Luminescence spectra and structure of novel MnF$_2$ heterostructures

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Abstract

Cathodo- and photoluminescence of MnF$_2$ thin epitaxial layers and MnF$_2$–CaF$_2$ superlattices on Si(1 1 1) has been studied at low temperatures. A blue shift of the main Mn$^{2+}$ broad band in MnF$_2$ films thinner than three monolayers is revealed. The shift is likely to be due to the change of the crystal structure from the tetragonal rutile-type characteristic of bulk crystals and thick layers to the cubic fluorite-type structure, as measured by RHEED and EXAFS.

Keywords: MnF$_2$ epitaxial layers; Cathodoluminescence; Photoluminescence; Structural transition

1. Introduction

The luminescence of MnF$_2$ bulk crystals at low temperatures is currently well understood [1–3]. A sharp and relatively weak exciton line E1 (18 419 cm$^{-1}$) was observed resulting from the magnetic dipole pure electronic transitions between the lowest excited $^4T_{1g}(^4G)$ and the $^6A_{1g}(^6S)$ ground states. A broader and stronger band owing to electric dipole exciton-magnon transitions and shifted to longer wavelengths was identified. This magnon sideband is a specific feature of antiferromagnetic ordering observed in bulk MnF$_2$ at low temperatures. A similar fine structure induced by different isoelectronic impurities with Mn$^{2+}$(Mg,Ca,Zn) was also recognized. Emission of these impurity excitons dominated in the spectra even for nominally pure crystals. In addition to the fine structure, a very broad band ($\approx 50$ nm) with a maximum at $\approx 575$ nm was observed. It had a characteristic shortwavelength threshold at $\approx 546$ nm and a long-wavelength tail extending over 650 nm. The broad band was attributed to the phonon (or, possibly, phonon plus magnon) assisted transitions [3].

In spite of the fact that the luminescence of bulk MnF$_2$ has been studied extensively, to our knowledge, no luminescence work has been done on MnF$_2$ epitaxial films. We have studied cathodoluminescence (CL) and photoluminescence (PL) spectra as well as their relevance to the crystal structure of MnF$_2$ epitaxial layers and MnF$_2$–CaF$_2$ superlattices (SLs) grown by molecular beam epitaxy (MBE).

2. Samples and structural studies

Manganese fluoride heterostructures have been grown on Si(1 1 1) substrates in a conventional MBE-system at the Ioffe Physico-Technical Institute. The details of sample preparation were described in Ref. [4]. Below, we report on the luminescence measurements of the following samples: (a) MnF$_2$/CaF$_2$/Si(1 1 1) double heterostructures with the MnF$_2$ layer thickness from 1 to 280 nm and (b) MnF$_2$–CaF$_2$ superlattices on Si(1 1 1), consisting of 15 periods. Each period contained 3 ML of MnF$_2$ and 10 ML of CaF$_2$ or 2 ML of MnF$_2$ and 8 ML of CaF$_2$.  

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Electron diffraction measurements (RHEED) showed that the first 3 ML of MnF$_2$ grew coherently with the pseudomorphic CaF$_2$/Si(1 1 1) heteroepitaxial substrate, inheriting the cubic crystal structure. For thicker films, RHEED indicated the tetragonal rutile-type structure [5]. The SL crystal structure was characterized by a X-ray crystal truncation rod (CTR) scattering which revealed well-pronounced superstructure reflections, indicating a good crystalline quality of the SLs.

The EXAFS analysis showed that in thin MnF$_2$ layers (≤ 3 ML), the fluorite structure, which does not exist under normal conditions, prevailed over the rutile structure, and the content ratio of the two components strongly depended on the thickness of the MnF$_2$ layer. Therefore, thin MnF$_2$ layers coherently grow in the fluorite structure on CaF$_2$ and the structure changes to the rutile one with increasing layer thickness.

3. Cathodo- and photoluminescence

The CL setup used consisted of a modified commercial scanning electron microscope (JEOL JSM-6400) including a continuous flow He cryostat. The typical exciting electron beam energy was 5 keV. To avoid undesirable damage of the structures by the beam, the beam current was maintained below 6 nA in most experiments and the beam was scanned to cover the rectangular spot on the sample of $300 \times 225 \mu m^2$ in size. The spectra were measured using a grating polychromator equipped with a LN-cooled charge-coupled device as a detector. The typical accumulation time of the spectra was 10–100 s. No correction of the spectral response was made. The setup sensitivity was sufficient for the measurement of samples with the MnF$_2$ layer thickness of 3 ML. However, the use of a diffusion pump for pumping the microscope chamber, did not allow us to conduct reliable measurements below 30 K.

Fig. 1 shows CL spectra obtained at 30 K for the samples with 13 ML (curve a) and 3 ML (curve b) MnF$_2$ layers. The spectrum of the 13 ML thick film has an asymmetric broad band with a maximum at ~ 586 nm, a short-wavelength threshold at 545 nm and a long wavelength tail. The spectrum is very similar to the Mn$^{2+}$ broad band observed for bulk MnF$_2$. The spectrum of the 3 ML MnF$_2$ film appear to be quite different. Its maximum is shifted by ≈ 10 nm towards the shorter wavelength. The shift of the short-wavelength edge of the band is estimated as 15–20 nm. Some additional bands in the blue and green regions can also be seen.

Cathodoluminescence spectra of the SLs with 2 and 3 ML MnF$_2$ layer thickness are shown by curves a and b in Fig. 2, respectively. One can see that the positions of the band maxima are practically the same and are very close to that observed in the 3 ML MnF$_2$ film. At the same time, they differ from that of the 13 ML film (see Fig. 1a). The observed changes in the CL spectra from thin (2–3 ML) to thicker (13 ML) MnF$_2$ films correlate with the structural transition from the cubic to rutile phase in thin MnF$_2$ epitaxial layers revealed by RHEED [5] and later confirmed by EXAFS studies [6].

Photoluminescence spectra were measured at 5 and 80 K, using an Ar$^+$ laser ($\lambda = 488$ nm), a grating monochromator and a photomultiplier. The sensitivity of the PL apparatus allowed studies of relatively thick MnF$_2$ films starting from 15 to 20 ML.

Fig. 3 shows the PL spectra obtained at 5 K for MnF$_2$–CaF$_2$ superlattices of various MnF$_2$ layer thickness: (a) 2 ML, (b) 3 ML.

![Fig. 1. Normalized cathodoluminescence spectra obtained at 30 K for MnF$_2$ epitaxial films of various thickness: (a) 13 ML, (b) 3 ML.](image1)

![Fig. 2. Normalized CL spectra obtained at 30 K for MnF$_2$–CaF$_2$ superlattices of various MnF$_2$ layer thickness: (a) 2 ML, (b) 3 ML.](image2)
wavelength (\(\sim 575 \text{ nm}\)) for the starting material and thick films. The band is broadened and its maximum is shifted by \(\sim 10 \text{ nm}\) to the blue region in SL.

The short-wavelength edge of the main MnF\(_2\) band reveals a fine structure (Fig. 4). The bulk MnF\(_2\) spectra show a number of sharp lines (curve a). Two strongest lines can be identified as magnon sidebands of the excitons bound by Mg\(^{2+}\) and Ca\(^{2+}\) residual impurities [3]. We have found that the PL spectra of the films are rather different, and well-pronounced steps are recognized in them. Only one step with a threshold wavelength of 539.1 nm is seen in the spectrum of the sample grown at moderate (200°C) temperature (curve b). However, there are two steps in the sample grown at moderate (200°C) temperature (curve c). A diffuse peak at 545.5 nm is also observed. In addition, a higher energy step at \(\sim 530 \text{ nm}\) is well-pronounced in this spectrum. Having in mind the CL data described above, this feature can be attributed to the assumption that some Mn\(^{2+}\) ions in the MnF\(_2\) layers grown at moderate temperatures have a cubic environment in addition to the dominating tetragonal phase. It would be natural to attribute the only step in the film grown at a higher temperature to the rutile phase of MnF\(_2\). The observed shift to the blue region can be related to the tensile strain which is expected in this film because of the larger thermal expansion coefficient of the fluoride films, as compared with the Si substrate.

The disappearance of the sharp lines in the PL spectra is, probably, partly due to the film purification because the vapour pressure of MgF\(_2\) and CaF\(_2\) is much lower than that of MnF\(_2\) at typical working temperature of the MnF\(_2\) effusion cell. The other important effect which could smooth the lines is the broadening of the lines caused by inhomogeneous strain in the epitaxial MnF\(_2\) films.

The cathodo- and photoluminescence studies have shown a considerable difference in the spectra of films and those of bulk crystals with the rutile-type structure. The observed blue shift of the Mn\(^{2+}\) broad band in thin (\(\leq 3 \text{ ML}\)) layers correlates with their fluoride-type structure measured by RHEED and EXAFS.

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