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MBE-growth of novel MnF_2–CaF_2 superlattices on Si(111) and their characterization

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Abstract

Novel short-period MnF_2–CaF_2 superlattices (SLs) on Si(111) substrates have been grown by molecular beam epitaxy. The thickness of a MnF_2 layer was 1–3 molecular layers. Reflection high-energy electron diffraction studies indicated the fluorite type of crystal structure of these layers. Fluorescent extended X-ray absorption fine structure measurements supported this observation. Atomic force microscopy measurements showed a flat surface morphology of the SLs. X-ray diffraction measurements revealed well-pronounced superstructural reflections. The width of their ω-curve did not exceed 2.5 arc min, which indicated a good crystal quality of the SLs.

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Keywords: Molecular beam epitaxy; MnF_2–CaF_2 superlattices; Structural characterization; Metastable phase

1. Introduction

It is known that the crystal structure and physical properties of ultrathin (a few monolayers) films can be very different from those of bulk crystals [1,2]. However, the amount of material in such a film in many cases is insufficient for studies of their properties or their applications. The growth of short-period pseudomorphic superlattices (SLs) helps much in solving this problem and enables a more detailed characterization of the crystal structure and physical properties of material in ultrathin films.

Manganese fluoride has the tetragonal rutile-type structure and is a wide energy band gap insulator with a distinct antiferromagnetic ordering below 67 K. Owing to the simple crystal structure and optical anisotropy, MnF_2 bulk crystals have been used as a model material for studying the magnetic ordering in optical spectra [3–5]. Together with the interesting magnetic properties, MnF_2 is attractive because of its capability to crystallise in different modifications at high temperatures or pressures [6]. Though the growth and properties of alkaline-earth fluoride films, grown by molecular beam epitaxy (MBE), have been studied extensively, less attention has been given to MnF_2 films [7,8].

Reflection high-energy electron diffraction (RHEED) studies have recently shown that the first

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three monolayers (ML) of MnF_2 on CaF_2/Si(111) heteroepitaxial substrates have the cubic fluorite-type crystal structure [9,10]. In the present work, we demonstrate the feasibility of growing short-period pseudomorphic MnF_2–CaF_2 SLs with a MnF_2 layer thickness from 1 to 3 ML. The SLs have been characterized by RHEED, atomic force microscopy (AFM), X-ray crystal truncation rod (CTR) scattering, high-resolution X-ray diffraction (HRXRD) and fluorescence-extended X-ray absorption fine structure (EXAFS).

2. Experimental

Fluoride SLs were grown at the Ioffe Physico-Technical Institute. After a standard chemical cleaning, silicon substrates were loaded into a MBE chamber and cleaned thermally at 1250°C in ultra-high vacuum. RHEED images were taken at 15 keV using a sensitive CCD camera.

After the thermal cleaning, the Si(111) surface showed a clear 7×7 superstructure below 830°C. Calcium and manganese fluoride layers were grown from MnF_2 and CaF_2 molecular beams produced by sublimation of small pieces of the fluorides in effusion cells with amorphous carbon crucibles.

A pseudomorphic CaF_2 buffer layer was grown on a silicon surface using the two-step technique [11]. In this work, three SLs were grown and characterised: the first two contained 1 ML and 2 ML of MnF_2, respectively, and 8 ML of CaF_2 in each period, the third one had 3 ML MnF_2 and 10 ML of CaF_2 in each period. All SLs consisted of 15 periods.

Just after the growth, the surface morphology of the structures was examined by an atomic force microscope P4-SPM-MDT (produced by NT-MDT, Zelenograd, Russia) operating in the tapping mode.

CTR measurements were carried out at the beamline BL6A at the Photon Factory in Tsukuba (Japan) using synchrotron radiation from the 2.5 GeV storage ring and imaging plates (IPs) as a detector [12,13]. The X-ray wavelength was set at 1.600 Å.

HRXRD measurements were conducted at the Rigaku X-ray Research Laboratory using an ATX-E high resolution X-ray diffractometer, equipped with a Cu rotating anode high-power generator. The incident X-ray was monochromated with a Ge(220) channel-cut crystal.

EXAFS measurements were performed at the beamline BL12C of the Photon Factory. The EXAFS spectra were measured at the Mn K-edge in the fluorescence-detection mode using a 19-channel Ge SSD.

3. Results and discussion

3.1. Epitaxial relations for a MnF_2 film on Si(111)

Because MnF_2 and Si have different crystal lattice symmetry (tetragonal and cubic, respectively), a reasonable matching between the layer and the substrate can occur only for some special orientations. For the MnF_2 growth on Si(111), there are two main possibilities:

- pseudomorphic growth in the cubic (fluorite-type) crystal structure
- growth of a relaxed film in the rutile structure characteristic of bulk MnF_2 crystals under normal conditions

The cubic fluorite-type phase of MnF_2 has been identified in Ref. [6] at high pressures and temperatures (HPT). Using these data, the lattice parameter of this phase at room temperature has been estimated to be 5.27 Å. The same value was also obtained by extrapolation of the $Mn_xCa_{1-x}F_2$ solid solution lattice parameter to $x = 1$ [14]. Thus, the mismatch between a MnF_2 film with the fluorite-type structure and a Si substrate is about -3% at RT. One can expect that the critical thickness of cubic MnF_2 film growth will be only a few monolayers.

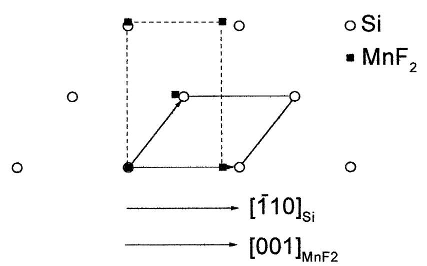

Fig. 1. Matching of the MnF_2(110) and Si(111) planes.

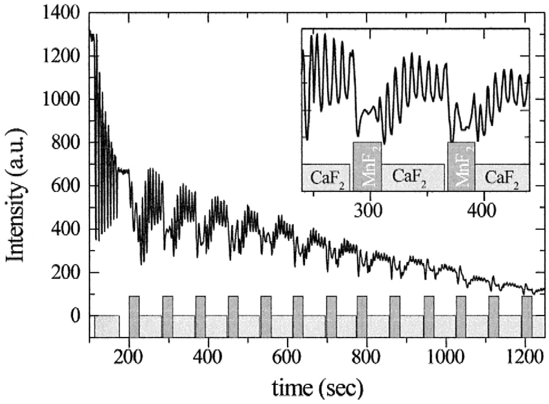

Fig. 2. RHEED specular beam intensity during the growth of the $[MnF_2\ 2\ ML/CaF_2\ 8\ ML]_{15}$ SL. Electron energy 15 keV, the electron beam azimuth $[\bar{1}10]$ and incidence angle 0.5°.

For a relaxed MnF_2 film, a reasonably good matching takes places if the film growth plane is (110) and $[001]_{MnF_2} \| [\bar{1}10]_{Si}$ (Fig. 1). In this case, the MnF_2 surface unit cell is a centered rectangle with the dimensions $6.88 \times 3.31\ Å^2$. The misfits between the silicon and manganese sites along the $[\bar{1}12]_{MnF_2}$ and $\| [\bar{1}10]_{Si}$ directions are $+2.8\%$ and -15.3%, respectively. Because of the three-fold symmetry of the Si (111) surface, a three-domain growth of a MnF_2 film with the rutile structure is expected. Manganese fluoride epitaxial growth has been recently observed in both fluorite and rutile phases [9,10].

3.2. RHEED studies of MnF_2–CaF_2 SLs growth

Because the surface unit cell of the MnF_2 rutile phase is twice as large as that of the cubic phase, there are additional reflections in the RHEED patterns from the rutile phase with respect to the cubic phase. During the growth of all SLs, only reflections from the cubic lattice were observed. Fig. 2 shows specular beam intensity oscillations in the RHEED pattern during the growth of the $[MnF_2\ 2\ ML/CaF_2\ 8\ ML]_{15}$ SL. The oscillations were observed during the whole growth process, and this allowed us to monitor the thickness of each SL layer. The shape of the oscillations is almost the same in each period, which indicates the stability of the growth conditions. The lower average diffracted intensities and oscillation amplitudes are due to microscopic roughness at low (RT) growth temperature.

3.3. AFM measurements

As was mentioned in Section 2, the MnF_2–CaF_2 SLs were grown at RT on pseudomorphic CaF_2 buffer layers. One can see in Fig. 3a the typical surface morphology of the buffer layer measured by

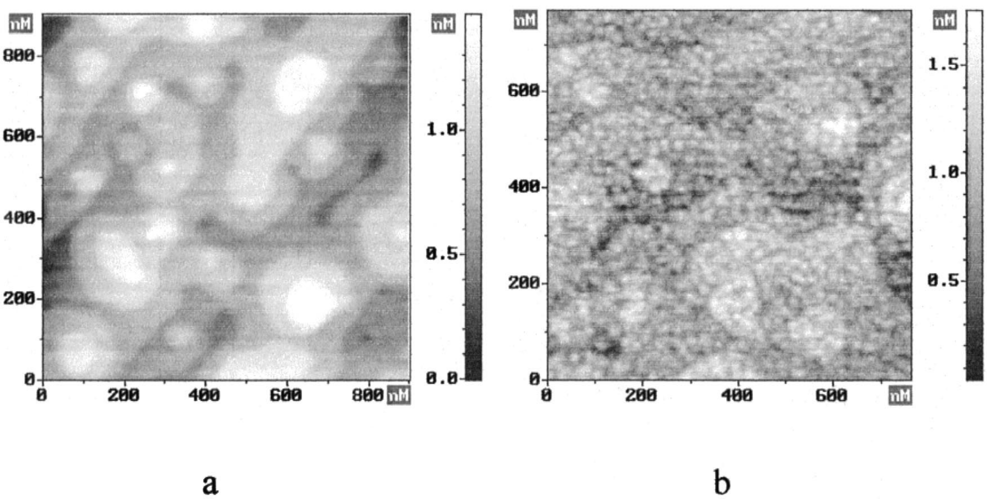

Fig. 3. AFM images of (a) a 3-nm CaF_2 buffer layer grown on Si(111) at 700°C, (b) the $[MnF_2\ 2\ ML/CaF_2\ 8\ ML]_{15}$ fluoride SL grown at room temperature.

an atomic force microscope. The surface is flat, the variations of its height in a 900×900 nm^2 square does not exceed 5 ML. 100–200-nm wide terraces are atomically smooth and surrounded with steps of one molecular layer thick. Width of the terraces is determined by the surface diffusion of CaF_2 molecules at high temperature (700–770°C). After growth of the [MnF_2 2 ML/CaF_2 8 ML]$_{15}$ SL at RT, the surface remained on the average flat (Fig. 3b). One can see, however, that it is not ideally smooth and small 20-nm islands cover the terraces.

3.4. XRD studies

3.4.1. CTR-scattering

Fig. 4 shows an IP image measured from the [MnF_2 2 ML/CaF_2 8 ML]$_{15}$ SL. In addition to the 111 reflection where both the SL and Si-substrate contribute to the scattering, two 311 reflections can be clearly seen. In the latter case, the contributions are spacially separated. This separation is due to so-called type-B epitaxial relation at the CaF_2/Si(111) interface grown at high temperature [15], where the epitaxial layer is rotated by 180° around the normal to the substrate surface. No superstructure features can be observed around the 311 reflection of the substrate. This clearly indicates the type-A (without the rotation) epitaxial relations between CaF_2 and MnF_2 layers in the SL.

3.4.2. High-resolution measurements

Fig. 5 presents a high-resolution $2\theta/\omega$ curve obtained for the [MnF_2 3 ML/CaF_2 10 ML]$_{15}$ SL grown on Si(111). In addition to the highest peak from the Si substrate, a number of superstructural reflections are clearly seen. They provide a convincing evidence for an additional periodicity in the structure. It was found that the width of the ω-curve for different satellites was less than 2.5 arc min. This shows a good crystal quality of the SL. Distinct interference fringes clearly seen on the curve indicate the flatness of the surface and interface.

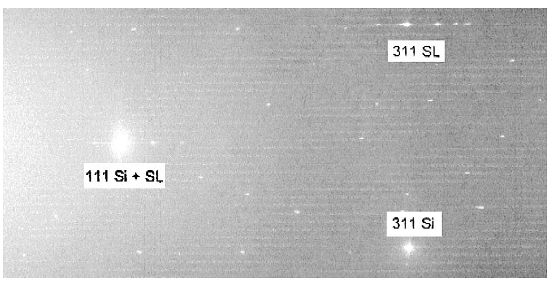

Fig. 4. CTR scattering from the [MnF_2 2 ML/CaF_2 8 ML]$_{15}$ SL.

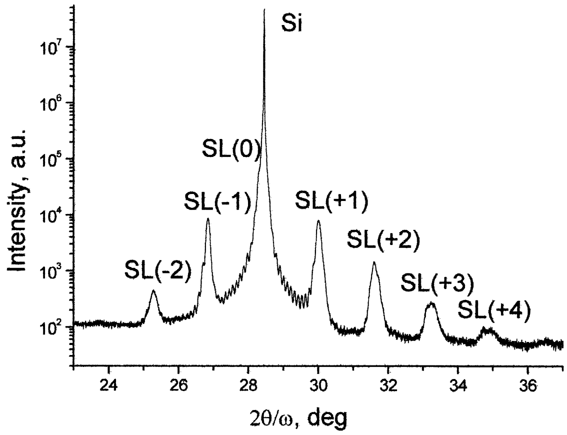

Fig. 5. HRXRD from the [MnF_2 3 ML/CaF_2 10 ML]$_{15}$ SL.

3.5. Fluorescence-EXAFS studies

In the [MnF_2 1 ML/CaF_2 8 ML]$_{15}$ SL, the EXAFS spectrum showed a very clear structure specific for fluorite MnF_2. This means that the MnF_2 crystal was forced to change its structure from rutile to fluorite by the epitaxial growth between the fluorite CaF_2 layers. This analysis of EXAFS spectrum supports the RHEED observation. With increasing thickness of MnF_2 layers, there is an admixture of rutile MnF_2. In the [MnF_2 13 ML/CaF_2 8 ML] double heterostructure, the EXAFS spectrum showed the rutile MnF_2 structure.

4. Conclusion

Summarizing the above, we have demonstrated the feasibility of epitaxial growth of novel MnF_2–CaF_2 superlattices with MnF_2 layer thickness from 1 to 3 ML. It was found from RHEED and EXAFS measurements that MnF_2 in these SLs has the cubic fluorite-type structure, unlike bulk MnF_2 crystals having the tetragonal structure of rutile.

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