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The microstructure of Al-doped ZnO thin films by a sol-gel dip-coating method

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These days, thin film metal oxide semiconductor have been intensively studied for optical and electronic device applications. As a II-VI compound semiconductor, zinc oxide (ZnO) is a wide band gap semiconductor ($E_g = 3.3 \text{ eV}$) at room temperature with a Wurtzite crystal structure. In particular ZnO can be employed as the transparent conducting oxide (TCO) in solar cell applications due to its advantages of low cost, high productivity, and excellent electrical conductivity. In this paper, aluminum doped zinc oxide polycrystalline thin films (AZO) have been prepared on glass substrates by a sol-gel dip-coating process. The quantity of aluminum in the solution was 1.0 at.%. After deposition, the films were pre-heated at 350 °C for 10 minutes and then the films were inserted in a furnace and post-heated at 500, 550, 600, 650, 700 °C for 1.5 h. We investigated the structural and microstructural properties of AZO thin film through X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis, respectively. Also we studied the electrical resistance and transmittance of specimens to employ for TCO applications.

Key words: Al-doped ZnO, Transparent conducting oxide, Sol-gel process, Thin films.

Introduction

Over the past few years, transparent electrode materials with high transmittance and good electrical conductivity have been intensively investigated due to the development of flat panel displays, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), and solar cells [1]. Requirements for transparent electrode materials in these applications are stringent: transmittance in the visible wavelength range should be higher than 85%, a low resistivity (10^{-3} ~ $10^{-4} \Omega \cdot cm$), a high chemical stability, and also thermal stability [2-3]. Indium tin oxide (ITO) films have been widely employed as transparent conducting oxide (TCO) at present. However, ITO has some problems such as low stability, toxicity and high cost due to limited indium resources [4]. Unlike the more commonly used ITO, zinc oxide (ZnO) is a nontoxic and inexpensive material that has gained attention recently. It is also a chemically and thermally stable material. ZnO is a II-VI n-type semiconductor because of the Zn interstitials and oxygen vacancies [5]. It has a high exciton binding energy of 60 meV and a wide direct band gap of approximately 3.3 eV at room temperature [5]. Pure ZnO films have high visible transparency and low electrical conductivity [5]. For these reasons, ZnO has currently been proposed as a TCO material in place of ITO.

For the purpose of improving electrical, optical and chemical properties, ZnO can be doped with various dopants to form new materials for TCO films: Cudoped ZnO (CZO), B-doped ZnO (BZO), Ga-doped ZnO (GZO), In-doped ZnO (IZO), Sn-doped ZnO (SZO) and Al-doped ZnO (AZO) [6-9]. In particular, AZO thin films have been investigated as a TCO in recent times because AZO films have a low resistivity of $2-4 \times 10^{-4} \,\Omega \cdot cm$ which is similar to that of ITO films [10-11]. Also AZO films are wide band gap semiconductors ($E_g = 3.4-3.9 \text{ eV}$), which exhibit good optical characteristics in the visible and near-infrared (IR) regions [12]. In addition, the structural, optical and electrical properties of ZnO films are governed by the deposition parameters, post-treatment and deposition methods. Undoped and doped ZnO thin films have been prepared by a variety of thin film deposition techniques, such as chemical vapor deposition, DC and RF magnetron sputtering, electron beam evaporation, thermal plasma deposition, pulsed laser deposition, metal organic chemical vapor deposition (MOCVD), spray pyrolysis and a sol-gel method [13-21]. Among these methods, the sol-gel process is an attractive technique for fabricating thin films due to the homogeneity of the precursor, a large-area coating capability and mass-production with a low cost.

In this paper, AZO thin films have been prepared by a sol-gel dip-coating method, the effects of post-heat treatment conditions on the optical, electrical properties and microstructure are investigated.

Experimental Details

In these experiments, the thin films have been prepared by the sol-gel dip-coating method. As starting materials, zinc acetate dihydrate $(Zn(CH_3COO)_2 \cdot 2H_2O)$

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and aluminum chloride hexahydrate (AlCl₃ \cdot 6H₂O) were used. 2-methoxyethanol and monoethanolamine (MEA) were used as solvent and stabilizer, respectively. Zinc acetate dihydrate was first dissolved in a mixture of 2methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0 and the concentration of zinc acetate dihydrate was 0.7 mol/l. The Al dopant concentration was 1.0 at.% with respect to Zn. The solution was stirred at 60 °C for 2 h to yield a clear and homogeneous solution. After that, Conning glass 1737 was ultrasonically cleaned in acetone, methanol and D.I. water for 5 minutes. Then the AZO films were deposited on glass substrates by the sol-gel dip-coating method. After deposition by sol-gel dip-coating, the films were preheated at 350 °C for 10 minutes in a rapid thermal processor (RTP) to evaporate the solvent and remove organic residuals. Then the films were inserted in a furnace and post-heated in air at 500, 550, 600, 650, 700 °C for 1.5 h.

The crystalline structures of the specimens were analyzed by X-ray diffraction (XRD) patterns. X-ray diffraction 2θ scans were carried out by employing an X-ray diffractometer (Rigaku) with a Cu-K α source ($\lambda = 0.154056$ nm). The crystallite size has been calculated from the XRD data using the Debye-Scherrer formula. The surface microstructure was observed by a scanning electron microscope (SEM). The electrical resistance was measured by a four-point probe method. Optical transmittance measurements were carried out using a UV–VIS spectrophotometer.

Results and Discussion

Fig. 1 shows the XRD patterns of (500, 550, 600, 650, 700 °C) AZO thin films. It shows that all the films are polycrystalline and exhibit the hexagonal Wurtzite



Fig. 1. X-ray diffraction (XRD) 2θ scans with CuK_{α} radiation for Al-doped ZnO thin films post-heated at various temperatures of (a) 500 °C (b) 550 °C (c) 600 °C (d) 650 °C (e) 700 °C.

crystal structure [22]. The relative intensities of the (100), (002), (101) peaks tend to increase with an increase in the post-heating temperature. The increase in peak intensities indicates an improvement in the crystallinity of the films because it is generally noted that the crystallinity can be enhanced while increasing the annealing temperature [22].

The inserted figure shows (002) diffraction peaks in the 2 θ region from 33 ° to 35 °. These main peaks of the AZO films shift to a higher diffraction angle with an increase in the post-heating temperature. The increase of 2 θ of the (002) peak may be related to a decrease of the lattice parameters which comes from the oxygen deficiency and strain caused by crystallization during the post- heating process [10, 23].

As the microstructure of the AZO thin films has an influence on the electrical and optical properties for optical devices, it is very important to investigate the



Fig. 2. SEM micrographs of the Al-doped ZnO thin films post-heated at various temperatures of (a) 500 $^{\circ}$ C (b) 550 $^{\circ}$ C (c) 600 $^{\circ}$ C (d) 650 $^{\circ}$ C (e) 700 $^{\circ}$ C.



Fig. 3. Grain size of Al-doped ZnO thin films post-heated at various temperatures.

surface morphology of AZO thin films. Fig. 2 shows SEM micrographs of AZO thin films post-heated at 500-700 °C with an interval of 50 °C. It can be seen that the microstructure of the films is dense and homogeneous. By increasing the post-heating temperature, the grains become denser and larger which can be considered as a coalescence process induced by the thermal treatment. For ZnO nanoparticles, there are many Frenkel defects, such as Zn interstitials and oxygen vacancies at the grain boundaries [5, 22]. As a result, these defects are favorable to the coalescence process to make larger grains whit an increase the post-heating temperature [22]. These results, in agreement with the XRD analysis, indicated that the diffusion probability of ZnO and Al atoms on the surface can be controlled by the post-heating temperature.

In this case that the grain size is smaller than 100 nm, the full width at half-maximum (FWHM) can used to estimate the grain size, based on the XRD results, the average size D of the grains can be calculated using the Debye-Scherrer formula [24]:

$$D = \frac{k\lambda}{B\cos\theta} \tag{1}$$

where λ is the X-ray wavelength (0.154056 nm), θ is the Bragg angle, *k* is a fixed number of 0.9 and *B* is the FWHM of the (101) diffraction peak. The variation of grain size is shown in Fig. 3.

The grain size of the AZO thin films estimated by the Debye-Scherrer formula increases from approximately 21 to 39 nm as the post-heating temperature was increased from 500 to 700 °C which is similar to the SEM results, as shown in Fig. 2. Also, an increase in the grain size with increasing annealing temperature in ZnO films has been reported earlier [25]. By comparing the grain size of AZO films measured and estimated by SEM and the Debye-Scherrer formula respectively, we found that these are some strong relationships between the SEM images and XRD patterns. Since the grain size of AZO thin has a nano scale size, we can estimate the grain



Fig. 4. Sheet resistance of Al-doped ZnO thin films post-heated at various temperatures.



Fig. 5. Optical transmittance spectra of the Al-doped ZnO thin films post-heated at various temperatures.

size of AZO thin film by employing the Debye-Scherrer formula from the XRD.

Fig. 4 shows the sheet resistance of the AZO thin films post-heated at various temperatures of 500-700 °C. In general, by increasing the annealing temperature, the resistivity of AZO films decreases since the grain boundaries and crystal deficiencies of the film can be decreased [26]. As shown in figure 4, the sheet resistance was decreased from 500 to 650 °C with an increase in the post-heating temperature and then increased as the post-heating temperature increased up to 700 °C. We attribute this increased sheet resistance as coming from a decrease in the mobility of carriers caused by segregation of aluminum components (Al₂O₃) at the grain boundaries for the grain growth process [26]. A minimum sheet resistance of about $2.5 \times 10^3 \Omega / \Box$ was obtained at 650 °C.

The optical transmittance spectra of the AZO thin films post-heated at various temperatures of 500-700 °C in the wavelength from 300 to 800 nm are compared in Fig. 5. All of the films exhibited a good transmittance in the visible region. As the wavelength of incident

light decreased to the ultraviolet region, the transmittance of the AZO films decreased with a sharp fundamental absorption edge at around 380 nm wavelength. It was also found that the post-heating temperature does not have a critical effect on the transmittance of the AZO films over the visible range.

Conclusions

In our research, we fabricated transparent and conductive AZO thin films for transparent conducting oxide applications using a sol-gel dip-coating process. The effects of various post-heating temperatures on the optical, structural and electrical properties of the AZO films were studied. All the films were polycrystalline with a hexagonal Wurtzite crystal structure. The grain size increased with an increase in the post-heating temperature from 500 to 700 °C while the sheet resistance decreased up to 650 °C and a minimum sheet resistance was measured to be about $2.5 \times 10^3 \Omega / \Box$. Also, we obtained a good transmittance in the visible range.

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