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Growth, structure and optical properties of amorphous or nano-crystalline ZnO thin films prepared by prefiring-final annealing

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The structural, surface morphological, and optical characteristics of amorphous or nanocrystalline ZnO thin films deposited on soda-lime-silica glass substrates by a prefiring-final annealing process at various temperatures were investigated using X-ray diffraction analysis, a field emission-scanning electron microscope, a scanning probe microscope, a ultraviolet-visible-near infrared spectrophotometer, and photoluminescence (PL). The films exhibited an amorphous pattern even when finally annealed at 100 °C-200 °C for 60 minutes, while highly c-axis oriented ZnO films were obtained by prefiring at high temperature, 400 °C and 500 °C. A relatively high transmittance in the visible spectra range and clear absorption edges of the films were observed except for the film annealed at 100 °C. The PL spectra of amorphous ZnO thin films annealed at 100 °C -200 °C with strong near-band-edge (NBE) emission were observed while the defect-related broad green emission was nearly fully quenched. After high-temperature prefiring and final annealing at above 300 °C, the PL spectra of the films were greatly deteriorated, the UV peak was diminished.

Key words: ZnO thin films, Amorphous pattern, Transmittance, NBE emission.

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, as 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) material, 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 to be a promising material for light-emitting devices and semiconductor lasers with low thresholds in the ultraviolet (UV) region. Generally, the corresponding PL spectra obtained from ZnO thin films shows defectrelated deep-level emission [6, 7] (yellow-green emission around 510 nm and red emission around 650 nm) as well as UV NBE 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 concentrated on high-vacuum processes which are very expensive methods from the viewpoint of the system and source materials. To meet the industrial needs for commercially available ZnO devices, easier and cheaper deposition methods for ZnO films need to 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 have reported an accompanied single violet emission of ZnO prepared by CSD [16].

In this study, 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.

Experimental

A homogeneous coating solution was prepared by mixing Zn acetate [(CH₃COO)₂Zn·2H₂O] (Merck, Germany) and 2-methoxyethanol (HOCH₂CH₂OCH₃) (Merck,

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Fig. 1. Flow chart of the experimental procedure.

Germany). Since Zn acetate has a low solubility in 2methoxyethanol, 2-aminoethanol ($H_2HCH_2CH_2OH$) (MEA) (Merck, Germany) was added to obtain a 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 mixed solution was stirred for 2 h to obtain a homogeneous sol.

Prior to the coating process, SLSG substrates were cleaned in deionized water, immersed in an H_2O_2 solution, and finally rinsed in acetone.

The starting solution was spin-coated onto the cleaned substrates at 4000 rpm for 10 s in air. The asdeposited films were prefired at 100, 200, 300, 400, and 500 °C for 10 minutes 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, 200, 300, 400, and 500 °C for 60 minutes. Figure 1 illustrates the processing scheme for preparation of ZnO thin films.

The thicknesses of the finally annealed ZnO thin films were approximately 0.5-0.7 µm, as determined by observations of fracture cross-sections with a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Since the defects in the finally annealed films were largely affected by the elimination modes of the organics in the precursor during the CSDbased process and the structural and optical properties are 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 films was investigated by using a high resolution X-ray diffraction technique (HRXRD, X'pert-PRO, Philips, Netherlands). A CuK α (λ =1.54056 Å) source was used, and the scanning range was between $2\theta = 20^{\circ}$ and 70° . The surface morphology of the films was evaluated from FE-SEM micrographs. The growth mechanism and the surface roughness of the thin films were studied using a scanning probe microscope (SPM, PSIA, Republic of Korea). All SPM measurements were performed in air using the tapping mode. The transmittance in the visible range was measured using a 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 PL spectra of the samples were measured by a micro-PL system (LabRamHR, Jobin Yvon, France) using the 325 nm line of a He-Cd laser as the excitation source.

Results and Discussion

Figure 2 shows a TGA curve of the coating sol used in this study. 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. The TGA curve of the starting sol (heating rate: 2 K·minute⁻¹) dried at 80 °C for 24 h showed a large weight loss due to the vaporization and pyrolysis of organics was recognized in the stage of pyrolysis between 150-200 °C. Therefore, pyrolysis of the starting solution is complete below about 200 °C. Thus, to investigate the effects of temperatures during prefiring and final annealing, we prepared ZnO films via the above- mentioned prefiring and annealing conditions in



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



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

our experimental procedure.

Figure 3 shows the XRD curves of ZnO thin films deposited on SLSG substrates. A strong (002) peak is observed at 2θ =34° for the samples heat treated at above 300 °C. This indicates ZnO thin films prepared at above 300 °C by using the CSD process with the zinc acetate-2 methoxyethanol-MEA solution show a *c*-axis orientation, i.e., a growth vertical to the substrate surface. The *c*-axis orientation in the ZnO films prepared using a physically dry method can be understood by the 'grain-boundary movement' model proposed by Loder et al. [17]. According to this 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, oriented growth (*c*-axis orientation for ZnO films) is achieved.

From the report of Ohyama et al. [18], for ZnO films prepared using a CSD process 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 provides oriented crystal growth. The vaporization of 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 in denser ceramic films. Moreover, when the prefiring temperatures are too high (> $300 \,^{\circ}$ C), 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].

However, in this study, it should be noted that *c*-axis oriented ZnO thin films were obtained by prefiring at a high temperature, 400 and 500 °C, and heating at a high rate. This result suggests that structural relaxation of the precursor gel before crystallization, by heating the film at low rates or prefiring at low temperatures of 200-300 °C, is unessential for obtaining oriented ZnO films.

The films show an amorphous pattern even when finally annealed at 100-200 °C for 60 minutes, 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. 2.

We also observed that with an increase in heat treatment temperature, the full widths at half-maximum (FWHM) decrease from 0.64° at 300 °C to 0.37° at 500 °C, while the peak intensity shows an increase with annealing temperature, as shown in Table 1. These results

Table 1. The peak intensity and FHWM of the (002) reflection from ZnO/SLSG

Temperature	Peak intensity (cps)	FWHM (°)
100 °C	-	—
200 °C	_	-
300 °C	295	0.64
400 °C	930	0.50
500 °C	2296	0.37

Table 2. Lattice parameter c and d-length calculated from the XRD patterns of ZnO (002) reflection

d	С
-	—
-	_
2.6085 Å	5.2700 Å
2.6048 Å	5.2096 Å
2.5968 Å	5.1963 Å
2.6033 Å	5.2066 Å
	<i>d</i> - 2.6085 Å 2.6048 Å 2.5968 Å 2.6033 Å

indicate that the ZnO thin film prepared with zinc acetate-2 methoxyethanol-MEA solution and heat treated at high temperature can be expected to have high crystallinity. The increase in intensity of the (002) reflection at 400 °C and 500 °C is a direct indication of the large volume of material oriented with (002) planes perpendicular to the SLSG substrate surface.

On the basis of the XRD data, the lattice c parameter has been estimated to be 5.2700 Å, 5.2096 Å, and 5.1963 Å at 300 °C, 400 °C, and 500 °C, respectively, as shown in Table 2. These values are similar to the ASTM value of 5.2066 Å for bulk ZnO. The larger values of the lattice constant for the films heat treated at 300 °C and 400 °C compared to the standard powder value shows that the unit cell is elongated along the caxis, and that compressive forces act in the plane of the ZnO film. These compressive forces disappear as the heat treatment temperature is increased to 500 °C.

In order to investigate more exactly 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 $\varepsilon_z = (c-c_0)/c_0$, 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:

$$\sigma = [2c_{13}^2/2c_{13} - c_{33}(c_{11} + c_{12})/2c_{13}]e_z \tag{1}$$

where c_{ij} are elastic stiffness constant for ZnO. The elastic constants used were: 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 plotted as a function of the heat-treatment temperature in Fig. 4. The negative sign for the film heated at 300 °C and 400 °C indicates that the lattice constant c is elongated as compared to the unstressed powder; therefore, the



Fig. 4. Variation of the stress induced in the ZnO films as a function of the heating temperature.

film is in a state of elongation. The film becomes nearly stress free at 500 $^{\circ}$ C.

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:

$$D = k\lambda / B \cos \theta \tag{2}$$

where, λ =1.54056 Å is the wavelength of the CuK α radiation, k=0.9 is the correction factor, B is the FWHM of the ZnO(002) peak, and θ is the diffraction angle. The grain size increases with an increase in the annealing temperature above 300 °C from 12.96 nm at 300 °C to 22.19 nm at 500 °C.

Figure 5 shows FE-SEM micrographs of ZnO thin films after heat treatment at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C, respectively. A particulate structure is indistinct in all films except films treated at 400 °C and 500 °C. The FE-SEM image of the ZnO film prepared at 200 °C shows a different morphology compared to the other images; some cracklike texture probably due to vaporization of organics is visible on the surface of the film. There is no evidence of aggregation of particles and nano-sized particles were obtained in the films annealed at 400 °C and 500 °C.

Figure 6 shows typical SPM micrographs (1 μ m×1 μ m) of ZnO thin films obtained at the annealing temperatures of 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C. We can observe many regular and uniform grains in the SPM images of the films annealed at 300 °C, 400 °C and 500 °C. In the amorphous films annealed at low temperatures, below 200 °C, a relatively rough surface structure probably due to vaporize residual organics during annealing as seen in Fig. 6(a) and (b). As the annealing temperature increases to 500 °C, the surface morphology becomes rough by grain growth [Fig. 6(e)].

UV transmission measurements were carried out for optical characterization of the films. Fig. 7 shows the visible spectra in the wavelength range from 340 nm to 900 nm of ZnO thin films annealed at various temperatures on SLSG substrates. A relatively high transmittance in the visible spectral range and clear absorption edges of the films were observed except for the film annealed at 100 °C. The high transmittances of the films are attributed to the small particle size which eliminates light scattering [22]. The transmittance in the UV spectral 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 optical absorption coefficient α of the films can be calculated from the transmittance using the relationship:

$$I = I_0 e^{-\alpha t} \tag{3}$$

where *I* is the intensity of the 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 α from Eq. (3). It is well known that the



Fig. 5. FE-SEM images of ZnO thin films on SLSG substrates heat treated at various temperatures.



Fig. 6. Three-dimensional SPM images of ZnO thin films on SLSG substrates heat treated at various temperatures.



Fig. 7. UV-visible spectra of ZnO thin films on SLSG substrates heat treated at various temperatures.

absorption coefficient α for allowed direct transitions at a given photon energy hv can be expressed as:

$$\alpha \cong (h \nu - E_g)^{1/2} \tag{4}$$

where, *h* is Plank's constant, ν is the frequency of the incident photon, and E_g is the optical energy band gap of the film. By plotting α^2 versus $h\nu$ and extrapolating the linear position of the curves to α^2 is zero gives E_g . The estimated values of the band gap for ZnO films annealed at various temperatures by this extrapolation method [23] are 3.34 eV, 3.25 eV, 3.28 eV and 3.30 eV at 200 °C, 300 °C, 400 °C, and 500 °C, respectively, close to the instinsic band gap of ZnO (3.2 eV).

The PL spectra at room temperature of amorphous or nano-crystalline ZnO thin films on SLSG substrates



Fig. 8. The PL spectra at room temperature for ZnO thin films on SLSG substrates heat treated at various temperatures.

obtained by pyrolysis and annealing at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C are shown in Fig. 8 and Table 3. In the PL spectra, for the films annealed at below 200 °C, only a strong NBE emission is seen. This NBE peak has been previously attributed to the emission from a free exciton in the literature [24]. The intensity of NBE emission peaks increase with an increase of annealing temperature up to 200 °C and rapidly decrease again with an increase of annealing temperature from 300 °C to 500 °C. After high-temperature annealing above 300 °C, the PL spectra of the film were greatly deteriorated, and the UV peak was diminished. The PL intensity decreases at high-temperature by a thermally-activated non-radiative recombination mechanism. Choi and Ma [25] reported that the non-radiative recombi-

Table 3. The peak intensity, the peak energy and FHWM of the NBE emission peak from ZnO/SLSG

Temperature	Peak intensity (cps)	Peak energy (eV)	FWHM
100 °C	242020	3.10	50.8
200 °C	376098.6	3.14	28.7
300 °C	78168	3.13	24.9
400 °C	—	_	—
500 °C	_	_	-

nation centres were generated by 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 an annealing temperature of 200 °C is an optimum condition for the formation of a ZnO thin film with a strong single NBE emission. The defect-related broad green (deep-level) emission is not seen in all the samples except for the film annealed at 500 °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 vacancies (V_0) and impurities [26].

Apparently, the degradation of PL is in contrast with the XRD results, which have shown an improvement of crystal quality of the films. The crystallinity of the ZnO films annealed at 400 °C and 500 °C was superior to that of films annealed at low temperature, whereas the PL properties of the ZnO films annealed at 100 °C and 200 °C were better than those annealed at higher temperatures. For the film annealed at a low temperature, 200 °C, the FWHM value of the PL spectrum curve was 28.7 meV and this value is believed to be smaller than any previously reported value 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 [27] and strongly dependent on the predominant defect, which affects the deep-level emissions. Vanheusden et al. [28] and Chen et al. [5] reported that oxygen vacancies are responsible for the green emission. However, Zhang et al. [29] and Lin et al. [30] considered the green emission of ZnO films to be due to zinc vacancies and antisite O_{zn} , respectively.

The PL spectra of amorphous ZnO thin films with strong UV emission was observed while the visible emission was nearly fully quenched. These features can be explained reasonably by Wang et al. as follows [16]: (i) The higher degree of disorder likely leads to stronger emission than that of crystalline ZnO. (ii) Quantum confinement effects (QCE) occur when the particle radius is of the order of 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 a film. Therefore, these results indicate that the amorphous ZnO films obtained at low temperature are very 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 a CSD process with a zinc acetate - 2 methoxyethanol - MEA solution. From XRD analysis, the films exhibited an amorphous pattern even when finally annealed at 100 °C-200 °C for 60 minutes, while highly c-axis oriented ZnO were obtained by prefiring at a high temperature, 400 °C and 500 °C. A relatively high transmittance in the visible spectral range and clear absorption edges of the films were observed except for the film annealed at 100 °C. From the PL measurements, a strong NBE emission was observed for the ZnO films annealed at low temperature, below 200 °C, while the deep-level emission is almost undetectable except for the film annealed at 500 °C. These results indicate that 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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