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Photoluminescence properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films fabricated by the sol-gel deposition method

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The photoluminescence properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films fabricated by the sol-gel deposition method were studied. The Mg^{2+} content in the films was up to 0.36 and they had the ZnO wurtzite structure. The band gap of the films can be controlled between 3.40 and 3.93 eV by adjusting the Mg^{2+} proportions. Transmittance spectroscopy was used to characterize the excitonic structure of the alloys, which the excitonic character is clearly visible at room temperature. The intense ultraviolet photoluminescence was observed at room temperature. This emission is indicative of the excitonic nature of the material. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413948]

I. INTRODUCTION

There has been great interest in wide-band-gap semiconductors, because there is a strong commercial desire to produce efficient and lasing blue light emitting diodes and short-wavelength laser diodes. Now the most attention is focused on the GaN and ZnSe based materials.¹ As a member of the II–VI semiconductors, zinc-oxide (ZnO) is known to have a wide range of technological applications such as transparent conducting electrodes in solar cells and flat panel displays, surface acoustic wave devices, and chemical sensors. Recently, ZnO has become even more interesting because of the discovery of the ultraviolet (UV) lasing at room temperature.^{2–4}

To explore a material with a shorter UV emission, one of the key techniques is to dope other ions into the lattice. To obtain the high performance light emitting diodes (LED) devices, the key technique is to construct a heterojunction to realize double confinement actions for electrons and photons in optoelectronic devices. Modulation of the band gap while keeping the lattice constants similar to each other is essential for this purpose.⁵ Because the ionic radius of Mg^{2+} (0.57 Å) is similar to that of Zn^{2+} (0.60 Å), a wide range solubility of Mg in the zinc blend could have been obtained in the film.⁶ Recently, thin films of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys with larger band gaps than ZnO were obtained by pulsed laser deposition (PLD), laser ablation molecular-beam epitaxy (MBE) and rf magnetron sputtering on (0001)-sapphire substrates.^{7–9} x is up to 0.36 while keeping the ZnO hexagonal structure. The band gap can range from 3.36 to 4.00 eV. Quantum well heterostructures based on these films have achieved low-threshold stimulated emission or laser action up to room temperature.^{10,11}

Although there are many studies of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys and the heterostructures based on them, few reports focus on their photoluminescence (PL) properties. In this article the sol-gel deposition method was used to fabricate $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films and their PL properties were studied. The sol-gel

deposition technique has an advantage over other methods in that it does not require vacuum apparatus and has the potential to produce films with large areas and complicated forms on various substrates. In particular, in order to prepare thin films of compound semiconductors, the sol-gel process is known to have the distinct advantages of process simplicity, lower costs and ease of composition control.^{12,13}

II. EXPERIMENTAL PROCEDURE

The sol was composed of $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Mg}(\text{CH}_3\text{COO})_2$, and polyvinyl butyral (PVB) in ethanol solution. The total concentration of metal ions was controlled at 0.1 mol/L. The concentration of Mg^{2+} was adjusted to 0.01, 0.02, 0.04, 0.05, and 0.08 mol/L. The sols were spin coated on Si (100) and quartz substrates at 2500 r/min. After the spin coating, the substrates were first heated to 100 °C in air for 10 min to evaporate the solvent, then to 350 °C in O_2 for half an hour to eliminate the organic component in the film. This process may be repeated many times to reach the desired film thickness. After heating the sample was cut into several pieces for different experiments, then thermal annealing was performed for 1 h in an O_2 environment at 700 °C to crystallize the zinc oxide film. The infrared spectrum was measured by a BIO-RAD FTS-3000 spectrophotometer having a resolution of 4 cm^{-1} in the range 400–4000 cm^{-1} , indicating that there was not any organic component in the film above 350 °C.

The x-ray diffraction (XRD) was measured by a D/max-rA x-ray diffractometer (Rigaku) using $\text{Cu } K\alpha$ of 1.5418 Å to determine crystal structure. An UV-360 Spectrophotometer (Shimadzu) was used for the optical characterization. In photoluminescence, the excitation source was a He–Cd laser with a wavelength of 325 nm and a power of 50 mW, and the luminescence signals were detected by an UV Microlaser Raman spectrometer made in France.

III. RESULTS AND DISCUSSION

In order to determine the maximum x value in the thin film alloy with the unique ZnO wurtzite structure, the XRD

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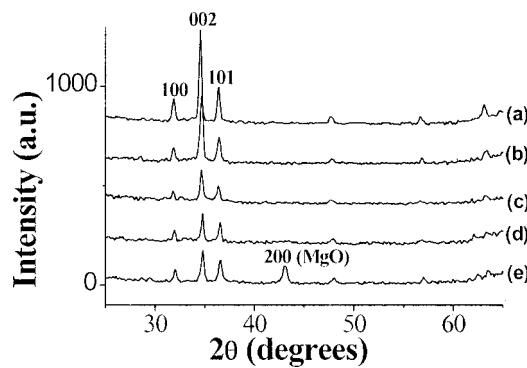


FIG. 1. XRD spectra of different $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films: (a) ZnO, (b) $x=0.05$, (c) $x=0.15$, (d) $x=0.36$, and (e) $x=0.46$.

pattern was employed. The XRD spectra of the films are shown in Fig. 1. There are three main peaks in the spectra, which belong to the (100), (002), and (101) directions of the ZnO wurtzite structure when the x value is not more than 0.36. Compared with ZnO thin films, the diffractive angle of the (002) direction is larger in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films. This result indicates that the Zn^{2+} ions are successfully substituted by Mg^{2+} ions in the ZnO lattice. Also, it can be seen that all these films are c -axis oriented and the c -axis orientation becomes weak when the Mg^{2+} content in the films increases. When the x value exceeds 0.36 an unimpurity peak located at 43° appears. It belongs to the cubic MgO structure. This result indicates that in order to keep the ZnO wurtzite structure the Mg^{2+} content in the film should not be more than 0.36.

Figure 2 shows the transmittance spectra of the films fabricated on a quartz substrate at room temperature. All the samples are high transparent in the visible region from 400 to 800 nm and have a sharp absorption band in the UV region. The excitonic nature of the films is clearly apparent in the spectra. Because the exciton binding energy is almost the same as ZnO (≈ 60 eV) in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films, the exciton peak remains present for all alloy compositions with increasing Mg concentration. By considering the exciton effect, the band gap (E_g) of these alloy films are estimated. The band gap is shown as a function of x in the inset of Fig. 2. The E_g increases almost linearly up to 3.93 eV for $0 \leq x \leq 0.36$, which indicates that the band gap can be tailor-

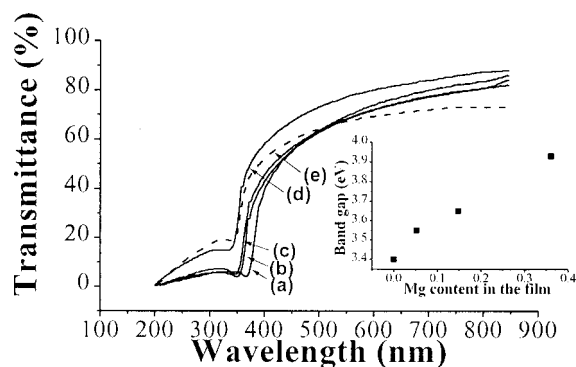


FIG. 2. Transmittance spectra of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films at room temperature: (a) ZnO, (b) $x=0.05$, (c) $x=0.15$, (d) $x=0.36$, (e) $x=0.46$ [the inset is the band gap (E_g) by considering exciton effect].

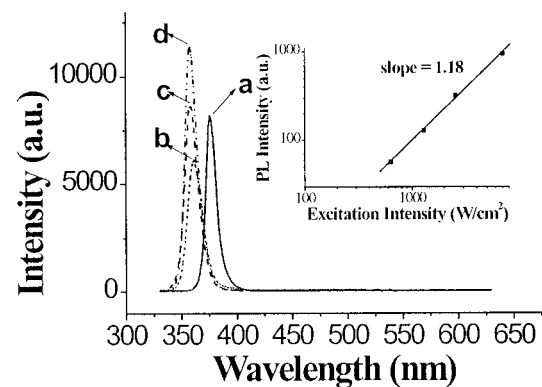


FIG. 3. Photoluminescence spectra for the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films with different Mg contents (a) ZnO, (b) $x=0.05$, (c) $x=0.15$, (d) $x=0.36$ samples at room temperature (the inset is the total photoluminescence energy as a function of excitation energy density).

made within this region. Because the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0 \leq x \leq 0.36$) alloy has the same structure as ZnO with a wider E_g , $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is a suitable material for potential barrier layers in ZnO based device and a good quality ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ heterojunction could be made.

The excitonic character of the films is also apparent in the photoluminescence spectra. The films were excited with the 325 nm line of a He-Cd laser (325 nm) and the intensity was controlled at 900 W/cm^2 . The photoluminescence spectra taken at room temperature are shown in Fig. 3 with $x=0, 0.05, 0.15$, and 0.36 . It can be seen that all the samples have only one peak located in the ultraviolet region of the spectra which originates from the excitonic near-band-gap emission. There are not any emission peaks related to Zn or O vacancy. The emission peak transfers from 3.3 to 3.46 eV as the Mg^{2+} content increases in the film. The luminescence peaks show a Stokes shift to the lower energy side of the absorption edge. This Stokes shift of the luminescence peaks is frequently observed in alloy semiconductors, where carriers feel different potentials depending on the local concentration and/or arrangement of the substituting elements. This effect is larger in ZnO than in III-V semiconductors, because the Bohr radius of excitons in ZnO is as small as 18 \AA and the excitons are therefore more sensitive to local inhomogeneity.¹⁴ The inset of Fig. 3 illustrates the integrated photoluminescence intensity as a function of excitation energy density for the $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ sample. The data are well described by a line of slope 1.18 on this logarithmic plot.

Taking into account free-exciton, bound-exciton, free-to-bound transitions, and the donor-acceptor pair recombination, the power dependence of the luminescence lines can be described by an $I \sim L^\kappa$ law, where I is the luminescence intensity and L is the excitation laser intensity, κ is a coefficient.¹⁵ For the excitation laser light with $h\nu$ exceeding the gap energy E_g , the coefficient κ is generally $1 < \kappa < 2$ for free- and bound-exciton emission. Based on this theory, our experimental data lie within this area which indicates that the photoluminescence of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film is due to the exciton transitions. Since the recombination process is excitonic, the full width at half maximum (FWHM) values of the

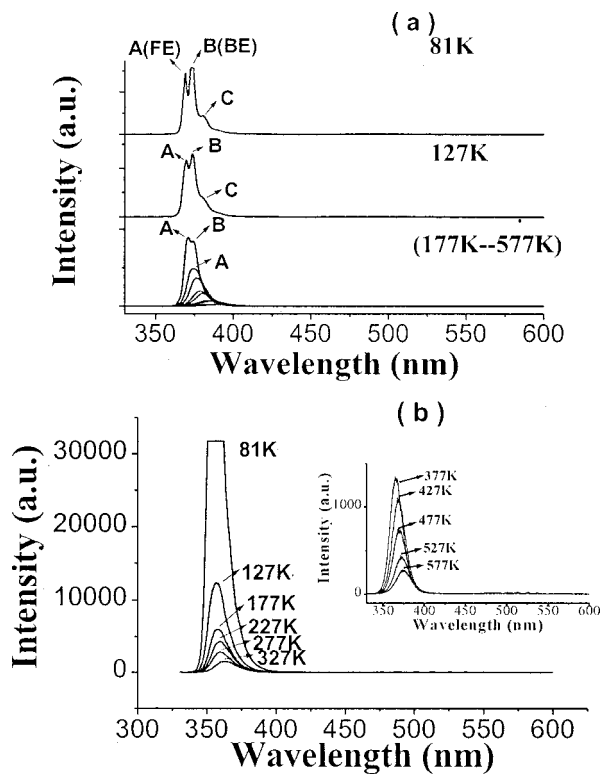


FIG. 4. PL spectra at different temperatures of (A) ZnO, (B) $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$.

spectra do not broaden dramatically with increasing Mg concentration.

The photoluminescence spectra of the $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ and ZnO samples at different temperature are shown in Figs. 4(a) and 4(b). It can be seen that the ZnO sample has three main peaks marked A, B, and C at low temperature (81 K). These peaks have been assigned to free exciton emission, excitons bound to neutral donors or acceptor transition and the phonon replicas of the free exciton, respectively. At room temperature, only the free exciton emission remains. But for the $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ sample there is only one peak in the spectra (from 80.9 K to room temperature). The exciton emission is still clearly visible when the temperature increases to 577 K. The PL intensity exponentially decreases in the higher-temperature region, mainly due to thermally activated nonradiative recombination mechanisms. This luminescence quenching is characterized by a relatively high activation energy. Comparing both of the spectra and considering the above results, we can draw the conclusion that the emission of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin film is mainly due to the free exciton transition. And the formula $I = I_0 / [1 + A \times \exp(-E_0/kT)]$ is used to calculate the free-exciton binding energy, where E_0 is the activation energy of the thermal quenching process, k_B is Boltzmann constant, I_0 is the emission intensity at 0 K, T is a thermodynamic constant and A is a constant.¹⁶ The total emission intensity (I) as a function of the temperature (K) is shown in Fig. 5. The solid line in Fig. 5 is the theoretical fit to the experimental data and we obtain $E_0 = 54.6$ meV. It is well agreement with the data of pure ZnO (59 eV).

In conclusion, the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films were obtained by sol-gel deposition method. The optical band gap

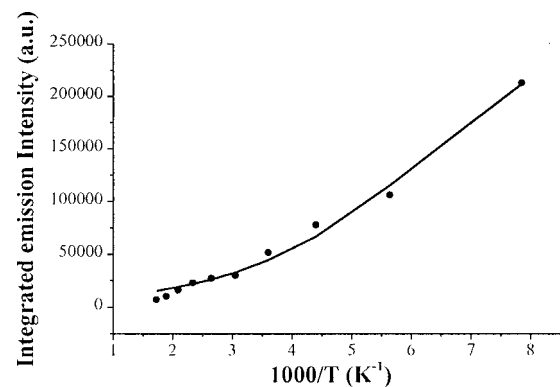


FIG. 5. Total emission intensity as a function of temperature.

could be tuned from 3.4 to 3.93 eV by adjusting the Mg content. Within this tuning range the crystal quality was sufficiently preserved to maintain the excitonic nature resulting in very efficient ultraviolet emission. The emission intensity depends on the excitation density. By comparing the photoluminescence of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with ZnO at different temperatures, we can attribute the UV emission from $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films to exciton transition. Thus, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films can be considered not only as barrier layers for the ZnO active layer, but also as an ultraviolet light emitting material.

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