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Room temperature UV emission of $Mg_xZn_{1-x}O$ films[☆]

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Abstract

II–VI wide band-gap semiconductor ternary $Mg_xZn_{1-x}O$ nanocrystalline films have been successfully formed on conductive glass from ZnO powder by electrophoresis deposition (EDP). In comparison with ZnO powder, the $Mg_xZn_{1-x}O$ films presented a more preferential crystalline orientation. Room temperature (RT) PL spectra of $Mg_xZn_{1-x}O$ films revealed a stronger band-edge ultraviolet (UV) emission and a narrower FWMH of 13 nm than that of ZnO powder. The UV emission peak of $Mg_xZn_{1-x}O$ film is located at the range of 375–381 nm with a small blue shift from that of ZnO powder. In addition, the ratio of PL peak intensity of band-edge emission to the deep-level emission in $Mg_xZn_{1-x}O$ films reached as high as 135:1 while compared with 23:1 of ZnO powder under the same He–Cd laser excitation level. Consequently, these electrophoretic deposition (EPD) $Mg_xZn_{1-x}O$ films exhibited a good quality for excitonic emission at RT. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, much attention has been given to II–VI semiconductor oxide ZnO and its ternary alloys. As an analogous material to GaN, ZnO has wurtzite crystal structure and direct wide bandgap. The room temperature (RT) bandgap of ZnO is 3.3 eV with emission in UV region. An outstanding feature of ZnO is its large excitonic binding energy of 60 meV leading to the existence and extreme stability of excitons at RT and/or even higher temperatures [1–4]. There have already been some reports about the excitonic lasing in high quality epitaxial ZnO films and ZnO nanocrystalline powder (known as random laser) under optical pumping at RT [5–10]. By alloying with MgO, the bandgap of the ternary alloys $Mg_xZn_{1-x}O$ could be tuned from 3.3 to 4 eV [11], which is available to form heterostructures with ZnO. Currently, stimulation emission induced by exciton–exciton scattering has been observed in $ZnO/Mg_xZn_{1-x}O$ multiquantum wells at up to RT [12]. Therefore, it makes ZnO-based compounds an excellent material system with potential applications for exciton-related photonic devices in the ultraviolet (UV) region.

A variety of deposition techniques have been employed to prepare ZnO films such as sputtering [13], pulsed laser deposition (PLD) [14], plasma-assisted molecule beam epitaxy (P-MBE) [15], laser-MBE [16] etc. Chemical method is attractive as it is simple, flexible and therefore economic with no special equipment needed. Electrophoretic deposition (EPD) has been widely used to deposit particles in the micron size range. It has also been adopted to deposit ZnO films [10,17–19]. Wong and Searson [18] reported the formation of ZnO particles by EPD. However, the intensity of the band-to-band emission was weak compared to the visible emission in their EPD films. Hence, the ratio R of emission intensity of near-band-edge (NBE) to that of the defect level (DL) ($R = I_{NBE}/I_{DL}$) from

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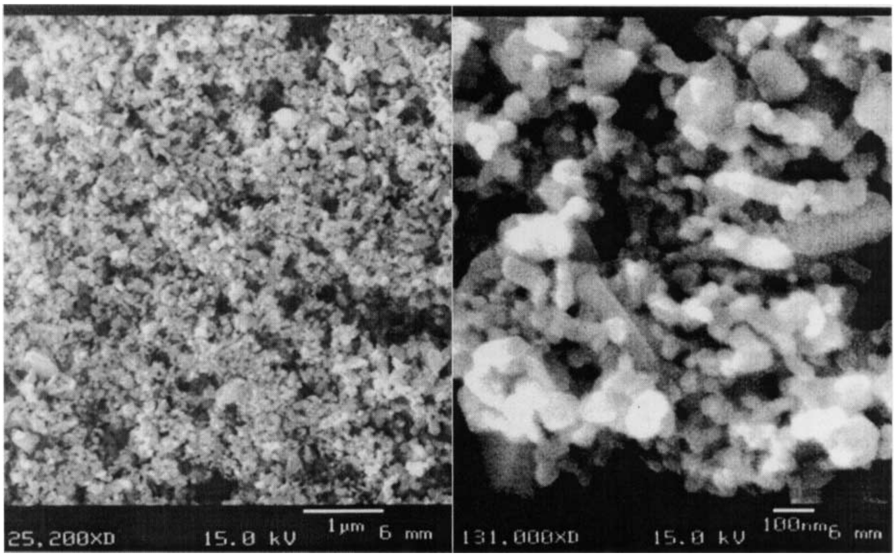

Fig. 1. SEM images of polycrystalline $Mg_xZn_{1-x}O$ film A (left: with low magnification; right: with high magnification).

their sample was as low as 1:2.1–1:2.3. In this communication, we report the fabrication of polycrystalline $Mg_xZn_{1-x}O$ films on conductive glass substrates by the EPD using ZnO powder. Structural and optical studies show that the $Mg_xZn_{1-x}O$ films with various small x values could be obtained from EPD. The film exhibiting higher emission ratio of R could be obtained from EPD. The band-edge emission indicated a strong excitonic photoluminescence with 13 nm of full-width of half maximum (FWHM).

2. Preparation of $Mg_xZn_{1-x}O$ films

In our experiments, the $Mg_xZn_{1-x}O$ films were fabricated from high purity ZnO nanocrystalline powder by EPD [17]. The substrate used in this experiment was conductive glass coated by F-doped SnO_2 film with sheet resistance of about 9.8 Ω. First, about 1.5 g/l ZnO powder and $Mg(NO_3)_2{\cdot}6H_2O$ were put into $O(CH_2CH_2OH)_2$. The mixture was then stirred well for 24 h to disperse the ZnO particles from their clusters and also mixed uniformly in the colloidal suspension. The concentration of the magnesium salt $Mg(NO_3)_2{\cdot}6H_2O$ was in the range of 10^{-4}–10^{-3} M/l. In this case, Mg^{2+} was provided by $Mg(NO_3)_2{\cdot}6H_2O$ and it was absorbed by the surface of the ZnO particles. The ZnO nanoparticles were, therefore, positively charged. A small piece of high purity graphite plate (2 × 10 × 20 mm) was chosen as an anode, while the conductive glass substrate that simultaneously served as a cathode was placed parallel to the anode. The distance between the two electrodes was about 1.5 cm. Depending on the concentration of magnesium compound and therefore the conductivity of the mixture, the voltage and current were in the range of about 140–160 V and 6–8 mA, respectively. During electrophoresis, a constant current was maintained. After about 10 min deposition and annealing at 450°C for 15 min in atmosphere in sequence, the $Mg_xZn_{1-x}O$ films with different x values less than 0.1 were obtained from different batches with various concentration of $Mg(NO_3)_2{\cdot}6H_2O$. After annealing, the color of the films turned into slightly white and semitransparent. The thickness of the films was about 2–3 µm determined from the cross section of the film by microscope. In our experiments, three pieces of $Mg_xZn_{1-x}O$ films A, B, C were fabricated with $Mg(NO_3)_2{\cdot}6H_2O$ concentrations of 5×10^{-3}, 6×10^{-3}, 7.5×10^{-3} M/l in solutions, respectively.

3. Morphology and structure of $Mg_xZn_{1-x}O$ films

The morphology of high purity ZnO powder, which was used for depositing $Mg_xZn_{1-x}O$ films, was analyzed by Hitachi H-9000NAR high resolution transmission electron microscope (TEM). The TEM image revealed that the powder contained nano-ZnO grains mostly indicating a regular hexagonal single crystalline structure. It was found from the TEM images that most of these ZnO particles oriented to [100] and [002]. The size of these dispersed ZnO particles was between 50 and 180 nm.

The morphology of $Mg_xZn_{1-x}O$ film A was observed by field emission scanning electron microscope (SEM). Fig. 1 shows the SEM secondary electron images of the $Mg_xZn_{1-x}O$ film A at low and high magnification, respectively. Apparently, the nano-particles assembled onto the substrate and formed the film with a fill factor of about 70%. The average size of the particles in the film was around

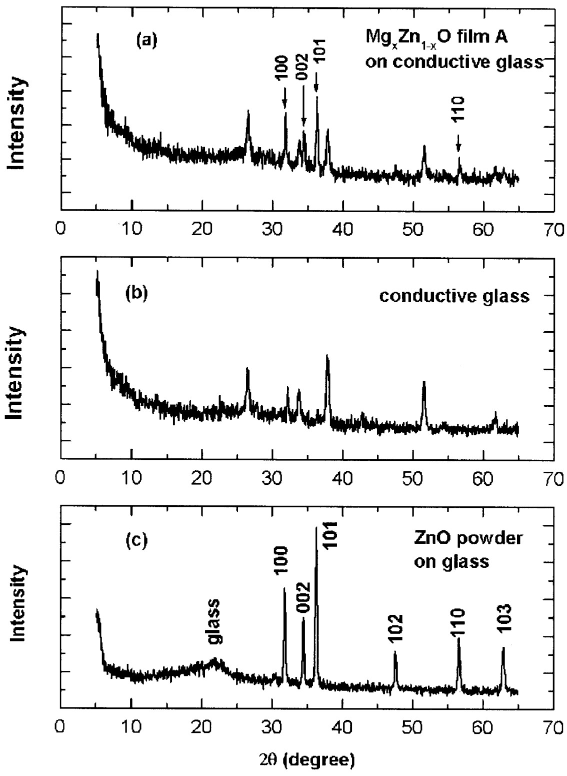

Fig. 2. Comparison of XRD spectrum between ZnO powder and $Mg_xZn_{1-x}O$ film. (a) Polycrystalline $Mg_xZn_{1-x}O$ film A on SnO_2-coated conductive glass, (b) SnO_2-coated conductive glass, (c) ZnO powder on glass.

50–70 nm. It seems that the dispersion sizes of the particles in the film are smaller than that of ZnO powder.

The typical XRD spectra of film A on SnO_2 coated glass, bare SnO_2 coated conductive glass and powder on glass were characterized by X'pert MRD-Philips diffractometer with CuKα line ($\lambda = 1.5418$ Å) as shown in Fig. 2(a)–(c), respectively. It can be seen from Fig. 2 that the XRD peaks were well indexed of ZnO for both powder and film except the peaks of substrates. Six peaks in powder occurred at $2\theta = 31.74$, 34.34, 36.26, 47.50, 56.62 and 62.90° corresponding to (100), (002), (101), (102), (110) and (103) directions of ZnO hexagonal structure. While in the XRD of the film, only the identified ZnO peaks of (100), (002), (101) and (110) appeared at positions with very small shift ($\Delta(2\theta) < 0.06°$). It indicated that both powder and film possessed polycrystalline hexagonal wurtzite structure. It was also found that the XRD linewidth of the peaks of the film was narrower than that of powder. It, therefore, reflected the enhancement of the crystallinity of the EPD film. Hence, it is reasonable to believe that the EDP films presented a more preferential crystalline orientation.

4. Photoluminescence of $Mg_xZn_{1-x}O$ films

Photoluminescence (PL) measurements of both the films and the powder were carried out at RT using our micro-PL system. In the PL measurements, a He–Cd laser with a wavelength of 325 nm and output power 27–30 mW was used as an excitation source. The typical PL spectra at RT are shown in Fig. 3, curves a and b corresponding to EDP film C and ZnO powder, respectively. Obviously, the bright near-band-edge (NBE) UV luminescence and well-suppressed deep-level emission (DL) (green band of about 2.4 eV) were consistently found in both samples. It was recognized that the green band emission in ZnO is associated with oxygen vacancies in the sample [3,20,21]. A common and visual method to evaluate the defect-level in ZnO as well as GaN film is to measure the ratio of $R = I_{NBE}/I_{DL}$. The chemically synthesized ZnO films usually

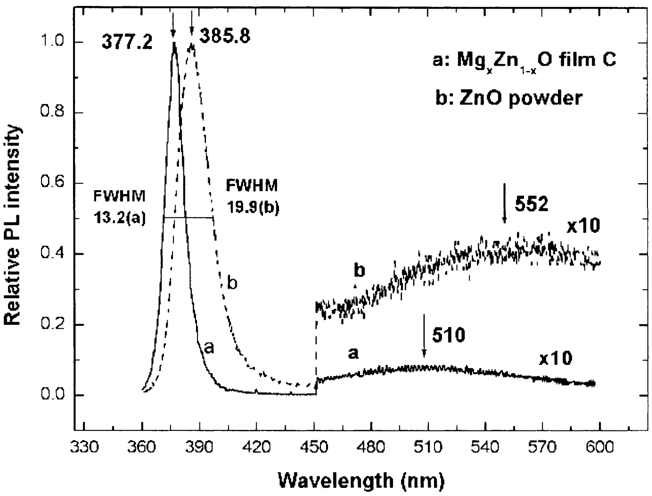

Fig. 3. Room temperature photoluminescence spectra of EPD polycrystalline $Mg_xZn_{1-x}O$ film C and ZnO powder (curve a — polycrystalline $Mg_xZn_{1-x}O$ film C; curve b — ZnO powder).

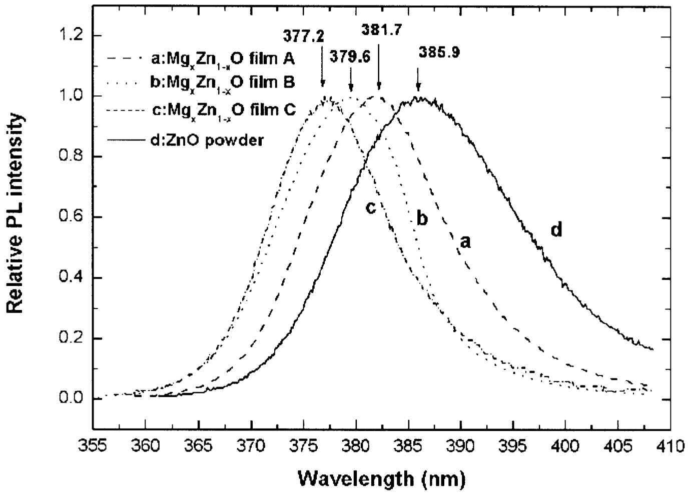

Fig. 4. Room temperature PL UV spectra of the EPD $Mg_xZn_{1-x}O$ films fabricated from different concentrations of $Mg(NO_3)_2 \cdot 6H_2O$ in solution and the ZnO powder (curve a — $Mg_xZn_{1-x}O$ film A with 5×10^{-3} M/l; curve b — $Mg_xZn_{1-x}O$ B film with 6×10^{-3} M/l; curve c — $Mg_xZn_{1-x}O$ film c with 7.5×10^{-3} M/l and curve d — ZnO powder).

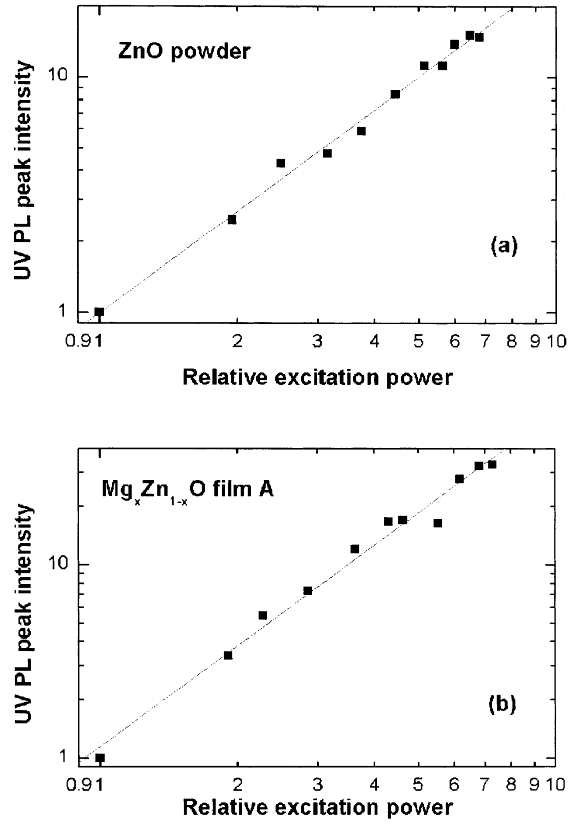

Fig. 5. The UV PL peak intensity dependence on excitation power. (a) The ZnO powder, (b) EPD $Mg_xZn_{1-x}O$ polycrystalline film A.

show much higher I_{DL} peak than I_{NBE}, whereas the epitaxial ZnO films grown by the MBE usually show R as large as 20:1 and can reach the stimulation emission at high excitations at RT [3]. In our experiments, at the same PL measurement configuration and excitation power of He–Cd laser, the intensity ratio R of near-band-edge emission I_{NBE} to deep level emission I_{DL} ($R = I_{NBE}/I_{DL}$) for the ZnO powder was 23:1, while in the EPD film A, B and C the ratio R reached as high as 53, 97 and 135:1, respectively. In other words, all the three $Mg_xZn_{1-x}O$ films have higher ratio of R than that of ZnO powder source. In particular, the higher the Mg composition in $Mg_xZn_{1-x}O$, the larger is the ratio R. From increasing ratio R, it may be understood that the incorporation of Mg helps to get enough oxygen in the ternary film during annealing. As a matter of fact, the optical emission behavior of our EPD films is not only better than the original ZnO powder but also comparable to that of the ZnO films formed by P-MBE [3] or laser pulsed deposition [14].

Fig. 4 presents the comparison of the near-band edge PL spectra of the ZnO powder and the three EPD $Mg_xZn_{1-x}O$ films with different Mg composition. Curves a–d in Fig. 4 are the UV PL spectra corresponding to the Mg_xZn_{1-x} films A, B, C and the ZnO powder, respectively. Obviously, the film deposited from the solution with higher Mg concentration exhibited a larger blue shift of PL peak related to that of their original ZnO powder [11].

In addition, the FWHM of UV near band-edge emission in the EDP films between 110 and 130 meV was obtained, which was narrower than 160 meV in the original ZnO powder. This value is also comparable to that of the typical FWHM of UV peak (~110 meV) in epitaxial MBE grown ZnO films [1]. Furthermore, it was also very interesting to note that the FWHM of the $Mg_xZn_{1-x}O$ films reduced with increasing concentration of $Mg(NO_3)_2 \cdot 6H_2O$ in the solution.

Eventually, the improvement of FWHM is consistent with the observations of preferred crystal orientation and the reduced dispersions of nanocrystalline size in the EPD films by the morphology and structure study. But the question whether and why Mg in the ternary $Mg_xZn_{1-x}O$ films could improve the FWHM of the UV spectra still remains.

It is known that the large exciton binding energy leads to a high exciton thermal stability in ZnO and its alloy $Mg_xZn_{1-x}O$ compounds at RT. Consequently, the excitonic radiative recombination should also be the dominant origin of the observed luminescence of the ZnO powder and $Mg_xZn_{1-x}O$ films at RT [21,22]. The dependence of UV PL peak intensity on the excitation power was measured as shown in Fig. 5(a) and (b) on logarithmic scale for $Mg_xZn_{1-x}O$ film A and ZnO powder, respectively. Both show a linear relation. The RT dominant emission in PL from free exciton at about 3.2 eV has evidenced in nanocrystalline ZnO and $Mg_xZn_{1-x}O$ films by several groups [3,20]. Considering the structure and PL spectra of the ZnO powder and the $Mg_xZn_{1-x}O$ films, it was found that the low x values are comparable to the ZnO and films reported. The near band-edge UV emission from 385 to 377 nm of our ZnO powder and EPD $Mg_xZn_{1-x}O$ films should be ascribed as free excitonic luminescence. Of course, further investigation is in progress.

5. Summary

In conclusion, ternary $Mg_xZn_{1-x}O$ nanocrystalline films with various small x values have been successfully fabricated from ZnO powder by EPD followed by annealing at 450°C in air. According to the different Mg composition, the UV peak of $Mg_xZn_{1-x}O$ films exhibited a different blue shift related to ZnO powder source. In comparison with the original ZnO powder, the $Mg_xZn_{1-x}O$ films showed a more preferential crystalline orientation. Room temperature PL spectra of $Mg_xZn_{1-x}O$ films revealed a stronger band-edge UV emission, a narrower FWMH about 13 nm and a much higher NBE to DL peak intensity ratio R (53:1 to 135:1 verses 23:1) than that of ZnO powder source, even though the EPD procedure was not optimized. All these demonstrated that our EPD $Mg_xZn_{1-x}O$ films exhibited a good quality for excitonic emission at RT. The EPD $Mg_xZn_{1-x}O$ film is a promising material system not only as barrier layers for the ZnO active layer, but also as an ultraviolet light emitting material.

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