White Light Emission from ZnS:Mn Thin Films Deposited on GaN Substrates by Pulsed Laser Deposition *

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(Received 19 April 2016)

ZnS:Mn thin films are grown on GaN substrates by pulsed laser deposition. The structure, morphology and optical properties are investigated by x-ray diffraction, scanning electron microscopy and photoluminescence (PL). The obtained ZnS:Mn thin films are grown in preferred orientation along β-ZnS (111) direction corresponding to crystalline structure of cubic phase. The deposition temperature has an obvious effect on the structure, surface morphology and optical properties of ZnS:Mn thin films. PL measurements show that there are two emission bands located at 440 nm and 595 nm when the films are deposited at temperatures from 100°C to 500°C. The relative integrated intensity of the blue emission and orange-red emission is determined by the deposition conditions. At the proper deposition temperature of 300°C, the color coordinate is closest to (0.33, 0.33). The ZnS:Mn films on GaN substrates can exhibit white light emission.

PACS: 68.55.−a, 78.55.Et, 78.67.Pt DOI: 10.1088/0256-307X/33/7/076802

Zinc sulfide (ZnS), as an important semiconductor optical material of II–VI compounds, with a wide band gap of 3.7 eV, has attracted much attention due to its unique properties and applications.[1−3] It has been extensively used in light emitting devices, electroluminescent devices, semiconductor lasers, flat panel displays, optical sensors, phosphors, solar cell window layers, and so on.[4−8] Due to its large band gap, ZnS can easily host different transition metal ions as luminescent centers.[9] Mn-doped ZnS nanostructures exhibit a prominent orange-red emission, which can be used as efficient phosphors. Recently, Mn-doped ZnS has aroused great interests for its applications in displays, white LEDs, optoelectronic devices and lasers due to its excellent optical and electrical properties.[10−13] Many approaches have been explored for preparation of ZnS:Mn thin films, including metal organic chemical vapor deposition (MOCVD),[14] rf magnetron sputtering,[15] molecular beam epitaxy (MBE),[16] chemical bath deposition (CBD),[17] and pulsed laser deposition (PLD).[18] Among these techniques, PLD is widely used for its ability to retain the film stoichiometry, fast deposition rate and simple substrate-heating setup. There are many reports on ZnS:Mn thin films fabricated by the PLD method on Si,[19] GaAs[20] and glass substrates,[21] while there are nearly no reports on the ZnS:Mn films deposited on GaN substrates. Due to its good light emission properties, GaN is one of the most promising candidates for the deposition of ZnS:Mn films. ZnS:Mn exhibits a strong orange-red emission, and GaN exhibits a strong blue emission. Their combination may be very interesting. The ZnS:Mn films deposited on GaN substrates have blue and orange-red dual color emissions, which can be used as a white light emitting device.

In this Letter, high quality ZnS:Mn films are deposited on GaN substrates by the PLD technique. The structure, surface morphology and optical properties as a function of deposition temperature are investigated. White light emission can be obtained by combining the orange-red light and blue light at proper deposition temperatures. This offers a cheap route for a white LED, which is significant for display technology.

For our experiments, the substrate is Mg-doped p-GaN films with a thickness of 1 μm (from the Inlead Technology Corporation, Taipei), deposited on sapphire (0001) wafers by metal organic chemical vapor deposition (MOCVD). ZnS:Mn films were deposited on GaN substrates by using the PLD technique. Before the films were deposited, GaN substrates were respectively rinsed in acetone, ethanol and de-ionized water by using an ultrasonic oscillator. The ZnS:Mn films were prepared by ablating a ZnS target containing 1 wt% Mn. A KrF excimer laser (COMPexPro 201, Coherent Inc.) was employed operating with a wavelength of 248 nm. The laser energy used to ablate the target was 300 mJ, with a repetition rate of 5 Hz. The vacuum chamber was evacuated to a base pressure of 10^{-7} Pa. The distance between the target and the substrates was 5 cm. ZnS:Mn thin films were deposited on GaN substrates at room temperature, 100℃, 300℃ and 500℃, respectively. The deposition

*Supported by the Science and Technology Plan Projects of Colleges and Universities in Shandong Province under Grant No J15LN33, the Scientific Research Foundation of Binzhou University under Grant No BZXYG1512, and the Doctoral Scientific Research Foundation of Binzhou University under Grant No 2014Y15.

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time was 30 min. After deposition, the samples were cooled to room temperature. The ZnS:Mn film thicknesses of the four samples are about 415, 400, 350 and 280 nm, respectively.

The crystallinity of ZnS:Mn films was carried out by using x-ray diffraction (XRD) (Rigaku D/MAX2500V diffractometer with Cu Kα radiation). Surface morphology was characterized by using a Hitachi S-4800 Field-emission scanning electronic microscope (FE-SEM). The photoluminescence (PL) spectra were measured at an excitation wavelength of 325 nm by using a He–Cd laser photoluminescence spectrometer (CVI Melles Griot) at room temperature. The emission spectra of PL were collected with an ARS SP2557 monochromator.

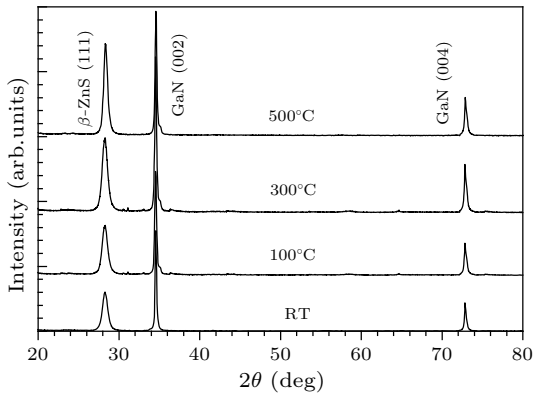

Fig. 1. XRD patterns of ZnS:Mn thin films deposited on GaN substrates at different temperatures. RT: room temperature.

Figure 1 shows the XRD patterns of ZnS:Mn films deposited on GaN substrates at different temperatures. For each of the samples, three diffraction peaks appear. The diffraction peaks at 34.1° and 72.8° correspond to (002) and (004) crystal facets of GaN, respectively. The clear diffraction peak at $2\theta = 28.4°$ corresponds to (111) plane of the zincblende structure,[9] indicating that all ZnS:Mn films are grown in preferential orientation. With the increase of the deposition temperature, the XRD peak intensity of ZnS:Mn films increases, indicating that the crystalline quality and grain size of the films are improved. The full width at half maximum (FWHM) can be used to evaluate the crystallinity, and smaller FWHM values indicate higher crystallinity of the films. Furthermore, the grain sizes can be approximately calculated from the FWHM of the β-ZnS (111) peak by using Scherrer's formula

$$D = K\lambda/\beta\cos\theta, \tag{1}$$

where D is the grain size (nm), K is the Scherrer constant (0.89), λ is the wavelength of the x-ray (0.154056 nm), β is the FWHM of the XRD peak at (111) in radians, and θ is the Bragg angle. The FWHM and grain sizes of ZnS:Mn films deposited on GaN substrates are listed in Table 1.

It can be seen that, with the increase of deposition temperature, the FWHM decreases and the grain size increases. The FWHM decreases from 0.676° to 0.528° and the grain size (D) increases from 23.1 nm to 29.5 nm when the deposition temperature increases from room temperature to 500℃. This indicates that the deposition temperature greatly affects the crystallinity of the ZnS:Mn films.

Table 1. FWHM and grain sizes of ZnS:Mn films deposited on GaN substrates.

Sample	FWHM (deg)	Size D
RT	0.676	23.1
100℃	0.661	23.6
300℃	0.588	26.5
500℃	0.528	29.5

Figure 2 shows the surface morphology of ZnS:Mn thin films grown on GaN substrates at different temperatures. With the increase of the deposition temperature, the surface morphology of the films is found to be continuous and dense. At higher deposition temperatures, the film surface is composed of larger grains. This phenomenon is in good agreement with the results obtained from XRD patterns. The improvement in surface morphology at higher temperatures is due to the accelerate migration of the sputtered atoms,[22] which forms a denser film with larger grains.

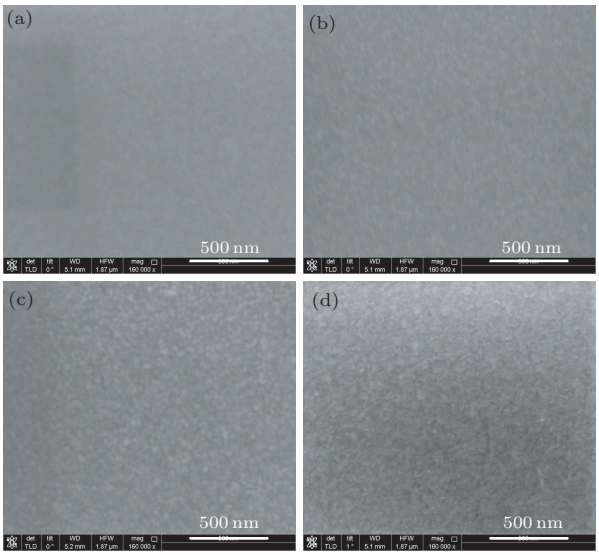

Fig. 2. Surface morphology of ZnS:Mn thin films grown on GaN substrates at different temperatures: (a) room temperature, (b) 100℃, (c) 300℃, and (d) 500℃.

Figure 3 illustrates the PL spectra of ZnS:Mn thin films grown on GaN substrates at different temperatures. It can be seen that there is only a blue emission band when the deposition is carried out at room temperature. With the increase of the deposition temperature, the orange-red light emission from ZnS:Mn appears. The blue emission at 440 nm is attributed to the combination of the sulfur vacancies from ZnS:Mn and the transition from the conduction band or shallow donors into deep Mg acceptor levels of GaN. The orange-red emission at 595 nm is assigned to the char-

acteristic $^4T_1$–$^6A_1$ transition of Mn^{2+} in ZnS, and its intensity increases with the deposition temperature. The blue emission intensity is enhanced when the deposition temperature increases from room temperature to 300℃, which may be related to the increasing sulfur vacancies and grain size. As the deposition temperature further increases to 500℃, the Mn^{2+} related emission intensity continues to increase, while the blue emission intensity decreases, due to the fact that the surface-defect state recombination is suppressed by the Mn emission. This is probably due to the fact that more Mn dopant occupies the host's vacancies, decreasing the numbers of the defect recombination.[12] In other words, a large number of Mn^{2+} ions are considered to replace the Zn^{2+} vacancies, leading to more $^4T_1$–$^6A_1$ transitions of Mn^{2+} in ZnS. Thus the intensity of blue emission related to Zn^{2+} vacancies is suppressed, and the intensity of orange-red emission related to the $^4T_1$–$^6A_1$ transition of Mn^{2+} is improved. For all of the samples, the change of the blue emission intensity indicates that the blue emission is the combination of the sulfur vacancies from ZnS:Mn and the Mg acceptor levels in GaN. The coexistence of two kinds of color (blue and orange-red) in ZnS:Mn shows that Mn impurity not only has completely doped in ZnS, but also changes the energy band structure by introducing impurity energy level.[13] On the other hand, a new energy transfer channel occurs in the Mn-doped ZnS films through the non-radiative relaxation to the $^4T_1$ excited state of Mn^{2+} ions, which can also suppress the blue emissions. In our experiment, the suppression is most obvious when the deposition temperature increases to 500℃. As the deposition temperature increases from 100℃ to 500℃, the relative (blue:red) integrated intensity ratios of the two intense, visible PL bands for ZnS:Mn/GaN are 1:0.79, 1:0.99 and 1:1.58, respectively. At the deposition temperature of 300℃, the relative (blue:red) integrated intensity ratio is 1:0.99. With the combination of the blue emission and the orange-red emission, a broad PL band (350–800 nm) is formed in the visible light region, and the ZnS:Mn/GaN composite system can exhibit intensive white light emission.

The above discussion indicates that the intensity ratio of the blue emission to the orange-red emission is influenced by the deposition temperature. In other words, the blue and orange-red dual colors can be tuned by the deposition temperature. To confirm this point, international commission on illumination (CIE) software is employed to calculate the color coordinate, as illustrated in Fig. 4. The detailed parameters for this calculation are listed in Table 2. From Fig. 4, it can be seen that the emissions of the ZnS:Mn/GaN samples can be used as a warm light source. The color coordinate of sample C is closest to $(0.33, 0.33)$ of white light. Therefore, ZnS:Mn thin films deposited on GaN substrates can emit white light, which can be used as white light LEDs.

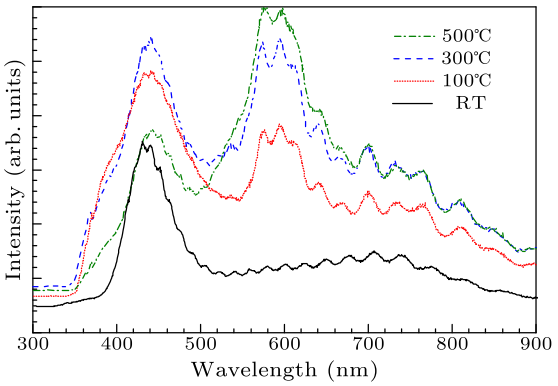

Fig. 3. PL spectra of ZnS:Mn thin films grown on GaN substrates at different temperatures.

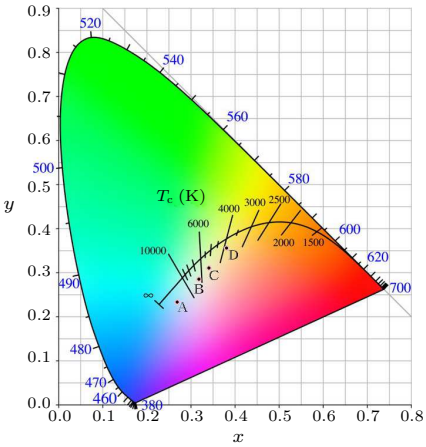

Fig. 4. Color coordinates of ZnS:Mn thin films deposited on GaN substrates at different temperatures: (A) room temperature, (B) 100℃, (C) 300℃, and (D) 500℃.

Table 2. Color coordinates and related parameters of ZnS:Mn thin films deposited on GaN substrates.

Sample	Color coordinate		Tristimulus values			Uniform color space	
	x	y	x	y	z	u'	v'
RT (A)	0.2698	0.234	51788	44932	95262	0.2523	0.4925
100℃ (B)	0.3188	0.2855	90308	80857	112077	0.2552	0.5142
300℃ (C)	0.3418	0.311	96380	87684	97903	0.2554	0.5228
500℃ (D)	0.3815	0.3559	109876	102502	75648	0.2551	0.5354

In summary, high quality ZnS:Mn thin films have been deposited on GaN substrates by the PLD method. When the deposition temperature increases, the XRD peak intensity of ZnS:Mn films increases, and the grain size increases from 23.1 nm to 29.5 nm. The deposition temperature affects not only the structure, morphology of the films but also the PL properties of ZnS:Mn thin films. The intensity ratio of

the blue emission (440 nm) to the orange-red emission (595 nm) can be tuned by varying the deposition temperature. At the proper deposition temperature of 300℃, ZnS:Mn/GaN composite can emit white light. Therefore, ZnS:Mn thin films have potential applications in optical devices and warm white light emitting devices.

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