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Substrate temperature dependence of structural and optical properties of $Zn_{0.4}Mn_{0.6}Se$ films

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Abstract

$Zn_{0.4}Mn_{0.6}Se$ thin films were grown on GaAs(100) substrates by HWE. The evolution of the crystal structure from the β-phase to the α-phase is characterized by x-ray diffraction patterns. The variation of the lattice constants for both the α-phase and the β-phase in the films is also investigated. The surface morphology is gradually roughened as the phase is changed. In the photoluminescence spectrum intra-Mn^{2+} transitions are observed and found to be substrate temperature dependent.

1. Introduction

Recently, magnetic semiconductors have attracted considerable interest due to the potential to create new classes of spin dependent electronic devices [1, 2]. $Zn_{1-x}Mn_xSe$ is well known diluted magnetic semiconductors (DMS), in which the Zn^{2+} cations of the host crystal are replaced with Mn^{2+} ions. In the DMS, the energy bandgap can be controlled by the composition of the transitional metal ions like other ternary alloys and several interesting characteristics such as magnetic, optical, and transport properties due to the sp–d interaction have been reported [3].

The crystal structure of bulk $Zn_{1-x}Mn_xSe$ is a zincblende type (β-phase) structure in the range of the Mn composition for $x < 0.35$ and a wurtzite (γ-phase) structure for $0.35 < x < 0.57$. At values of x beyond these ranges mixed phases occur. In general, bulk MnSe has a NaCl type (α-phase) structure [4]. ZnMnSe epilayers with metastable β-phase over the $x > 0.6$ composition range have been grown by molecular beam epitaxy and hot-wall epitaxy (HWE) [5, 6]. Phase transformations in semiconductor materials have been studied exhaustively, both theoretically and experimentally under pressure [7, 8]. In addition,

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some studies have reported that the crystal structure depends on the substrate orientation and the growth conditions [9, 10].

In this study, we report the HWE growth of $Zn_{0.4}Mn_{0.6}Se$ thin films on (100) GaAs substrates and discuss the dependence of the crystallographic properties on the substrate temperature. The optical properties of these films also were investigated by photoluminescence (PL) measurements.

2. Experimental details

$Zn_{0.4}Mn_{0.6}Se$ films were grown on GaAs(100) substrates by HWE. The GaAs substrates were ultrasonically cleaned by trichloroethylene, acetone, and methanol, in sequence, for 5 min each. They were then chemically etched at 50–60 °C in a $3H_2SO_4$:H_2O_2:H_2O solution for 1 min and rinsed by flushing de-ionized water. Just prior to the growth, thermal etching at 590 °C under approximately 2×10^{-7} Torr for 20 min was carried out to remove remaining impurities and oxidized layers.

5N Mn and ZnSe powder (Furuuchi Co., Japan) were used as the source materials. These were placed in different sections and heated independently. The temperature for ZnSe and Mn was controlled at 695 and 700 °C, respectively, and the substrate temperature was controlled from 240 to 400 °C. The chemical composition of the grown films was measured using energy dispersive x-ray spectrometry (EDX). The crystal structure and the surface morphology were determined by x-ray diffraction (XRD) and atomic force microscopy (AFM) (PSIA Corp. XE), respectively. PL spectra were taken using a He–Cd laser (325 nm), a 1 m monochromator, and a conventional photon-counting system.

3. Results and discussion

The Mn composition of all the grown films determined by EDX was about $x = 0.6$, indicating that the composition ratio of (Zn + Mn):Se was almost unity in all samples. The film thickness was about 1 μm.

Figure 1(a) shows the θ–2θ scan XRD spectra for several $Zn_{0.4}Mn_{0.6}Se$ films grown at different substrate temperatures. Diffraction peaks of (200) and (400) corresponding to α- and β-phase with GaAs(200) and (400) peaks were observed, indicating that $Zn_{0.4}Mn_{0.6}Se$ films with (100) crystal orientation were grown on the (100) GaAs substrate and the crystal structure of these films has a mixed phase of zincblende and rocksalt. In the films grown at low temperature, β-(400) diffraction peaks were dominant with some traces of α-(400) peaks. As the substrate temperature increased, the peaks related to β-phase became weaker, whereas the α-phase peaks became more dominant. This suggests that the crystalline structure of the grown films evolved gradually from the zincblende phase to the rocksalt phase with increasing substrate temperature and that the temperature of sample fabrication plays an important role in the phase formation of ZnMnSe films. The origins for the structural change as a function of substrate temperature have thus far not been well understood. However, ZnMnSe films with higher x composition appear to prefer the β-phase arranged on the zincblende (100) GaAs plane at low substrate temperature. As the substrate temperature increases, there seems to be a preference for the α-phase, because the Mn and Se atoms occupy the stable lattice sites due to the increase in the thermal energy for surface migration of adatoms.

The lattice constants for both the α-phase and the β-phase of $Zn_{0.4}Mn_{0.6}Se$ films were determined with each (400) diffraction peak angle of the XRD spectra, as shown in figure 1(b). With increasing substrate temperature, the value of observed lattice constants for α-phase

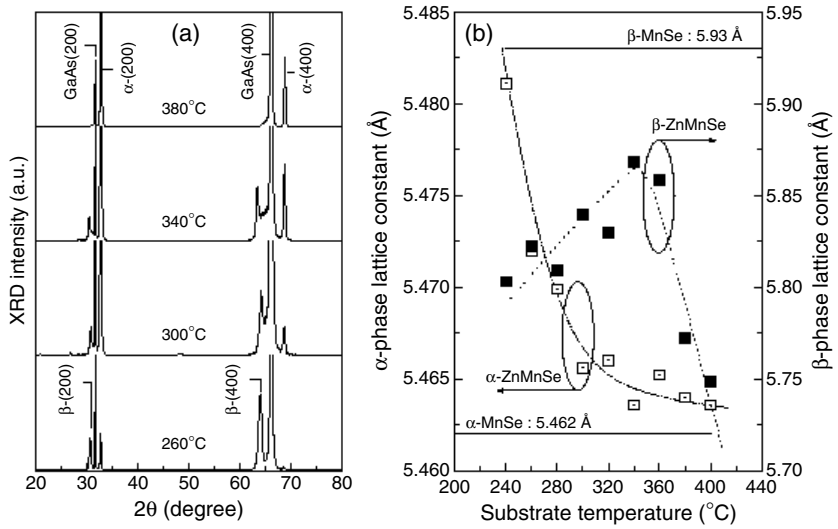

Figure 1. (a) XRD spectra of $Zn_{0.4}Mn_{0.6}Se$ films grown at 260, 300, 340, and 380 °C, and (b) the substrate temperature dependence of the lattice constants for both the α-phase and the β-phase of these films.

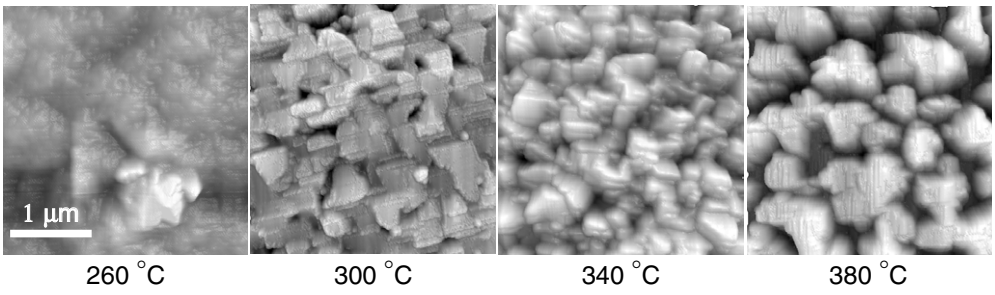

Figure 2. AFM surface morphologies for several $Zn_{0.4}Mn_{0.6}Se$ films grown at different substrate temperatures.

decreases rapidly and approaches that for bulk α-MnSe (5.462 Å [4]). Meanwhile the value for β-phase increases to that for β-MnSe (5.93 Å, [6]) up to 340 °C, followed by a decrease at higher substrate temperature. This phenomenon could be considered to result from migration of the Mn atoms preferentially to the rocksalt sites of the host crystal (stable MnSe) as the thermal energy for surface migration is increased. In addition, at temperature above 340 °C, the Zn atoms migrate selectively to the zincblende sites of the host crystal (stable ZnSe). Below 340 °C, the variation of the lattice constants for the β-phase is under investigation.

Figure 2 shows AFM surface morphologies for several $Zn_{0.4}Mn_{0.6}Se$ films grown at different substrate temperatures. The β-phase thin film grown at 260 °C displays a smooth surface. With increasing substrate temperature, the surface morphology is gradually roughened. This behaviour could be related to the structural change as a function of growth temperature.

The PL spectra at 10 K for several $Zn_{0.4}Mn_{0.6}Se$ films grown at different substrate temperature are shown in figure 3(a). Only emission peaks related to the intra-Mn^{2+} transition

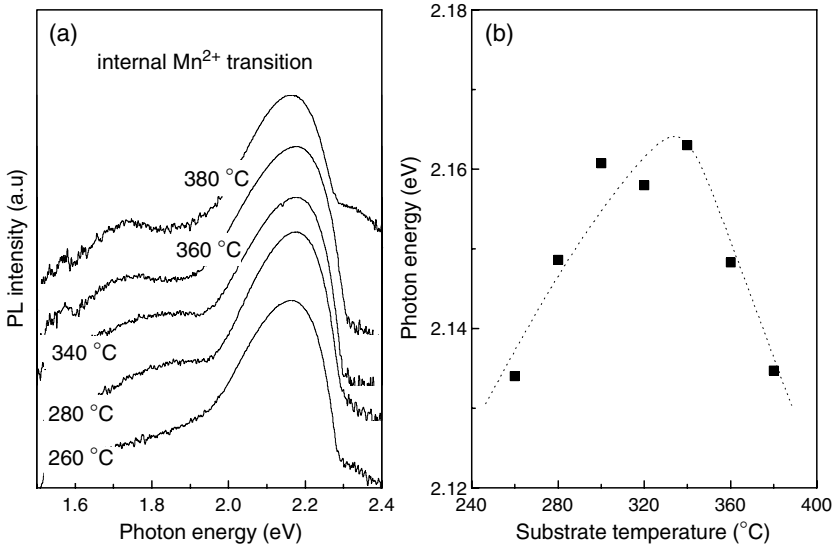

Figure 3. (a) The logarithmic PL spectra at 10 K for several $Zn_{0.4}Mn_{0.6}Se$ films grown at different substrate temperatures, and (b) the emission peak energy of the β-phase as a function of the substrate temperature.

($^4T_1 \rightarrow {}^6A_1$) are observed, and no other peaks such as near edge emission are observed in the spectra. The usual yellow emission band is observed dominantly at about 2.15 eV, which is caused by transition in the tetrahedral coordination $Mn^{2+}(3d^5)$ ions [6]. An emission peak in the octahedral coordination is revealed weakly near 1.7 eV [11], where the intensity increases with increasing substrate temperature. The emission peak energy of the β-phase as a function of the substrate temperature is shown in figure 3(b). With increasing substrate temperature, the peak energy blue-shifts up to 340 °C and then red-shifts. This is correlated with the variation of the lattice constants for the β-phase. In ZnMnSe epilayers with a zincblende structure, the intra-Mn^{2+} transition peak energy blue-shifts with an increased lattice constant [6].

4. Conclusions

$Zn_{0.4}Mn_{0.6}Se$ thin films with a (100) crystal orientation and a mixed phase of zincblende and rocksalt were grown on GaAs(100) substrates by HWE. The XRD spectra showed that the sample structure was changed from β-phase to α-phase with increasing substrate temperature. The lattice constants for α-phase approach that for bulk α-MnSe with increasing substrate temperature, while the value for β-phase increases up to 340 °C followed by a decrease at higher substrate temperature. This variation is explained by the surface migration of adatoms. The surface morphology, observed via AFM, is gradually roughened as the structure is changed. Intra-Mn^{2+} transitions in the tetrahedral and octahedral coordination at 10 K PL spectrum are observed at about 2.15 and 1.7 eV, respectively, and they are related to the phase change with increasing substrate temperature.

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