

Synthesis and temperature dependent photoluminescence of $Zn_{1-x}Mg_xO$ films grown by ultrasonic spray pyrolysis

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Abstract $Zn_{1-x}Mg_xO$ films were deposited on single crystal Si (100) substrates using ultrasonic spray pyrolysis under ambient atmosphere. A strong ultraviolet near-band-edge (NBE) emission was observed in the room temperature photoluminescence (PL) measurement for all the as-grown $Zn_{1-x}Mg_xO$ films, while the deep-level emission was almost undetectable, suggesting that the obtained $Zn_{1-x}Mg_xO$ -based films are well close to stoichiometry and of optically high quality. A distinct blue-shift of NBE emission peak from 386 nm to 358 nm was observed as the Mg concentration increases from 0% to 25 %. The photoluminescence spectra as a function of temperature were also investigated to examine the emission mechanism of $Zn_{1-x}Mg_xO$ films.

Introduction

ZnO and related Zn(Mg, Cd)O material system have attracted considerable attention as an excellent candidate for the next generation of ultraviolet light emitting and lasing devices [1–3]. For fabricating a double heterostructure light emitting device using ZnO active layer, two key techniques are critical, i.e. p-type doping and

band gap engineering in semiconductors. Great progress has been made recently on the p-type doping and p–n junction device based on ZnO material in our group [4–7], indicating a bright future of ZnO based optoelectronic device with extremely low cost. For further melioration of device performances, it was necessary to tune the band gap of ZnO (~3.37 eV) to produce compounds with band gaps wider or narrower than that of ZnO alone. $Zn_{1-x}Mg_xO$ compounds can be a suitable barrier layer for carrier confinement because its band gap can be modulated by its composition in the range of 3.37–4 eV while maintaining its lattice constant close to that of ZnO [8]. More efficient exciton-related emission process can be expected from the light-emitting devices based on ZnO/ZnMgO superlattices or quantum wells structure [9]. A number of methods have been previously employed to deposit $Zn_{1-x}Mg_xO$ films [8, 10], however, the choice of dopant and growth technique remains controversial [11–13]. The ultrasonic spray pyrolysis technique has been proved to be a simple and inexpensive method [4–7]. Nevertheless, there has been no report on the fabrication and especially the temperature dependent photoluminescence (PL) properties of $Zn_{1-x}Mg_xO$ films grown with ultrasonic spray pyrolysis system, although it is important for fully understanding the emission process and thereby crucial to device applications.

In this paper, $Zn_{1-x}Mg_xO$ films were deposited on single crystal Si (100) substrate with the relatively simpler process of ultrasonic spray pyrolysis. Temperature dependent photoluminescence (PL) spectra were employed to examine the emission properties of the $Zn_{1-x}Mg_xO$ films. Success in the tenability of $Zn_{1-x}Mg_xO$ bandgap and optical emission spectra at extremely low cost as reported here will greatly increase the potential applications for this material system.

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Experiment procedure

Ultrasonic spray pyrolysis was employed to grow the designed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films on Si (100) substrates under ambient atmosphere. The detailed deposition procedures have been described elsewhere [4, 10]. The thickness of films was controlled to be approximately 300 nm. In order to control the incorporation of Mg into $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films ranging from 0% to 25%, the Zn/Mg ratio in the precursor solution was accurately adjusted correspondingly. The experiment conditions have been optimized for the enhancement of UV emission performance in photoluminescence property.

The crystalline micromorphology were characterized by field emission scanning electron microscopy (SEM) (JEOL JSM 6700F). To investigate the optical properties of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films, photoluminescence (PL) measurements were performed at room temperature by a JY Microlaser Raman spectrometer using 325 nm line of a He–Cd laser as an excitation source.

Results and discussions

SEM images show that all the samples present good thickness uniformity, smooth dense surface, no visible pores and defects over the film. No evident change was observed in grain morphologies due to the incorporation of Mg into $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films. A typical SEM micrographs of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films was illustrated in Fig. 1.

Room temperature PL spectra for $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with x ranging from 0% to 25% are shown in Fig. 2. The inset on right top corner is the selected area magnification. The intensity has been normalized to clearly demonstrate the shift of peak position with Mg content in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films.

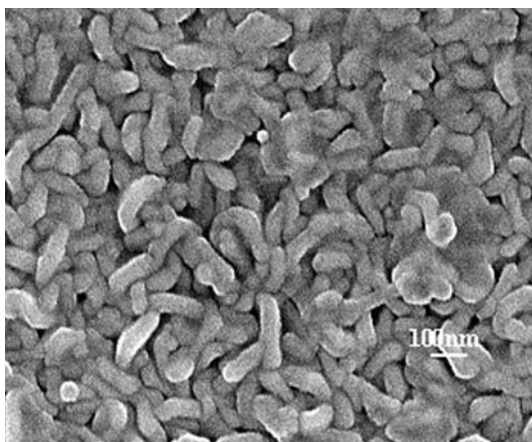


Fig. 1 A typical SEM micrographs of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ (here $x = 0.2$) films deposited on Si (100) substrate by ultrasonic spray pyrolysis

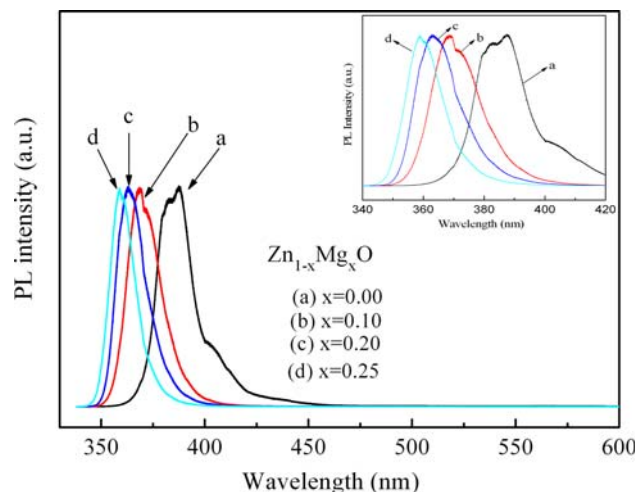


Fig. 2 Room temperature PL spectra from $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films as a function of Mg composition varying from 0% to 25%. The inset on right top corner is the selected area magnification

A strong near-band-edge (NBE) ultraviolet emission peak was observed for all the samples, which was generally considered to be originated from the radiative recombination of exciton in the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films [10, 14]. While the deep-level emission related to structural defects was almost undetectable, which indicates a very low concentration of oxygen vacancy in the ZnO based films [15–17]. It was well accepted that ZnO based films always possess some oxygen vacancy regardless of the growth technique used [8, 16, 17]. In this study, we believe that during the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films growth at atmosphere, a large amount of reactive oxygen would be available from the ambient atmosphere, which result in less intrinsic defects such as oxygen vacancies than the films deposited at high vacuum environment. Moreover, this results clearly indicate that Mg^{2+} can be incorporated into the ZnO lattice by ultrasonic spray pyrolysis due to the similarity in ionic radius between Mg^{2+} (0.71 Å) and Zn^{2+} (0.74 Å) [8]. The full width at half maximum (FWHM) of NBE emission peak was lower than 18 nm for all the samples. A distinct blue-shift of NBE emission position from 386 nm to 358 nm was observed as the Mg concentration increased from 0% to 25%. This trend of blue-shift has been observed previously in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films and was thought to be due to the augment of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ band gap caused by the incorporation of magnesium [10]. The same should be true for the case considered here. In other words, the optical emission spectra of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films can be precisely controlled between 3.21 eV and 3.46 eV in our system. Thus, the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films reported here can be considered as a suitable barrier layer for band gap engineering such as ZnO-based superlattices or quantum wells. It had been demonstrated that the PL spectra of ZnO based films

depend on the stoichiometry and microstructure of the materials [14–17]. Therefore, these results indicated that our $Zn_{1-x}Mg_xO$ films were well close to stoichiometry and of optically high quality.

In order to investigate the emission mechanism of $Zn_{1-x}Mg_xO$ films, the PL spectra from $Zn_{1-x}Mg_xO$ film were measured as a function of temperature. All the $Zn_{1-x}Mg_xO$ films (x ranging from 0% to 25%) exhibit similar behavior in the temperature dependent PL measurements. As an example, the temperature dependent PL spectra from $Zn_{0.75}Mg_{0.25}O$ film were presented in Fig. 3. Furthermore, the integrated emission intensity and full-width at half-maximum (FWHM) of NBE emission were calculated as a function of measured temperature, as shown in the inset of Fig. 3. As can be clearly seen from Fig. 3, the intensity of NBE emission decreases sharply while the FWHM of NBE emission peak increases almost linearly, with increasing temperature at all the temperature range, which was due to the thermally activated nonradiative recombination mechanisms [17, 18]. The temperature dependence of the bound excitonic emission intensity can be expressed by the equation [18]

$$I_T = I_0/[1 + A \exp(-E_A/k_B T)]$$

where E_A 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 the thermodynamic temperature, and A is the constant. However, due to the insufficient number of data, in particular at high temperature where the peaks are hardly resolved, we did not carry out the fitting. Similar performance had been carried out in the literature [18]. It

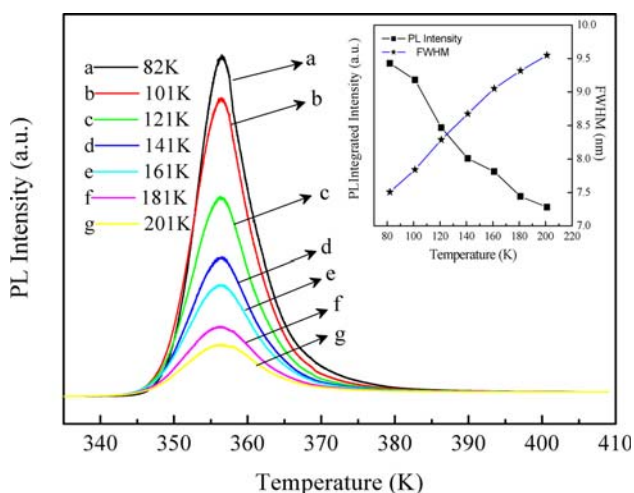


Fig. 3 PL spectra from $Zn_{0.75}Mg_{0.25}O$ thin films as a function of measured temperature. The inset was integrated emission intensity and full-width at half-maximum (FWHM) of NBE peak energy from $Zn_{0.75}Mg_{0.25}O$ film as a function of temperature

may be strange that no significant shift in NBE emission energy was observed. This result was not in agreement with those reported in literatures for bulk and epitaxial thin films [19, 20]. Thus, the exact origin and mechanism for the obtained PL emission have to be verified by further research.

Conclusions

In summary, $Zn_{1-x}Mg_xO$ films with x ranging from 0% to 25% were deposited on single crystal Si (100) substrate using ultrasonic spray pyrolysis under ambient atmosphere. A strong ultraviolet NBE emission was observed in the room temperature photoluminescence (PL) measurement for all the as-grown $Zn_{1-x}Mg_xO$ films, while the deep-level emission was almost undetectable, which indicate that the obtained $Zn_{1-x}Mg_xO$ films are well close to stoichiometry and of optically high quality. A distinct blue-shift of NBE emission peak from 386 nm to 358 nm was observed as the Mg concentration increased from 0% to 25%. In the temperature dependent PL spectra, the intensity of NBE emission decreases sharply with increasing temperature due to the thermally activated nonradiative recombination mechanisms.

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