Growth and structure of $\text{Mn}_x\text{Ca}_{1-x}\text{F}_2$ epitaxial films on Si(111)

N. L. Yakovlev, A. G. Banshchikov, R. N. Kyutt, N. S. Sokolov and L. Hirsch†
Ioffe Physico-Technical Institute, St Petersburg, Russia
†Universite Bordeaux 1, 351 Cours de la Liberation, 33405 Talence Cedex, France

Abstract. Molecular beam epitaxy was used to grow films of MnF$_2$ and CaF$_2$ solid solutions on Si(111) substrates. The composition of the solutions was measured using oscillations of reflection high energy electron diffraction, electron microprobe analysis and Rutherford backscattering and was in the range from 10% to 45% of MnF$_2$. In these solutions, step flow growth mode occurs even at relatively low temperature as 400°C in contrast to pure CaF$_2$. The films have cubic fluorite crystal lattice. Their lattice parameter measured using X-ray diffraction decreases linearly from 0.544 nm to 0.536 nm in the above range.

Introduction

Fluoride films grown by molecular beam epitaxy (MBE) on silicon substrates can be used for matching of lattice constant to that of materials grown above them [1]. The cubic CaF$_2$, SrF$_2$ and BaF$_2$ crystals are good insulators and lattice parameter of their solid solutions covers the range from 0.5463 to 0.620 nm. Smaller lattice parameters can be obtained in mixed Mn$_x$Ca$_{1-x}$F$_2$ crystals. Though MnF$_2$ bulk crystals have the tetragonal crystal lattice of rutile ($a = 0.486$ nm, $c = 0.328$ nm), these solid solutions have cubic fluorite lattice up to $x = 0.47$ with lattice parameter linearly decreasing to 0.5372 nm [2].

It was found recently [3] that very thin MnF$_2$ layers up to 3 molecular layers on the surface of CaF$_2$(111) can have cubic fluorite lattice. To compare their structure with that of MnF$_2$ and CaF$_2$ solid solutions we grew the solution films on Si(111) substrates by means of MBE. We measured their lattice parameters using X-ray diffraction (XRD) and surface morphology using atomic force microscopy (AFM). As a prospective, manganese compound films may have magnetic properties attractive for micro-electronics.

Film growth

The structures were grown at the Ioffe Physico-Technical Institute. After standard chemical cleaning, silicon substrates were loaded into the MBE chamber and cleaned thermally at 1250°C in ultra high vacuum. Reflection high energy electron diffraction (RHEED) images from the Si(111) surface below 830°C showed a clear 7 × 7 superstructure. Because of molecular mode of sublimation of the fluorides, the stoichiometry of the film is kept automatically, so CaF$_2$ was deposited from one source, MnF$_2$ from the other one.

Oscillations of RHEED specular beam intensity were used to monitor the fluoride growth, Fig. 1, which was carried out in 3 stages: (1) CaF$_2$ 7 monolayers (ML) at 700°C to form well ordered interface, then at 400°C (2) CaF$_2$ several ML and (3) CaF$_2$ and MnF$_2$ from the two sources up to the thickness of 300 nm. The change of the oscillation period from (a) to (b), Fig. 1, indicates the mixture composition, which is presented in the table.

The composition of the layers was determined independently by standard electron microprobe analysis (EMA) using Camebax system. In several samples, Rutherford back
Table 1. Structural parameters of the films with different MnF$_2$ content determined by RHEED, EMA and RBS. All lattice parameters are percents of normalized deviation from respective parameter of silicon: $(a_{\text{film}} - a_{\text{Si}})/a_{\text{Si}}$. 

<table>
<thead>
<tr>
<th>MnF$_2$ content (%)</th>
<th>Parameters</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>RHEED</td>
<td>EMA</td>
</tr>
<tr>
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<td>0</td>
</tr>
<tr>
<td>750</td>
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<td>784</td>
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<td>42</td>
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<tr>
<td>778</td>
<td>50</td>
<td>43</td>
</tr>
</tbody>
</table>

Fig. 1. RHEED intensity oscillations during the deposition of: (a) 8 monolayers of CaF$_2$, (b) Mn$_{0.34}$Ca$_{0.66}$F$_2$. Electron energy 15 keV, beam azimuth [110].

Fig. 2. RBS spectrum from Mn$_{0.4}$Ca$_{0.6}$F$_2$ film 300 nm thick in random scattering geometry. The energy of incident 4He$^+$ ions is 2 MeV.

Fig. 3. AFM image of the surface of Mn$_{0.4}$Ca$_{0.6}$F$_2$ film 300 nm thick. Tapping mode, resonance frequency 512 kHz.
scattering (RBS) measurements with 2 MeV 4He$^+$ ions were carried out at the University of Bordeaux. A random RBS spectrum is shown in Fig. 2. It allows determination of MnF$_2$ content and indicates also that the distribution of Mn is uniform through the depth of the film. The values of MnF$_2$ content measured by different methods are quite close, see the table, their deviation can be regarded as the errorbar.

We found that during the growth of the solid solutions in the range of 10% to 40% of MnF$_2$ content, the growth mode was different from that of pure CaF$_2$ at 400°C. In the latter case, the surface became rough with 30 nm high hills on a 300 nm film, RHEED image consisted of transmission spots. In the former case, the RHEED image during the whole MBE process contained only two dimensional reflections from (111) face of cubic fluorite lattice. AFM images from these structures showed that step flow growth mode occured, Fig. 3. The large width of the single layer terraces indicates larger migration length of the molecules of the both fluorides here with respect to that in the case of CaF$_2$. Similar behaviour was observed also during MBE of CaF$_2$ and MgF$_2$ solid solutions [4]. This means that the presence of MgF$_2$ or MnF$_2$ molecules inhibits nucleation of two dimensional islands. (Molecular surface migration is known for ionic compounds [5].)

**Lattice parameters**

Lattice parameters of the solid solutions were measured by XRD using a double-crystal two-circle diffractometer with CuKα radiation. The curves, Fig. 4, are θ − 2θ scans (Bragg scans) across 531 reflections, one at the incident grazing angle, the other at the diffracted grazing angle. In this geometry, both normal (a$^{531}_{\text{nor}}$) and lateral (a$^{531}_{\text{lateral}}$) lattice parameters can be calculated from the measured positions of the peaks. The normal lattice parameter can be obtained also from θ − 2θ scans across symmetric 111 Bragg reflection (a$_{\text{nor}}^{111}$). These parameters normalized with reference to silicon (a$_{\text{Si}} = 0.543$ nm) are presented in the table. The agreement between the values of the normal parameter obtained from different reflections confirms the selfconsistency of the measurement. In the curves of the sample with 10% MnF$_2$, the peaks from the film and the substrate overlap, thus only normal lattice parameter could be measured.

The difference between the normal and lateral parameters is due to the thermal strain of the films [6]. During cooling of the samples from 400°C to room temperature thermal shrinking of the fluoride crystal is −0.7% because of larger thermal expansion of the fluoride with respect to silicon [7]. Assuming the Poisson ratio for the solid solutions to be the same as for CaF$_2$ (p = 0.96), we can calculate their lattice constants for free crystal,

![Fig. 4. θ − 2θ scans across 531 reflection in XRD of Mn$_{0.34}$Ca$_{0.66}$F$_2$ film: (a) grazing diffraction, (b) grazing incidence.](image)

![Fig. 5. Lattice parameter versus the composition of CaF$_2$ and MnF$_2$ solid solutions.](image)
\[ a_{\text{film}} = \left( a_{\text{nor}} + pa_{\text{lat}} \right)/(1 + p) \], see the table. The value of residual planar strain in the films lies in the range between -0.2% and -0.4%. Assuming that it does not fall out of this range also for the sample with 10% MnF₂, we calculated its lattice constant also.

The dependence of the lattice constant of the solid solution films is plotted in Fig. 5. The solid line is the dependence obtained for bulk crystals [2]. The both dependences are close to each other, however in all the films, the lattice constant is smaller than in the bulk. Part of this difference may be due to changes of elastic properties of the crystal with admixture of MnF₂. The other possible reason may be the presence of vacancies which are practically always formed during MBE [8]. Extrapolation of the obtained dependence to \( x = 1 \) gives the lattice constant of cubic MnF₂ 0.527 nm. This value is very close to 0.528 nm extrapolated from XRD measurements of cubic MnF₂ existing at pressure 20 to 50 kbar above 300°C [9], to 1 bar and room temperature.

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References