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Properties of Al Doped ZnO Thin Film Prepared by Simple Casting Process

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Abstract

Aluminum doped zinc oxide (AZO) thin films were prepared by a simple doctor blade technique. A solution of zinc acetate mixed with aluminum chloride was used as precursor, which was casted on the glass substrate. The influences of annealing temperature on properties of the films were evaluated by X-ray diffraction, scanning electron microscope, UV-visible spectrophotometer and four point probe technique. The electrical conductivity and optical energy band gap of AZO films had been increased when Al concentration increased, due to the effect of the atom of Al dopant in the ZnO films.

Keywords: Zinc Oxide;Al dopant; Thin Film

1. Introduction

At present, metal oxide materials have attracted attention in the study due to many advantages in properties of those materials [1]. Among metal oxide materials, zinc oxide (ZnO) is a material that has gained widespread interest due to its suitability for many applications. Zinc oxide materials can be used in a variety of devices such as gas sensor, solar cell, memory device, photodetector etc. due to excellent of ZnO properties [2-3].

It is well known that the compositional or composite materials are used for the development and improvement material's properties. In case of chemical doping in ZnO material, the structure parameters can be manipulated that affect to properties of material. Wide variety of applications can be prepared such as transparent electrode, spintronic etc. [4-6]. However, the aluminium doped ZnO (AZO) has been studied for use as a variety of devices such as ion sensor, transparent conducting electrode etc. [7-8], which the properties of AZO have improved. The aluminium atom that doped into ZnO may be either substituted or occupied as the interstitial site in AZO, resulting in a change in properties of the AZO.

In this work, the aluminium doped zinc oxide thin film had been prepared by simple convective doctor blade. The prepared AZO film was annealed at 450 °C in ambient to improve properties of films. The effect of aluminium dopant in ZnO thin films has been studied.

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2. Experimental

Zinc acetate and aluminium chloride were used as starter materials. At first, the zinc acetate was dissolved in deionized water with concentration of 0.1 M with volume of 50 ml. Aluminum chloride was used as aluminium dopant source while the concentration of mixed solution was fixed at 0.1 M. After that, 0.3 g of monoethanolamine (MEA) was added to precursor solution as stabilizer to prevent precipitation of precursor solution. The solution was stirred until occur clear and homogeneous solution. To prepare thin film, the convective doctor blade technique was applied to fabricate thin film with the speed of 1 mm/s. Prior use, glass substrate had been cleaned by alcohol process with ethanol, isopropane, and acetone, respectively. The precursor solution was dropped on glass substrate that thickness of precursor had been controlled by kapton tape at the both edges of glass substrate. After prepare films, the thin film was annealed at temperature of 450 °C of 2 hour in air. The properties of Al doped ZnO thin films were characterized by X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), UV-Vis spectroscopy, four-point probe, respectively.

3. Results and Discussion

Fig. 1. shows the surface morphology and cross section images of Al doped ZnO thin films. It was found that the thickness of the films occurred about 180-270 nm. The surface morphologies of the films exhibit the grain-like structure. The grain size of AZO had been increased with increasing the doping concentration of Al. Moreover, the roughness of film morphology is also decreased when concentration of Al had been increased.

To perform the electrical properties of AZO films, the resistivity of AZO films at various Al dopants was measured as shown in Fig. 2. It was found that the resistivity of AZO depends on the concentration of Al dopant. The resistivity is decreased with increasing of Al concentration. The resistivity of AZO in this work are in agreement with the electrical properties of Al doped ZnO that prepared by RF magnetron sputtering and sol-gel method [4, 9].

Optical properties are an important parameter for optoelectronics application of AZO thin film. Optical transmittance spectra of AZO films with various Al contents at the annealing temperature of 450 °C are shown in Fig. 3. It can be seen that all AZO films exhibited optical transparent behaviour with optical visible light transparency more than 60%. The optical absorption edge was observed in region of 340-360 nm. To obtain the optical energy band gap (E_g) of AZO, the absorption coefficient (α) was evaluated from [8]:

$$\alpha = \left(\frac{1}{t}\right)\ln\left(\frac{1}{T}\right) \tag{1}$$

Where t is the thickness and T is the transmittance of AZO film. In other reports, the structure of ZnO has a direct energy band gap therefore the optical energy band gap (E_g) of AZO can be performed from following relations [8]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{2}$$

Where hν is photon energy, A is a constant parameter. The relation of $(\alpha h\nu)^2$ and photon energy (hν) are shown in Fig. 4. The optical energy band gap (E_g) of AZO was estimated

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from the extrapolation of the linear region to the x-axis or zero optical absorption and the values of E_g of AZO films depicts as the inset of Fig. 4. It was found that the optical energy band gap of AZO films had been increased when Al concentration increased. It can be explained by Burstein-Moss effect. In the Burstein-Moss effect, the band gap of Al-ZnO film increased due to the donor electron was filled in occupy states in the conduction band. Therefore, the valence electrons desired an alternately excited energy level. Thus, the optical energy band had been shifted to higher value [10]. As a result of the ion of aluminium occupied into the structure of zinc oxide and then bringing the charges are increased. This result is consistent with the results of the resistivity of AZO film.

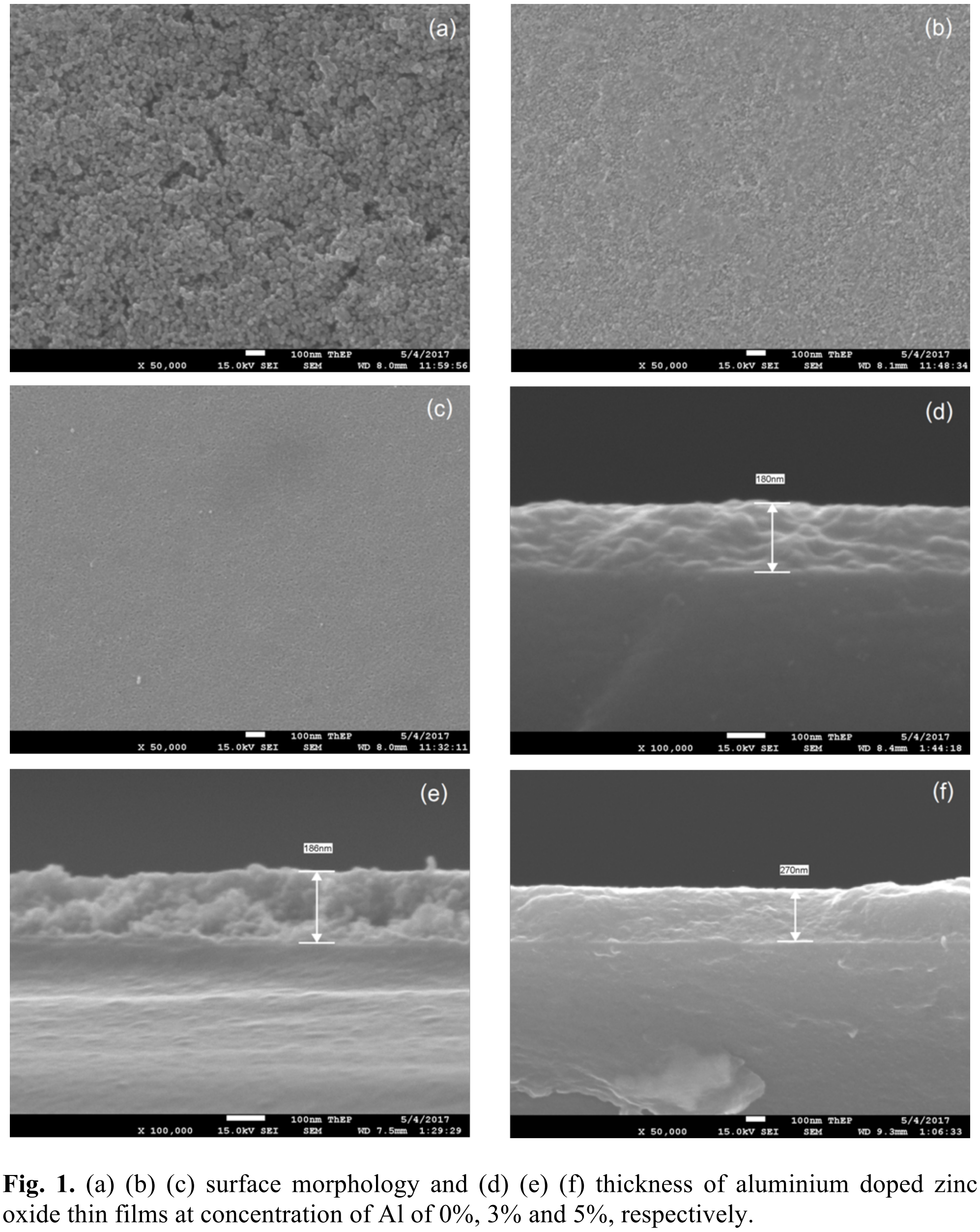


Fig. 1. (a) (b) (c) surface morphology and (d) (e) (f) thickness of aluminium doped zinc oxide thin films at concentration of Al of 0%, 3% and 5%, respectively.

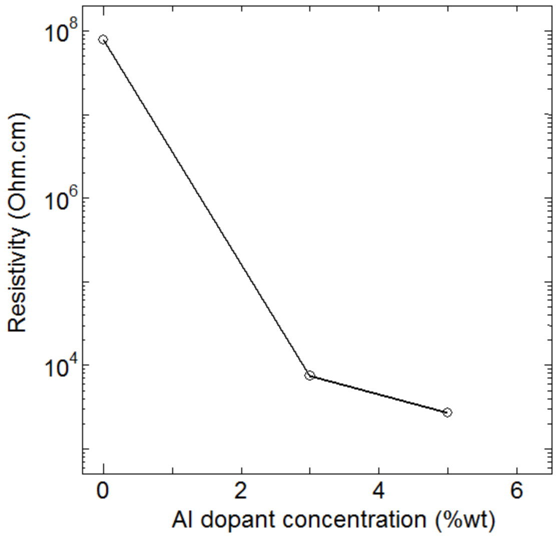


Fig. 2. electrical resistivity of aluminium doped zinc oxide thin films at various al dopant concentrations.

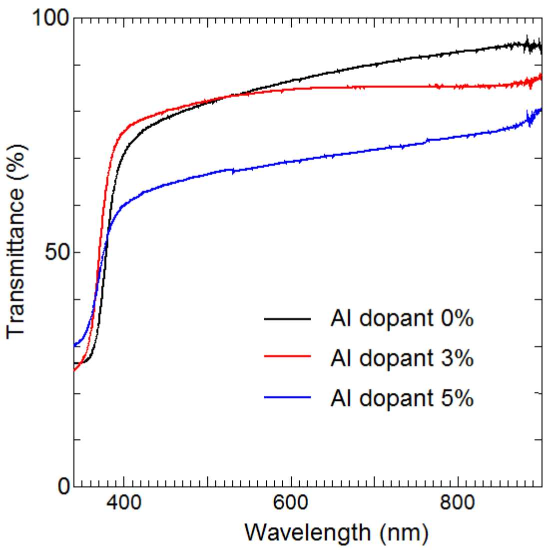


Fig. 3. Optical transparent spectra of aluminium doped zinc oxide thin films.

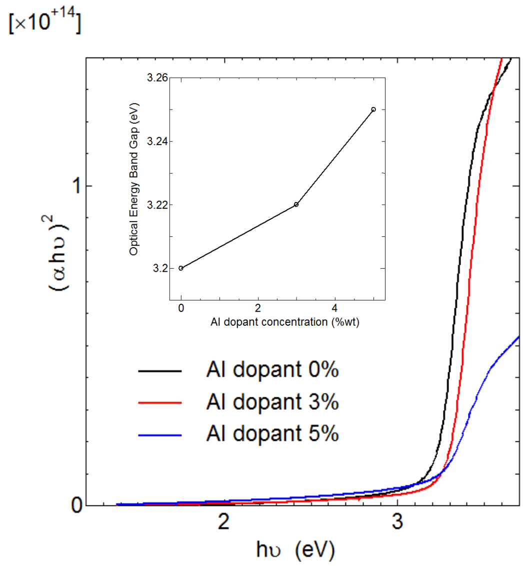
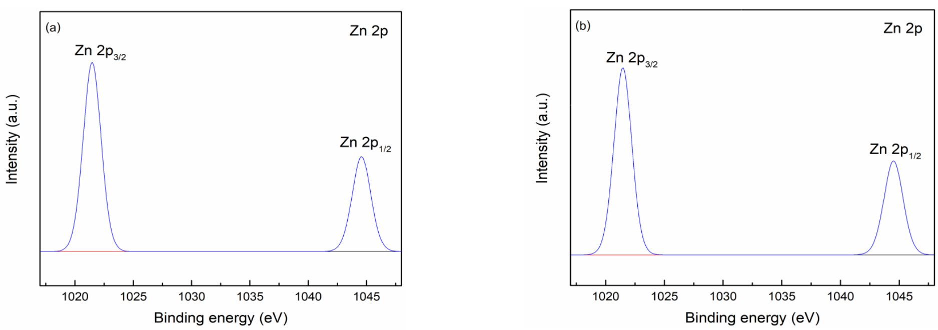


Fig. 4. plots of $(\alpha h\nu)^2$ vs. $h\nu$ of aluminium doped zinc oxide thin films and the inset depicts the the optical energy band gap (E_g) of AZO film.

To obtain more information of structural properties of AZO film, the X-ray photoelectron spectroscopy was used to investigate chemical bonding of AZO film. Fig. 5. exhibits the zinc (Zn 2*p*), oxygen (O 1*s*), and aluminium (Al 2*p*) photoelectron peaks in XPS spectra. The peaks of Zn 2p were found at binding energy of 1020.9 eV and 1044.0 eV that corresponds with the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ [4]. It can be seen that the main peaks was observed at the peaks of Zn 2*p*, which is slightly different when the aluminium dopant had been increased. The peak of O 1*s* was resolved with four of Gaussian peaks at peak position centres of 530, 531, 532 and 533 which defined as OI, OII, OIII, and OIV, respectively. The OI peak was attributed to the ion of O^{2-} on the wurtizite structure of hexagonal ZnO. The OII is attributed as the oxygen deficient regions on ZnO structure. The OIII peak at binding energy of 531 eV is attributed as the loosely bonded oxygen of the AZO at the surface of thin film due to effect of chemisorption of oxygen impurity. In case of XPS spectra peak of Al 2*p*, the peak was observed at binding energy of 74.2 eV. That means the incorporation of Al atom into the Zn site of ZnO structure [7]. The binding energy of OIV peak can be indicated as the absorption of moisture molecule into AZO film.



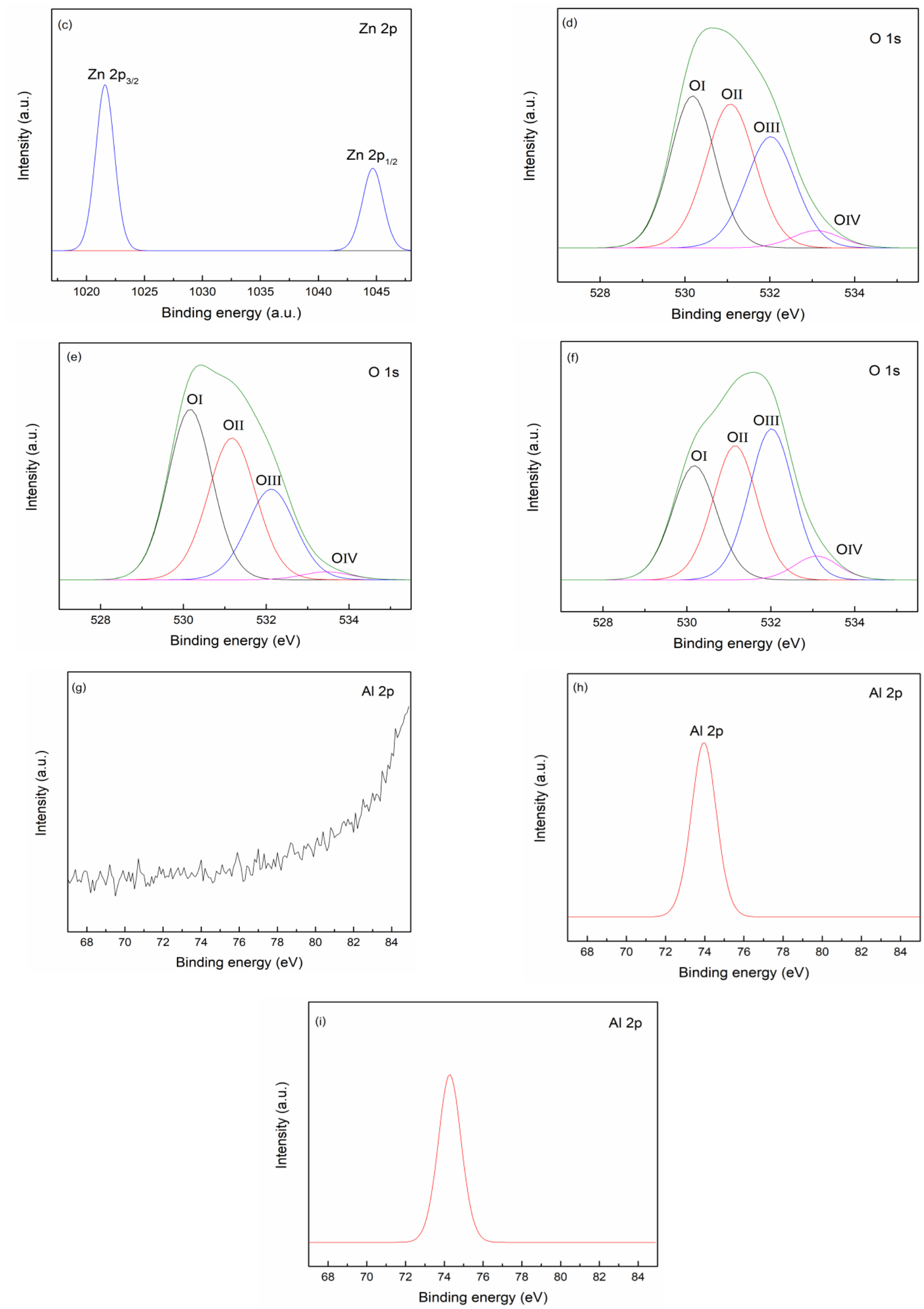


Fig. 5. XPS spectra of Al doped ZnO thin films with various Al dopant concentration of (a) Zn 2*p* of ZnO, (b) Zn 2*p* of Al dopant 3%, (c) Zn 2*p* of Al dopant 5%, (d) O 1*s* of ZnO (e) O 1*s* of Al dopant 3%, (f) O 1*s* of Al dopant 5%, (g) Al 2*p* of ZnO, (h) Al 2*p* of Al dopant of 3%, and (i) Al 2*p* of Al dopant of 5%, respectively.

4. Conclusion

Aluminum (Al) doped zinc oxide (ZnO) thin films were prepared by a simple doctor blade technique. The thickness of AZO films occurred about 180-270 nm. The surface morphologies of the films show the grain-like structure with the grain size of AZO had been increased with increasing the doping concentration of Al. The electrical conductivity and optical energy band gap of AZO films had been increased when Al concentration increased. That can be explained by Burstein-Moss effect which result is consistent with the results of the resistivity of AZO films. The XPS results exhibited the incorporation of Al atom into the Zn site of ZnO structure.

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