Synthesis of Al Doped ZnO Thin Films from ZnO Powder Mixed with Al Wire Targets by Using Asymmetric Bipolar Pulsed-dc Magnetron Sputtering System

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Abstract

The thin films of Al doped ZnO were grown on glass substrate at room temperature from three targets of Al wires mixed ZnO powder with sputtered area ratio of Al wire to ZnO powder of 0%, 5% and 15% by using an asymmetric bipolar pulsed-dc magnetron sputtering system. The effect of Al doping on structural, electrical and optical properties of ZnO thin film were investigated. The X-ray diffraction patterns showed that Al doped ZnO thin film are polycrystalline of hexagonal wurtzite structure with preference orientation in (002) plane. By increasing Al wires area ratio from 0% to 15%, the resistivity of the films was decreased from 231.45 mΩcm to 5.20 mΩcm. The optical transmittance spectra of all films show that the maximum value reaches to 90% in the visible region. These results showed that the thin films obtained from Al wire mixed ZnO powder target by using an asymmetric bipolar pulsed-dc magnetron sputtering system was successfully deposited on glass substrate, the resistivity can be decreased by increasing Al content with low effect on optical transparent properties of the film.

Keywords: Al doped ZnO, optical transmittance, resistivity, sputtering, ZnO films

Introduction

Recently, the thin films of transparent conducting oxides (TCOs) are important for a large number of application consisting of solar cell, touch screens, light emitting diodes and photodetectors. Among many TCOs materials, indium doped tin oxide (ITO) film is the mostly used because of high visible transmission and low electrical resistivity (Boonyopakorn, Rangkupan, & Osotchan, 2018). However, indium is an expensive and very rare materials, so it is very necessary to find its replacement. Al doped Zinc oxide (AZO) thin films have received increasing attention because of its advantages including low resistivity, high visible transmittance, low cost and less toxic (Zhou, Zhang, Tan, Zhang, & Zhang, 2012).

There are many techniques have been used for preparing the AZO films, such as spray pyrolysis (Muiva, Sathiaraj, & Maabong, 2011), sol-gel (Tari et al., 2012), magnetron sputtering (Ou, Lai, Yuan, Cheng, & Kao, 2016), etc. However, sol-gel method seems not useful due to high cost of raw material and cracking of thin film during drying, the thin film obtained from spray pyrolysis method has non-uniformity of film with larger grain size (Jeyaprakash, Ashok kumar, Kesavan, & Amalarani, 2010). The magnetron sputtering is the most commonly used due to the surface of the films is very smooth, film thickness is easily controlled by fixing the operating parameters and simply adjusting the deposition time (Alnajjar, 2012). Recently, Pulsed dc magnetron sputtering is a relatively new sputtering method that has been used for thin film preparation. Pulsing the magnetron discharge in the mid frequency range (10-200 kHz) stabilizes plasma, prevents arcing and yields high deposition rates (Pimpabute, Burinprakhon, & Somkhunthot, 2011). It thus very interesting to deposit Al doped ZnO thin film by using pulsed dc magnetron sputtering and compare the structural, electrical and optical properties to other methods.

There are many typical sputtering targets have been used for deposition AZO thin film such as compacted of ZnO/Al_2O_3 powder (Stamate, 2020), Metallic Zn-Al (Chaves et al., 2019) and etc., but there have not been reported of the use of target made of alloy mixed powder. Therefore, it is interesting to prepare thin film with Al wires mixed ZnO powder targets and investigate its properties.

In this work, the Al doped ZnO films were deposited on glass substrate by an asymmetric bipolar pulsed dc magnetron sputtering method. The effect of Al doping on structural, electrical and optical properties of ZnO films are presented.

Methods and Materials

Target Preparation

Sputtering targets were made from 99.999% pure Al wires and pure ZnO powder which were compacted with pressure of 86.7 MPa on a circular copper base in the sputtered area ratio of ZnO:Al were 100:0, 95:05 and 85:15 as show in Figure 1. The thin films were deposited on glass substrate at room temperature under argon gas pressure of 60 mTorr, discharge current of 120 mA, fixed positive pulse voltage 100 V, and pulsed frequency 17.2 kHz.

(a) (b) (c)

Figure 1 Sputteing targets Al wire mixed ZnO powder before and after sputtering process. The target has the sputtered area ratio (a) ZnO:Al_100:0, (b) ZnO:Al_95:05 and (c) ZnO:Al_85:15

Investigation Negative Deposited Voltage

In the pulsed-dc sputtering process, the positive ion of argon gas is accelerated by negative voltage pulse to surface of target to knock off atom on target become to plasma. The suitable negative voltage can be obtained by increasing voltage of negative pulse and investigated optical emission of atom in plasma during sputtering process. The optical spectrum of plasma was analyzed to identify elemental atoms comparable to the atomic spectrum database of NIST (Atomic Spectra Database Lines, 2020).

In this research, the suitable negative deposited voltage of pulsed-dc sputtering of each target was investigated via optical emission of plasma during sputtering process using spectrometer (getSpec-2048 spectrometer, Sentronic GmbH). The optical emission of plasma obtained from suitable negative voltage of each target was showed in Figure 2

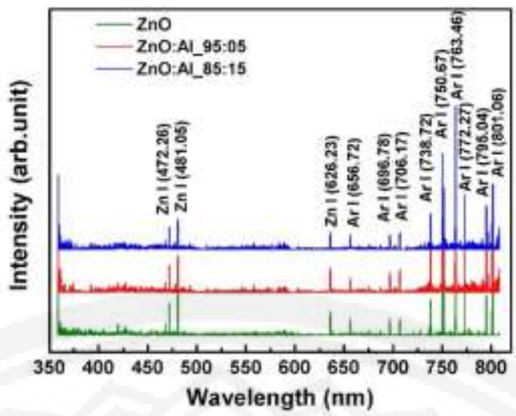
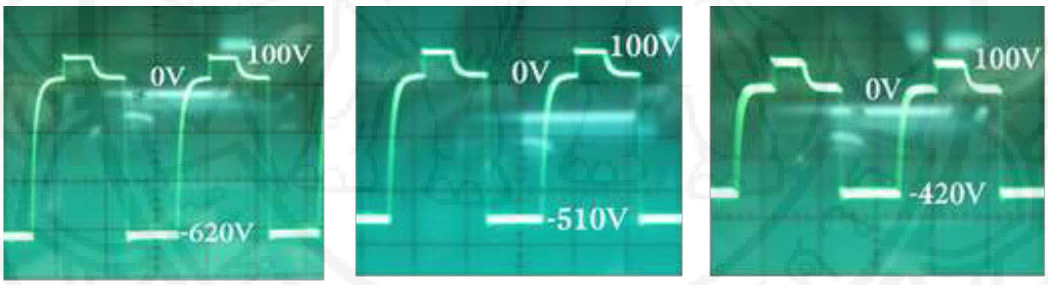


Figure 2 The optical emission of plasma from suitabel negative votage of during sputtering process of targets of ZnO:Al_100:0, ZnO:Al_95:05 and ZnO:Al_85:15

The suitable negative voltage chracteristic of plasma pulsed was captured from screen of high frequecy Oscilloscope as shows in Figure 3. The optical emission spectra shows optical emission of Zn at the wavelegth of 472.26 nm, 481.05 nm and 626.23 nm, while optical emission of Ar atoms were found in the wavelegth over than 650 nm. The optical emission of Al and O were not observed cuase of the wavelength optical emission of the atoms are out of measurent range of spectrometer. The Zn spectra indicating that these negative voltage increases the Ar ion energy sufficient to knock off atoms on sputtering targets. These voltage chracteristic were used to deposit thin films in this work.



(a) (b) (c)

Figure 3 The suitable negative voltage chracteristic of plasma pulsed obtained from target of (a) ZnO:Al_100:0, (b) ZnO:Al_95:05 and (c) ZnO:Al_85:15

Thin films characterization

The crystal structures were analyzed using x-ray diffraction (XRD) using Philips Model PW 1830 with a radiation wavelegth of 0.15406 nm (CuK_{α_1}, at 30 kV and 30 mA). The film thickness was measured using Tolansky's method. The optical properties of the ZnO and Al-doped ZnO thin films were evaluated from the optical transmission which were recorded by a UV-VIS-NIR spectrophotometer (UV-VIS-NIR 3101 PC, Shimadzu Ltd., Japan) in the wavelength range of 300-2000 nm. The resistance of the films were investigated from I-V (current-voltage curves) measured by using digital multimeter (Keithley model 617) and the resistivity were analyzed using Ven der Pauw four point probe method.

Results and Discussion

Structure properties

The Figure 4 shows X-ray diffraction spectra of thin film prepared from different sputtering targets. The XRD patterns of all films shows the polycrystalline structure of Wurtzite Hexagonal with strong peak of plane (002) and weak peaks of diffraction planes (102), (103) and (004) (using JCPDS 89-1397 as reference). These XRD peaks are in good agreement with other reports (Baneto et al., 2014; Chaves et al., 2019).

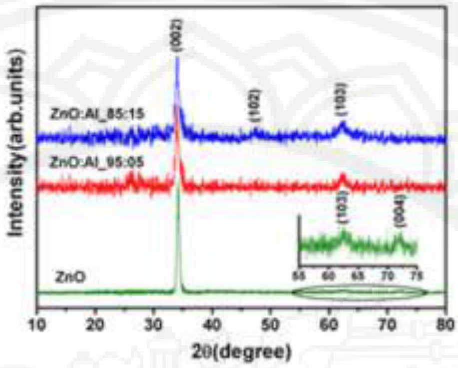


Figure 4 XRD patterns of Al doped ZnO films prepared with different sputtering targets

The lattice spacing between planes of the XRD peaks were calculated from the Bragg's formula (Ilican, Caglar, & Caglar, 2010):

$$2d_{hkl}\sin\theta = n\lambda \quad (1)$$

where d_{hkl} is the lattice spacing, θ is diffraction angle, λ is wavelength of radiation, (hkl) is Miller indices and n is diffraction order (n= 1,2…). The lattice constants a and c were calculated by using the following relation (Prabhu, Venkateswara, Sesha, & Siva, 2013):

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2} \quad (2)$$

The table 1 shows the lattice constants a and c of the thin film samples obtained from ZnO, ZnO:Al_95:05 and ZnO:Al_85:15 targets are well matched with standard values of JCPDS databased (Card No. 89-1397).

Table 1 The d-spacing of the XRD peak and lattice constants a and c of the film obtained from ZnO ZnO:Al_95:05 and ZnO:Al_85:15 targets compared to JCPDS database 89-1397

XRD planes	JCPDS 89-1397		ZnO		ZnO:Al_95:05		ZnO:Al_85:15	
	2θ	d(Å)	2θ	d(Å)	2θ	d(Å)	2θ	d(Å)
(002)	34.38	2.606	34.17	2.624	34.05	2.633	34.02	2.635
(102)	47.48	1.913	-	-	-	-	47.38	1.918
(103)	62.78	1.479	62.58	1.484	62.24	1.491	62.36	1.489
(104)	72.46	1.303	71.89	1.313	-	-	-	-
a(Å)	3.253		3.233		3.265		3.236	
c(Å)	5.213		5.250		5.266		5.269	

The average grain sizes (Table 2) of thin films were calculated from the full width at half maximum (FWHM) of the (002) XRD peak using Scherrer's formula (Prabhu et al., 2013):

$$D = \frac{0.89\lambda}{\beta \cos\theta_B} \qquad (3)$$

where D is average grain sizes, β is full width at half maximum (FWHM) and θ_D is diffraction angle. The calculated results show that all films exhibited nano-grain size which decreases with increasing Al concentration. The grain size was decreased from 22.0 nm for ZnO film to 13.1 nm and 12.3 nm for ZnO:Al_95:05 film and ZnO:Al_85:15 film, respectively. These grain size values are close to grain size of ZnO:Al films grown from ceramic target which was increased from 15 nm to 22 nm with increasing film thickness (Alnajjar, 2012).

Table 2 The size of FWHM of The XRD Plane Peak (002) and the crystalline grain size of thin film ZnO, ZnO:Al_95:05 and ZnO:Al_85:15

Thin films	FWHM(B_s)	Grain size D(Å)
ZnO	0.508°	220
ZnO:Al_95:05	0.766°	131
ZnO:Al_85:15	0.806°	123

Thin films thickness

The Figure 5 shows Fizeau fringes image observed due to interference in multiple beam interferrometric technique (Tolansky's method) (Tolansky, 1948). The thin films thickness was obtained from image using the following formula:

$$t = \frac{h\lambda}{2I} \qquad (4)$$

where t is thin film thickness, λ is monochromatic wavelength (obtained from sodium light tube, 589.3 nm), h is step height and I is fringes spacing. The results of calculated thickness are showed in Table 3 and this thickness was used for calculate resistivity in next section.

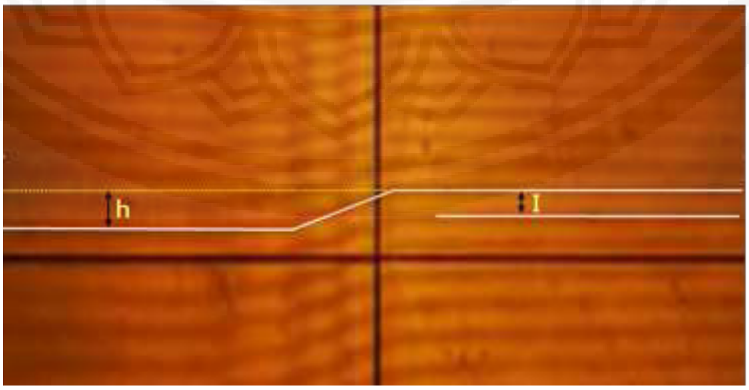


Figure 5 Fizeau fringes image of Al doped ZnO films prepared from ZnO:Al_85:15 target

Electrical properties

Thin film resistance was evaluated from I-V curves measured using Ven der Pauw four point probe method (Van der Pauw, 1958). Thin film resistivity was calculated using the following equation:

$$\rho = \frac{\pi t}{\ell n2}\left[\frac{R_{ab,dc} + R_{bc,ad}}{2}\right]F \quad (5)$$

where ρ is resistivity, t is film thickness, $R_{ab,dc}$ and $R_{bc,ad}$ are resistance and F is correction factor obtained by using the following relation:

$$\frac{R_{ab,dc} - R_{bc,ad}}{R_{ab,dc} + R_{bc,ad}} = \left(\frac{F}{\ell n2}\right)\operatorname{arccos}h\left[(\exp\frac{\ell n2}{F})/2\right] \quad (6)$$

The results of calculated resistivity are showed in table 3

Table 3 The film thickness and electrical resistivity of thin film ZnO, ZnO:Al_95:5 and ZnO:Al_85:15

Thin films	Thickness(nm)	R_{abcd}	R_{bcad}	$(R_{abcd}+R_{bcad})/2$	F	ρ(mΩcm)
ZnO	773.9	569.26	759.75	664.51	0.993	231.45
ZnO:Al_95:05	457.5	21.69	29.41	25.55	0.992	5.26
ZnO:Al_85:15	625.3	16.84	18.39	18.39	0.998	5.20

The resistivity was found of 231.45 mΩcm for ZnO thin film and decreased to 5.26 mΩcm and 5.20 mΩcm for ZnO:Al_95:05 and ZnO:Al_85:15 thin films, respectively. The minimum resistivity 5.20 mΩcm of Al doped ZnO thin films in this work is close to resistivity of 2.01 mΩcm obtained from AZO films deposited from 1 wt% Al_2O_3 -doped ZnO targets (Boonyopakorn et al., 2018) and close to 2.67 mΩcm of Al-doped ZnO thin film prepared by off-axis magnetron sputtering (Ou et al., 2016). These results indicate that the resistivity of thin film in this work was decreased with increasing Al and suitable for using as electrode thin film.

Optical properties

The optical transmission was measured by using air as reference, the transmission spectra of all thin film samples illustrated interference fringes in the wavelength range of 400-2000 nm as shows in Figure 6. The maximum transmission is varied between 90% and 80% in the visible region which is similar to other reports (Ou et al., 2016; Seawsakula et al., 2017). The interference fringes intensity drops in the wavelength range of 500-600 nm and absorption edges at around 450 nm indicated that the thin films exhibit high absorbent in UV. By increasing Al content, the optical transmittance was slightly decreased in visible region and clear decreased in near infrared region. This results shows that the all of film suitable candidates to be transparent electrode.

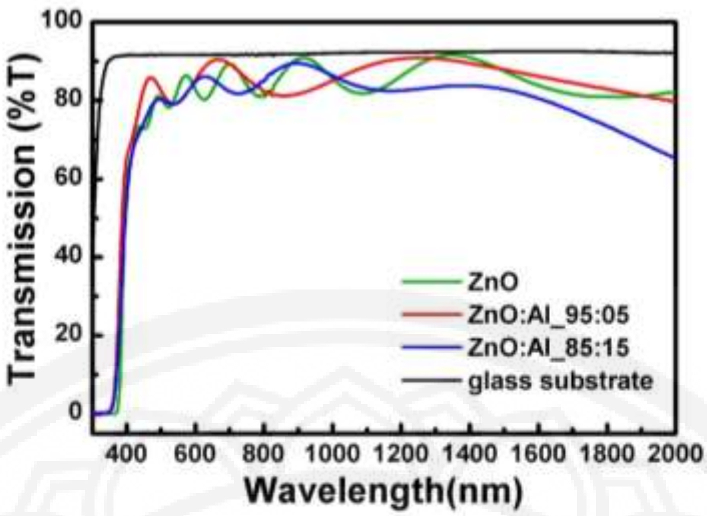


Figure 6 Optical transmission of glass substrate and Al doped ZnO films obtained from different sputtering targets

Conclusion and Suggestions

The thin films of Al doped ZnO were successfully deposited on glass substrates from Al wires mixed ZnO powder targets using an asymmetric bipolar pulsed dc sputtering system. The effect of Al doping on structural, electrical and optical properties has been investigated. The XRD Diffraction patterns of all films showed that the structures were hexagonal and that the average grain size can reduce by increasing Al doping. The electrical resistivity was increased with increasing Al concentration on the films. The transmittance spectra showed high transmission over >80% in visible region.

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