

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF ALUMINUM DOPED ZINC OXIDE THIN FILMS AT DIFFERENT ANNEALING TEMPERATURES

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ABSTRACT

The Al doped ZnO thin films with doping concentration of 1 at.% have been prepared using sol-gel spin-coating method and have been annealed at temperatures of 350~500 °C. The thin films were characterized using x-ray diffractometer (XRD), UV-Vis-NIR spectrophotometer and current voltage (I-V) measurement system for structural, optical and electrical properties characterization, respectively. XRD pattern reveals the improvement of c-axis orientation with annealing temperatures. The Urbach energy as calculated from transmittance spectra increased with annealing temperatures. I-V measurement results revealed improvement in electrical properties of the thin films with annealing temperatures.

INTRODUCTION

ZnO is a versatile and technologically important material with direct band gap energy of 3.3 eV and large exciton binding energy of about 60 meV [1]. It is transparent in visible range region, non-toxic, readily available and stable against thermal and chemical reaction. ZnO is naturally n-type semiconductor material mainly caused by its native intrinsic defect; Zn interstitial and O vacancies [2]. Due to its excellent properties, ZnO has been used in various kind of electronic and optoelectronic devices such as solar cell [3], light emitting device [4], and gas sensor [5].

Since the performance of ZnO based devices partly depend on the quality of ZnO thin film, it is important to prepared ZnO thin films which are not only good in the optoelectronic and structural properties but also good in electrical properties. Doping and annealing process are indentified as among of the techniques which could improve ZnO properties. In this study, we have prepared Al doped ZnO thin films at concentration of 1 at.% through sol-gel spin-coating method. The doping concentration is fixed at 1 at.% because it have been reported that the value is the optimum parameter

to obtain low resistance thin film [6]. The effects of annealing temperature on the Al doped ZnO thin film properties were investigated in this work.

METHODOLOGY

The sol of ZnO thin films preparation was prepared using zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) as a precursor material, aluminum nitrate nanohydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) as a dopant material, 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) as a solvent and monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$, MEA) as a stabilizer. Zinc acetate and aluminum nitrate was first dissolved in 2-methoxyethanol solution followed by additional of MEA to produce 0.4M zinc acetate solution. The quantity of aluminum nitrate was controlled to achieved 1 at.% Al doping in ZnO. The molar ratio between MEA and zinc acetate was fixed at 1. The solution was stirred at 80°C for 3 hr by hotplate magnetic stirrer and then aged at room temperature for 24 h to yield a clear and homogeneous solution. ZnO thin films were deposited on the glass substrates by spin-coating technique. The precursor solution was dropped 10 times onto the substrates, which were spin at 3000 rpm for 60 s. After the spin-coating process, the films were dried at 150°C for 10 min to evaporate the solvent and to remove organic residuals. The spin-coating and drying procedures were repeated 10 times to increase the film thickness. The films then were annealed under an ambient atmosphere from 350 to 500 °C for 1 h. The structural properties of the thin films were investigated using X-ray diffractometer (XRD, Bruker AXS D8 Advance). The optical properties of ZnO thin films were examined by UV-Vis-NIR spectrophotometer (Cary 5000). The current-voltage (I-V) measurements were conducted by using 2 probes and power supply system (Advantest R6243). The thicknesses of the thin films were estimated using Scanning Electron Microscope (SEM, JEOL JSM6360LA) to be 0.54, 0.61, 0.47, 0.64 and 0.98 μm for as deposited sample, samples annealed at 350, 400, 450 and 500 °C, respectively.

RESULTS AND DISCUSSION

Structural Properties of ZnO Thin Films

XRD pattern of Al doped ZnO thin films at different annealing temperatures are shown in Figure 1. Crystalline phase were identified according to JCPDS powder diffraction file (#36-1451). 5 peaks correspond to ZnO wurtzite structure in the 2 θ region of 25-60 ° were appeared in the XRD spectra which have been identified as (100), (002), (101), (102) and (110) orientation. It could be observed that all annealed thin films have preferential growth at (002) orientation or along c-axis indicating the thin films growth is perpendicular to the substrates. It also could be seen that as deposited samples has very weak peaks compared to the annealed samples to indicate amorphous phase in ZnO thin films structure. Sharper peaks were obtained for thin film annealed at higher temperature which showed the crystallinity improvement of Al doped ZnO thin films with annealing temperatures. The diffraction peak of Al_2O_3 phase was not observed from XRD measurements indicating Al^{3+} substitutionally doped in ZnO structure. Full width at half maximum (FWHM) of (002) orientation peaks were obtained from XRD spectra to be 0.512, 0.372, 0.381 and 0.359 ° for thin films annealed at 350, 400, 450

and 500 °C, respectively. The FWHM values are used to calculate grain size according to the Scherrer's formula as indicates by following equation (Eq. 1) [7]:

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (\text{Eq. 1})$$

where D is the grain size, λ is the X-ray wavelength of 1.54 Å, B is the FWHM of the (002) plane in radian and θ is the diffraction angle correspond to (002) plane. From the calculation, the grain sizes are 17.0, 23.3, 23.0 and 24.2 nm for thin films annealed at 350, 400, 450 and 500 °C, respectively. Taking consideration of experiment error in this study, the size of ZnO grain in the thin films tends to increase with annealing temperature. The grain size increment may attribute from particle merging activity at high annealing temperature. High annealing temperature will provide sufficient energy for atom rearrangement process which the atoms will occupy the correct sites in the crystal lattice. Thus, at higher annealing temperature, the grains with lower surface energy become larger, while the growth orientation becomes stronger that lead to crystallinity improvement of ZnO structure [8].

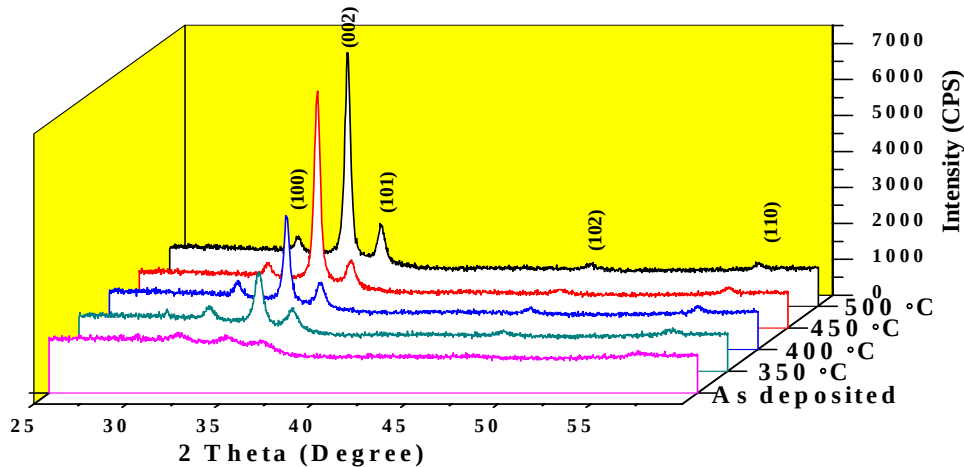


Figure 1: XRD spectra of ZnO thin films at different annealing temperatures.

Optical Properties of ZnO Thin Films

Figure 2(a) shows transmittance spectra of Al doped ZnO thin films as a function of annealing temperatures. All films have a good transmittance above 80% in the 400-1500 nm region. The average transmittance in the visible region (400-800 nm) for as deposited sample, samples annealed at 350, 400, 450 and 500 °C are 84.1, 84.0, 82.5, 83.4 and 85.7 %, respectively. It also could be observed that a sharp absorption edge at wavelengths of about 370 nm present in the spectra indicating the absorption properties of ZnO in the UV region. The optical absorption at absorption edge corresponds to the transition from valence band to conduction band and is close with ZnO band gap energy.

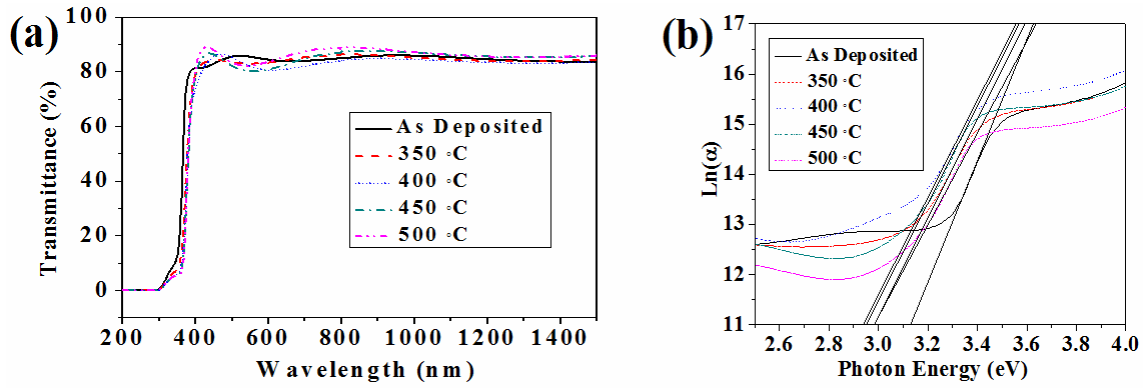


Figure 2: (a) The transmittance spectra and (b) Ln (α) vs photon energy plot of ZnO films with annealing temperatures.

Figure 2(b) shows the plot of Ln (α) vs photon energy to characterized structural disorder or defects of Al doped ZnO thin films with annealing temperatures. The graph was plotted using following equation (Eq. 2) [9]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_0}\right) \quad (\text{Eq. 2})$$

Where α is absorption coefficient, E_0 is the Urbach energy and α_0 is a constant. The α values of all samples as a function of wavelength were obtained using Lambert's law as shown by equation below (Eq. 3):

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (\text{Eq. 3})$$

The possible defects in the thin films which affect on band tailing phenomenon are shown by a parameter known as Urbach energy [10]. The reciprocal gradient of the plot's linear portion as shown in Figure 2(b) will give the value of Urbach energy. From the plots, the Urbach energy of as deposited sample, samples annealed at 350, 400, 450 and 500 °C are 82.5, 101.5, 102.0, 104.0 and 108.9 meV, respectively. The result shows the Urbach energy increase with annealing temperatures. The result suggested the defect generation of Al doped ZnO thin films increase with annealing temperatures which caused band tail widening. The broadening of donor levels into impurity band which merge with conduction band in the forbidden gap is might be a factor which could related to the phenomenon in this work. The condition is due to increment of carrier concentration with annealing temperature as a result of more incorporation of Al^{3+} in the ZnO lattice structure by higher thermal energy obtained at higher annealing temperature.

Electrical Properties of ZnO Thin Films

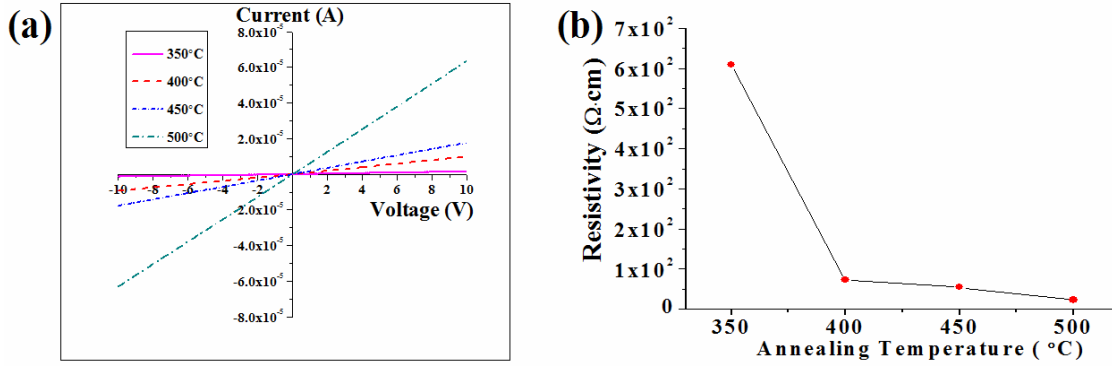


Figure 3: (a) I - V curve and (b) resistivity of ZnO thin films with annealing temperatures.

I - V measurement plots for Al doped ZnO thin films at different annealing temperatures are shown in Figure 3(a). Gold (Au) was used as the metal contacts in the measurement. The result indicates the Ohmic behavior of thin films with linear I - V curve observed for all annealed thin films. It also could be observed that the current value at fixed voltage increase with annealing temperatures to indicate the enhancement of electron conductivity as annealing temperature is increased. From the I - V curves, the resistivity, ρ of Al doped ZnO thin films were calculated using following equation (Eq. 4):

$$\rho = \left(\frac{V}{I} \right) \frac{wt}{l} \quad (\text{Eq. 4})$$

Where V is supplied voltage, I is measured current, t is the film's thickness, w is the electrode width and l is the length between electrodes. The calculated resistivity obtained in this work to be 609, 73, 55 and 23 Ωcm^{-1} for thin films annealed at 350, 400, 450 and 500 °C, respectively. The plot of Al doped ZnO thin films resistivity with annealing temperatures is shown in Figure 3(b). It could be concluded that the resistivity of the thin films are decreased with annealing temperatures up to 500 °C. The improvement of the crystallinity with annealing temperature is believed to be one of the factors which contributed to the decrement in electrical conductivity at higher annealing temperatures [11]. Besides that, the increment of carrier concentration by the ionization of oxygen vacancies with annealing temperature also contributed to the increment of electrical conductivity at higher annealing temperature [12]. As have been shown by optical measurement result, the increment of Urbach energy might be the evidence of Al^{3+} substitutionally incorporation increment in ZnO lattice structure with annealing temperatures which increase the electron concentration thus reduce the resistivity of ZnO thin film. At higher annealing temperature also, the films densification process occurs as the result of particle merging activity which reduces oxygen adsorption on the grain boundaries [13]. The condition reduce carrier trapping phenomenon in the thin film to increase the conductivity of ZnO thin film. In polycrystalline structure, the crystalline order is limited to small regions called grains. The grain boundary is the area or region between adjacent grains. At the grain boundaries, the atomic arrangement is

less ordered than inside the grain. Also at the grain boundary, the foreign atoms such as oxygen tend to accumulate. The conduction electrons near the grain boundary is believed are attracted towards and trapped in grain boundaries with the present of oxygen atoms. The condition create depletion region close to the grain boundaries which act as barrier for electrons to flow from one grain to another grain. The oxygen desorption in the grain boundaries with annealing temperatures is believed to be important factor which enhance electron mobility in the films to increase conductivity at higher annealing temperature.

CONCLUSION

ZnO thin films were prepared on glass substrate by the sol-gel spin-coating method. The structural, optical and electrical properties of the films at different annealing temperatures were investigated. From XRD result, (002) oriented Al doped ZnO thin films were successfully prepared on amorphous glass substrate. The crystallinity properties as well as c-axis orientation were increased with annealing temperatures. All films exhibit high transparency in the visible region with average transmittance above 80 %. The Urbach energy study suggested the widening of band tailing increased in Al doped ZnO thin film as annealing temperature increased. Current-voltage (I-V) measurement study indicates resistivity of ZnO thin films decrease with the increasing of annealing temperatures up to 500°C.

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