium fluoride has a considerably higher lattice parameter (5.80 Å) than calcium fluoride (5.46 Å) and silicon (5.43 Å); therefore a noticeable influence of the strain on the initial stages of growth and on the formation of the interface is expected. Here we report on recent studies of SrF_2 growth on Si(001) focusing mainly on atomic force microscopy (AFM) and valence band ultraviolet photoemission (UPS) results. A more extended study including reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED), and X-ray photoemission (XPS) will be presented elsewhere. The results indicate that although there are some similarities there exist considerable differences between the growth modes of SrF_2 and CaF_2 on Si(001).

2. EXPERIMENTAL

The experiments were conducted in part at the Ioffe Physical-Technical Institute (St. Petersburg, Russia) and in part at the Department of Materials Engineering of the University of Modena and Reggio Emilia (Modena, Italy).

Deposition of SrF_2 was carried out at a pressure below 1×10^{-7} Pa using a home built effusion cell, consisting of a graphite crucible which was heated up to about 1100ºC to produce a SrF_2 molecular beam. The typical flux values used were in the range of 1-7 monolayers per minute (1 nominal monolayer (ML) corresponding to a thickness of 2.9 Å on Si(001)).

Silicon substrate heating was provided either by indirect heating, passing electric current through a heater filament located closely behind the substrate (Russia) or by direct heating, passing current through the substrate itself (Italy). The substrate temperature was monitored with an optical or IR pyrometer and additionally with a tungsten-rhenium thermocouple (Russia).

Si(001) *n*-type substrates were used with a miscut angle of 1-3 mrad with respect to the (001) plane. They were cleaned prior to SrF_2 deposition, the procedure consisting of a standard chemical Shiraki treatment followed by flashing the surface up to 1100-1200ºC in UHV conditions. The surface morphology of the SrF_2/Si(001) interfaces was measured in tapping (semi-contact) mode with an ambient air P4-SPM NT-MDT atomic force microscope. Typical resolution of the AFM was 10-15 nm laterally and 1-2 Å in the direction of the surface normal. Photoemission was carried out using He I photons ($h\nu$ = 21.2 eV) generated in a differentially pumped discharge lamp (Vacuum Generators). Angle-integrated spectra were acquired with a double pass cylindrical mirror analyzer (PHI) with an energy resolution of 100 meV. All spectra were taken at room temperature, after allowing the sample to cool down after deposition.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology

As observed by LEED and RHEED [2,4] the clean Si surfaces used in this study present terraces which are all parallel to each other and equal in extension, showing alternated 2×1 and 1×2 reconstructions. All the step edges appear to be 1 monolayer high when measured with the AFM. AFM images taken on the SrF_2/Si(001) surface at different nominal coverages are shown in Figure 1. At the initial stage of SrF_2 growth at 750ºC (Figure 1a) thin fluoride nanostripes less than 10 nm in width are seen to develop on the Si terraces running either along the [110] or [$1\,\bar{1}\,0$] directions of the substrate depending on the Si dimer orientation within the terrace. As a consequence of growth, the terraces on Si(001) are reorganized during the formation of the first layer. This is analogous to what is

observed on the CaF_2/Si(001) system [2-4]. At the completion of the first layer the surface presents terraces twice as wide separated by steps of SrF_2 twice as high, with respect to the clean Si(001). At increasing fluoride coverage, in the range from 2 to 20 ML, SrF_2 grows in a step flow mode (Figure 1b). The surface consists of atomically flat terraces separated by steps of ~3 Å in height. AFM images show that the step edges tend to form 90º angles with each other. This indicates a (001) orientation of the fluoride layers. No triangular shaped islands characteristic of a (111) growth direction are observed. RHEED patterns (not shown) are sensitive to whether the [110] e-beam direction is along or across the steps. With the electron beam across the steps a reconstruction is observed with arcs following a 1/3 periodicity. The on-the-arc-periodicity is 1 or 1/2 depending on coverage. With the electron beam along the steps the on-the-arc-periodicity is 1/3 at ~1 ML and then becomes 1/N at higher coverage.
When SrF_2 is deposited at T = 400ºC, flat triangular islands form on the Si surface with heights of a few ML (Figure 1c). This suggests a (111) orientation of the SrF_2 lattice in the direction normal to the surface plane.

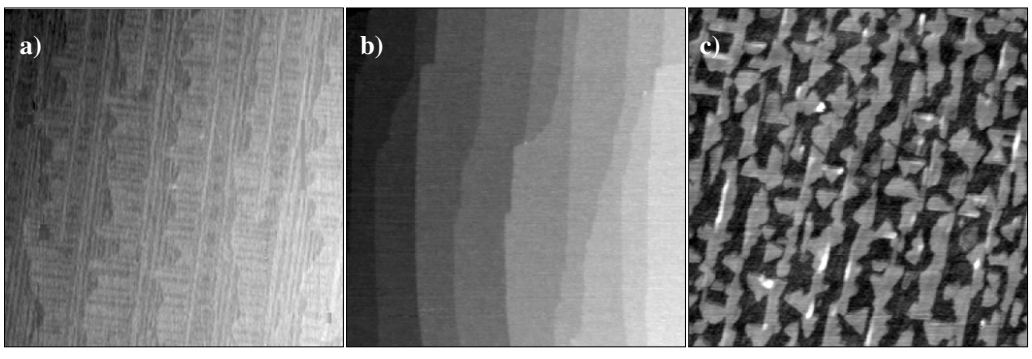

Figure 1. (a) AFM image taken at 0.5 ML of SrF_2 coverage with the substrate held at 750°C during growth. (b) AFM image taken at high coverage in the same growth conditions as in panel (a). (c) AFM image taken at 0.5 ML of SrF_2 coverage with the substrate held at 400°C during growth. The scan size is 900 × 900 × 3 nm.

The (111) orientation is also confirmed by RHEED, where streaks at low coverage and 3D diffraction spots at higher coverage show a mixture of two (111) lattices rotated 90º with respect to each other. At low coverage, the persistence of a 2×1 RHEED diffraction pattern suggests the presence of clean Si surface regions in between the triangular islands. This is in agreement with observations on CaF_2/Si(001) at low deposition temperatures [2].

3.2 Valence band

Valence band spectra taken with 21.2 eV photons on films of different nominal thicknesses prepared at different substrate temperatures (400°C and 700°C) are shown in Figure 2. The clean surface spectrum is also reported for comparison. It presents distinct features that correspond to emission from surface states at about 0.8 eV of binding energy and other structures at higher energy in agreement with literature results [5]. From the initial deposition stages at high temperature, at sub-monolayer coverage (Figure 2a), the features of the clean Si surface are severely damped. A distinct feature, which can be ascribed to emission from the F 2*p* valence band appears at about 1 ML of coverage, centred at about 8.6 eV of binding energy. This feature evolves with coverage, first with the emergence of a pronounced shoulder at 10.8 eV, then with the developing of a more complex structure between 8 and 12 eV of binding energy. While the narrow F 2*p* structure observed at low coverage can be associated with an interface-reacted fluoride layer, the large structure observed at high coverage is associated with the development of the bulk-like F 2*p* valence band of the SrF_2 film, similarly to the case of CaF_2/Si(001) [2,3].

It is noteworthy that the spectrum taken at 0.3 ML of coverage in Figure 2a does not show any signal related to fluorine. This is also the case in x-ray photoemission (not shown). This result can be taken as evidence of molecular dissociation occurring at high deposition temperatures. In particular, complete depletion of fluorine is observed, while Sr appears to be present at the surface (from the XPS results) even at extremely small coverage. An analogous behaviour was also reported with CaF_2/Si(001)[4]. In the inset of Figure 2a, a magnification of the valence band region below 5 eV is shown. A new feature is observed at about 1.5 eV of binding energy, which can be associated to the Sr 5*s* state in the dissociated interface layer. This is in agreement with observations by M.A. Olmstead et al. for dissociative SrF_2 chemisorption on Si(111) at high temperature [6].
When deposition is carried out at low substrate temperature (Figure 2b) there is no evidence of molecular dissociation at the interface (also with XPS). The broad structure centred at about 9.2 eV is associated with the F 2*p* valence band in the triangular nano-dimensional fluoride islands. It can be noticed that at 7 ML coverage the F 2*p* feature broadens and shifts towards higher binding energies, as expected for bulk SrF_2. The difference in the emission lineshape at low and high temperature can be related to the different morphology and resultant dimensional effects of the films in the two cases.

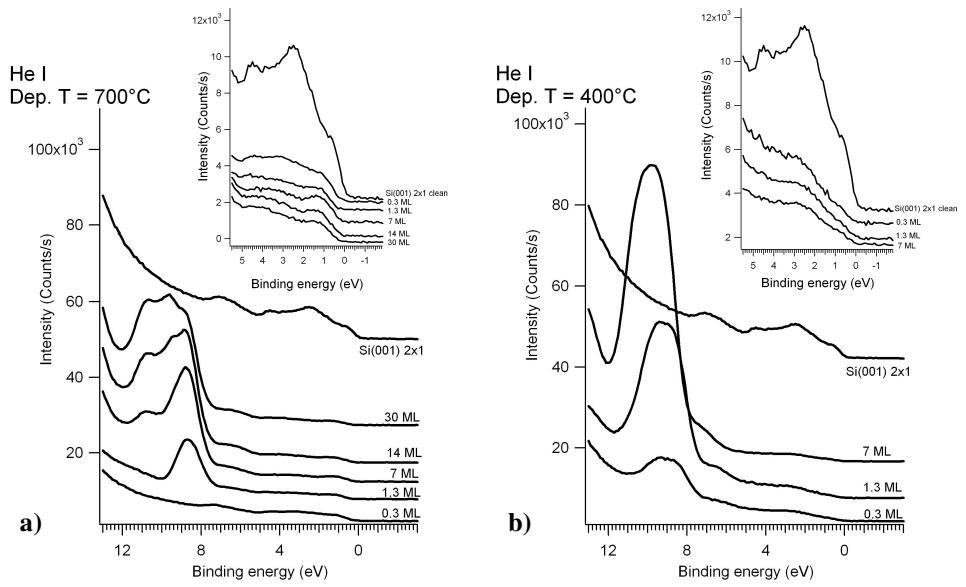

Figure 2. UPS spectra taken after (a) high and (b) low deposition temperature as a function of coverage. The zero of the binding energy refers to the Fermi level position (measured on the Ta clips in electrical contact with the Si sample). For visualization purposes spectra have been shifted on the vertical scale with respect to each other.

At variance with deposition at high temperature, no Sr induced features, which can be related to dissociated molecules, are observed the top of the valence band (inset of Figure 2b). Instead, a progressive reduction of the clean Si structures is observed.

4. CONCLUSIONS

At low substrate temperatures (around T = 400°C), flat triangular SrF_2(111) islands develop which are a few monolayers in height and with four possible orientations rotated by 90°. At high substrate temperatures (700-750°C), after the transformation of the initial two-domain (2×1 + 1×2) Si(001) surface into a single domain fluoride surface (similar to the CaF_2/Si(001) case), SrF_2 shows a very flat

(001) surface, which is quite unexpected for fluorides because of the high surface energy associated with (001) surfaces. Photoemission in the region of the valence band shows trends similar to those observed previously for CaF_2 growth on Si(001) [2,3]. This shows that at elevated temperatures there is molecular dissociation and suggests a reaction between Si and the first layer of SrF_2.

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