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Morphology of alkali halide thin films

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Abstract

Two alkali halide adsorbate–substrate systems were investigated by atomic force microscopy (AFM) working in contact mode. Adsorbate film orientation relative to the substrate was determined from the arrangement of the atomic steps of the substrate and the edges of the forming islands. In this work we present experimental results obtained for systems: NaCl/LiF(0 0 1) and LiF/NaCl(0 0 1), which exhibit a strong tendency of the self-assembly into regular structures.

Keywords: Alkali halides; Nanostructures; Thin films

1. Introduction

In the age of nanotechnology, a variety of film/substrate systems showing stress-induced self-organization into regular patterns are becoming important. Such systems can be exploited in future technological applications [1–6]. Alkali halides are promising wide band gap insulators, which can serve as templates for the guided growth of nanostructured thin films or individual nanometer-scale objects with specific functionalities [7–11]. Furthermore, 1D structures, like nanowires, can be grown on alkali halide prestructured surfaces. For example, iron nanowire arrays [12], as well as gold nanowire arrays [13] have been prepared by shadow deposition on a self-organized grating template produced by annealing the NaCl(1 1 0) surface. In general, the heteroepitaxy is a promising tool for materials engineering and advanced devices production. It is well known that the lattice mismatch in heteroepitaxy can result in a variety of periodic superstructures. Such superstructures can serve as templates for synthesis of new materials and devices. The studies of alkali halide thin films, in this respect, play an important role because of their simplicity among insulators and because they span a wide range of lattice constants ranging from 0.4017 nm for LiF to 0.7325 nm for RbI.

Recently many attempts have been made to build ordered structures of organic molecules on alkali halide surfaces [14–16]. Such structures are very appealing for the development of future integrated nanoelectronic devices [17]. In our opinion, it is reasonable to expect that good nanostructured templates can be obtained by the heteroepitaxy of an alkali halide on foreign alkali halide crystal. Since the late 1980s, such an epitaxial growth of one alkali halide on another alkali halide has been investigated by Yang and Flynn [18,19] and Saiki et al. [20,21]. It was argued that for misfits smaller than 20% the films grow epitaxially in the layer-by-layer mode, while in the island mode for larger misfits. Furthermore, the adlayers grow with their (1 0 0) planes parallel to the (1 0 0) substrate surface plane. It is known from experiments that a large misfit between the lattice constants of film and substrate may not hinder epitaxial growth. For the accommodation of the misfit, various interface structures (including dislocations, stacking faults, surface corrugations and carpet-like structure) were proposed [22–26]. Kiguchi et al. [27] have observed that the lattice distortion in the adlayer relaxes more rapidly for systems where the film lattice constant is larger than that of the substrate (i.e. a system with a positive misfit) as compared to systems where the film lattice constant is smaller than that of the substrate (i.e. a negative misfit system). The difference between the two cases was attributed to the fact that the elongation of ionic bonds can be accomplished easier than compression.

Up to now, very few atomic force microscopy studies of the growth of alkali halide films on alkali halide crystals have been reported. Mayer et al. [28] have shown that some asymmetry can exist for KBr ultrathin films on NaCl(1 0 0) and for NaCl on KBr(1 0 0). Namely in the positive misfit system, KBr on

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NaCl(1 0 0) grows in compact rectangular islands of double and triple layer height with the bulk lattice constant of KBr. Such a system exhibits a superstructure with the periodicity of the least common multiple of the NaCl and KBr lattice constants. On the other hand, the negative misfit system, NaCl on KBr(1 0 0), grows in more defected islands of monolayer height and adapt the lattice constant of the substrate. Recently [29,30], it was shown that some heteroepitaxial thin films of alkali halides can get nanostructured as a result of annealing. For example LiF as well as NaCl thin layers deposited on Si(0 0 1) substrate at room temperature consist of small grains arranged rather randomly. But after the annealing at elevated temperatures the grains transform into 3D rectangular-shaped islands, surrounded by free substrate areas. Such nanostructures result from the Ostwald ripening and the interface stress induced by the lattice mismatch and thermal expansion coefficient difference. In this work we study NaCl/LiF(0 0 1) and LiF/NaCl(0 0 1) systems.

2. Experimental

The experiments were performed in UHV STM/AFM Omicron VT system (base pressure $< 10^{-8}$ Pa). The AFM images were acquired with a silicon triangular tip (Nanosensors, spring constant of 0.3 N/m) working under soft contact. Alkali halide substrates were prepared by single crystal cleavage immediately before being loaded into the vacuum chamber of the AFM microscope. Before experiments, the LiF or NaCl (6 mm × 6 mm × 1 mm) was degassed by heating to 300 °C for an hour. Alkali halides are known to be very susceptible to radiation damage in the halogen sublattice when exposed to ionizing radiation. Therefore, in the present work we do not use any technique involving ionizing radiation to characterize the alkali halide substrates and deposited adlayers. For determination of the orientation of the substrate and the relative orientations of deposited films we have observed the alignment of substrate crystal edges, atomic steps at the substrate and the island edges. It is well known that alkali halides surface steps are oriented predominantly, but not exclusively, along the [1 0 0] and [0 1 0] lattice directions. The directions of these steps (so-called low-index directions) are also parallel to the macroscopic orientation of the crystal edges. Before the thin layers preparation, the LiF and NaCl sources were heated in vacuum for several hours. The film thickness was monitored using quartz microbalance. The substrate temperature, during annealing, was measured using a type K thermocouple, spot-welded to the sample holder of the heater unit. Unfortunately, such an arrangement of the thermocouple gives rather poor accuracy in the sample temperature measurements.

3. Results and discussion

In the following, we concentrate on the NaCl/LiF(0 0 1) and LiF/NaCl(0 0 1) systems with lattice constants 0.5628 nm for NaCl and 0.4017 nm for LiF. The thermal expansion coefficients are 44 ppm/K and 37 ppm/K (for NaCl and LiF, respectively).

The AFM images of NaCl/LiF(0 0 1) system are presented in Fig. 1. The image in Fig. 1a shows the topography of the layer as deposited at room temperature. As it is seen in Fig. 1a, the small grains are randomly scattered all over the substrate, showing no preferential directions. After annealing at about 250 °C, the initial small grains transform into much larger ones, oriented preferentially along the ⟨1 0 0⟩ substrate directions. The rectangular-shaped pits, visible in this figure, in some cases can be considered as uncovered areas of the substrate. The comparison of the images depicted in Fig. 1a–c indicates that either massive self-diffusion or massive desorption of the adlayer or both processes take place during the film/substrate system annealing. In this experiment the annealing temperature was only about 250 °C and 300 °C (and lasted for a few minutes), therefore it is reasonable to assume that stress-induced diffusion is the dominant process in this system. However, in general, partial desorption of the overlayer can occur due to the heat generated during conversion of the as deposited, unordered, film into a phase consisting of relatively larger crystallites. Such a partial desorption have been observed during annealing of thin films of some gasses (Ar, N_2, O_2) deposited at 2 K [31]. The effect of the annealing-induced (partial) desorption of the cryodeposited gas was easily detected as a spike of pressure in the experimental chamber. Since, in the cases considered here, we have not observed any distinct rise of pressure during the annealing process, it is reasonable to argue that the observed nanostructurisation in the systems studied goes mainly via diffusion. In our opinion, partial desorption of the film is an important re-organization process next to diffusion. This is consistent with the low value (0.1 eV) of the activation energy for diffusion of NaCl molecule on the NaCl surface [18,19]. To understand the obtained results we have to assume that the activation energy for diffusion of NaCl molecule over the LiF(0 0 1) substrate is not much larger.

The image depicted in Fig. 1b indicates that the Ostwald ripening, island coalescence and the rectangular-shaped pits formation develop together. The effect of the interface–strain relaxation via the reduction of interface area, which is a consequence of the free energy minimization, is clearly seen in Fig. 1d, showing the topography of the system after annealing at 300 °C. As one can see, the effective area of the interface is substantially reduced in favour of uncovered substrate, thus indicating that the epilayer–substrate interface is energetically very costly. A careful inspection of several images of annealed NaCl/LiF(0 0 1) systems has not revealed any inclination of the top surfaces of the nanostructured layer relative to the substrate surface. Furthermore, the islands are very narrow and substantially elongated along [1 0 0] or [0 1 0] substrate directions. It should be noted that the difference in thermal expansion coefficients in NaCl/LiF(0 0 1) and LiF/NaCl(0 0 1) systems amounts about 7 ppm/K. This difference can be considered as an additional (next to the large misfit) driving force to the massive adlayer material rearrangement via diffusion and probably via desorption. Since in the systems of the alkali halide on foreign alkali halide, important for the relaxation is the lattice misfit, the mechanisms based on stacking fault model and ‘‘carpet-like’’ structure [23,25,26,32]