# Mg doping reduced full width at half maximum of the near-band-edge emission in Mg doped ZnO films

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Sol–gol method was employed to synthesize Mg doped ZnO films on Si substrates. The annealing temperature-dependent structure and optical property of the produced samples were studied. An interesting result observed is that increasing Mg concentration in the studied samples induces the full width at half maximum (FWHM) of their near-band-edge (NBE) emission decrease and the defect related emission of the corresponding sample suppresses drastically. The possible mechanism of the observed result is discussed.

**Keywords:** doping, ZnO, photoluminescence

**PACC:** 7280E, 8140T

## 1. Introduction

ZnO is a semiconductor with a large exciton binding energy of 60 meV which results in more efficient excitonic emission at room temperature.[1] Recently, ZnO is of great interest because of many promising applications in light emitting diode and laser device.[2−4] It is well known that among the wide band gap semiconductors, addition of dopants often induces dramatic changes in their electrical and optical properties. A few studies have suggested that ZnO doped with transition metal ions could possess interesting optical properties.[5,6] MgO is the prototype of an ionic compound semiconductor with wide band gap of 7.8 eV, and Mg substitution in ZnO leads to an increase in the band gap depending on the Mg contents.[7] The dramatic property of Mg doped ZnO films may possess the potential application for nanoscale resonant tunneling devices thus has attracted much interest and extensively study. Ohotomo *et al.*[8] alloyed ZnO with MgO using the pulsed laser deposition (PLD) and reported increase in band gap in the alloy. Lin *et al.* studied Mg doped ZnO films using sol–gol deposition and attained a band gap with 3.4 eV.[9] Kukreja *et al.* achieved a band gap of about 3.8 eV by alloying ZnO with MgO.[10]

Although the extensive studies have been contributed to Mg doped ZnO, the study on the doping induced narrowing of its near-band-edge (NBE) emission as well as varying the defect related emission is few. In this paper, sol–gol method is employed to synthesize Mg doped ZnO films on Si substrates, and the annealing temperature-dependent structural as well as the optical property of the produced samples are studied. The results indicate that increasing of Mg content markedly enhances the efficiency of band edge emission and restrain the visible emission as well. Increasing annealing temperature results in a blueshift of the ultraviolet (UV) peak of the corresponding samples; however, broadens the full width at half maximum (FWHM) and decreases the intensity of their UV peak. A possible change process of Mg doped ZnO films during preparation is proposed to explain the corresponding mechanism.

## 2. Experimental

$Zn_{1-x}Mg_xO$ films with the nominal composition of $x = 0$, 0.005, 0.01, 0.015, 0.02, and 0.03 were synthesized via the sol–gol method. $Zn(CH_3COO)_2{\cdot}H_2O$, $Mg(CH_3COO)_2{\cdot}H_2O$ and polyglycol (PEG) were added to methanol. PEG was used as a stabiliser. $NH_3.H_2O$ was added to methanol to create the alkaline environment (pH∼9), and the resulting mixture was stirred at 50 °C, which served as the coating solution after cooling to room temperature. The solution was dropped onto Si substrates which were rotated at 3000 rpm for 30 s. After depositing by spin coating, the films were dried at 120 °C for 10 min. The pro-

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cedures from coating to drying were repeated 6 times to get the final films. The films were then inserted into a furnace and annealed in air at 400, 450, 500 and 550 °C for 4 h, respectively. The structure of the films was investigated by x-ray diffraction (XRD). Photoluminescence (PL) measurements were performed at room temperature by using a He–Cd laser (325 nm) as the excitation source.

## 3. Results and discussion

Figure 1 shows XRD patterns of pure and doped ZnO thin films with different Mg concentrations (0, 0.5, 1.0, 1.5, 2.0, and 3.0 at%) annealed at the temperature of 550 °C for 4 h. All films exhibited only the peaks in the range of 34.37°–34.46° which belong to the ZnO(002) indicating that the single-phase $Zn_{1x}Mg_xO$ films have grown without phase separation. As can be seen from the inset of Fig. 1, the peaks of $Zn_{1x}Mg_xO$ (002) moves from 34.37° to 34.46° as the Mg content increased to 3 at% and the corresponding lattice parameters extracted from XRD data changed from 0.5214 nm to 0.5201 nm. Since the ionic radius of $Mg^{2+}$ (0.066 nm) is smaller than that of $Zn^{2+}$ (0.074 nm) the decreasing of the lattice constant implies the substitution of Mg to Zn in the studied films.[11]

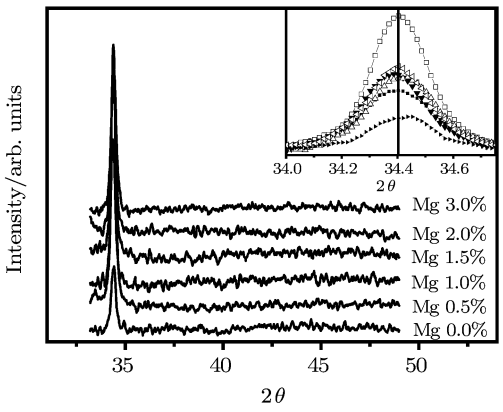



**Fig. 1.** XRD patterns of Mg doped ZnO thin films on Si substrates annealed at 550 °C.

Figure 2 shows XRD patterns of $Zn_{1x}Mg_xO$ ($x$ = 2 at%) films annealed in the range of 400–550 °C All films exhibited only the $Zn_{1x}Mg_xO$(002) peaks in 34.40° indicating that the $Zn_{1x}Mg_xO$ films are of single-phase without phase separation observed within the limitation of XRD resolution. The calculated lattice constant $c$ is of 0.5208 nm smaller than that of pure ZnO film, conforming that Mg was introduced into the film and lodged on the Zn position. There is no observed shift of the peaks of $Zn_{1x}Mg_xO$(002) as the annealing temperature varied from 400 °C to 550 °C, indicating that the structure of the studied films did not change within the measurement resolution.

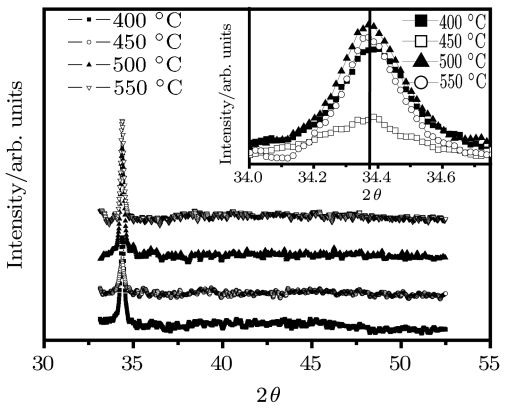



**Fig. 2.** XRD spectra of $Zn_{1-x}Mg_xO$ ($x$ = 2%) films annealed at the temperature of 400 °C, 450 °C, 500 °C and 550 °C, respectively.

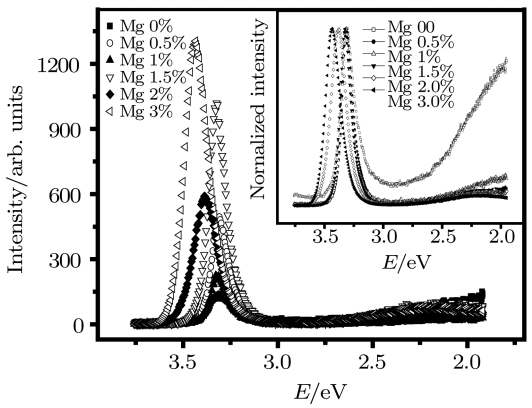



**Fig. 3.** Room temperature PL spectra of Mg doped ZnO thin films on Si substrates annealed at 550 °C. The inset shows the PL spectra with normalized intensity.

Figure 3 shows the PL spectra of $Zn_{1-x}Mg_xO$ films annealed at 550 °C. It can be seen that the spectra of all the samples consist of a strong UV emission and a broad visible emission, corresponding to the near-band-edge and the deep-level defects emission in ZnO.[12,13] Compared with each spectrum in Fig. 3, one can see that with increasing Mg content in the sample, the intensity of UV emission increases. The inset of Fig. 3 is the normalized intensity of the PL. From the inset, it is clear to see that the UV peak blueshifted significantly with increasing the concentration of Mg, while the intensity of defect related emission suppressed with increasing of Mg concentration, confirming the reducing of the density of deep-level defects in the studied samples due to Mg doping.[14,15]

Figure 4 shows the Mg concentration-dependent UV PL emission energy (left axis) and the corresponding peak width (right axis) of the sample annealed at 550 °C. From Fig. 4, it is clear that as the Mg concentration increased to 3 at% gradually, the UV PL emission of the corresponding samples blueshifted from 3.278 eV to 3.438 eV with their FWHM decreased from 153 meV to 98 meV. The blueshift in band-gap energies of Mg doped ZnO films is ascribed to electronic structure modifications.[16] When the Mg content is less than 4 at%, the majority of Mg ions are likely substituted in the Zn sites of ZnO.[17] As Mg content increases, the contribution of Mg 3s-like states becomes dominant at the bottom of the conduction band. Since Mg 3s-like states are higher than that of Zn 4s level, the band gap of $Zn_{1-x}Mg_xO$ is broaden with increasing Mg concentration by heightening the bottom of the conduction band.[16–18] The FWHM values of UV peaks decreased with increasing Mg content indicating that the improved crystal quality is attributed to the introduction of Mg in ZnO films.

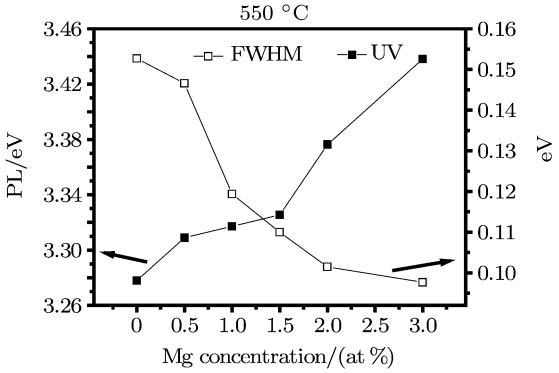



**Fig. 4.** UV luminescence energy and FWHM values of UV peaks of $Zn_{1-x}Mg_xO$ films annealed at 550 °C.

Figure 5 shows PL spectra of $Zn_{1x}Mg_xO$ ($x = 2$ at%) films annealed in the range of 400–550 °C. All films exhibited an intensive UV emission and a weak and broad visible light emission band which possibly induced by oxygen vacancies.[19] As seen in Fig. 5, with increasing of annealing temperature, the UV emission peaks blueshifted with the intensity decreases gradually as indicated in detail in the inset of Fig. 5. (The inset of Fig. 5 is the annealing temperature-dependent intensity of the normalized spectra). The inset of Fig. 5 clearly indicated that the UV emission blueshfited, and the visible emission band redshifted with their normalized intensity increased as annealing temperature increased. The above results indicate that the relevant defects in $Zn_{1-x}Mg_xO$ films increase as annealing temperature increases.

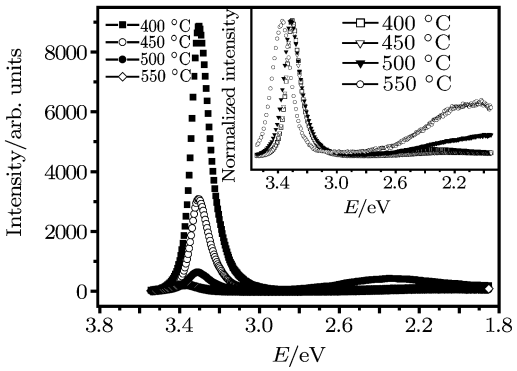



**Fig. 5.** Room temperature PL spectra of $Zn_{1-x}Mg_xO$ ($x = 2\%$) films annealed at the temperature of 400, 450, 500, 550 °C, respectively. The inset shows the PL spectra with normalized intensity.

Figure 6 shows the temperature-dependent UV emission energy and the emission peak FWHM. The solid squares stand for the data of energy position of UV and the open circles are for the values of FWHM. It can be seen from Fig. 6 that the energy of UV peak increases from 3.30 eV to 3.37 eV as annealing temperature increased from 400 °C to 550 °C, while the FWHM of UV peak of the corresponding samples increased from 0.11 eV to 0.15 eV. Such effects could be resulted from that the increaed anealing temperature promotes Mg diffusing into ZnO crystal lattice.

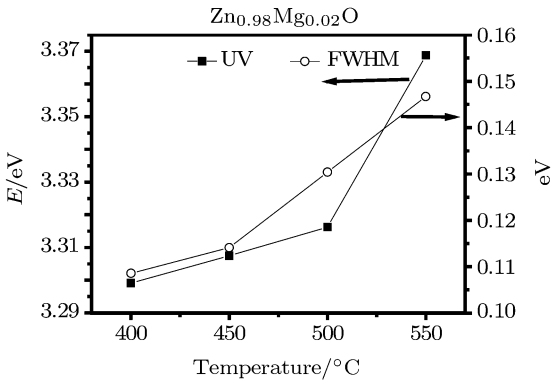



**Fig. 6.** The UV luminescence energy and FWHM values of UV peaks of $Zn_{1-x}Mg_xO$ ($x = 2\%$) films annealed at the temperature of 400, 450, 500, 550 °C, respectively.

Now, we return to discuss the interesting result observed in Mg concentration modulated the FWHM of the UV emission as indicated in Fig. 4. The FWHM of the UV emission in ZnO is sensitive to the quality of its crystal and the defect and distortion of its lattice. The decreasing of the FWHM of the UV emission

with increase Mg concentration in ZnO films suggested that the doped Mg in ZnO is perfectively substituted Zn in ZnO lattice while the introduced distortion is very low. As known, the visible emission of ZnO or the doped ZnO is believed to originate from the point defects. The drastically suppressed visible PL emission in the studied samples in the paper indicated the properly introducing Mg replace Zn in ZnO without introducing point defects significantly. Such the result suggested that elaborately introducing Mg to replace Zn in ZnO lattice not only results in increase in the gap in the doped ZnO, but also promotes the quality of its crystalline. Therefore, Mg is a mineralizer in Mg doped ZnO. Elaborately introducing Mg in ZnO could effectively reduce the density of intrinsic point defects in ZnO, which can properly explain the dramatically decrease of the FWHM of the UV emission and drastically suppress the visible PL emission in Mg doped ZnO when the concentration of Mg increased as indicated in Fig. 4. Moreover, introduce of Mg in ZnO also results in the decrease of nonradiative recombination processes in the doped ZnO.[20] However, the mineralization effect of Mg in ZnO is sensitive to the temperature of sample synthesis. Increasing the temperature of the sample synthesis weakens the Mg mineralization effect and induces Mg component fluctuations in the compositions.[21] Such an effect is responsible for the widening of the FWHM of the UV emission as indicated in Figs. 5 and 6. Although the aforementioned image could qualitatively understand the observed result in Fig. 4, the detailed understanding of the mechanism of Mg as mineralizer in Mg doped ZnO should be studied more and now is undergoing.

## 4. Summary

Sol–gol method was employed to synthesize Mg doped ZnO films on Si substrates with different Mg concentration. The annealing temperature-dependent structure and the optical property of the produced samples were studied. The particularly interesting finding in this paper demonstrated that elaborately introducing Mg concentration within 3% doped in ZnO results in not only the increasing of its band gap but also narrowing its UV peak FWHM and depressing its defect related emission.

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