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Tunable blue and orange emissions of ZnS:Mn thin films deposited on GaN substrates by pulsed laser deposition

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ABSTRACT

ZnS:Mn thin films have been grown on GaN substrates by pulsed laser deposition, and their structures and optical properties have been investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), photoluminescence (PL), and electron paramagnetic resonance. The ZnS:Mn thin films have a cubic structure that is oriented mainly along the (1 1 1) plane. The crystal quality was optimized by varying the deposition conditions. Room temperature PL measurements with a 325 nm excitation source show that there are three emission bands located at 434 nm, 465 nm and ~600 nm. The intensity ratio of the blue emission bands (434 nm, 465 nm) to the orange (600 nm) was determined by the deposition conditions. The broad orange emission consisted of two emission bands centered at 590 and 615 nm, and it exhibited a red shift for measurement temperatures between 5 and 70 K, followed by a blue shift at temperatures up to 300 K. The tunable blue and orange dual color emissions make this material a candidate for use as a warm white lighting emitting device.

1. Introduction

II–VI semiconductors have attracted much attention due to their unique properties and applications [1]. Zinc sulfide has been studied for a variety of applications, including light-emitting diodes, electroluminescent devices, flat panel displays, optical sensors, phosphors, etc. [2]. As a compound semiconductor, ZnS is a direct wide band gap material with a band gap energy of E_g=3.7 eV [3]. Because of its large band gap, ZnS can easily host different transition metal ions as luminescent centers. Experimental results have shown that nanostructures doped with Mn^{2+} ions exhibit a prominent yellow emission, which enables their use as efficient phosphors. Mn-doped ZnS crystals have good luminescent properties and are currently of great interest for application to white LEDS and optoelectronics because of their pronounced electrical and magnetic properties [4]. Researchers have shown promising results with this class of materials [5,6], including ZnS:Mn^{2+} nanoparticles [7–11], nanowires [12], and nanoribbons [13].

Thin films are very important in the production of devices. ZnS films have been deposited by a variety of techniques, such as metal organic chemical vapor deposition (MOCVD) [14], chemical bath deposition (CBD) [15], sol–gel deposition [16], sputtering [17], radio frequency (RF) magnetron sputtering [18], molecular beam epitaxy [19], atomic layer epitaxy [20] and pulsed laser deposition (PLD) [21]. Among these techniques, PLD is widely used for its low substrate-heating requirement, ability to retain the film stoichiometry, simple setup and fast deposition rate, so it is very convenient to obtain film by using PLD in laboratory. There are reports of ZnS:Mn thin films fabricated by the PLD technique on silicon wafers [22,23], ITO-coated glass [24] and glass [25]. On the hand, the widely used white GaN-based LED is by the method of encapsulation with $Y_3Al_5O_{12}$:Ce, Gd (YAG:Ce, Gd) phosphors. As Mn-doped ZnS exhibits a strong yellow emission, it is a good candidate of phosphors in LED. The ZnS:Mn films deposited on GaN substrates have blue and orange dual color emissions and can be used as a white light emitting device.

Till now, there are no reports on the optical and morphological properties of ZnS:Mn films deposited on GaN substrates, therefore, in this study, high quality ZnS:Mn films were deposited on GaN substrates by the PLD method, and the effects of the deposition and annealing temperatures on the optical properties of these ZnS:Mn thin films were investigated. Our results show that the blue and orange dual color emissions can be tuned by changing the deposition and annealing temperatures. The orange emission at approximately 600 nm consists of two emission bands at 590 nm and 615 nm, for which the peak positions are fixed but the intensity ratio of the emission at 590 nm to the emission at 615 changes with the temperature.

2. Experimental

In the present work, ZnS:Mn films were deposited on GaN substrates by ablating a stoichiometric home-made target using

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the pulsed laser deposition technique. The Mn doping concentration in the prepared ZnS:Mn target was 2%. The thin films were deposited with a KrF excimer laser (Coherent COMPexPro 200) operating at 248 nm. The laser energy used to ablate the target was 320 mJ, with a repetition rate of 5 Hz. The vacuum chamber was evacuated by a turbo-molecular pump to a base pressure of 5.0×10^{-4} Pa and filled with Ar gas at a flow rate of 10 sccm. ZnS:Mn thin films were deposited on GaN substrates at room temperature (named #A1), 300 °C (#A2) and 500 °C (#A3) under an annealing treatment at a temperature of 500 °C for 1 h. The samples deposited at room temperature were unannealed (#B1) and annealed at 300 °C (#B2) and 500 °C (#A1). The deposition time and annealing time were 30 min and 60 min, respectively. The substrate was installed at a distance of 40 mm from the target surface. After deposition, the samples were allowed to cool to room temperature.

Various measurement tools were utilized throughout the experimental procedure. Structural characterization of the thin films was carried out using X-ray diffraction (Shimadzu XRD-7000). Morphological analyses were performed using a FESEM (Hitachi S-4800). PL spectra of the films were recorded at an excitation wavelength of 325 nm using a He–Cd laser photoluminescence spectrometer (Edinburgh EPL-375).

3. Results and discussion

3.1. Structure characterization and morphology

Typical X-ray diffraction (XRD) patterns for ZnS:Mn films deposited at different deposition temperatures and annealing temperatures are shown in Fig. 1. Fig. 1a shows the XRD patterns of ZnS:Mn thin films deposited at room temperature (#A1), 300 °C (#A2) and 500 °C (#A3), with an annealing treatment at 500 °C for 1 h. Fig. 1b shows the XRD patterns for films deposited at room temperature: unannealed (#B1), annealed at 300 °C (#B2) and 500 °C (#A1) for 1 h. All ZnS:Mn thin films exhibited a clear peak at $2\theta = 28.4°$, which arises from the (1 1 1) plane of the zinc-blende structure, indicating that all films were highly oriented along the ⟨1 1 1⟩ direction. The full width at half maximum (FWHM) can be used to evaluate the crystallinity, where smaller FWHM values correspond to higher crystallinity of the film. As shown in Fig. 1, the crystallinity increases at higher deposition and annealing temperatures. Furthermore, the crystallite (grain) sizes (D) can be calculated from the FWHM of the most intense broadening of the (1 1 1) XRD peak to determine the crystal quality using Scherrer's formula

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos(\theta_{hkl})} \quad (1)$$

where D is the crystallite size, λ is the wavelength of the X-ray, β_{hkl} is the FWHM of the diffraction peak at (1 1 1) in radians, and θ_{hkl} corresponds to the Bragg angle. The structural parameters of the ZnS:Mn thin films deposited on GaN substrates are shown in Table 1. The crystallite size (D) increased from 36.3 nm to 45.5 nm when the deposition temperature increased from room temperature to 300 °C and increased further to 47.1 nm at a deposition temperature of 500 °C. The first three rows of Table 1 show that the annealing temperature greatly affects the crystallinity of the ZnS:Mn thin film, with higher annealing temperatures corresponding to increasing crystallinity.

The morphologies of the ZnS:Mn films on GaN substrates were investigated by SEM and FESEM measurements, as shown in Fig. 2. Fig. 2 shows FESEM images of the prepared samples: (a) image of #A1 (RT, 500 °C), (b) image of #A2 (300 °C, 500 °C), (c) image of #A3 (500 °C, 500 °C), (d) image of #B1 (RT, RT), (e) image of #B2 (RT, 300 °C), and (f) cross-sectional FESEM images of sample #A3. The film thickness of the ZnS:Mn film prepared at a substrate temperature of 500 °C was estimated to be approximately 500 nm from the cross-sectional FESEM images, as shown in Fig. 2 (f). The film morphology was found to be continuous and dense, and the surface was composed of larger grains for the films deposited or annealed at higher temperatures; this finding is consistent with the results of the XRD analysis. The improvement in morphology is caused by the migration of the sputtered atoms, which forms a denser film with larger grains.

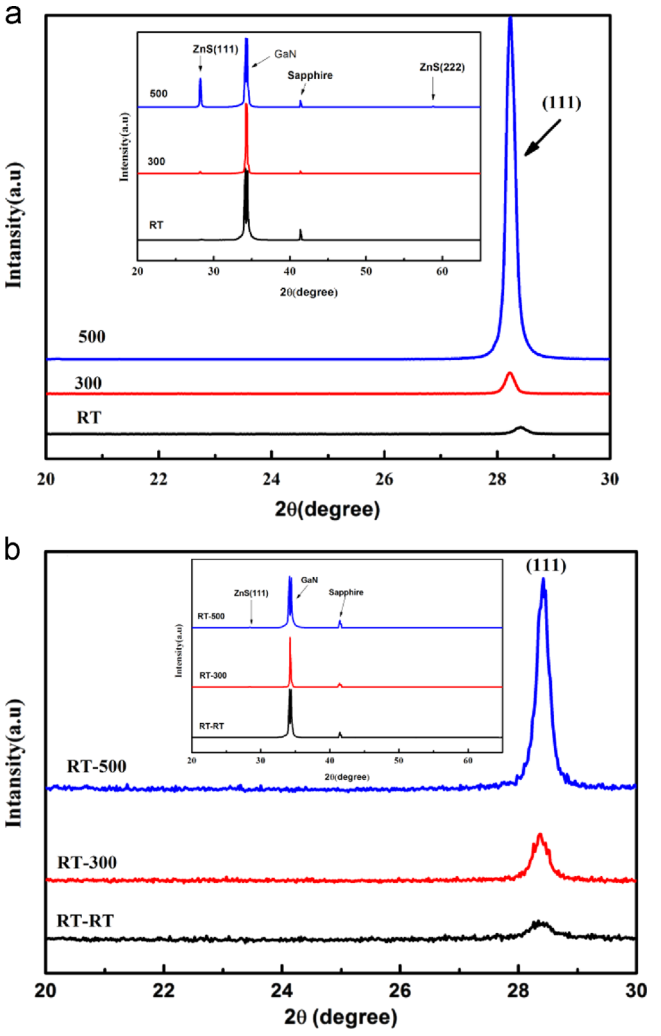

Fig. 1. XRD patterns of ZnS:Mn thin films deposited on GaN substrates: (a) patterns of three samples at different deposition temperatures: #A1 (RT), #A2 (300 °C), #A3 (500 °C) all annealed at a temperature of 500 °C for 1 h and (b) patterns of three samples deposited at room temperature and annealed at different temperatures for 1 h: #B1(RT), #B2 (300 °C), #A1 (500 °C). Inset in each figure is the XRD patterns with θ changing from 20° to 70°.

Table 1
Structure parameters of zinc-blende ZnS:Mn thin films deposited on GaN wafers.

Sample	Preferred orientation	FWHM(°)	Size D
RT-unannealed	(1 1 1)	0.365	24.7
RT-300	(1 1 1)	0.291	31
RT-500	(1 1 1)	0.25	36.3
300–500	(1 1 1)	0.198	45.5
500–500	(1 1 1)	0.192	47.1