Morphology of thin SrF_2 films on InP(111) as studied by RHEED

S. Heun, M. Sugiyama, S. Maeyama, Y. Watanabe, and M. Oshima
NTT Interdisciplinary Research Laboratories, 3-9-11 Musashino-shi, Tokyo 180, Japan
Tel.: +81-422-59-2521, FAX: +81-422-59-3576, e-mail: heun@aela.ntt.jp

Abstract
We studied the growth of SrF_2 on InP(111) with reflection high energy electron diffraction (RHEED). In this paper the surface and bulk crystalline structure of 50 Å SrF_2 grown on two InP(111) surfaces prepared in different ways is compared. HF-etching of the InP(111) substrate resulted in a rough surface, whereas an As-treatment produced a flat surface without superstructure. After annealing of the SrF_2 films at 500°C for 10 minutes the film deposited on the HF-etched surface showed a texture, whereas the film deposited on the As-treated InP(111) surface is epitaxial even without twinning.

1. Introduction

The alkaline earth fluorides are a very promising material for the growth of insulating layers on semiconductors. Their crystalline structure (fluorite) is very similar to the diamond or zinc blende structure of commonly used semiconductors [1]. Also the lattice matching for appropriately chosen material combinations is very good, for example -1.2% in the case of SrF_2 on InP [2]. So an epitaxial growth can be expected. In addition the alkaline earth fluorites are good insulators with a large band gap (10-12 eV) [3], and they are quite easy to deposit because they sublime as molecules [2].
It is reported that SrF_2 grows in (111) facets if deposited at 380°C on InP(100) [4]. Therefore the SrF_2(111) plane seems to be the energetically favoured one, and a film with a smaller surface roughness can be expected. Due to the low non-congruent evaporation temperature of InP [5] the available range of deposition temperatures is limited. Due to this fact and because we wanted to compare with our previous results obtained for SrF_2 on InP(100) [6] we decided to grow the SrF_2 at RT.

2. Experimental

The experiments were performed in an ultra high vacuum (UHV) chamber located at the Photon Factory (PF), Tsukuba, Japan. The system consist of an analysis chamber and a chamber for molecular beam epitaxy (MBE) connected by a transfer chamber. Sample preparation and RHEED measurements were done in the MBE chamber. Arsenic and SrF_2 were deposited from K-cells. After deposition SRPES measurements were made at the beamline BL-1A in the PF. These experiments will be described in a forthcoming paper [7].
Samples were mirrorlike polished 350 µm thick n-type InP(111)-B (±0.5°), which were S-doped (2×10^{19} cm^{-3}). The samples were mounted on a Mo sample holder.
The film thickness calibration for these experiments was problematic. Due to trouble with the x-ray source a calibration using the attenuation of the XPS In 3d peak was not possible. So the film thickness was determined to be 50 Å ± 20% using cross sectional transmission electron microscopy (TEM).

3. Results and Discussion

3.a. SrF_2 on HF-etched InP(111)

As was shown for InP(100) [6], an HF treatment is a suitable way to remove the native oxide from an InP surface. So for the here discussed experiments an InP(111) sample with native oxide was etched in a 10% HF/90% ethanol solution for 10 minutes at RT. Subsequently the sample was transferred under ethanol into the UHV chamber. As discussed in [6], the HF treatment results in a slight fluorine contamination of the InP surface. This was also observed for the InP(111) sample. The valence band of this sample as measured with SRPES (photon energy 100 eV) was superimposed with an F 2p peak [7]. To remove this F contamination the sample was annealed at 300°C for 5 minutes. After this treatment the SRPES F 2p peak had disappeared [7]. This surface was studied with RHEED. Figure 1a shows the picture obtained in [01$\bar{1}$] direction, whereas fig. 1b was measured in [$\bar{2}$11] direction. In both directions a spotty transmission pattern was obtained which indicates a rough surface. A superstructure was not observed. This result is similar to that obtained for the HF-etched InP(100) surface [6]. The RHEED pattern of the InP(111) surface seems to be more streaky compared to the InP(100) surface. Therefore one could conclude that the roughness of the InP(111) surface is smaller than that of the InP(100) sample prepared under the same conditions. But since even small variations of the angle of incidence of the electron beam can change an RHEED pattern from streaky to spotty, this observation should be interpreted with utmost caution. Due to the transfer mechanism of our chamber the orientation of the sample with respect to the electron beam can easily vary within 1°.
50 Å SrF_2 was deposited at RT on this rough and clean InP(111) surface. Then the film was annealed at 500°C for 10 minutes. The RHEED patterns measured on this surface are shown in fig. 2. A superposition of streaks and spots is obtained which indicates a rough crystalline surface of the film. From scanning electron microscopy (SEM) and SRPES measurements it is clear that the film is continuous [7]. The distance of the streaks in [01$\bar{1}$] direction is smaller than for the same direction on the uncovered InP substrate so one could assume a superstructure on the film surface. But because the streaks are not equidistant this possibility can be excluded. On the other hand, assuming a texture of the film this RHEED pattern can be understood. In case of a texture crystallites are rotated with respect to the surface normal, and all in-plane-directions occur with the same probability. This is illustrated in fig. 3 where the (111) plane of the reciprocal lattice of the fluorite structure is shown. Three digits are referring to the cubic bulk unit cell of fluorite, which is shown in fig. 4a, whereas two digits refer to the hexagonal surface unit cell [8]. If the SrF_2 grows epitaxially the [01$\bar{1}$] direction of the film corresponds to the [01$\bar{1}$] direction of the underlying substrate. The spots obtained for this epitaxial case in [01$\bar{1}$] direction are the bulk Bragg points (000), (02$\bar{2}$) and multiples of them. The crystal truncation rods (CTR) belonging to those points are visible in the RHEED picture shown in fig. 2a. The other streaks in this picture can be identified as the (10), (20) and (21) CTRs (and, of course, equivalent rods) of crystallites with their [11$\bar{2}$] or [14$\bar{5}$] directions parellel to the [01$\bar{1}$] direction of the InP substrate. For a better understanding the streaks in fig. 2a are labelled. The spacing of the measured streaks agrees well with the predicted spacing from the model. The spacing values are listed in table 1.
Compared to the other streaks the intensity of the (20) streak is very weak so that it is nearly invisible in fig. 2a. To explain this the structure factor S of the basis of the fluorite unit cell has to be calculated. This is defined as [9]

$$S(hkl) = \Sigma_j f_j \exp[-i2\pi(x_j h + y_j k + z_j l)]$$

where $r_j = (x_j, y_j, z_j)$ gives the position of the j-th atom of the basis in real space, f_j its atomic form factor, (hkl) denotes the indices of a reciprocal bulk lattice point, and the sum includes all atoms of the basis. The intensity of a reciprocal lattice point is proportional to SS^*, where S^* is the complex conjugate of S. The positions r_j of the atoms of the basis are given in ref. [10]. Atomic form factors for F and Sr were taken from ref. [11]. The resulting structure factors and intensities are listed in table 1. The intensity of the (22$\bar{2}$) spot which is located on the (20) rod is one order of magnitude lower than that of the (11$\bar{1}$) spot on the (10) rod which agrees well with the measured intensities.
It is well known that electron bombardment changes the morphology of thin films of alkaline earth fluorides [2]. This was observed also during our RHEED measurements. During the measurement in the [011] direction the intensity of the streaks decreased, while the intensity of the background increased simultaneously. This indicates an increasing density of point defects on the surface. This implies that the subsequently taken photograph in the [$\bar{2}$11] direction is not as sharp as the previous one taken in the [01$\bar{1}$] direction. In fact the RHEED pattern of the [$\bar{2}$11] direction as shown in fig. 2b is very weak and a transmisson pattern. Anyway, it is astonishing that no texture streaks are visible. The pattern can be explained with an epitaxial film. Even if the density of point defects increased drastically during the measurement in the [01$\bar{1}$] direction, it is very unlikely that the film rearranged from a textured to an epitaxial one. Much more probable is the following explanation: the texture is not ideal, i.e. not all directions in the (111) plane have the same probability, but there is a preferential orientation as given by the substrate. In the very weak RHEED pattern measured in the [$\bar{2}$11] direction only the dominating streaks are visible, and they belong to the crystallites with the same orientation as the substrate.

3.b. SrF_2 on As-treated InP(111)

In analogy to our previous work on SrF_2 on InP(100) we prepared another sample in an arsenic treatment. To our knowledge only one paper is published which deals with an As-treated InP(111) surface [12], but the authors did not examine the structure of this surface in detail. We annealed the sample under As_4 flux (10^{-5} mbar) at 500°C for 10 minutes, cooled it down to RT, and then annealed it again without As_4 flux at 500°C

for 10 minutes. The resulting RHEED pattern is shown in fig. 5. It shows a bright 1x1 and is produced from a flat surface without superstructure.

On this surface 50 Å SrF_2 was deposited at RT, and subsequently the film was annealed at 500°C for 10 minutes. The corresponding RHEED patterns are shown in fig. 6. Again the measurement in $[01\bar{1}]$ direction was done first. The pictures show a spotty 1x1, so the film is epitaxial and rough. The picture taken in $[01\bar{1}]$ direction shows weak intensity in the middle between the integer order CTRs. But a 2x1 reconstruction on a film with such a large roughness is very unlikely. On the other hand it is well known that surface roughness broadens the CTR [13]. So these weak streaks are more likely caused by tails of the (10) and $(0\bar{1})$ rods. This is illustrated in fig. 7.

The picture taken in the $[\bar{2}11]$ direction is very weak, as in the case of SrF_2 on HF-etched InP(111), but this time the position of the reciprocal lattice points on the CTR can be determined. Figure 8 shows a cut of the Ewald space along the $[\bar{2}11]$ direction. The asymmetry between $(1\bar{1})$ and $(\bar{1}1)$ rod is illustrated. In case of twinning the $(1\bar{1})$ and the $(\bar{1}1)$ rods are equivalent, as also illustrated in fig. 8. The measured RHEED pattern shows a clear asymmetry between the $(1\bar{1})$ and the $(\bar{1}1)$ rod as shown in fig. 6b. So we can conclude that within the sensitivity of RHEED the film is epitaxial without twinning.

4. Conclusion

As in the case of the InP(100) surface, the HF-etching resulted in a rough InP(111) surface whereas the As-treatment produced a flat and well ordered surface. However, in contrast to the InP(100) case no surface reconstruction was observed on the As-treated InP(111) surface. On these surfaces SrF_2 was deposited at RT and subsequently annealed at 500°C for 10 minutes. Both SrF_2 films were crystalline. However, SrF_2 grows on the HF-etched surface with a texture, whereas it grows epitaxially, even without twinning, on the As-treated InP(111) surface. Although the reason for this difference is still unclear, there is hope to correlate these structural data with the results of SRPES measurements [7].

RHEED has again shown to be a useful tool with severe limitations. Any quantitative analysis beyond counting of reciprocal points is very difficult due to the dynamical nature of electron diffraction. Even in the kinematical limes of low energy electron diffraction (LEED) [13] the problem of electron beam induced film damage remains. To overcome this difficulty, x-ray diffraction seems to be the method to employ. Corresponding measurements are in progress.

Acknowledgements

Special thanks to Hiroki Hibino and Masato Tomita for fruitful discussions on RHEED and electron microscopy, respectively.

References

[1] G. Couturier, A. Chaouki, H. Ricard, A. S. Barriere and C. Haw: J. Vac. Sci. Technol. B 5 (1987) 870
[2] J. M. Phillips, L. C. Feldman, J. M. Gibson and M. L. McDonald: Thin Solid Films 107 (1983) 21
[3] T. K. Paul and D. N. Bose: J. Appl. Phys. 67 (1990) 3744
[4] W. Weiss et al.: Surf. Sci. 268 (1992) 319
[5] G. J. Davies et al.: Appl. Phys. Lett. 37 (1980) 290
[6] S. Heun, M. Sugiyama, S. Maeyama, Y. Watanabe, and M. Oshima: accepted for publication in Appl. Surf. Sci.
[7] S. Heun, M. Sugiyama, S. Maeyama, Y. Watanabe, and M. Oshima: to be submitted to Phys. Rev. B
[8] F. Jona, J. A. Strozier Jr. and W. S. Yang: Rept. Progr. Phys. 45 (1982) 527
[9] C. Kittel: Introduction to Solid State Physics, John Wiley & Sons New York 1976
[10] R. W. G. Wyckoff: Crystal Structures, Interscience Publishers New York 1965
[11] P. A. Doyle and P. S. Turner: Acta Cryst. A 24 (1968) 390
[12] M. Kubo and T. Narusawa: J. Vac. Sci. Technol. B 8 (1990) 697
[13] J. Wollschlager, J. Falta, and M. Henzler: Appl. Phys. A 50 (1990) 57
[14] K. Saiki, Y. Sato, K. Ando and A. Koma: Surf. Sci. 192 (1987) 1

(hk)	00	10	11	20	21
distance between (00) and (hk) in model	0	1	$\sqrt{3}$	2	$\sqrt{7}$
distance between (00) and (hk) in measurement	0	1	1.7	2	2.6
first bulk bragg point on (hk)-rod	(000)	(111)	(022)	(222)	(133)
structure factor S of this bulk bragg point intensity ~ $S \cdot S^*$	11.6	6.9	4.6	2.2	6.9 - 1.2i
	135	18	21	5	49