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Influence of Annealing Temperature on Optical Properties of Al Doped ZnO Nanoparticles via Sol-gel Methods

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Abstract. Zinc oxide (ZnO) thin films have become technologically important materials due to their wide range of electrical and optical properties. The characteristics can be further adjusted by adequate doping processes. The effect of dopant concentration of Al, heating treatment and annealing in reducing atmosphere on the optical properties of the thin films is discussed. Undoped and aluminum-doped zinc oxide (AZO) thin films are prepared by the sol-gel method. Zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine are used as precursor, solvent and stabilizer. In the case of AZO, aluminum nitrate nanohydrate is added to the precursor solution with an atomic percentage equal to 0 %, 1 %, 2 % and 3 % of Al. The multi thin layers are transformed into ZnO upon annealing at 450 °C and 500 °C. The optical properties such as transmittance, absorbance, band gap and refractive index of the thin films have been investigated by using UV-Visible Spectroscopy (UV-Vis). The results show that the effect of aluminium dopant concentration on the optical properties is depend on the post-heat treatment of the films. By doping with Al, the transmittance spectra in visible range increased and widen the band gap of ZnO which might due to Burstein-moss effects.

INTRODUCTION

Nanotechnology in science materials with dimensions around 1 nm to 100 nm has changed scientific viewpoint and the pathways for old problems remained unsolved through the previous technologies [1]. Moreover nanotechnology gives out more points in great potential for benefit to humankind. ZnO is a part of inorganic compound with unique physical and chemical properties known as zincate and occurs rarely in nature. ZnO have high chemical stability and electrochemical coupling coefficient for broad absorption range as well as very high photo- stability [2]. ZnO have large binding energy of 60 MeV [3] and strong exciton emission which would allow stable high-yield luminescence from ZnO nanostructures even at room temperature. Due to their wide band gap (3.37 eV) properties, ZnO suitable in various application in photo electronic and electronic devices such as for devices that producing acoustic waves, field of emitter, gas sensors [4], pH sensors [5] and also solar cells [6].

ZnO nanoparticles can be prepared in large scale production but with low cost and simple method such as alkali precipitation [7], thermal decomposition, hydrothermal synthesis, sol gel methods, sonochemically methods [8], micro emulsion, and any other routes. Sol gel method attract the attention of chemists due to their low cost preparation and ease to integrate with semiconductor silicon technology. ZnO is normally introduced and doped with group III elements such as boron, gallium, indium or aluminum in order to improve and develop optical transmittance and optical energy band gap of ZnO thin films by modifying its electrical, optical, magnetic, and chemical-sensing properties. Al-doping concentration played a major role on the enhancement of transparency and the shift of optical bandgap of ZnO thin films [9]. Another positive effect of doping with these materials is the ability to stabilize the film at high temperature. By varying and finding the best temperature in thermal annealing,

the improvement of crystal quality can be implemented and the structure defect in materials can be reduced. Furthermore, annealing at higher temperature also provides a mechanism for the substitution of a zinc atom in the presence of an impurity in a process that is effectively akin to doping ZnO [10]. In this paper, we report the effect of annealing temperature as well as Al dopant concentration on optical properties of undoped ZnO.

MATERIALS AND METHODOLOGY

In order to study the effect of aluminium concentration and thermal treatment on the optical properties of Al-doped ZnO thin films, undoped ZnO, 1%, 2% and 3% of Al were prepared by sol-gel method with annealing temperature of 450 °C and 500 °C by using a furnace. As a starting material, Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in a solvent of 2-methoxyethanol at a room temperature and monoethanolamine (MEA) was added as a stabilizer. MEA acts, at the same time, as a base and a complexing agent [10]. The molar ratio of MEA to zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) was maintained at 1.0 and the concentration of zinc acetate was 0.1 M. The solution was stirred at 75 °C for 2 h yield a clear and homogeneous solution, which served as a coating solution after cooling to room temperature. The solution was aged for 1 day at room temperature. The films were coated using dip coating technique due to their simple and cheap technique for deposition of thin oxide films, but it requires soluble reagents. The solvents were evaporated and dried at 250 °C with a heating rate of 5 °C/min in an oven after each successive coating to evaporate the solvent and remove organic residuals. The preheat-treatment temperature of 250 °C is sufficient for the complete evaporation of organic compound. The procedures from coating to drying were repeated two times until the required thickness of the sintered films is obtained. The films were then annealed in air for crystallization at two different post-heat-treatments temperatures 450 °C and 500 °C for 1 h.

RESULTS AND DISCUSSIONS

Figure 1 shows the optical absorbance of the prepared thin film at temperature of 450 °C and 500 °C. The absorbance of all samples were decreases as the wavelength increases in the visible region. The samples exhibit low absorbance compared to undoped ZnO when doped with Al. From Fig. 1(b), undoped ZnO with annealing temperature of 500 °C has a highest absorbance and the lowest absorbance is obtained at Al dopant 3%. By doping with Al, the absorption edge of a degenerate semiconductor is shifted to shorter wavelengths with increasing carrier concentrations. The optical absorption at absorption edge corresponds to the transition from valence band to conduction band, while the absorption edge shifting to the lower energy relates to some local energy levels caused by some intrinsic defects [11].

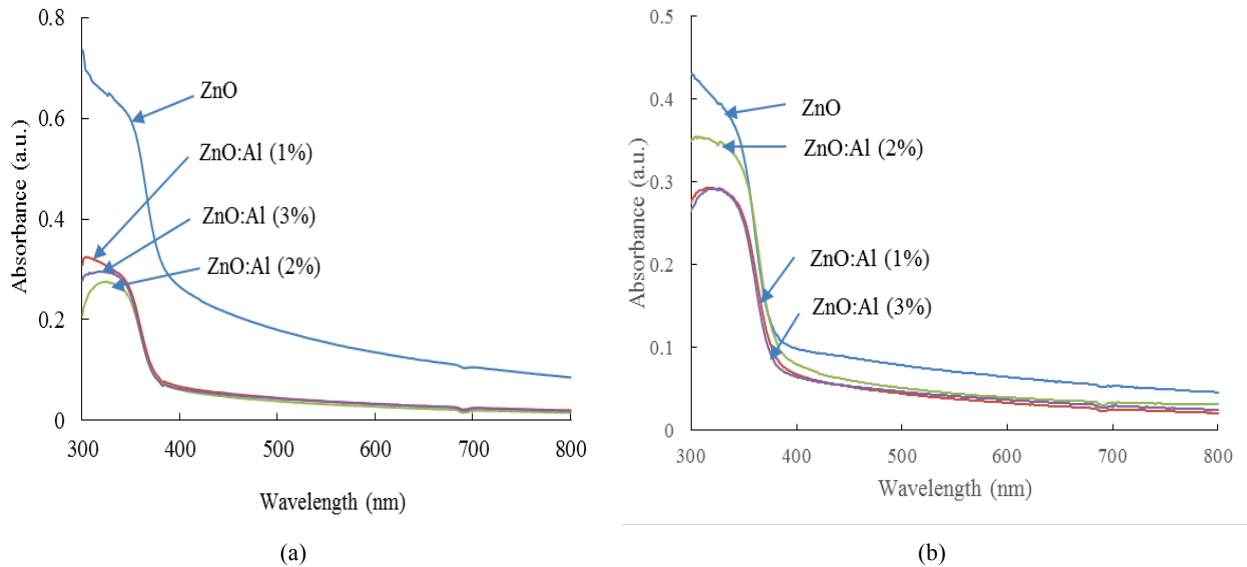


FIGURE 1. Absorbance spectra of Al doped ZnO at annealing temperature of (a) 450 °C and (b) 500 °C

In addition, increase of the carrier concentration with increasing annealing temperatures implies that more Al atoms diffuse into ZnO layer and replace partial of the Zn^{2+} sites at elevated temperature. When the annealing temperature is increased from 450 °C to 500 °C, the process would result in the precipitation of AlO_x and consequently decrease the carrier concentration [12] as the absorption edge shifted to higher wavelengths as shown in Fig. 2.

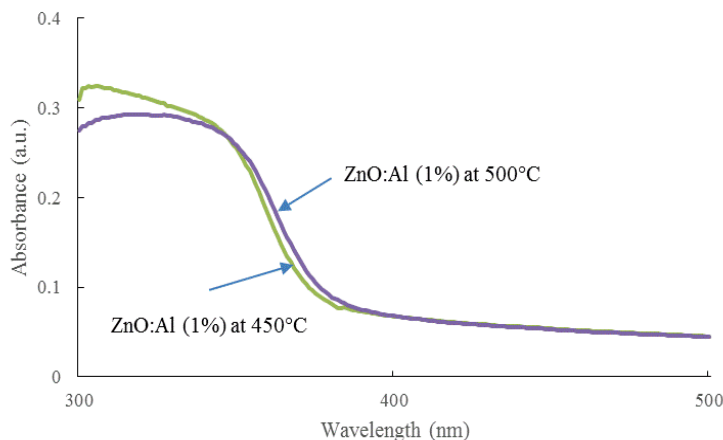


FIGURE 2. Absorbance spectra of doped ZnO with 1% Al at annealing temperature of 450 °C and 500 °C

Figure 3 shows optical transmittance of undoped ZnO thin film and doped ZnO thin film with 1%, 2% and 3% of Al dopant. The transmittance in this wavelength range from 300 nm to 800 nm is improved upon Al doping. All of the films exhibited a good transmittance in the visible region. Fig. 3(a) shows that the highest optical transmission is at Al dopant of 3% that is 95.37% while the lowest optical transmission is at undoped ZnO thin film which is around 81% in value. Meanwhile, Fig. 3(b) shows that the highest optical transmission is at Al dopant of 3% which is around 94.2% while the lowest optical transmission is at undoped ZnO thin film which is 89.5% in value. The higher the Al dopant concentration, the higher the optical transmission obtained. As the wavelength of incident light decreased to ultraviolet region, the transmittance of AZO films decreased with a sharp fundamental absorption edge at around 355 nm of wavelength. Increasing of Al doped ZnO thin film visible transmittance is due to the widening of the optical bandgap which is always explained by the Burstein-Moss theory [13]. The optical transmittance spectra of ZnO and AZO thin films exhibit an improved visibility with higher post-annealing temperature. The higher activation energy provided in higher temperature has improved the ZnO transparent thin films atoms to form better crystal lattice [14]. Generally, the quality of ZnO thin films improves with increasing annealing temperature [15]. Aluminium atoms doped into ZnO lattice elevate the free charge carriers and broaden the optical bandgap [16].

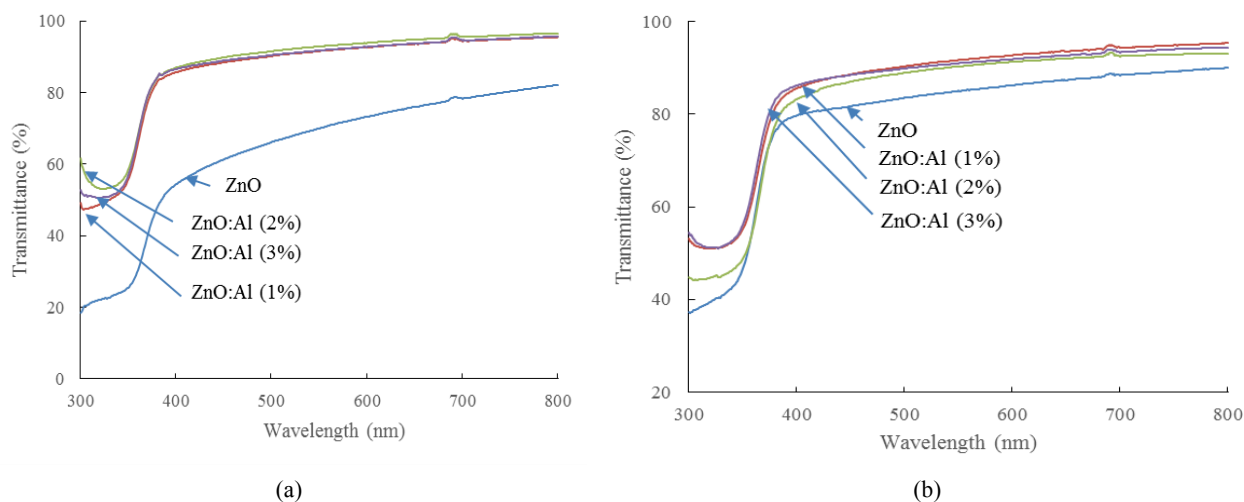


FIGURE 3. Transmittance spectra of Al doped ZnO at annealing temperature of (a) 450 °C and (b) 500 °C.

Figure 4 shows the refractive index of Al doped ZnO at annealing temperature of 450 °C and 500 °C. Fig. 4(a) shows that undoped ZnO has the highest refractive index which is around 4.0 at wavelength of 300 nm and at annealing temperature of 500 °C, the refractive index around 3.0 as shown in Fig. 4(b). This was calculated from the formula of refractive index, n of ZnO from equation (1) with R represent reflectance value.

$$n = [1 + (R) 0.5 / 1 - (R) 0.5] \quad (1)$$

When ZnO is doped with Al, the refractive index reduced, since the ionic radii of Al^{3+} is smaller than that of Zn^{2+} , the substitution of Al ions into the Zn^{2+} site is the cause for reducing the lattice expansion along the c-axis direction [12].

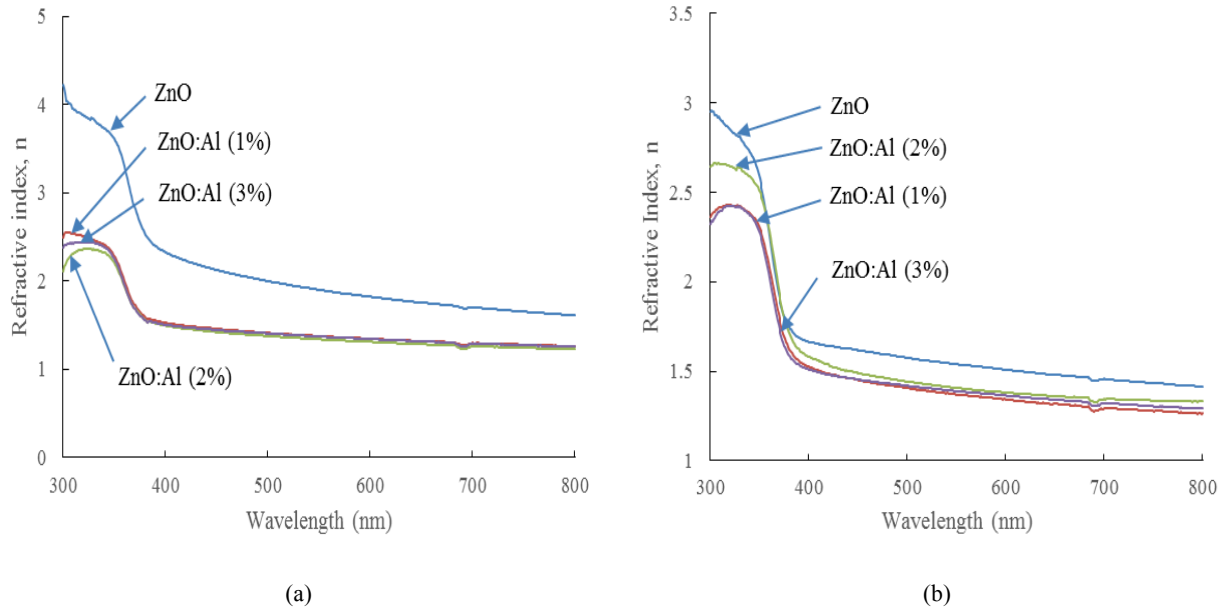


FIGURE 4. Refractive index spectra of Al doped ZnO at annealing temperature of (a) 450 °C and (b) 500 °C.

Typically, the optical band gap (E_g) of direct band gap materials can be obtained by plotting and extrapolation of $(\alpha h\nu)^2$ vs. $h\nu$, where α and $h\nu$ are the absorption coefficient and the photon energy, respectively. Band gap energy estimated from the absorption edge of the films is shown in the Fig. 5. Figure 5(a) shows that undoped ZnO thin film has a band gap of 3.25 eV at 450 °C, and it increases to 3.37 eV and 3.38 eV at Al dopant of 1% and 2% respectively, and the highest energy band gap is at Al dopant 3% which is 3.39 eV. As shown in Fig. 5(b), the undoped ZnO thin film has a band gap of 3.30 eV at 500 °C, and it increases to 3.34 eV and 3.35 eV at Al dopant of 1% and 2% respectively, and the highest energy band gap is at Al dopant 3% which is 3.37 eV, which might be due to relaxation of growth induced strain in them [15].

The possible mechanism taking responsibility on this widening of the band gap is the quantum size effect of the nanocrystalline structure of the films [17]. The feature regarding the increase of optical band gap with increasing doping concentration may be attributed to the truth that N or Al dopant may increase the carrier concentration of the film resulting in the carrier-induced wideness of band gap, well-known as Burstein-Moss effect [18]. It is observed that the band gap increases roughly for undoped ZnO with increase in annealing temperature, which is thought to be the formation of defects at higher temperatures [19]. There are other factors that explain the increase in energy band gap. For instance the effect of O_2 absorption by the film and referred to as the Burstein-Moss process. Defects such as O/Zn ratio increases with annealing temperature which leads to variations in the electronic properties [20].

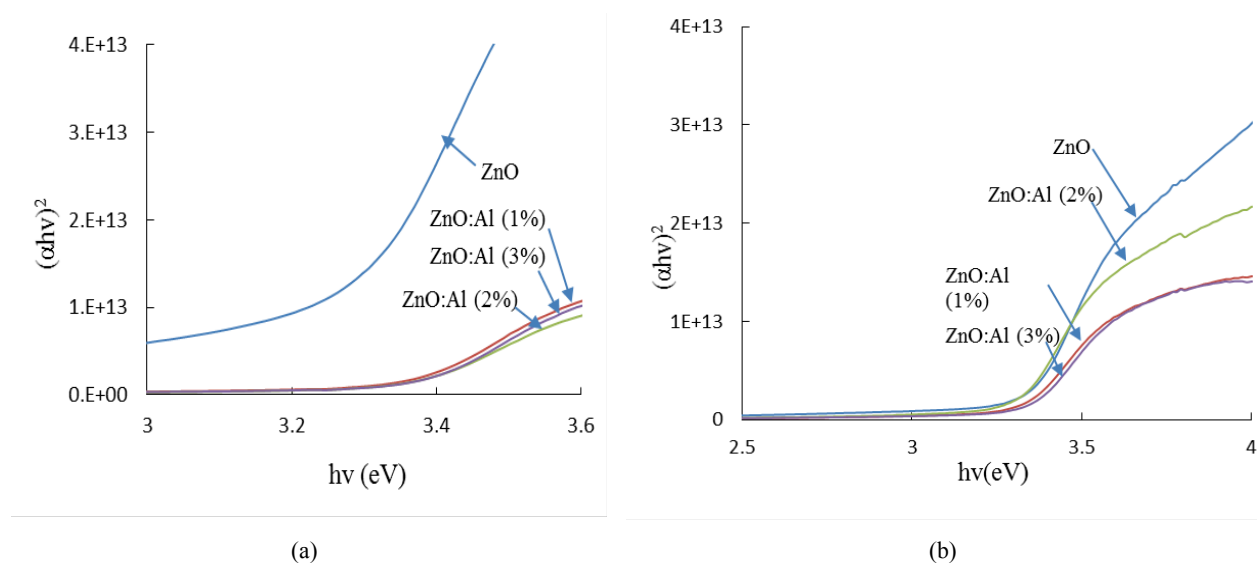


FIGURE 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Al doped ZnO thin films at annealing temperature of (a) 450 °C and (b) 500 °C.

CONCLUSIONS

As a conclusion, annealing temperature does play an important role in contributing the energy band gap obtained as the band gap increase when temperature increase from 450 °C to 500 °C. The highest band gap obtained at temperature 450 °C at percentage of 3% Al, the highest Al dopant concentration which the value is 3.39 eV which is near to the value of direct wide band gap energy of Zn, 3.37 eV therefore can be applied in photonics applications. The lowest band gap is obtained at temperature 450 °C of undoped ZnO thin film which is 3.25 eV. Besides, the TCO of Al dopant also does influence the optical properties of the ZnO thin films by improving its optical transmittance from 81% to 89.5% at different temperatures.

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