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Study of Structure, Surface Morphology and Optical Property on ZnO: Al Thin Films as Anti-Reflecting Coating

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Abstract: The significant influences of substituting low concentration Al at Zn-site as an anti-reflecting coating (ARC) for $Zn_{1-x}Al_xO$ compound on structure; morphology and optical property have been studied. The $Zn_{1-x}Al_xO$ sample with $x = 0, 5, 10$ and 15 wt.% were synthesized via a sol gel method. The films obtained from the sol gel method have been annealed at $400^\circ C$ for 2 h. The XRD, SEM and AFM have been applied for characterizing the structure and the morphology of the film. XRD spectra show all samples exhibit hexagonal structure. The morphological measurements show that particle size decreases with increasing the concentration of Al. These films exhibit a denser and compact film's structure that could be effective in light trapping in thin film solar cells. The optical property has been characterized using UV-Visible-NIR spectrometer. The values of band gaps increase as the concentration of Al increases. The increase of the band gap is acceptable as a requirement for good anti-reflecting coating element. Therefore these films can be applied as anti reflecting coating thin film solar cells.

Key words: ZnO, sol gel, thin films, structure, band gap

INTRODUCTION

ZnO is one of the metal-oxide semiconductors that have been studied as functional materials for devices such as UV-light emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensing, solar cells and structural material such as window material for display. As one of the promising metal oxide materials in the semiconductor field due to its potential properties, ZnO has received considerable attention in the recent years (Look, 2001; Shan *et al.*, 2004a, b). ZnO has a wide energy band gap about 3.3 eV and a large exciton binding energy of 60 meV at room temperature (Shan and Yu, 2003). Thin films of ZnO have many advantages such as they can be fabricated in small and large scale, low cost production and are widely compatible with microelectronic technology, circuit and anti reflecting coating for solar cells. As-grown ZnO usually exhibits n-type conductivity with a wide band gap. The n-type conductivity might be caused by intrinsic defects, interstitial zinc and oxygen vacancies. It is thought that aluminium could increase the conductivity of ZnO. Electrical conductivity of ZnO can be increased by doping with group 3 elements such as aluminium, boron, gallium and indium, or group 7 elements such as fluorine (Nunes *et al.*, 2002). There were various methods to produce Al doped ZnO films such as sputtering (Lee *et al.*, 2007), pulsed laser deposition (Liu *et al.*, 2007) and sol gel methods (Zhou *et al.*, 2007). The sol gel process is known to have the distinct advantage of process simplicity and easy control of the film

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composition. The aim of this study is to examine the influence of Al content on structure, morphology and optical property ZnO films, in order to apply as anti reflecting coating thin film solar cells and to improve its efficiency.

MATERIALS AND METHODS

In this study aluminium doped ZnO thin films were prepared by sol gel and spin coating methods on glass substrates. The solution of Al doped ZnO was prepared by sol gel method with $x = 0, 5, 10$ and $15 \text{ wt.}\%$ ($\text{Zn}_{1-x}\text{Al}_x\text{O}$). Isopropanol and diethanolamine were used as a solvent and a stabilizing agent, respectively. Zinc acetate dihydrate and aluminium nitrate were used for sources of Zn and Al. The zinc acetate dihydrate was first dissolved in a mixture isopropanol and diethanolamine for 1 h at 70°C , 0.2 M of aluminium nitrate mixed in ethanol was added in the solution of zinc acetate. The isopropanol was added to adjust the solution concentration to 0.5 M of the zinc acetate. The solution was stirred for 2 h at 70°C to yield a clear solution. The solution could be used after the solution was cooled to room temperature. The Al doped ZnO thin films were deposited on glass substrate using spin coater with three times deposition of solution. The substrates were cleaned by methanol and acetone before the deposition of the films. The films were spin coated on the substrates at 2500 rpm . This procedure was repeated three times to get 3 layers of sample. After deposition, the substrates were annealed at 400°C for 2 h. The structures of Al doped ZnO thin films were studied by X-ray diffractometry. SEM and AFM observed morphology and roughness of this film's surface. The optical transmittance was measured by optical spectroscopy using UV-Vis-NIR spectrometer. Range of this spectrometer is between $300\text{-}900 \text{ nm}$.

RESULTS AND DISCUSSION

Figure 1 shows that all samples consist mainly of three peaks corresponding to (100), (002) and (101) lattice plane diffraction of the hexagonal ZnO structure. The Al doped ZnO films have a strong diffraction peak at 5% Al doped ZnO sample. It means that 5% Al doped ZnO sample leads to slightly bigger crystallite and better crystallinity than others sample. Moreover, the peak intensities of films decrease with increasing of Al content, it indicates that the increase in Al could deteriorate crystallinity of ZnO owing to stress induced by ion misfit between Zn and Al and segregation of Al in ZnO's grain boundary (Zhou *et al.*, 2007).

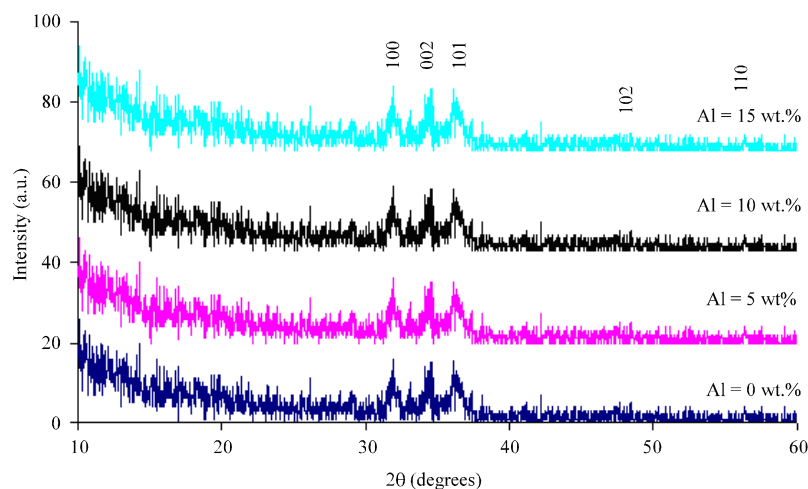


Fig. 1: XRD Spectra of the Al doped ZnO films

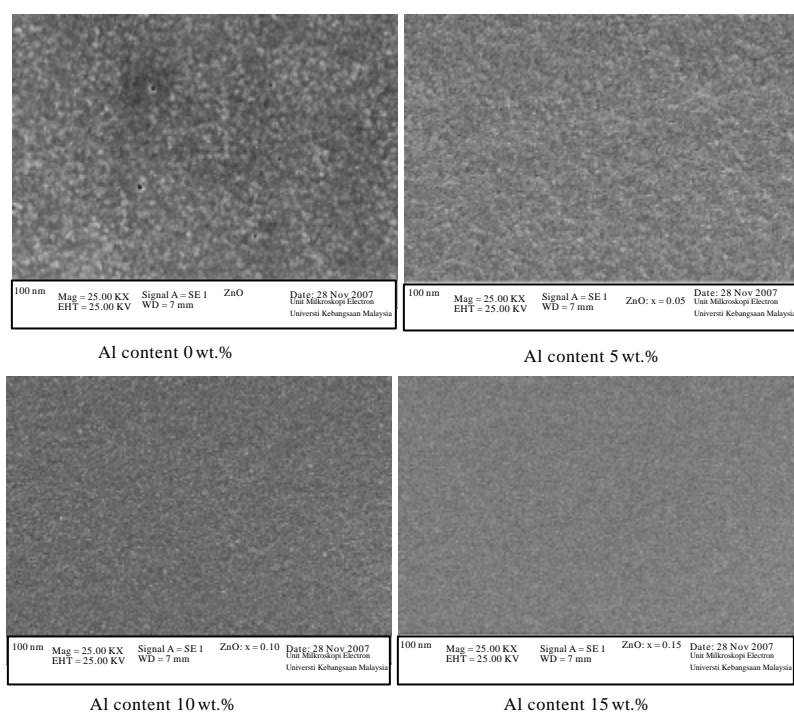


Fig. 2: SEM micrographs of the Al doped ZnO

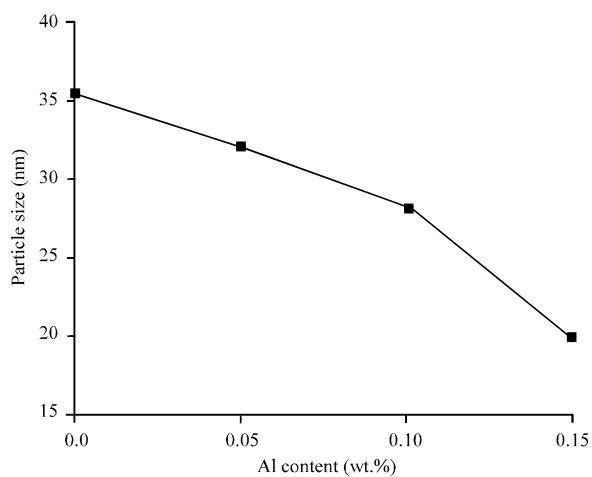


Fig. 3: Relation between Al content and particle size of ZnO films

The SEM photographs of the Al doped ZnO thin films with various Al contents are shown in Fig. 2. The surface morphology of the films strongly depends on the Al contents. It is found that the surfaces are continuous and smooth with increasing Al contents. These films exhibit porous microstructures and spherical crystalline particles. The particle sizes of the Al doped ZnO films are shown in Fig. 3. Thus, it is found that the films become denser giving to the Al. Particle sizes become

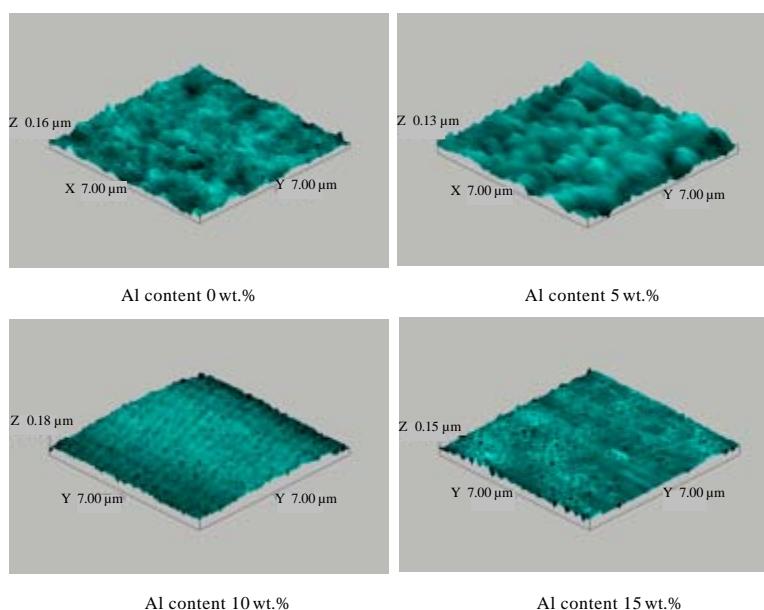


Fig. 4: AFM images of the Al doped ZnO films

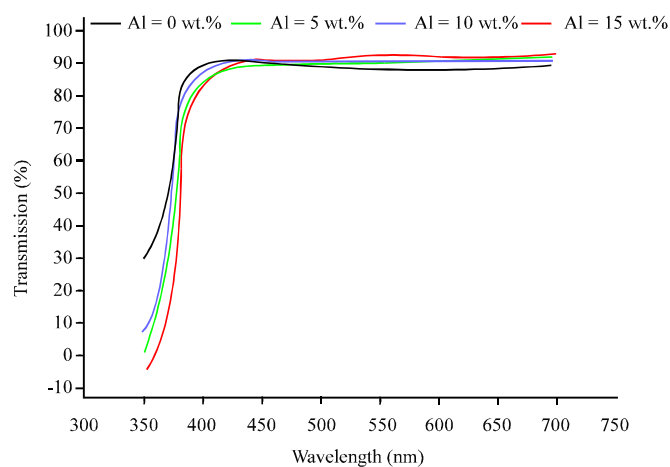


Fig. 5: Effect of dopant compositions on the optical transmittance of the Al doped ZnO thin films

smaller when Al content increases. Particle sizes for Al content 0, 5, 10 and 15 wt.% are 35.28, 32.14, 28.16 and 20 nm, respectively. The change in particle size can be explained to be due to a difference in ionic radius between 0.074 nm for Zn and 0.057 nm for Al (Nunes *et al.*, 2002).

Figure 4 shows the atomic force microscopy (AFM) images of the films Al doped ZnO with different compositions. The surface of Al free ZnO film is larger than those of Al doped ZnO. The RMS average surface roughness of the films decreased with increasing Al content is 20 to 10 nm. It is found that 15% Al doped ZnO has the smoothing surface than those of other specimens.

The transmission characteristics of the Al doped ZnO films were measured by a UV-visible spectrometer. The spectra of the samples are presented in Fig. 5. The films show 85-92% optical

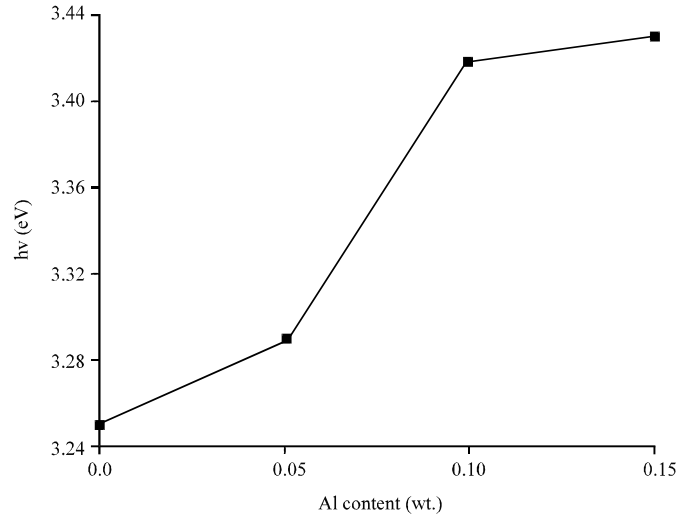


Fig. 6: Relation between Al content and band gap energy

transmission in the visible range, which is important for solar cells application. The 5% Al doped ZnO film has high transmittance, i.e., 92% for wavelength over 400 nm. This value is the highest transmittance than other samples. This could be due to the fact that the 5% Al doped ZnO film present more voids than the 10 and 15% Al doped ZnO film, which may lead to decreasing in optical scattering. High transmission shows that the Al doped ZnO films could absorb light at wavelength over 400 nm.

The transmission data have been applied for evaluating the band gap energy of the films. In order to calculate the optical band gap energy (E_{opt}) of the thin films, we assume the absorption coefficient:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad (1)$$

where, T is transmittance and d is the film thickness. Structure of ZnO has a direct band gap and the absorption edge for the direct interband transition is given by:

$$(\alpha h\nu)^2 = C(h\nu - E_{opt}) \quad (2)$$

where, C is a constant for direct transition, h is the Planck's constant and ν is the frequency of the incident photon. Figure 6 shows relation between Al content and band gap energy for Al doped ZnO thin films with various Al content. The optical band gap energies determined from obtained spectra are 3.25, 3.29, 3.42 and 3.43 eV for Al doped ZnO thin films with Al content 0, 5, 10 and 15 wt.% respectively. According to Moss-Burstein theory, in heavily doped ZnO films, the donor electrons occupy states at the bottom of the conduction band. Since the Pauli's principle prevents states from being doubly occupied and optical transition are vertical, the valence electrons require extra energy to be excited to higher energy state in the conduction band. Therefore, the band gap energies of the Al doped ZnO films are broader than that of the ZnO pure film.

CONCLUSION

The Al doped ZnO thin films were prepared by the sol gel method with different composition of Al as dopant. The XRD pattern show that the samples are polycrystalline and exhibit the single

phase of ZnO with hexagonal structure. The surface morphology of the films strongly depends on the composition of Al. High transmission of films shows that the Al doped ZnO films could absorb light at wavelength over 400 nm. The value of band gap energy is slightly increased as concentration of Al increases. The increase in the band gap fulfills a requirement for a good anti-reflecting coating element.

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