

Preparation of ZnO Thin Films with UV Emission by Spin Coating and Low-temperature Heat-treatment

Bo-An Kang and Ju-Hyun Jeong*

Department of Biomedical Engineering, Nambu University, Republic of Korea

*Department of Ophthalmic Optics, Konyang University, Republic of Korea

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Purpose: This research is that prepare amorphous or crystalline ZnO thin films with pure strong UV emission on soda-lime-silica glass (SLSG) substrates by low-temperature annealing. **Methods:** Growth characteristic and optical properties of the amorphous or nano-crystalline ZnO thin films prepared on soda – lime – silica glass substrates by chemical solution deposition at 100, 150, 200, 250 and 300°C were investigated using X-ray diffraction analysis, ultraviolet – visible – near infrared spectrophotometer, and photoluminescence. **Results:** The films exhibited an amorphous pattern even when finally annealed at 100°C~200°C for 60 min, while crystalline ZnO was obtained by pre-firing at 250 and 300°C. The photoluminescence spectrum of amorphous ZnO films shows a strong NBE emission, while the visible emission is nearly quenched. **Conclusions:** These results indicate it should be possible to cheaply and easily fabricate ZnO-based optoelectronic devices at low temperature, below 200°C, in the future.

Key words: ZnO thin film, Chemical solution deposition, Photoluminescence spectrum

Introduction

Zinc oxide based coatings are of much interest in science and technology due to their interesting potential applications¹⁻³, such as in thermoelectric and gas sensor devices, transparent electrodes, selective surfaces, piezoelectric devices, etc. The wide range of applications is a result of the fact that ZnO is both a piezo-electric and electro-optic (EO) materials, and a semiconductor which possesses a wide band gap (3.3 eV)⁴. The most unique property of ZnO is its large exciton binding energy of 60 meV, which is much larger than those of GaN (24 meV), ZnSe (19 meV) and ZnS (39 meV)⁵. Because of this large binding energy, the exciton is stable at room temperature even in bulk crystals. Owing to these properties, ZnO is considered as a promising material for light-emitting devices and semiconductor lasers with low thresholds in the ultraviolet (UV) region. Generally, the corresponding photoluminescence (PL) spectra obtained from ZnO

thin films shows defect-related deep-level emission^{6,7} (yellow-green emission around 510 nm and red emission around 650 nm) as well as UV near-band-edge emission around 380 nm, which strongly depends upon the preparation methods and growth conditions.

Using molecular beam epitaxy (MBE), rf magnetron sputtering, metal organic chemical vapor deposition (MOCVD) and other methods, high quality ZnO layers have been grown and their structural and optical properties have been extensively studied⁸⁻¹¹. However, most of the reports on the UV emission of ZnO films have been concentrated on high-vacuum processes which are very expensive method from the viewpoint of system and source materials. To meet the industrial needs for the commercially available ZnO devices, the easier and cheaper deposition methods for the ZnO film should be developed. Chemical solution deposition (CSD) is another attractive technique for obtaining thin films and has the advantages of easy control of the film composition and

Corresponding Author Address: Ju-Hyun Jeong, 685 Gasuwon-dong, Seo-gu, Daejeon 302-718, Korea
TEL: +82-42-600-6333, E-mail: jerngju@konyang.ac.kr

easy fabrication of a large-area thin film at low cost¹²⁻¹⁵. Only a few researchers reported that there was accompanied single violet emission of ZnO prepared by CSD¹⁶.

In this work, we first report a simple and efficient method to prepare amorphous or crystalline ZnO thin films with pure strong UV emission on soda-lime-silica glass (SLSG) substrates by low-temperature annealing.

Methods

A homogeneous coating solution was prepared by mixing Zn acetate $[(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}]$ (Merck, Germany) and 2-methoxyethanol ($\text{HOCH}_2\text{CH}_2\text{OCH}_3$) (Merck, Germany). Since Zn acetate has low solubility in 2-methoxyethanol, 2-aminoethanol ($\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) (MEA) (Merck, Germany) was added to obtain clear solution (concentration: 0.6 mol Zn acetate/L2-methoxyethanol). The molar ratio of MEA to Zn acetate was fixed at 1.0. The mixing solution was stirred for 2 h to obtain a homogeneous precursor solution.

Prior to coating process, SLSG substrates were cleaned in deionized water, immersed in H_2O_2 solution, and finally rinsed in acetone. The starting solution was spin-coated onto the cleaned substrate at 4000 rpm for 10 sec in air. The as-deposited film was pre-fired at 100°C, 150°C, 200°C, 250°C and 300°C for 10 min in air. The coating process was repeated 13 times to prepare a thick coating of ZnO. Then the final annealing was performed in air at 100°C, 150°C, 200°C, 250°C and 300°C for 60 min.

The thickness of the finally annealed ZnO thin film was approximately 0.5~0.7 μm , as determined by F20 (Filmetric Inc., San Diego, U.S.A.) using reflection spectrum and the observation of fracture cross-section with a field emission – scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan) of the precursor solution was performed (heating rate: 2°C/min, in air). The crystallinity of the ZnO thin films was investigated by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). A $\text{CuK}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) source was used, and the scanning range was between $2\theta = 20^\circ$ and 70° . The transmittance in the visible range was measured using UV – visible – NIR spectrophotometer (CARY 500 Scan, Varian, Australia). The transmittance was automati-

cally calibrated against that of a bare SLSG substrate as a reference sample, and the absorption coefficient was obtained from the transmittance curve. Room temperature photoluminescence (PL) spectra of the samples were measured by micro-PL system (LabRamHR, Jobin Yvon, France) using 325 nm line of a He-Cd laser as the excitation source.

Results and Discussion

Fig. 1 shows TGA curve of the precursor solution used in this work. A larger weight loss corresponding to pyrolysis of the precursor solution began around 130°C and was completed just below about 200°C, as shown in Fig. 1. TGA curve of the precursor solution (heating rate: 2°C/min) showed large weight loss due to the vaporization and pyrolysis of organics were recognized in the stage of pyrolysis at 150~200°C. Therefore, pyrolysis of the precursor solution is completed below about 200°C. Thus, to investigate the effects of temperatures during pre-firing and final annealing, we prepared ZnO films via the above-mentioned pre-firing and annealing conditions in our experimental procedure.

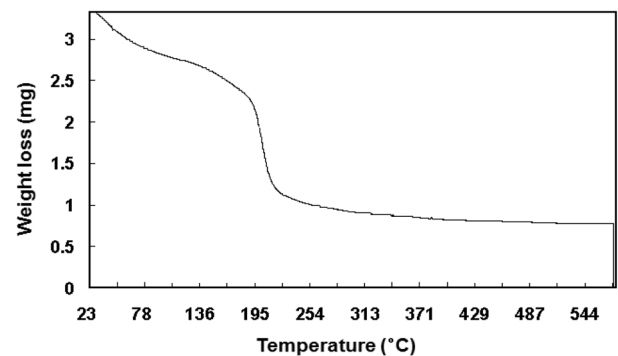


Fig. 1. TGA curve of the precursor solution used in this work.

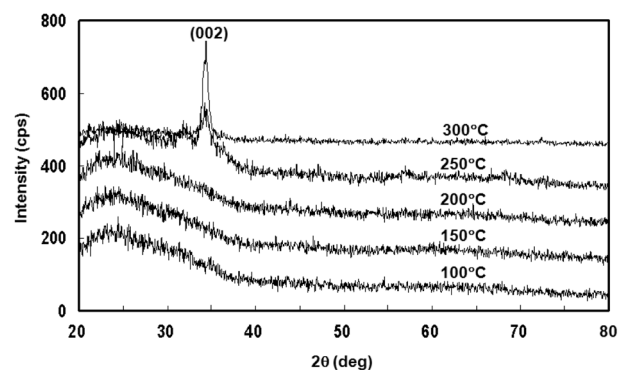


Fig. 2. HRXRD spectra of the ZnO thin films on SLSG substrates heat treated at various temperatures.

Fig. 2 shows the XRD curves of ZnO thin films deposited on SLSG substrates. A (002) peak with a weak (100) reflection is observed at $2\theta=34^\circ$ for the samples heat treated at 250 and 300°C. The films show an amorphous pattern even when finally annealed at 100~200°C for 60 min, which implies the most of the processes occurring up to 200°C are mainly related to removal of organic compounds in precursor, as shown in Fig. 1. On the basis of the XRD data, the lattice *c* parameter has been estimated to be 5.2284 and 5.2700 Å at 250 and 300°C, respectively. This value is similar to the ASTM value of 5.2066 Å for the bulk ZnO. The larger value of lattice constant for the film at 250 and 300°C compared to the standard powder value shows that unit cell is elongated along the *c*-axis, and that compressive forces act in the plane of the ZnO film.

UV transmission measurements were carried out for optical characterization of the films. Fig. 3 shows the visible spectra in the wavelength range from 300 nm to 900 nm of the ZnO thin films annealed at various temperatures on SLSG substrates. A relatively high transmittance above 80% in the visible spectra range and clear absorption edges of the films were observed except the film annealed at 100°C. The transmittance in the UV spectra region decreased abruptly near 3.2~3.3 eV, resulting from band – to – band transition. In this transition, UV absorption occurs due to the excitation of electrons from the filled valence band to the conduction band. The slopes of the absorption edge are sharpened and there is an obvious shift of the absorption edge to longer wavelength with increasing processing temperature.

The optical absorption coefficient α of the films can be

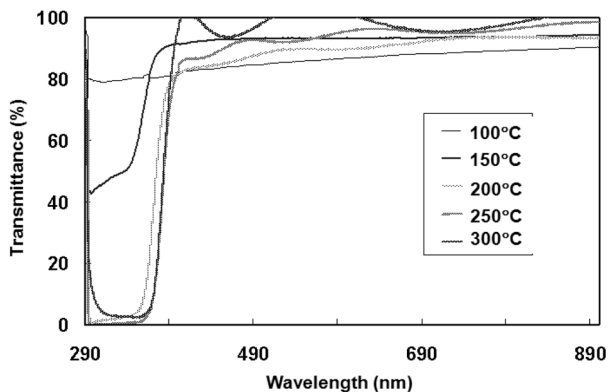


Fig. 3. UV-visible spectra of the ZnO thin films on SLSG substrates heat treated at various temperatures.

calculated from the transmittance using the relationship,

$$I = I_0 e^{-\alpha t} \quad (1)$$

where *I* is the intensity of transmitted light, *I*₀ is the intensity of the incident light, and *t* is the thickness of the ZnO film. As the transmittance is defined as *I*/*I*₀, we obtain a from Eq. (1). It is well known that the absorption coefficient α for allowed direct transitions at a given photon energy *hν* can be expressed as,

$$\alpha = (h\nu - E_g)^{1/2} \quad (2)$$

where, *h* is Plank's constant, ν is the frequency of the incident photon, and *E*_g is optical energy band gap of the film. By plotting α^2 versus *hν* and extrapolation the linear position of the curves to plotting α^2 is zero is *E*_g. The estimated values of the band gap for the ZnO films annealed at various temperatures by an extrapolation method¹⁷ are 3.41 eV, 3.34 eV, and 3.30 eV at 150°C, 200°C, and 250°C, respectively, close to the intrinsic band gap of ZnO (3.2 eV). As can be seen clearly, *E*_g values decrease from 3.41 eV to 3.30 eV with an increase of heating temperature. In other words, the optical energy band gap of our films becomes shorter as heating temperature increases.

The PL spectra at room temperature of amorphous or nano-crystalline ZnO thin films on SLSG substrates obtained by pyrolysis and annealing at 100°C, 150°C, 200°C, 250°C and 300°C is shown in Fig. 4. In the PL spectra, only a strong near-band-edge (NBE) emission is seen for all films except film annealed at 150°C. This NBE peak has been previously attributed to the emission from free exciton in the literature¹⁸. After annealing at

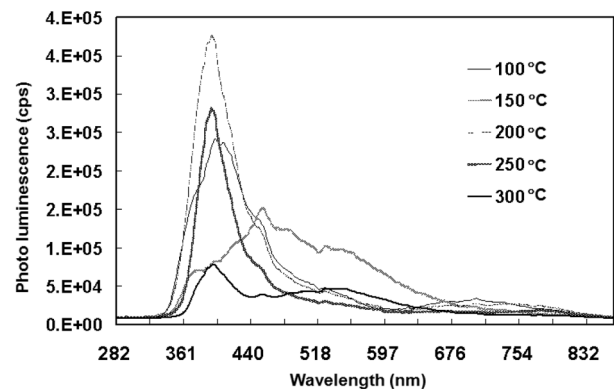


Fig. 4. The PL spectra at room temperature for the ZnO thin films on SLSG substrates heat treated at various temperatures.

250°C and 300°C, the PL spectra of the film was slightly deteriorated, the UV peak was diminished. M. Choi et al.¹⁹ reported that the non-radiative recombination centres were generated by the oxygen vacancies, which increase with increasing temperature. For the film annealed at 200°C, the largest NBE peak intensity in the PL spectra was observed. This indicates that the annealing temperature of 200°C is an optimum condition for the formation of ZnO thin film with a strong single NBE emission. A distinct defect-related broad green (deep-level) emission is not seen in all the samples except the film annealed at 150°C. The origin of the green luminescence is still in dispute, but it is usually attributed to emission related to grain boundary defects and other interior defects such as oxygen vacancy (VO) and impurities²⁰.

Apparently, for the film annealed at low temperature, 200°C, the FWHM value of the PL spectrum curve was 28.7 meV and this value is believed to be comparable with any previously reported values of ZnO films prepared by chemical solution deposition.

The PL spectrum of amorphous ZnO thin films with strong UV emission was observed while the visible emission was nearly fully quenched. The features can be explained reasonably by Z. Wang et al. as follows¹⁶: (i) The higher degree of disorder likely leads to intensity emission stronger than that of crystalline ZnO. (ii) Quantum confinement effects (QCE) occur when the particle radius is of the order the exciton Bohr radius (1.8 nm, ZnO). Although it is difficult to obtain the exact diameter of amorphous ZnO, we assume that the sizes of amorphous ZnO are smaller than 1.8 nm.

It is well understood that PL spectra depend on the stoichiometry and the microstructure of the film. Therefore, these results indicate that the obtained amorphous ZnO films at low temperature are well close to stoichiometry and of optically high quality. Our findings show that the PL property of the ZnO thin films is improved because the grain size decreases with low-temperature annealing.

Conclusions

In this study, amorphous or nano crystalline ZnO thin films were grown on inexpensive SLSG substrates using chemical solution deposition with a zinc acetate – 2 methoxy ethanol – MEA solution. From XRD analysis, the

films exhibited an amorphous pattern even when finally annealed at 100°C~200°C for 60 min, while crystalline ZnO was obtained by pre-firing at 250 and 300°C. A relatively high transmittance in the visible spectra range and clear absorption edges of the films were observed except the film annealed at 100°C. From the PL measurement, a strong NBE emission was observed for the ZnO film annealed at 200°C, while the deep-level emission is almost undetectable except the film annealed at 150°C. These results indicate it should be possible to cheaply and easily fabricate ZnO-based optoelectronic devices at low temperature, below 200°C, in the future.

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스핀코팅 및 저온열처리에 의한 자외선 발광특성을 갖는 산화아연 박막의 제조

강보안 · 정주현*

남부대학교 의료공학과, *건양대학교 안경광학과

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목적: 본 논문은 저온열처리로 비결정 또는 결정 ZnO 박막의 UV emission 가능하다는 것이다. **방법:** 화학적 용액법을 이용하여 소다-라임-실리카 유리 위에 100, 150, 200, 250 및 300°C로 열처리하여 비정질 및 나노 결정질 ZnO 박막을 제조하였으며, 박막의 성장 특성 및 광학적 특성을 X-선 회절 분석법, 자외선-가시광선-근적외선 분광법 및 발광분석법을 통하여 분석하였다. **결과:** 100°C~200°C에서 60분간 열처리된 박막은 비정질 특성을 나타내고 있었으며, 250°C 및 300°C로 열처리된 박막에서는 ZnO 결정상이 나타났다. 비정질 ZnO 박막의 PL분석에 의하면 매우 강한 Near-band-edge emission이 나타났으며, Green emission은 거의 검출되지 않았다. **결론:** 앞으로는 저온에서 ZnO 광전자소자를 쉽게 제조할 수 있을 것이다.

주제어: 산화아연 박막, 화학적 용액법, 발광곡선