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Sol-gel Derived-highly Transparent c-axis Oriented ZnO Thin Films

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Purpose: A simple and efficient method to prepare nanocrystalline ZnO thin film with pure strong UV emission on soda-lime-silica glass substrates by low-temperature annealing was improved. **Methods:** Crystal structural, surface morphological, and optical characteristics of nanocrystalline ZnO thin films deposited on soda-lime-silica glass substrates by prefiring final annealing process at 300°C were investigated by using X-ray diffraction analysis, field emission-scanning electron microscope, scanning probe microscope, ultraviolet-visible-near infrared spectrophotometer, and photoluminescence. **Results:** Highly c-axis-oriented ZnO films were obtained by prefiring at 300°C. A high transmittance in the visible spectra range and clear absorption edge in the ultra violet range of the film was observed. The PL spectrum of ZnO thin film with a deep near band edge emission was observed while the defect-related broad green emission was nearly quenched. **Conclusions:** Our work will be possibly adopted to cheaply and easily fabricate ZnO-based optoelectronic devices at low temperature, below 300°C, in the future.

Key words: ZnO thin film, Nanocrystalline, Transmittance, Photoluminescence

Introduction

Zinc oxide based coatings are of much interest in science and technology due to their interesting potential applications[1-3], such as in thermoelectric and gas sensor devices, transparent electrodes, selective surfaces, piezo-electric 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 studied[8-11]. 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 easy fabrication of a large-area thin film at low cost[12-15]. Only a few researchers reported that there was accompa-

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nied single violet emission of ZnO prepared by CSD[16].

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

Experimental

A homogeneous coating solution was prepared by mixing Zn acetate [$(CH_3COO)_2Zn \cdot 2H_2O$] (Merck, Germany) and 2-methoxyethanol ($HOCH_2CH_2OCH_3$) (Merck, Germany). Since Zn acetate has a low solubility in 2-methoxyethanol, 2-aminoethanol ($H_2HCH_2CH_2OH$) (MEA) (Merck, Germany) was added to obtain clear solution (concentration: 0.6 mol Zn acetate / L 2-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 sol.

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 10sec in air. The as-deposited film was prefired at 300°C for 10 min in air. The coating process was repeated 13times to prepare a thick coating of ZnO. Then the final annealing was performed in air at 300°C for 60 min. Fig. 1 illustrates the representative processing scheme for preparation of ZnO thin film.

The thickness of the finally annealed ZnO thin film was approximately 0.5~0.7 μm, as determined by observations of fracture cross-sections with field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Since the defects of finally annealed film were largely affected by the elimination modes of the organics in the precursor for the CSD-based process and the structural and optical properties were vital for semiconductor devices especially for light emitting devices, it is necessary to study how these properties are affected by prefiring and thermal annealing. Thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan) of the coating sol was performed. The crystallinity of the ZnO thin film was investigated by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). A CuKα (= 1.54056Å) source was used, and the scanning range was between $2\theta = 20^o$ and 70^o. The surface morphology of the

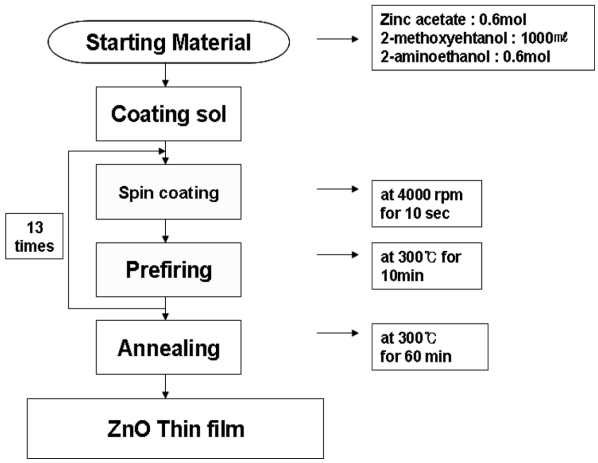

Fig. 1. Flow chart of the experimental procedure.

film was evaluated from FE-SEM micrograph. The growth mechanism and the surface roughness of the thin film were studied by using a scanning probe microscope (SPM, PSIA, Korea). All SPM measurements were performed in air using the tapping mode. The transmittance in the visible range was measured using UV-visible-NIR spectrophotometer (CARY-500 Scan, Varian, Australia). The transmittance was automatically 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 sample was 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. 2 shows TGA curve of the coating sol used in this work. A larger weight loss corresponding to pyrolysis of the starting sol began around 130°C and was completed just below about 200°C, as shown in Fig. 1. TGA curve of the starting sol (heating rate: 2°C/min) dried at 80°C for 24 h showed large weight loss due to the vaporization and pyrolysis of organics were recognized in the stage of pyrolysis at 150°C~200°C. Therefore, pyrolysis of the starting solution is completed below about 200°C.

Fig. 3 shows the XRD curve of ZnO thin film deposited on SLSG substrates. A strong (002) peak is observed at 2θ~34° for the sample heat treated at 300°C. This indicates the ZnO thin film prepared at 300°C by using CSD with zinc acetate-2 methoxyethanol-MEA solution show a *c*-axis orientation, i.e., a vertical growth to the substrate sur-

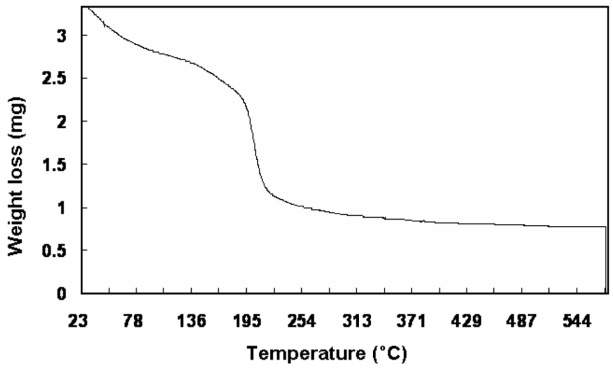

Fig. 2. TGA curve of the coating sol used in this work.

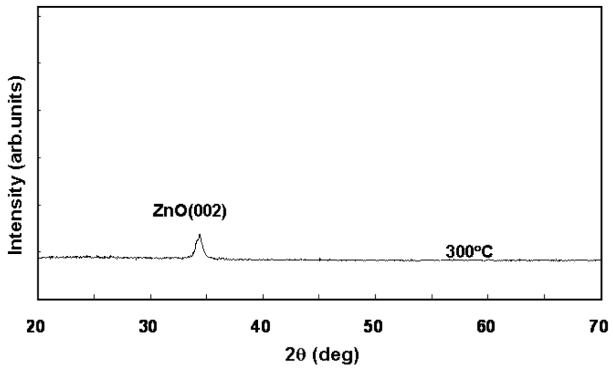

Fig. 3. HRXRD spectra of the ZnO thin film on SLSG substrate heat treated at 300°C.

face. The *c*-axis orientation in the ZnO films prepared by using a physical dry method can be understood by the 'grain-boundary movement' model proposed by Loder *et al.*[17].

According to that model, at the very first stage of film growth, certain grains with particular orientations start to grow. By thermodynamical coalescence of crystallites during film growth, orientation growth (*c*-axis orientation for ZnO films) is achieved. From the report of Ohyama *et al.*[18], for the ZnO films prepared by using a CSD with zinc acetate 2 methoxyethanol MEA solution, removal of the solvent and the organic substances produced by acetate decomposition prior to crystallization may be one of the key factors that provide oriented crystal growth.

The vaporizationof the solvents, the decomposition of the zinc acetate, and the crystallization of the zinc oxide may occur almost simultaneously when the heating rate is high. Since the structural relaxation of the gel film, which is induced by the solvent vaporization and acetate decomposition, can take place only before the crystallization, the simultaneous vaporization, decomposition, and crystallization may give the film less chance to be structurally relaxed[18]. On the other hand, when the heating rate is low, the gel film is given enough time to structurally relax before crystallization, resulting indenser ceramic films. Moreover, when the prefiring temperatures are too high (> 300C), vaporization of the solvents, and thermal decomposition of the zinc acetate may take place abruptly and simultaneously with the crystallization, disturbing the unidirectional crystal growth[18].

We also observed the full width at half-maximum (FWHM), 0.64 at 300°C. This result indicates that the ZnO thin film prepared with zinc acetate 2 methoxyethanol MEA solution and heat treated at low temperature can be expected to have relatively high crystallinity.

On the basis of the XRD data, the lattice *c* parameter has been estimated to be 5.2700Å at 300°C. This values are similar to the ASTM value of 5.2066Å for the bulk ZnO. The larger value of lattice constant for the film heat treated at 300°C compared to the standard powder value shows that the unit cell is elongated along the *c*-axis, and that compressive forces act in the plane of the ZnO film.

In order to more exactly investigate the structural properties of ZnO films, we calculated the stress in the film. The calculation of the film stress is based on the bixial strain model[19]. Film strain $\varepsilon = (c_{film} / c_0) / c_0$, where c_0 is the strain-free lattice parameter measured from ZnO powder sample. To drive the stress of the film parallel to the film's surface, we used the following formula[19], which is valid for a hexagonal lattice:

$$\sigma_{film} = [2c^2_{13} / 2c_{13} - c_{33}(c_{11} + c_{12}) / 2c_{13}]\varepsilon \quad (1)$$

where c_{ij} are elastic stiffness constant for ZnO. The elastic constant were used: $c_{11} = 208.8$ GPa, $c_{33} = 213.8$ Gpa, $c_{12} = 119.7$ Gpa, and $c_{13} = 104.2$ Gpa[20]. The stress of the film can be estimated using Eq. (1) and is -0.2835×10^{10} dyne/cm^2. The negative sign for the film heated at 300°C indicates that the lattice constant *c* is elongated as compared to unstressed powder; therefore, the film is in a state of elongation.

From the FWHM and the peak position of the ZnO (002) peak, the grain size *D* was derived from the well-known Scherrer's relation[21] as below,

$$D = k\lambda / B\cos\theta \quad (2)$$

Where, $\lambda = 1.54056$Å is the wavelength of the CuKα radiation, $k = 0.9$ is the correction factor, *B* is the FWHM of the ZnO (002) peak, and θ is the diffraction angle. The

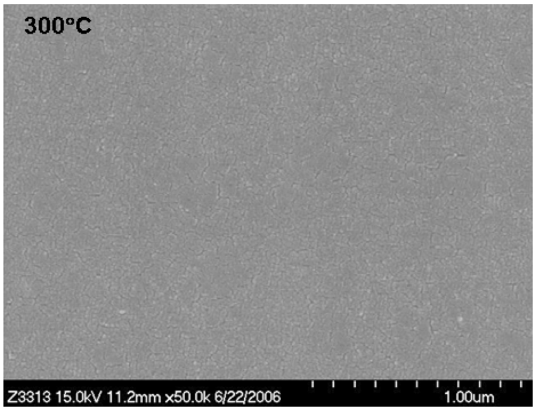

Fig. 4. FE-SEM image of the ZnO thin film on SLSG substrate heat treated at 300°C.

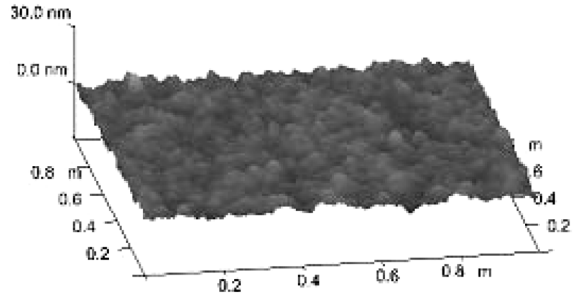

Fig. 5. Three-dimensional SPM image of the ZnO thin film on SLSG substrate.

rain size is determined to be 12.96 nm.

Fig. 4 shows the FE-SEM photograph of the ZnO thin film after heat treatment at 300°C. Particulate structure is indistinct. There is no evidence of aggregation of particles and nano-sized particles were obtained in the film.

Fig. 5 shows typical SPM micrographs (1 μm × 1μm) of the ZnO thin film obtained at the annealing temperature of 300°C. We can observe many regular and uniform grains in the SPM images of the film after annealing.

UV transmission measurement was carried out for optical characterization of the films.

Fig. 6 shows the visible spectra in the wavelength range from 340 nm to 900 nm of the ZnO thin film after annealing on SLSG substrate. A relatively high transmittance in the visible spectra range and clear absorption edge of the film were observed. The high transmittance of the film is attributed to the small particle size which eliminates light scattering[21]. 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.

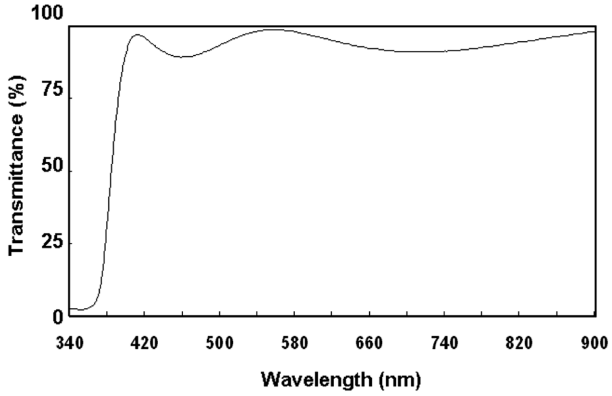

Fig. 6. UV-visible spectra of the ZnO thin film on SLSG substrate.

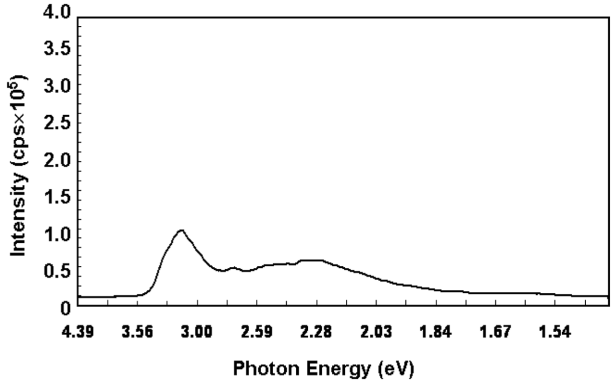

Fig. 7. The PL spectra at room temperature for the ZnO thin film on SLSG substrate.

The optical absorption coefficient of the film can be calculated from the transmittance. The estimated value of the band gap for the ZnO film by an extrapolation method[22] are 3.25 eV close to the intrinsic band gap of ZnO (3.2 eV).

The PL spectra at room temperature of nano-crystalline ZnO thin film on SLSG substrate obtained by pyrolysis and annealing at 300°C shown in Fig. 7. In the PL spectra, only a near-band-edge (NBE) emission is seen. This NBE peak has been previously attributed to the emission from free exciton in the literature[23]. The defect-related broad green (deep-level) emission is not seen. 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 (V_O) and impurities[24].

In this work, for the film annealed at low temperature, 300°C, the FWHM value of the PL spectrum curve was 24.9 meV and this value is believed to be smaller than any previously reported values of ZnO films prepared by

CSD. Several important properties based on ZnO, such as electroluminescence (EL) and PL, are strongly related to the defect formation. Many researchers reported that green-orange PL emitted from ZnO films is probably due to different point defects[25] and strongly dependent on the predominant defect, which affects the deep-level emissions. Vanheusden *et al*.[26] and Chen *et al*.[5] reported that oxygen vacancies are responsible for the green emission. However, Zhang *et al*.[27] and Lin *et al*.[28] considered the green emission of ZnO films to be due to zinc vacancies and antisite O_{zn}, respectively.

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

Conclusions

In this study, nano-crystalline ZnO thin film was grown on inexpensive SLSG substrate using a CSD with a zinc acetate-2 methoxyethanol- MEA solution. From XRD analysis, the film exhibited a highly c-axis oriented ZnO. A relatively high transmittance in the visible spectra range and clear absorption edge of the film were observed. From the PL measurement, a deep NBE emission was observed for the ZnO film annealed at low temperature, 300^{o}C, while the deep-level emission is almost undetectable. This result indicates that it should be possible to cheaply and easily fabricate ZnO-based optoelectronic devices at low temperature, below 300^{o}C, in the future.

Acknowledgment

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졸-겔법에 의한 c-축 배향성을 가진 고투과율 ZnO 박막의 제조

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(2007년 10월 25일 받음, 2007년 11월 20일 수정본 받음)

목적: 저온에서 열처리에 의해 소다-라임-실리카 유리 위에 강한 UV방사 나노결정 ZnO박막을 단순하고 효율적 방법으로 개선하고자 한다. **방법**: 소다-라임-실리카 유리 위에 코팅되고 전열처리 및 300°C의 후열처리를 행하여 제조된 나노 결정질 ZnO 박막의 결정 구조적, 표면 형상적 및 광학적 특성을 X-선 회절 분석, 전계방사 주사형 전자현미경, 원자간력 현미경, ultra violet - visible - near infrared spectrophotometer 및 photoluminescence를 이용하여 분석하였다. **결과**: 가시광 영역에서 높은 투과율과 자외부에서 뚜렷한 흡수밴드를 갖는 c-축으로 고배향된 ZnO 박막을 300°C의 후열처리를 통하여 얻을 수 있었다. 비교적 뚜렷한 near band edge 발광을 보이는 photoluminescence 스펙트럼이 나타났으며, 결함에 의한 완만한 녹색 발광은 거의 관찰되지 않았다. **결론**: 앞으로 본 연구는 300°C 이하의 저온에서 저렴하고 쉽게 ZnO을 기초로한 광전기 소자에 적용될 것이다.

주제어: ZnO 박막, 나노결정질, 투과율, Photoluminescence