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Influence of substrate temperature on ultraviolet emission of ZnO films prepared by ultrasonic spray pyrolysis

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ZnO films were deposited on MgO substrates (ZnO/MgO) by ultrasonic spray pyrolysis. Substrate temperature varied from 200 to 350°C. The crystallographic properties and surface morphologies of the ZnO/MgO films were studied by X-ray diffraction and scanning electron microscopy. The properties of photoluminescence (PL) for the films were investigated by dependence of PL spectra on the substrate temperature and the ambient temperature. Ultraviolet (UV) emission peak (3.37 eV) was dominantly detected at 18 K, which sustained at 300 K with a reduced value of the peak energy. The ZnO/MgO films prepared at 350°C showed the strongest UV emission peak at 18 and 300 K among the films in this study.

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1. Introduction

ZnO films have been widely studied for the applications as electrical and optical devices [1–3]. Recently ZnO films are particularly attracting more attention as a candidate material for ultraviolet (UV) optical devices due to their wide band gap (3.37 eV) and large exciton binding energy (60 meV) [4–6].

ZnO has a wurtzite structure and shows n-type semiconductor properties by oxygen vacancies and/or excess zinc. It is also reported [7–9] that ZnO films show photoluminescence (PL) in the region of UV and visible light. The cause of the UV emission is known to be bound exciton complexes [10–13] and that of visible light is oxygen vacancies [14] and interstitials [15].

ZnO films have been prepared by many techniques; RF magnetron sputtering [16], sol-gel method [17], chemical vapour deposition [18], spray pyrolysis [19, 20], MBE [20–23]. However, most of the repots on the UV emission of ZnO films have been concentrated on MBE which are very expensive method from the viewpoint of system and source material. In order to meet the industrial needs for the commercially available ZnO devices, the easier and cheaper deposition methods for the ZnO film should be developed. Recently, ultrasonic spray pyrolysis (USP) is considered to be a very useful method because of the simplicity of facilities and the low cost of the raw materials [24].

Several materials have been used as substrates for the deposition of ZnO films. Among them, MgO is known to be one of promising substrates for obtaining high quality ZnO films due to its relatively low price and low mismatched interface with ZnO (9%).

In this paper, we prepared ZnO films on MgO substrates (ZnO/MgO) by the USP method. The structural, electrical and PL properties were studied as a function of substrate temperature and ambient temperature. Narrow and high emission peaks in the UV region were observed from the samples prepared above 250°C.

2. Experimental procedure

ZnO films were grown on the (100) MgO substrates by the USP method. In the USP process, zinc acetate (Aldrich, 99.999%) diluted in methanol was selected as the zinc precursor at a concentration of 0.01 mol/l. Aerosols produced by nebulizing the solution are transported to the reactor by nitrogen gas at a flow rate of 2 l/min. The substrate temperature varied from 200 to 350°C in the span of 50°C. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the crystallographic properties and the surface morphologies of the films, respectively. We used Cu K_α

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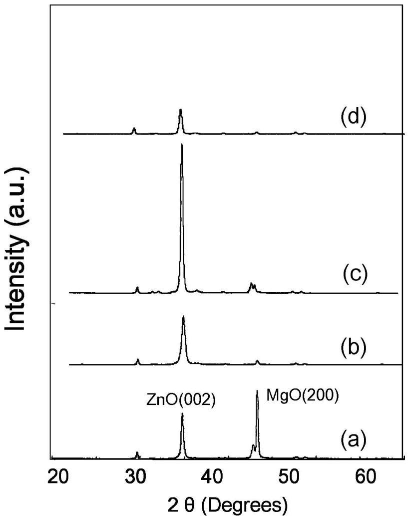


Figure 1 XRD spectra of ZnO/MgO films deposited at substrate temperature of: (a) 200°C, (b) 250°C, (c) 300°C, and (d) 350°C.

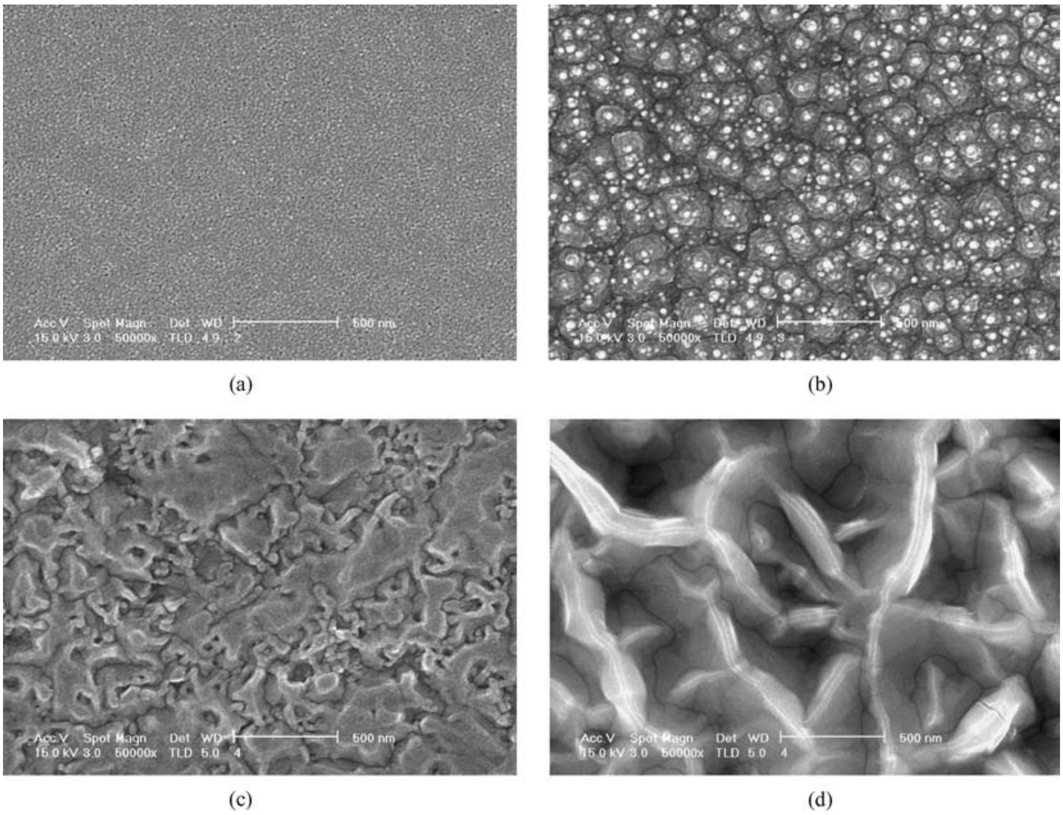
($\lambda = 0.1542$ nm) radiation for the XRD and the 2θ was between 20° and 60°. The film thickness was measured from the cross section SEM micrographs of the films. PL measurements were carried out with a 325 nm CW He-Cd laser. The excitation power was about 55 mW and the diameter of the laser beam was around 1.8 mm. The PL measurements were conducted at the ambient temperature of 18, 100, 200 and 300 K. The resistivity of the films was measured by the four-point probe method.

3. Results and discussion

XRD patterns of ZnO/MgO films grown at substrate temperature of 200, 250, 300 and 350°C are shown in Fig. 1. XRD results show that the ZnO films have a polycrystalline structure with a preferred orientation of (002). The highest (002) ZnO peak is observed from the films grown at 300°C. Gain sizes obtained using the Scherrer's equation are between 22 and 40 nm.

Fig. 2 is SEM micrographs of the ZnO films corresponding to Fig. 1. The merge and enlargement of neighboring grains with increasing substrate temperature is observed. The grain sizes observed in SEM usually appear larger than those calculated by Scherrer's equation, which is attributed to the conglomeration of unclear small grains in SEM micrographs. The SEM image of the ZnO film prepared at 350°C shows a very different morphology comparing to other images; it looks mixture of pyramid-type grains founded in annealed films.

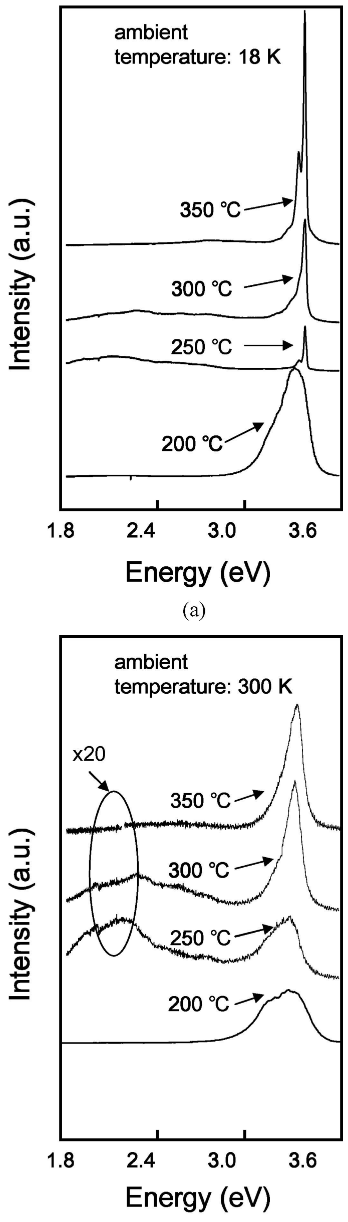
PL measurements were conducted for the ZnO films prepared at 200, 250, 300 and 350°C; the measurements were carried out at the ambient temperature of 18, 100, 200 and 300 K, respectively. PL spectra of the ZnO films measured at 18 and 300 K are shown in Fig. 3. UV peak at 3.37 eV with its LO-phonon replica (~3.30 eV) was dominantly observed at 18 K from most films. The origin of the peak at 3.37 eV is normally assigned to free excitons [25, 26]. The peak is decreased to 3.30 ± 0.02 eV as the ambient temperature increases to 300 K. Table I summarizes the energy and full-width-half-maximum (FWHM) of the



(a) (b)

(c) (d)

Figure 2 SEM micrographs of ZnO/MgO films deposited at substrate temperature of: (a) 200°C, (b) 250°C, (c) 300°C, and (d) 350°C.



(a)

(b)

Figure 3 PL spectra of ZnO/MgO films prepared at 200, 250, 300, and 350°C. The ambient temperature of (a) and (b) is 18 K and 300 K, respectively.

TABLE I The peak energy and FWHM of the UV emission peak from ZnO/MgO films

	18 K		300 K	
Substrate temperature (°C)	Peak energy (EV)	FWHM (meV)	Peak tnergy (eV)	FWHM (meV)
200	3.30	236	3.27	323
250	3.37	24	3.28	262
300	3.37	28	3.31	124
350	3.37	19	3.30	114

peaks. The low-temperature (18 K) UV peak (3.30 eV) of the film grown at 200°C is found to be much lower than that of the other films, which is resulted from the immature crystalline structure due to the low substrate temperature. The emission peak intensity of the films increases as substrate temperature increases except the film grown at 200°C. The smaller peak intensity of the film grown at 250°C than that of the film grown at 200°C is thought to be due to the rougher surface as shown in Fig. 2; the rough surface causes the scattering of the emitted light. The UV peak intensity of the film grown above 200°C reduces abruptly at room-temperature (300 K). The PL intensity decreases in high-temperature by the thermally activated nonradiative recombination mechanism. We believe that the nonradiative recombination centres are generated by the oxygen vacancies which increase with increasing substrate temperature. FWHM of the peaks decreases with increasing the ambient temperature. The large low-temperature FWHM (236 meV) of the film grown at 200°C is the other evidence for the immature crystalline structure. The broad peaks of visible light were observed between 2.10 and 2.28 eV at room temperature which reduced much for the films grown at 350°C. The origin of the visible light is attributed to defects: oxygen vacancies [14], zinc interstitials [15] etc. Fig. 4 shows the resistivity of the ZnO/MgO films as a function of substrate temperature. The resistivity of the film grown at 350°C drops to 6.4 × 10^{-4} Ωcm which corresponds to the electron concentration of 3×10^{20} cm^{-3}. The high concentration of electron is another evidence for the oxygen vacancies and zinc interstitials. It is supposed that the screening of defects by the electrons reduces the visible light emission of the films grown at 350°C in spite of a high concentration of defects in the films.

We studied an ambient temperature dependence of the UV emission properties: peak energy and FWHM. The ZnO films deposited at the substrate temperature of 300 and 350°C showed a distinguishable UV peak above 200 K. So, we present the results of the films grown at 300 and 350°C. The peak energy dependence on the ambient temperature is shown in Fig. 5a. A band-gap shift results in the peak energy variation with temperature. Electron-phonon interaction and lattice expansion are considered

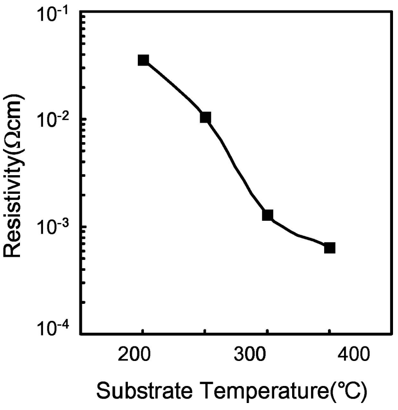


Figure 4 Resistivity variation of ZnO/MgO films with substrate temperature.

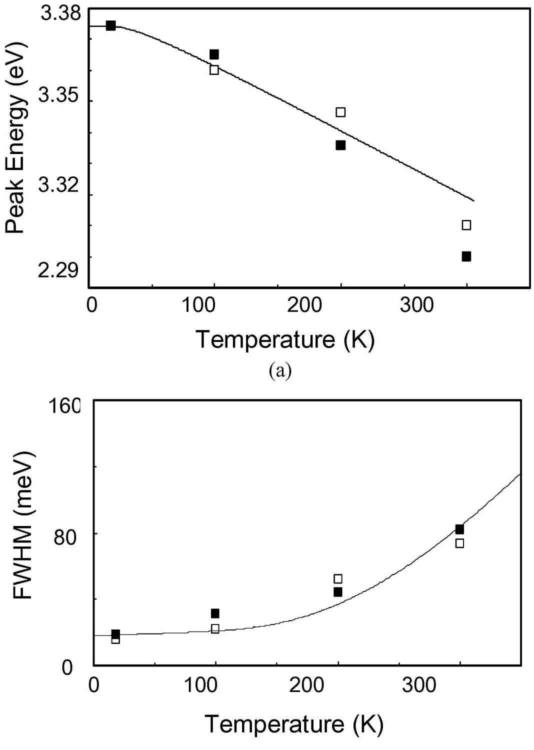


Figure 5 (a) The peak energy and (b) FWHM of the UV emission peak of ZnO/MgO films as a function of the ambient temperature. Closed squares and open squares are the experimental data of the films grown at 300 and 350°C, respectively. The solid curves represent the theoretical fitting results based on the Equation 1 and 2.

to be origin of the band-gap shift as a function of temperature. Both phenomena effect on the band-gap shift with a very similar mechanism. O'Donnell and Chen [26] simplified the overall contribution of phonons in a one term using Bose-Einstein statistical factor and average phonon energy. The equation is given by [26]

$$E(T) = E(0) - \lambda[\coth(<\hbar\ \omega>/2\kappa \mathrm{T}) - 1] \qquad (1)$$

where $E(0)$ is an exciton energy at 0 K, λ is a proportional coefficient and $<\hbar\omega>$ is an average phonon energy. Our experimental data are fitted to Equation 1. $E(0)$, λ and $\hbar\bar{\omega}$ are obtained as approximately 3.37 eV, 20.0 meV and 8.0 meV from the Fig. 5a. The fitted λ is very similar to the value (20.9 meV) obtained from the low-temperature absorption spectra of ZnO films grown by laser-molecular-beam epitaxy [22]. Estimated $\hbar\bar{\omega}$ (8.0 meV) is lower than the maximum energy of a low-frequency group of ZnO bulk phonons (12 meV). The temperature dependence of FWHM is shown in Fig. 5b. The FWHM of the UV emission peak increases as the ambient temperature increases. The broadening of the peaks is attributed to the exciton-phonon scattering. The temperature dependence of FWHM has been described by the theoretical equation given by [27]

$$\Gamma(T) = \Gamma(0) + \gamma T + \Gamma/[\exp(\hbar\omega/\kappa \mathrm{T}) - 1] \qquad (2)$$

where $\hbar\bar{\omega}$ is a LO phonon energy, $\Gamma(0)$ is the broadening parameter at 0 K, γ is the coupling strength of an exciton-acoustic phonon interaction and Γ is a parameter describing exciton-LO phonon interaction. The experimental data were compared with the theoretical curve drawn by Equation 2. Makino *et al.* [22] have studied on the effects of temperature on FWHM for ZnO films prepared by MBE. We used the parameter values deduced by Makino *et al.* [22] for the calculation of Equation 2. In Equation 2, $\hbar\bar{\omega}$ is assumed to be 72 meV which is the LO phonon energy of bulk ZnO [28]. There is a relatively good matching between the experimental data and the theoretical curve, which confirms that the broadening of peaks is due to the exciton-phonon scattering.

In this experiment, we observed room-temperature UV emission from ZnO films prepared by ultrasonic spray pyrolysis. Even though lots of questions on the mechanism of the emission remain to be solved, the ZnO films by the ultrasonic spray pyrolysis can be one of the promising candidates for the UV optical devices.

4. Conclusions

ZnO films were successfully grown on MgO substrates by an ultrasonic spray pyrolysis method. Substrate temperature varied from 200 to 350°C. The ZnO/MgO films have a polycrystalline structure with a preferred orientation of (002). The grains in the ZnO films changed from a small island-like form to a big mountain-range-like shape as substrate temperature increases. PL properties were measured at 18, 100, 200 and 300 K, respectively. UV emission at 3.37 eV with its phonon replica was dominantly observed at 18 K from most films. The emission peak intensity of the films increases with substrate temperature except the film grown at 200°C. The UV peak intensity of the film grown at 200°C is exceptionally high, the cause of which is still being studied. The broad peaks of visible light were observed between 2.10 and 2.28 eV at room temperature which reduced much for the films grown at 350°C. The resistivity of the films deposited at 350°C decreases to 6.3 × 10 −4 Ω. It is supposed that the screening of defects by the electrons reduces the visible light emission of the films grown at 350°C. In spite of incomplete study on the mechanism of the UV emission, the ZnO films prepared by the ultrasonic spray pyrolysis are one of the promising candidates for the UV optical devices.

Acknowledgments

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