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The ultraviolet emission mechanism of ZnO thin film fabricated by sol–gel technology

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Abstract

ZnO thin films were successfully deposited on SiO_2/Si substrate by sol–gel technology. The as-grown ZnO thin films were annealed under an ambient atmosphere from 600 to 900 °C by rapid thermal annealing (RTA) process. X-ray diffraction and scanning electron microscopy analyses reveal the physical structures of ZnO thin films. From PL measurement, two ultraviolet (UV) luminescence bands were obtained at 375 and 380 nm, and the intensity became stronger when the annealing temperature was increased. The strongest UV light emission appeared at annealing temperature of 900 °C. The chemical bonding state in ZnO films was investigated by using X-ray photoelectron spectrum. The mechanism of UV emission was also discussed.

Keywords: ZnO; Sol–gel processes; Films; Optical properties

1. Introduction

ZnO is a versatile material and has emerged as a promising candidate for wide applications in the fields of electronics[1] and surface acoustic wave devices.[2] Due to its large exciton binding energy of 60 meV and the wide band-gap of 3.3 eV, thin films of ZnO have been applied in many optoelectronic devices such as short wavelength light emitting diodes[3] and transparent electrode.[4]

Generally, ZnO exhibits luminescence bands in the UV and visible regions.[5,6] It is reported that UV emission originates from the exciton transition.[7] However, most of the discussions were focused on the effects of physical structure on the intensity of UV emission.[8,9] Fewer articles were mentioned about the relationship between the chemical state of the surface of ZnO films and the intensity of UV emission. In this study, ZnO thin films were prepared by a facile and inexpensive sol–gel technique. The relationships between physical and chemical characteristics and PL properties were investigated. The mechanism of UV emission was also discussed based on these analyses.

2. Experimental

ZnO thin films were deposited on the SiO_2/Si substrates by sol–gel technique. Fig. 1 shows the flow chart of the preparation of ZnO films. The sol was prepared using zinc acetate dehydrate ($Zn–(OOC–CH_3)_2{\cdot}2H_2O$), 2-methoxyethanol ($C_3H_8O_2$) and monoethanolamine ($C_2H_7NO$, MEA). Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio for MEA to zinc acetate was fixed at 1.0 and the concentration of zinc acetate was 0.6 mol l^{-1}. The resultant solution was stirred at 120 °C for 1 h and then refluxed at 80 °C for 1 h to yield a clear and homogeneous solution, which served as the coating solution. The precursor solution was dropped onto SiO_2/Si substrates, which were rotated at 1000 rpm for 10 s and then rotated at 2000 rpm for 20 s. After depositing by spin coating, the films were dried at 270 °C for 3 min to evaporate the solvent and remove organic residuals. The spin-coating and preheating procedures were repeated four times. The films were then post-heated under an ambient atmosphere from 600 to 900 °C for 1 h by rapid thermal annealing (RTA) process.

The thermal decomposition behavior of a ZnO solution was examined and analyzed by using thermogravimetry–differential thermal analyzers (TG/DTA), carried out by a PerkinElmer

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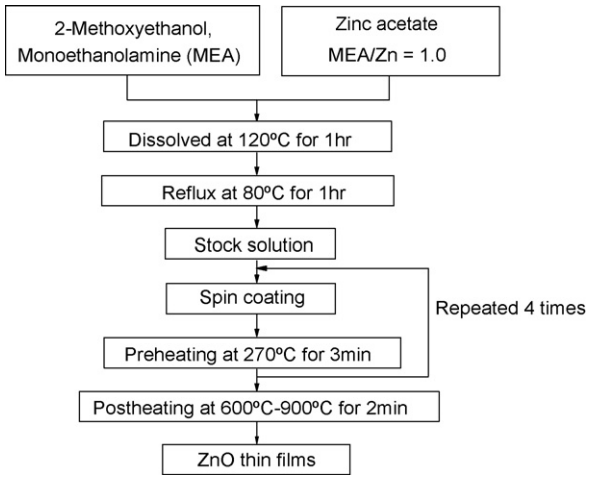

Fig. 1. Flow chart of sol–gel technique for ZnO thin films.

Diamond TG/DTA. Crystalline characteristics of thin films were obtained by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer and Philips XL-40FEG field emission scanning electron microscope (FESEM) was used to analyze the surface morphologies and grain structures. The diverse luminescent characteristics of ZnO films annealed at various temperatures were investigated through the photoluminescence (PL) measurement with a He–Cd laser of 325 nm. X-ray photoelectron spectroscopy (XPS) was carried out for chemical analysis of ZnO films by a Fison (VG) ESCA210 instrument. All measurements were performed under room temperature.

3. Results and discussion

Generally, the thermal decomposition behavior of the precursor is complicated especially with various kinds of organic molecules contained. The possible reaction routes were estimated by thermal analysis. Fig. 2 shows the TG/DTA curves of the dried ZnO gel. The TGA curve illustrates an overall reaction with a measured weight loss of 70% at 270 °C, which may be due to the combustion of resultant organics such as ethoxy group and MEA. The decomposition involves many thermal effects. Three small and one large exothermic peak were observed at around 126, 170, 270 and 360 °C, respectively. The first three peaks at 126, 170 and 270 °C may be due to the combustion

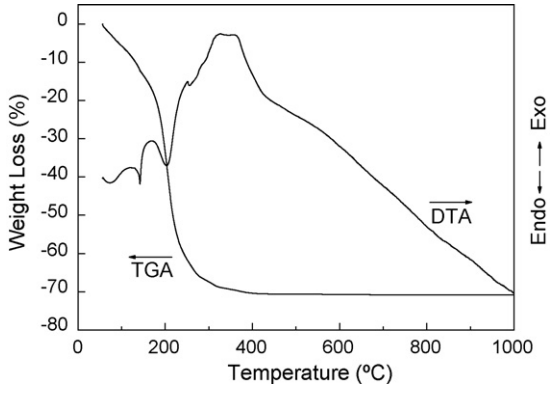

Fig. 2. TG/DTA analysis of ZnO precursor.

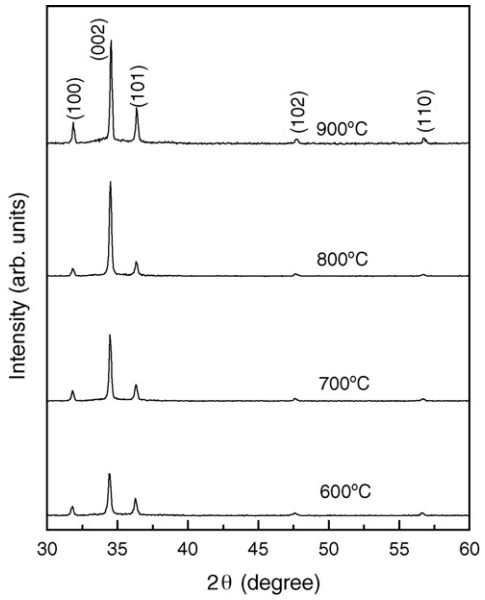

Fig. 3. XRD patterns of ZnO films annealed at various temperatures.

of 2-methoxyethanol, MEA and other residual organics, respectively. The large exothermic peak around 360 °C results from the formation of ZnO since no further weight loss can be observed at temperature higher than 400 °C.

Fig. 3 shows the X-ray diffraction patterns of sol–gel-synthesized ZnO thin films after post-annealing under various temperatures. The peaks identified correspond to (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) plane reflections for Wurzite-type ZnO. Among these diffraction peaks, the (0 0 2) diffraction located at 34.5° is the most intensive. The intensity of ZnO (0 0 2) diffraction peak increased as the annealing temperatures were increased from 600 to 900 °C. The spectrum reveals that ZnO thin film exists a preferred (0 0 2) orientation after annealing at high temperature. The mechanism of the *c*-axis oriented ZnO films can be attributed that the value of surface free energy of ZnO (0 0 2) plane is minimum at the growth stage.[8] In addition, the full-width at half maximum (FWHM) for ZnO (0 0 2) peak decreases with the increasing annealing temperatures of 600 °C (0.225°), 700 °C (0.200°), 800 °C (0.191°) and 900 °C (0.193°). According to the Scherrer's equation,[10] the calculated grain sizes of ZnO films should increase with the increased annealing temperatures.

Fig. 4 shows the surface morphologies of ZnO films annealed at 600, 700, 800 and 900 °C for 1 h, respectively. It is obvious that the particle size increased with the increased annealing temperature, which is consistent with the FWHM results. The surface structure and grain boundary also became denser and clearer at higher annealing temperatures. According to Li et al.,[11] the atoms would obtain enough energy to occupy the proper sites in the crystal lattices and grains with lower surface energy would become larger at higher temperatures.

The PL spectra for ZnO thin films were shown in Fig. 5. There exists two emission peaks located at 375 and 380 nm, which correspond to the ultraviolet (UV) emission. The intensities of both UV emission peaks were increased gradually when the annealing temperature was increased. According to Chatterjee et al.,[9] the

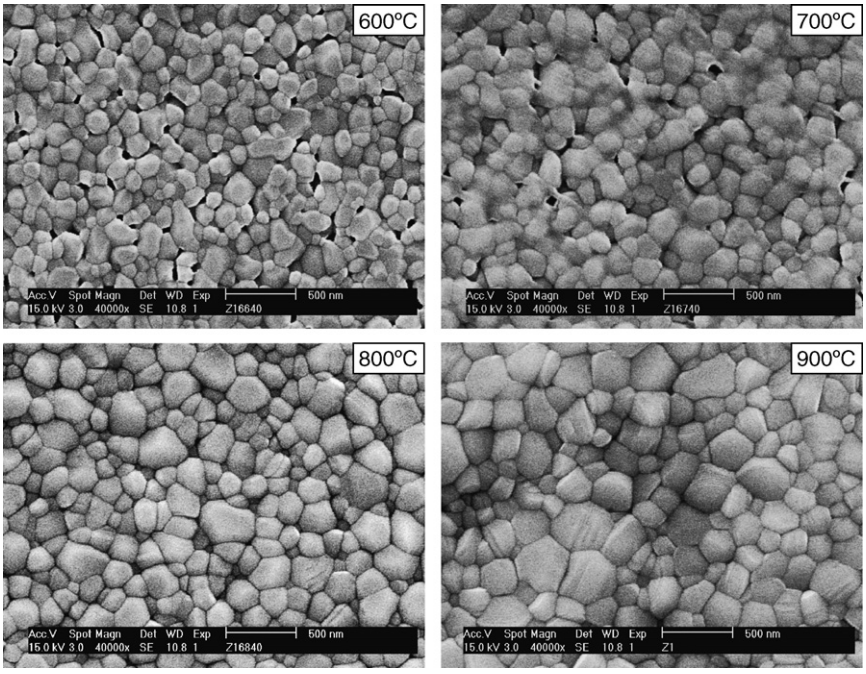

Fig. 4. Surface morphologies of ZnO films annealed at various temperatures.

increased intensity of UV emission was dependent of the grain size and crystal orientation. In this study, the grain size, ZnO (0 0 2) diffraction intensity and UV intensity all increased with the increased annealing temperature. The results are consistent with the tendency of Chatterjee's report. However, comparing the two emission peaks, the intensity of 380 nm is sharper and stronger than that of 375 nm and reaches the maximum at 900 °C. Besides, the increased intensity of 375 nm is not as strong as that of 380 nm. Many studies have been carried out to investigate the mechanism of UV emission of ZnO thin films and some reports indicated that the UV emission might be due to the band-to-band transition and the free exciton recombination.[8,10] The near band edge emission of 375 nm was believed to be resulted from the band-to-band transition because it corresponds to the electron energy of about 3.3 eV, which is close to the band gap of ZnO thin films. Another UV emission at 380 nm was considered to be due to the free exciton recombination in ZnO as discussed. However, the energy difference of 375 and 380 nm is 44 meV, which is smaller than the exciton binding energy of 60 meV. The exciton Rydberg constant related to the exciton binding energy is dependent of the reduced effective mass μ and the static dielectric constant ε. ($R \propto \mu/\varepsilon^2$) The dielectric constant obtained in this study is larger than the dielectric constant value of ZnO bulk. The result was considered to responsible for the key factor of the shrinking binding energy.

The XPS analysis is used to investigate the chemical state of ZnO films. The O 1s spectrum was found to consist of two components, centered at 530.1 and 532.0 eV, as shown in the inset of Fig. 6. The lower binding energy is attributed to O–Zn bonding and the other is attributed to O–H bonding due to chemisorbed oxygen on the films.[12,13] As shown in Fig. 6, it is obvious that the relative intensity of O–Zn bonding increased when the annealing

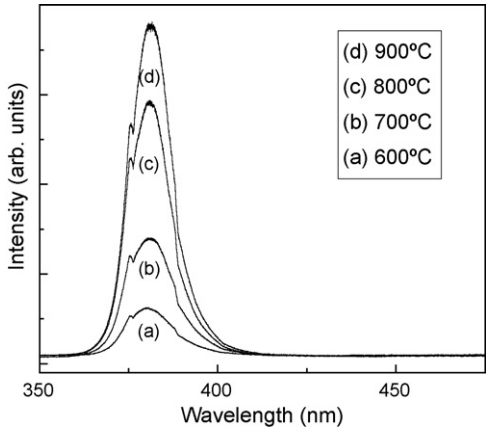

Fig. 5. PL spectra of ZnO films annealed at various temperatures.

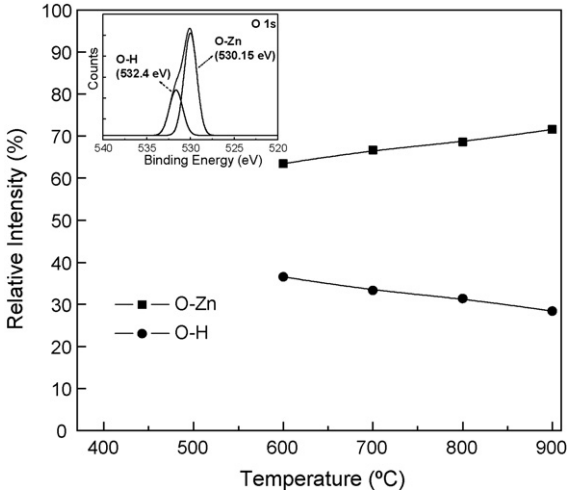

Fig. 6. The relative intensity in O 1s of ZnO films.

temperature increased, whereas that of O–H bonding decreased. The tendency reveals that more zinc and oxygen atoms were bonded as annealing at higher temperature and the crystallinity of ZnO thin film was improved. The result can be confirmed by the XRD spectrum shown in Fig. 3. Nevertheless, there were some zinc or oxygen ions still existed as interstitial in ZnO film, which might act as non-radiative recombination centers and reduce the emission intensity. As reported,[14] the improved crystallinity can decrease the non-radiation recombination and increase the radiation recombination for carriers and avail the existence of the free exciton. Similar results were also obtained in this study. Therefore, as the excited electrons returned from conduction band to valence band, they would fall on the exciton states, which is a little lower than the bottom of conduction band, firstly and then jumped to valence band. As a result, the related emission of exciton recombination was also located at UV spectrum. However, other report mentioned about visible light emission with a similar process.[15] The authors indicated that the O/Zn ratio of as-grown sample which was preheated at 275 °C is 1.044 (oxygen-rich), which indicated that the post-annealing might generate more defects and produce visible light emission. In this study, the O/Zn ratio of ZnO thin film annealing at 900 °C is approximate to 1, which means a stoichiometric thin film was obtained and results in pure UV emission. Based on the analysis above, the strong UV emission at 380 nm can be considered to be effected by free exciton recombination and the diminution of non-radiative centers.

4. Conclusions

In summary, ZnO thin films were prepared by sol–gel technique at room temperature and annealed under various temperatures from 600 to 900 °C. The intensity of UV emission, centered at 375 and 380 nm, increased with the increased temperature, which was consistent with the increased grain size of ZnO films. The emission peak at 375 nm was considered to be owing to the band-to-band transition. According to XPS analysis, the emission peak at 380 nm could be attributed to the free exciton recombination which was resulted from the bonding condition of zinc and oxygen atoms during annealing at high temperature. The excitons were considered to be the dominant role for UV emission in this emission peak.

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