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Abstract. Al doped ZnO (AZO) thin films were deposited using dc magnetron sputtering on corning glass substrate has successfully done. After deposition, the samples were annealed in vacuum ambient at temperature of 300 ^{o}C with variation in annealing duration of 0, 30, and 50 minutes, respectively. The structural, optical and electrical properties of these films have been investigated as a function of annealing duration. Thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectrometer and I-V measurements. AZO thin films without annealing treatment was showed amorphous structure. However, after annealed at 30 and 50 minutes, the films obtained were polycrystalline with a hexagonal wurtzite structure and preferred orientation in the (002) plane. Average optical transmittance of the AZO thin films was over 85%. In Addition, the electrical resistivity is reduced from 1.85 x 10^{6} Ωcm to 1.93 x 10^{2} Ωcm when applying annealing treatment. It's can be concluded, the annealing treatment in vacuum ambient was improved the crystallinity and simultaneously improved optical and electrical properties of AZO films.

1. Introduction

Transparent conducting oxides (TCOs) have been intensively investigated as the application for optical and electrical applications, such as thin film photovoltaics, flat panel displays and light emitting diodes. TCO thin films should have low resistivity, high transmittance in the visible region, and high thermal/chemical stability. At present, ZnO-based TCO films have attracted considerable interest due to is high thermal stability, non-toxicity and phenomenally low cost. For the purpose of improving the electrical conductivity and optical transmittance of ZnO thin films, group III elements such as boron, aluminum, gallium, and indium are usually introducing to ZnO [1-4]. At present, Al-doped ZnO (or AZO) thin films as TCOs film have most attention, due to the advantage of AZO thin film is wide bandgap semiconductor materials (E_g = 3.3 to 3.7 eV) resulting in the optical transmittance properties in the visible regions [5]. The growth of ZnO thin films has been carried out by various methods, including pulse laser deposition (PLD) [6], metal organic chemical vapor deposition (MOCVD) [7], pyrolysis [8], sol-gel spin coating [9], and rf magnetron sputtering [10]. In this study AZO thin films were grown on corning glass using the homemade DC magnetron sputtering method under consideration that DC magnetron sputtering was able to produce good quality thin films with simple process and low production costs. The annealing influence is considered as an effective technique to modify intrinsic defects and improve electrical properties [11-12].

2. Methods

In this research, homemade DC magnetron sputtering was used to grow AZO thin films. The stages of thin film growth begin with the makes of AZO targets, substrate preparation, and the growth of AZO thin films. AZO sputtering target 2 inch in diameter is prepared using raw materials ZnO (99.99%) and Al_2O_3 (99.99%), the total mass of the AZO target is 10 grams with a mole fraction ratio of Al_2O_3 is 3%. The mixture of ZnO and Al_2O_3 was synthesized using a solid-state reaction, calcined at 500 °C for 4 hours, and sintered at 750 °C for 5 hours. AZO thin films were grown on a corning glass substrate. Substrate preparation is done by cutting 1x1 cm^2 of corning glass. The substrate is cleaned using methanol in an ultrasonic bath for 15 minutes to remove contamination on the surface of the substrate, then repeated using acetone for 10 minutes. The substrate is cleaned with water and dried with nitrogen spray. Before the growth of the film, the sputtering reactor was vacuumed to a pressure of 1 mTorr, then argon gas flowed up to pressure deposition of about 500 mTorr during the growth of the AZO film for 120 minutes.

AZO thin films are grown at a temperature of 400 °C with 40 watt plasma power for 120 minutes. The post-growth annealing treatment was carried out with a sputtering reactor under vacuum at a temperature of 300 °C. The annealing duration varied was 0, 30, and 50 minutes. The AZO thin film crystal structure was analyzed using X-ray diffraction (XRD). Scanning electron microscopy (SEM) is used for thin film surface morphology analysis. UV-vis spectrometer is used for the analysis of the optical properties of films. The electrical properties of films was analyzed using I-V measurements.

3. Results and Discussion

The XRD pattern of AZO thin films grown with DC magnetron sputtering with different annealing duration of 0, 30, and 50 minutes, respectively is shown in Figure 1. The un-annealed AZO film shows the absence of crystal peaks in the XRD pattern, meaning that the film has an amorphous structure. AZO films with a duration of 30 and 50 minutes showed the presence of crystal peaks in the XRD pattern with a polycrystalline structure. In previous studies, AZO grown on a preparatory glass substrate with the same growing and annealing conditions, the resulting AZO film has an amorphous structure [13]. Data from XRD analysis including angle 2θ, *hkl* plane, *d*-spacing, FWHM, and crystallite size are shown in Table 1. AZO films with annealing duration of 30 and 50 minutes have a hexagonal wurtzite structure and grown along the direction (002) plane. Its means that the dominant film grows in the c-axis direction and is perpendicular to the substrate plane. The highest peak intensity (002) occurs when the AZO film was annealed at duration of 50 minutes. When the AZO film was annealed for 30 minutes, peaks (100) and (102) were not observed. Although peaks (100), (101), (102), (103) and (110) are observed in the XRD pattern, no secondary phases and clusters are found, such as Al_2O_3 and $ZnAl_2O_4$ which indicate that the Al atoms substitute Zn in hexagonal and Al^{3+} lattices can be interstitial sites ZnO or Al may be separated into non-crystalline regions in grain boundaries and form Al-O bonds [14].

From the data in Table 1, its appears that the peak angle value of 2θ for (002) peaks shifts to an angle smaller than 34.67° when the film is annealed for 30 minutes to 34.42° when the film is annealed for 50 minutes, which indicates the occurrence of incorporated Al^{3+} interstitial site of ZnO [14]. To test the quality of AZO films can be seen from the angle of 2θ of (002) peak, full width at half maximum (FWHM) of (002) peak and grain size as shown in Table 1. The FWHM value for AZO that were annealed for 50 minutes was 0.47° lower than the 30 minute is 0.62°. The grain size of the AZO film that was annealed for 50 minutes (18.3 nm) was also greater than the 30 minutes film (14.0 nm). This condition shows that the film that was annealed for 50 minutes had better crystalline quality compared to the film that was not annealed or was annealed for 30 minutes. Due to the annealing duration effect can be said that increasing of the annealing duration was improved the crystallinity of the films, which is the annealing duration of 50 minutes.

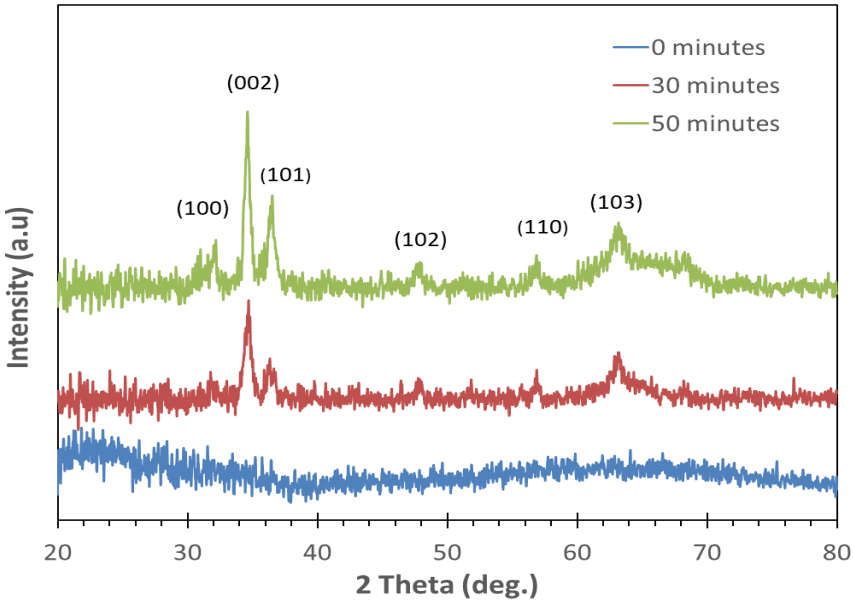

Figure 1. XRD spectrum of AZO thin film with different annealing duration of 0, 30, and 50 minutes.

Table 1. XRD analysis data from AZO thin film samples were scaled for a duration of 0, 30, and 50 minutes.

Film AZO	2-theta (deg.)	*hkl* plane	d_{hkl} (ang.)	FWHM (deg.)	Size (nm)
#AZO-0	-	-	-	-	-
#AZO-30	34.67	(002)	2.585	0.62	14.0
	36,29	(101)	2.473	0.69	12.7
	57.00	(110)	1.615	0.51	18.7
	63.02	(103)	1.474	1.60	6.2
#AZO-50	32.13	(100)	2.784	0,60	14.4
	34.42	(002)	2.592	0.47	18.3
	36.42	(101)	2.465	0.63	13.8
	47.63	(102)	1.908	0.61	14.9
	56.87	(110)	1.617	0.29	32.6
	63.04	(103)	1.473	2.00	4.8

AZO thin film microstructure influences the electrical and optical properties for the application of optoelectronic devices, therefore it is very important to investigate the surface morphology of AZO thin films. Figure 2 shows the surface microstructure of the AZO film that was annealed with different duration of 0, 30 and 50 minutes. Visually, there is a surface morphology difference between AZO films annealed by 0, 30, and 50 minutes. The AZO film that is not annealed (Figure 2a) shows that the microstructure tends to be amorphous, porous appearance and connection between grains are not compact. Whereas the AZO film that was annealed for 30 minutes (Figure 2b) and 50 minutes (Figure 2c) appears to have a more homogeneous arrangement of grains and connections between grains appear to be compact and more dense with grain arrangement. When annealing is done, the mobility of the atoms is faster so that it increases the density grain. Annealing post growth treatment increases AZO crystalline homogeneity as FWHM peak value (002) of AZO film is annealed at lower annealing duration. The SEM also shows grain size of AZO film in nanocrystalline scale as the data from XRD analysis. But usually the results of observations of grain size with SEM appear larger than the data

from XRD analysis results. Grain boundary and grain size greatly affect the electrical and optical properties of AZO films.

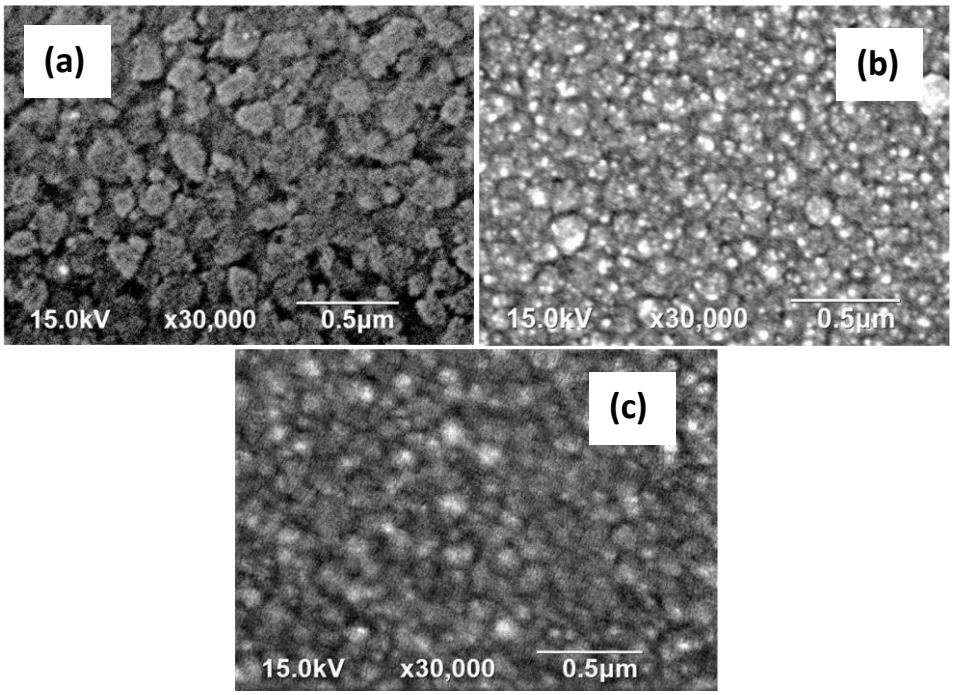

Figure 2. SEM images of AZO thin film with different annealing duration of (a) 0, (b) 30, and (c) 50 minutes.

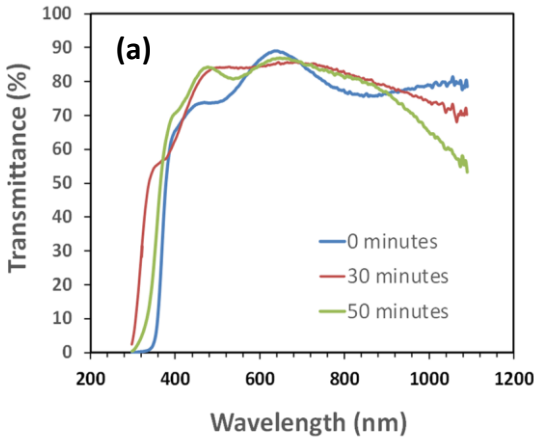

Figure 3a. Optical transmittance of AZO thin films as function of duration annealing (0, 30, and 50 minutes).

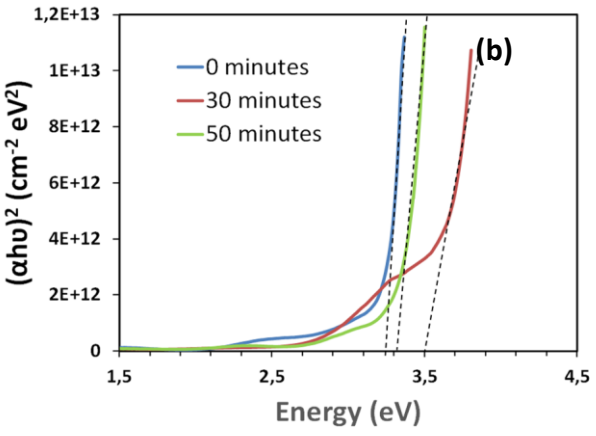

Figure 3b. The energy gap of the AZO films estimated by the extrapolation of the linear part of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots.

Figure 3 (a) shows optical transmittance as a function of wavelength from AZO thin films annealing at 0, 30 and 50 minutes. Un-annealed AZO thin films have an average optical transmittance value of 82.1% in the visible light region. When the thin film was annealed for a duration of 30 and 50 minutes, it showed an increase in the optical transmittance value of AZO films in the visible light region to an average of 85.0% and 85.4%, respectively. This increases in optical transmittance value is related to the better quality of AZO film crystals when apply annealing treatment.

An obvious absorption edge and interference phenomenon could be observed in the transmission spectra for all AZO thin films, which indicated that smoot and homogeneous surfaces of AZO thin films were obtained. The reduction in optical transmittance in the infrared region is most probably related to an increase in light reflection due to an increased charge carrier density. It is know that TCOs behave as metallic materials in the infrared region, and thus are reflective [13]. The optical bandgap E_g is obtained by extrapolating linear portions of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$), as shown in Figure 3 (b), where α is the absorption coefficient. The sharp absorption edge can be accurately determined for the high quality AZO thin film by linear fit. Optical bandgap from AZO films was annealed at 0, 30, and 50 minutes were 3.24 eV, 3.50 eV and 3.32 eV, respectively. In general, annealing treatment has increased the optical bandgap of AZO thin films.

Based on the optical bandgap, its can be said that the absorption edge of AZO un-annealed shift to higher energy (blueshift) for AZO with an annealed. Increases of the annealing duration was affected on the carrier concentration blocking the lowest state in the conduction bands, as known as a Burstein-Moss effect [14]. The broadening of the optical bandgap can be calculated with equation:

$$\Delta E_g = \left(\frac{h^2}{2m_{vc}^*}\right)(3\pi^2 n)^{2/3} \quad (1)$$

where ΔE_g is the shift of the doped ZnO compared to undoped ZnO, m_{vc}^* is the reduced effective mass, h is Planck's constant, and n is the carrier concentration. It's clearly to said that the optical bandgap would increase with increasing the carrier concentration of the film.

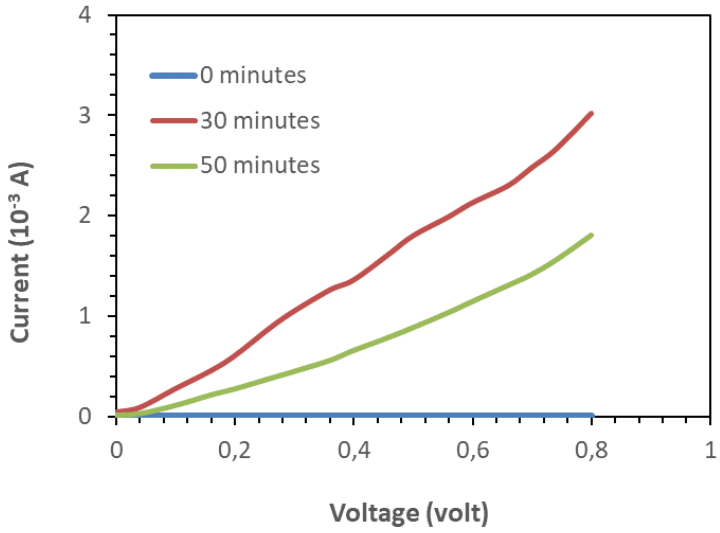

Figure 4. I-V meausurement of AZO thin films.

Table 2. Resistivity and conductivity of AZO thin films.

Annealing (minutes)	Resistivity (Ω cm)	Conductivity $(\Omega\ cm)^{-1}$
0	1.85×10^{6}	8.80×10^{-7}
30	1.93×10^{2}	5.26×10^{-3}
50	4.04×10^{2}	2.64×10^{-3}

AZO sample I-V measurements were carried out using the two probes method at room temperature shown in Figure 4. AZO thin film samples showed the electrical properties of ohmic conduction behavior. The results of the resistivity and conductivity calculations of AZO films are shown in Table 2. The resistivity of AZO films that are not annealed have a very high resistivity value due to the

amorphous film structure. When analyzed for the duration of 30 and 50 minutes, the resistivity value of AZO film grown on corning glass substrate decreased very significantly from 1.85 x 10^6 to 4.04 x 10^2 Ωcm. This condition did not occur when the film was grown on preparatory glass substrate in previous studies [13]. This decrease in resistivity or increase in conductivity is consistent with data on optical bandgap and the Burstein-Moss effect on AZO films was annealed for 30 and 50 minutes. The annealing duration treatment has increased the concentration of charge carriers on AZO films grown on a corning glass substrate.

4. Conclusion

AZO thin films were grown on a corning glass substrate with DC magnetron sputtering. The effect of annealing duration of 0, 30, and 50 minutes has been investigated, respectively. XRD analysis shows that the film was annealed has grown in the direction of the 002) plane, along the c-axis perpendicular to the substrate. Surface morphology shows the transition between amorphous structures into crystal structure. AZO optical bandgap film increases when annealing is performed. When the annealing duration is 30 minutes, the AZO film optical bandgap increases up to 3.50 eV and is consistent with its resistivity value due to the Burstein-Moss effect. The AZO thin film also shows better optical transmittance greater than 85% in the visible light region.

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