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Effects of aluminium doping concentration on properties of AZO films prepared by RF magnetron sputtering technique

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Abstract

In this research, the aluminium-doped zinc oxide films were prepared from undoped and 1 – 5 weight percentage (wt.%) of Al_2O_3 doped ZnO ceramic targets by RF magnetron sputtering technique in order to study the effect of Al doping concentration on the properties of prepared AZO films. The AZO films were deposited on glass slides at room temperature and post-annealed at 500°C in vacuum for 1 hour. Atomic percentage (at.%) of Al compositions, film structures and electrical-optical properties were characterized. It was found that at.% of Al doping concentration were 3.45, 5.77, 6.12, 11.18 and 12.77 in the films deposited from 1 – 5 wt.% Al_2O_3 doped targets, respectively. Carrier concentration and optical band gap also improved with increasing Al doping concentration. It implied that higher Al doping concentration increased Al substitutions for Zn atoms. However, excess Al doping concentration has no longer contributed to Al substitution but played a role of electron traps resulting in the decrease of carrier concentration and optical band gap. From XRD spectra, it was found that undoped and 3.45 at.% Al-doped ZnO films showed preferred orientation in (002) plane which drastically decreased and disappeared with higher Al doping concentration but, on the other hand, (100) and (101) peaks started to be detected. Therefore, the increase of Al doping resulted in the change of orientation and poor crystallinity. As a result, the Hall mobility decreased because of dominant grain boundary scattering. Minimum resistivity of 2.01 x 10^{-3} Ω.cm was achieved for the AZO films with 3.45 at.% Al doping concentration.

Keywords: Al_2O_3–doped ZnO targets, AZO films, Al-doping concentration and RF magnetron sputtering

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1. Introduction

Transparent conducting oxide (TCO) films have been widely used in many applications [1 - 3] because of their high visible transmission and low electrical resistivity. There are many kinds of TCO such as doped indium oxide, doped tin oxide and doped zinc oxide. Among these kinds of TCO, the tin-doped indium oxide (ITO) film is mostly used in the applications. However, the indium is a rare and expensive element. Therefore, there are many efforts for researchers to prepare other low-cost, good quality and indium-free TCO films [2, 4, 5]. Aluminium-doped zinc oxide (AZO) film is especially attractive due to its good electrical property with high transmission in visible light region comparable to ITO. In addition, the raw materials used for preparations of the AZO targets are low-cost, abundant in nature and non-toxic especially for the magnetron sputtering technique.

Unique combinations of electrical and optical properties of the TCO films have resulted from good crystalline structure and high carrier concentration with high mobility. For AZO film, the charge carriers have originated from intrinsic oxygen vacancies and substitutions of Al^{3+} into Zn^{2+} sites of zinc oxide structure. Various deposition techniques can be used to prepare the AZO films including DC and RF magnetron sputtering [1 - 8]. For magnetron sputtering technique, the oxygen vacancy and Al^{3+} substitution are dependent on deposition parameters such as working pressure [4], sputtering power [9], substrate temperature [10, 11], target to substrate [12] and oxygen partial pressure [13] which are wildly investigated. In addition, the Al doping concentration is an important parameter that has effects on properties of the deposited AZO films.

In this work, the AZO films were prepared by RF magnetron sputtering technique at room temperature from undoped and 1 – 5 weight percentage (wt.%) of aluminium oxide doped zinc oxide target and post-annealed at 500°C in vacuum. Effects of Al doping concentrations in deposited film on crystal structure and electrical-optical properties of the AZO films were studied.

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2. Methods

AZO sputtering targets were prepared by mixing zinc oxide powder (ZnO, 99.7%) with different weight percentages (wt.%) of aluminium oxide powder (Al_2O_3, 99.99%) ranged from 0 to 5 wt.% for 5 hours. Mixed powders were crushed by ring-mill machine (Model: 1A, Rocklabs) and pressed into the plates with a diameter of 82.2 mm and sintered at a temperature of 1,300°C in air for 3 hours resulting in AZO ceramic targets with a diameter of about 74.1 mm. After that for AZO film preparations, 2.5 x 2.5 cm^2 glass slides were used as substrates. They were ultrasonically cleaned in acetone and ethyl-alcohol respectively for 10 minutes each, and blow dry with nitrogen gas before putting in the vacuum chamber. Target to substrate distance was fixed at 8 cm. The AZO films were prepared in the home-built sputtering system at room temperature working at a frequency of 13.56 MHz (Cito 1310, Comet). Before sputtering process, the vacuum chamber was evacuated to the base pressure of about 1.0 x 10^{-5} mbar by rotary and diffusion pumps. Ultra-high purity argon gas (99.995%) was then filled into the vacuum chamber. The AZO films were deposited at working pressure and RF power of 5.0 x 10^{-3} mbar and 100 W, respectively. Before coating, the target was pre-sputtering for 5 minutes and deposition times were calibrated in an interval of 30 – 45 minutes for film thickness of 300 nm for all conditions. The film thicknesses were determined by scanning electron microscope (SEM) measurements at the cross-sections of the deposited film/glass substrate. After that the deposited films were annealed at 500°C for 1 hour in vacuum. After annealing, the crystal structures of annealed films were characterized by X-ray diffraction technique (D8 diffractrometer, Bruker). The electrical and optical properties were analyzed by Hall (HMS-3000, Ecopia) and UV-Vis-NIR (UV-3600, Shimadzu) measurements, respectively. In addition, the atomic percent (at.%) of Al composition in the film structure were also investigated by energy dispersive X-ray (EDX) spectroscopy (SU3500, Hitachi).

3. Results and discussion

3.1 Atomic percentages of Al doping concentration and crystal structure

Atomic percentages (at.%) of Al doping concentration in AZO films deposited from undoped and doped ZnO target are shown in Table 1, which, as expected, at.% Al increased from 3.45 to 12.77 for 1 – 5 wt.% Al_2O_3 doped in the target. XRD spectra of the AZO films deposited from all prepared targets are shown in Figure 1. For undoped and 1 wt.% Al_2O_3-doped targets, the deposited films showed hexagonal wurtzite structure of the ZnO (ICDD: 01-089-0510) [14] with preferred orientation in (002) plane at $2\theta = 34.54°$ and 34.74°, respectively. It can be noticed that the 2θ value of undoped ZnO film is very close to standard value ($2\theta = 34.45°$). However, for 3.45 at.% Al-doped ZnO film, the 2θ value have shifted to higher angle. The shifted angle may be attributed to different ionic radii between Zn^{2+} and Al^{3+} which are 72 pm and 53 pm, respectively.

Table 1 at.% of Al and the electrical properties of AZO films deposited from the 0 – 5 wt.% of Al_2O_3-doped ZnO ceramic targets

wt.% of Al_2O_3 doped in AZO targets	at.% of Al doping concentration
0	-
1	3.45
2	5.77
3	6.12
4	11.18
5	12.77

Because of the substitution of Al atoms in Zn sites, the length of *c*-axis is expected to be shorter. In addition, the difference of ionic radii between Zn^{2+} and Al^{3+} also has effect on the crystal structure of the films. As can be seen in the Figure 1, the (002) peak drastically decreased and disappeared for 11.18 or higher at.% Al doped ZnO films. This result is consistent with that prepared by spray pyrolysis technique at a substrate temperature of 420°C with different atomic percentages (at.%) from 0 – 10 at.%, as reported by Muiva *et al.* [5]. Decrease of the (002) peak may be described in term of stress appeared in the film structure which originated from over limit of Al substitutions in the Zn sites. High stress in the film structure resulted in the loss of periodic arrangement and, consequently, poor crystallinity in the film structures. In addition, Mamat *et al.* [15] also suggested that at higher Al doping concentration, due to larger nuclear charge of Al^{3+}, the extrinsic Al^{3+} capture more oxygen in competition with Zn^{2+} which decrease crystallinity and hexagonal structure of the films. From Figure 1, it was also observed that there are low intensities (100) and (101) peaks appeared for Al-doped ZnO films which are a few higher with increasing at.% Al doping concentration. This result represented that higher at.% Al leads to the change of crystal orientation into other directions rather than the *c*-axis perpendicular to the substrate surface which is in accordance with those of other authors [5, 15, 16].

3.2 Electrical and optical properties

1) Electrical properties

Electrical properties of the AZO films doped with various at.% Al doping concentration are shown in Figure 2. It can be seen that the carrier concentration was improved with the increase of at.% Al in the film which implied higher Al substituting for Zn atoms in the film structure. Maximum carrier concentration of

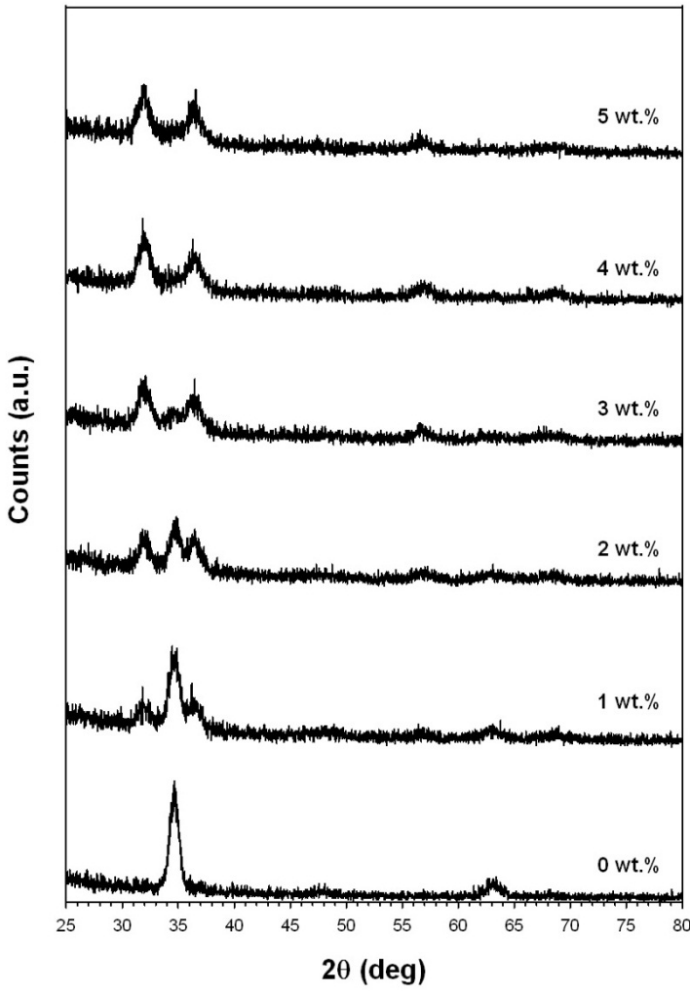

Figure 1 XRD spectra of AZO deposited from Al_2O_3 doped ZnO targets in the range of 0 – 5 wt.%

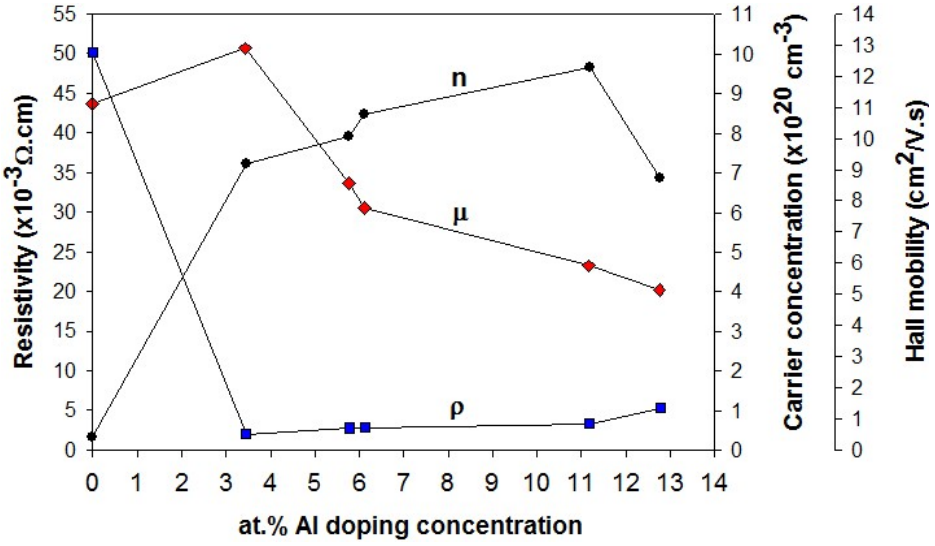

Figure 2 Electrical properties of deposited AZO at various at.% Al doping concentrations

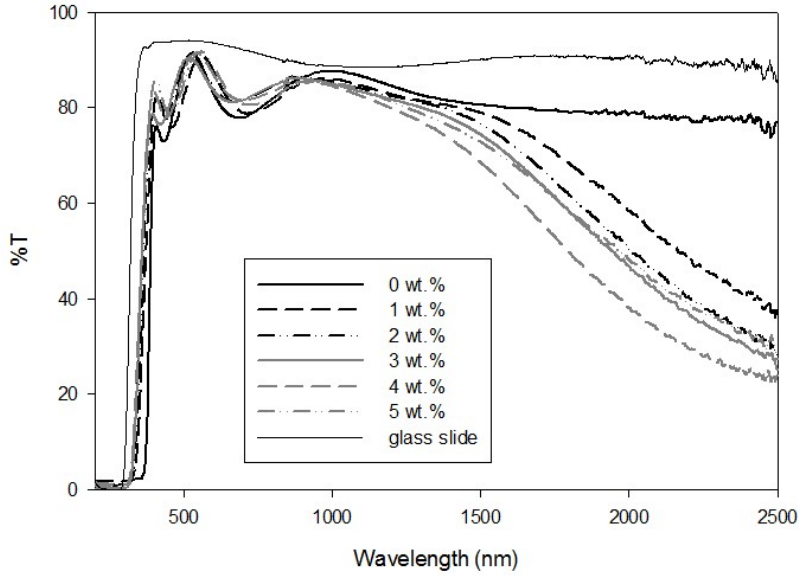

Figure 3 Optical properties of AZO films deposited from 0 – 5 wt.% doped ZnO target

9.67×10^{20} cm^{-3} was achieved for 11.18 at.% Al doping concentration. However, further increase of Al in the film structure, the carrier concentration was reduced to 6.86×10^{20} cm^{-3}. Therefore, the over limit of Al doping concentration have not contributed to Al substitutions for the Zn atoms but, on the other hand, they may segregated to grain boundaries or interstitial sites and acted as electron traps in the film structure. This result is consistent with that reported by El Manounia *et al.* [16]. For Hall mobility, it varied in the opposite direction with carrier concentration. The Hall mobility decreased with increasing at.% Al doping concentration. Maximum Hall mobility was 12.89 $cm^2/V.s$ for 3.45 at.% Al which decreased to 5.15 $cm^2/V.s$ as the at.% Al was increased to 12.77. The decrease of Hall mobility was also reported by Zhao *et al.* [2]. Decrease of Hall mobility may be described in term of grain boundary scatterings which are due to the lattice distortion in the film structure with higher at.% Al doping concentration, as previously discussion.

2) Optical properties

Optical properties of undoped and Al doped ZnO films are shown in Figure 3. Average transmissions for all films in visible region are higher than 80%. Optical band gaps of the AZO films were determined from equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where α is the optical absorption coefficient, $h\nu$ is the incident photon energy and A is a constant for direct transition. The optical absorption coefficient can be calculated from an equation $\alpha = (1/d)\ln(1/T)$, where d is the film thickness and T is the transmission of AZO films.

By plotting graphs between $(\alpha h\nu)^2$ vs. $h\nu$, as shown in Figure 4, the optical band gap (E_g) for direct transition can be determined by extrapolation the linear absorption edge part of curve to obtain the interception on energy axis. It was found that the optical band gap of ZnO film is 3.24 eV and become higher to 3.47, 3.58, 3.66 and 3.68 eV for increasing at.% Al doping concentration from 3.45 to 11.18, respectively. However, the optical band gap become smaller to 3.65 eV for 12.77 at.% Al. Variation of the optical band gap is relevant to the carrier concentration in the film structures which is attributed to Burstein-Mass effect which describes the blue-shift of absorption edge of a degenerate semiconductor with increasing the carrier concentration.

4. Conclusions

The AZO films were prepared from undoped and 1 – 5 wt.% Al_2O_3 doped ZnO ceramic target by the RF magnetron sputtering technique and annealed at 500°C in vacuum for 1 hour. It was found that the at.% of Al in the film structure increased from 3.45 to 12.77 at.% as the wt.% of Al_2O_3 doped from 1 to 5 wt.%, respectively. The crystal structure, electrical and optical properties of deposited films were affected by different at.% of Al doping concentrations. Higher at.% of Al doping concentrations increased the Al substitutions in Zn sites resulting in poor crystallinity and the increase of carrier concentration and optical band gap. However, because of poor crystallinity, the grain boundary scattering was dominant which contributed to lower Hall mobility. It was also found that

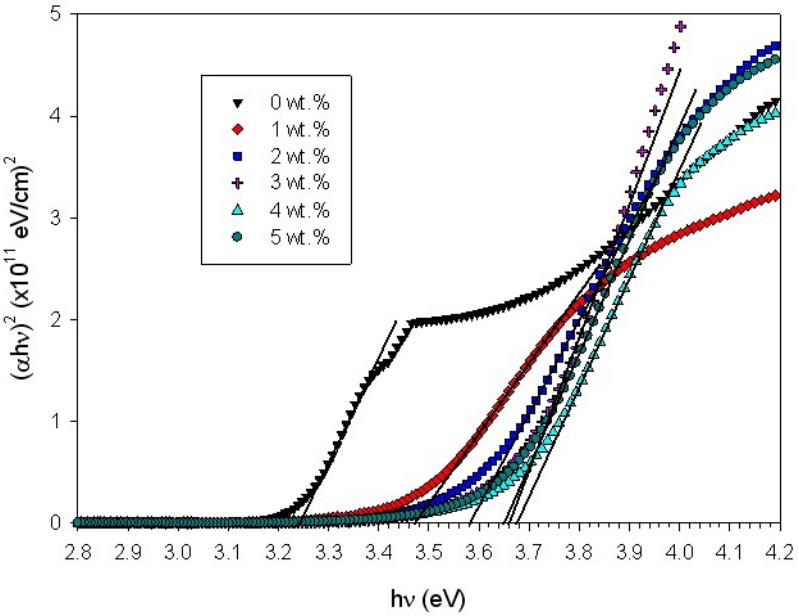

Figure 4 Optical band gap determination of AZO films deposited from 0 – 5 wt.% doped ZnO target

limitation of wt.% of Al_2O_3 doped in the target was 4 wt.% with 11.18 at.% Al doping concentration in the film structure. Excess Al doping concentration in the film structure plays a role of electron traps. From experimental results, it can be concluded that, in sputtering technique, at.% of Al doping concentration in the film structure can be easily controlled by wt.% of Al_2O_3 doped in sputtering target which have effects on the film structure and properties of deposited AZO films.

From the experimental results, it can be seen that the crystal structure has low crystallinity with increasing Al doping concentration which resulted in lower carrier mobility. In order to improve the crystallinity of film structure, the AZO may be deposited in higher RF power and higher substrate temperature before post-annealing process. Better crystallinity can decrease the grain boundary scattering and improve the electrical property of deposited AZO films.

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