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Structure, Optical and Electrical Properties of Al-doped ZnO Thin Film Grown in Hydrogen-Incorporated Sputtering Gas

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Keywords : Sputtering, Al-doped ZnO, hydrogen, low power density

Abstract : Low RF power density was used for preparing transparent conducting Al-doped ZnO (AZO) thin films by RF Magnetron Sputtering on Corning 1737 glass. The dependence of films' structural, optical and electrical properties on sputtering gas, film's thickness and substrate temperature were investigated. Low percent of incorporated H_2 in Ar sputtering gas has proven to reduce film's resistivity and sheet resistance as low as 4.1 x 10^{-3} Ω.cm. It also formed new preferred peaks orientation of (101) and (100) which indicated that the *c*-axis of AZO films was parallel to the substrate. From UV-VIS-NIR Spectrophotometer analysis, it further showed high optical transmittance at about ~ 90% at visible light spectra (400 - 700 nm).

1. Introduction

Research of the Al-doped ZnO (AZO) transparent conducting films are currently attracting much attention for application in many electronic devices ranging from TFT, OLED, and particularly for window layer thin film solar cells [1-3]. ZnO is a 3.4 eV direct band gap material at 300 K with hexagonal wurtzite structure [4]. It presents outstanding characteristics from good optical quality, stability, and excellent piezoelectric [5] and semiconducting properties [6]. Recently, Al-doped ZnO becomes an attractive alternative material for replacing Indium-Tin Oxide (ITO) as a promising transparent conducting oxide due to its advantages such as inexpensive, abundant and harmless materials.

It has been known ZnO exhibits strong *n*-type conductivity even the source of the conductivity is still in controversy. For many years the *n*-type conductivity has traditionally been attributed to the native defect. However, Van de Walle [7-8,] has found strong evidence that hydrogen acts as a source of conductivity for ZnO. This behavior is very different from hydrogen in other semiconductors, in which it only acts as a compensating center and always counteracts the conductivity. Recently, few experiments confirmed this new evidence, such as Cox *et.al* [9] and Hoffman *et.al* [10] using muon spin rotation and electron paramagnetic resonance technique. The molecular structure was further confirmed by infrared spectroscopy. Other progress was reported by Kilic [11] *et.al* by generalized the hydrogen doping behavior in various oxides recognizing that there exists a hydrogen pinning level at about 3.0 ± 0.4 eV below vacuum for all oxide.

Few methods have been reported on the preparation of hydrogen-doped ZnO or preparation of AZO films by introducing H_2 gas such as; DC sputtering, MBE, RF Magnetron sputtering, ion implantations, MOCVD and ion beam sputtering [12-17]. Among these various deposition techniques, RF Magnetron sputtering has shown advantage such as offers safety, avoids the use of toxic gas, performs high deposition rate at low temperature, easy to expand to large scale glass substrate, low cost and simple.

In this study, we investigated the characterization of sputtered Al-doped ZnO thin films by incorporating low percent H_2 in Ar sputtering gas.

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2. Experimental Details

Corning glass 1737 was used as a substrate for deposited AZO films using RF magnetron sputtering. A sintered ceramic target with a mixture of 98 wt% ZnO (purity 99.99%), 2 wt% Al_2O_3 (purity 99.99%) and 69 mm in diameter placed at the distance 50 mm below the substrate. 0.7 mm thick of Corning glass 1737 substrate were sliced into 10 x 10 mm in size and cleaned in organic cleaning; acetone, ethanol, distilled water and following by nitrogen gas drying in order to eliminate contaminants level. Various film thickness were obtained by varying the deposition time. The deposition conditions are given in the Table 1. Deposition was performed at various working pressure and film' s thickness was obtained by varying deposition time. Throughout all experiments, the target was *pre-sputtered for 15 minutes* before actual deposition begin in order to remove for removing any contamination on the target' s surface.

Crystallinity and crystal orientation of thin films were examined by X-Ray Diffractrometer using Cu Kα radiation with λ = 1.5405 Å (Rigaku DMAX 2500, Japan). Plane view and cross section were observed using Scanning Electron Microscope (Hitachi S-4100, Japan). Surface roughness and morphology were examined by Atomic Force Microscope (Nanoscope IIIa, Digital Instruments, USA). The optical transmittance and optical band gap were determined by UV-Vis-NIR Spectrophotometer (Cary 500 Varian, USA) with spectral range 300-1000 nm and Four-point probe was used for electrical resistivity and sheet resistance measurement.

Tabel 1. Deposition Parameter

Parameter	Condition
Power density (watt/cm^2)	0.8
Sputtering gas	Argon and Argon+3%H_2
Working pressure (10^{-2} Torr)	2 and 4
Substrate temperature (^{0}C)	150 and 200
Film thickness (nm)	150 - 430

3. Results and Discussion

3.1. Structure

Most papers reported that sputtered AZO thin films are highly textured, with the *c*-axis perpendicular to the substrate surface at (002) orientation. In this report, we observed strong dominated peaks of (100) and (101) which occurred at films deposited with mixture Ar-3%H_2. No Al_2O_3 peak was detected from the XRD patterns. This may be due to aluminum *substitute zinc in the hexagonal* lattice or aluminum segregating to the non-crystalline region in grain boundary.

Crystal orientation of the films evaluated by XRD showed in Fig. 1. The XRD peaks for films with thickness 150 nm had low crystallinity indicated by weak peaks either in (002), (100) or (101) corresponded to 34.4^0, 31.8^0 and 36.1^0 from JCPDS card No. 36-1451. Optimum crystallinity for deposited films were obtained with working pressure 2 x 10^{-2} Torr for mixture argon+3% hydrogen and 4 x10^{-2} Torr for pure argon sputtering gas.

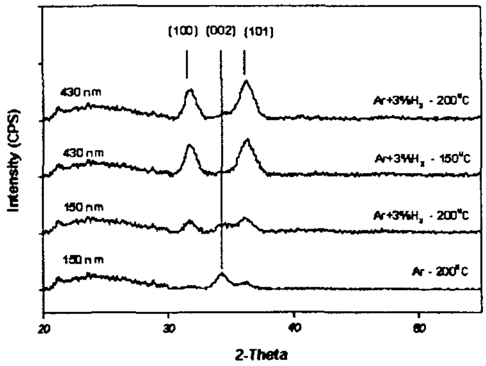


Fig. 1. X-ray Diffraction pattern of AZO films at various thickness and temperature

Peak of (002) showed at films deposited with pure argon whereas peak of (100) and (101) were always existed at films deposited with mixture argon-3% hydrogen. This (100) and (101) peaks existence due to the presence of incorporated hydrogen in mixture sputtering gas were also observed by other reports [18,19]. The peaks of (100) and (101) indicated that the *c*-axis of films was parallel to the substrate, or the *a*-axis was perpendicular to the substrate. It was clear that incorporated H_2 has enhanced the relative intensity of (100) and (101) peaks. This unique structural change originated from the reduction of oxygen content due to the continuous hydrogen addition during deposition process [19].

The XRD patterns also showed the dependence of crystallinity on film' s thickness and substrate temperature. As the increasing the film' s thickness and substrate temperature, the films' crystallinity were increased indicated by the increasing of (100) and (101) peaks intensity.

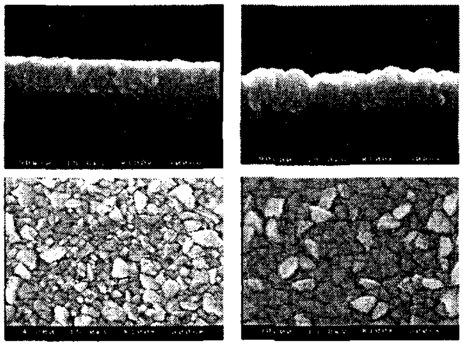

(a) (b)

Fig. 2. SEM micrograph of deposited 150 nm thick AZO films (a) in pure Ar, (b) Ar-3% H_2 sputtering gas

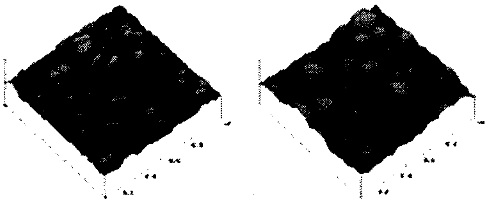

(a) (b)

Fig. 3. AFM surface morphology of deposited 150 nm thick AZO films (a) in pure Ar, (b) Ar-3% H_2 sputtering gas

Fig. 2 shows SEM images of AZO films' plane section and columnar structure with films thickness at 150 nm deposited at 200^0C substrate temperature. At 150 nm film deposited with pure argon gas showed well defined columnar structure. Incorporated small percent of hydrogen to sputtering argon gas produced dominated spherical shape which has disappeared the columnar structure and the difference became more apparent at 430 nm film thickness.

Complementary analysis between XRD and SEM showed evidence between presence of incorporated hydrogen *in* sputtering gas which has contributed to produce new preferred (100) and (101) orientation and therefore transformed films structure into spherical shape, whereas deposited film with (002) orientation only grown as well defined columnar structure at pure argon gas.

Fig.3. demonstrates AFM morphology *for deposited AZO films* at 150 *nm*. Film' s surface morphology more clearly showed the effect of incorporated H_2 in sputtering gas as describe in XRD and SEM analysis previously.

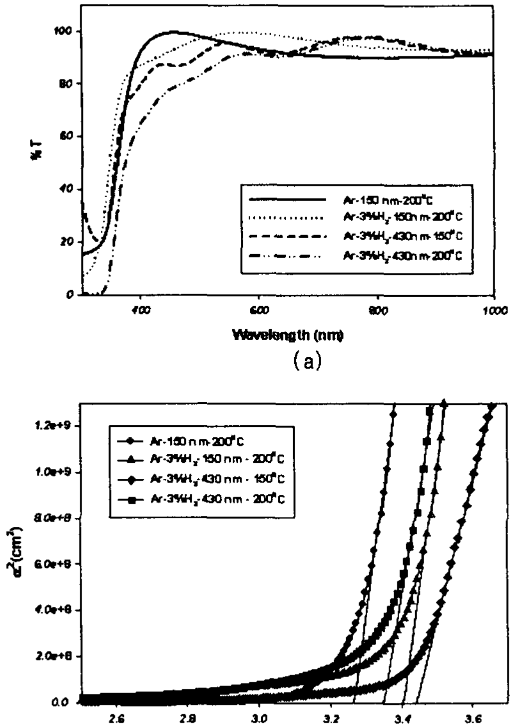
3.2. Optical Properties

The dependence of AZO film' s optical transmittance from spectral range 300-1000 nm on various substrate temperature, thickness and hydrogen presence is shown in Fig. 4.a. At 150 nm, substrate temperature effect was slightly increased the optical transmittance in blue region or near-UV region, both in film deposited with pure argon and mixture argon and 3% hydrogen. Here the presence of hydrogen has given high optical transmittance similar to film deposited with pure argon gas. However, due to the thickness effect the film' s blue region transmittance was decreased obviously as film' s thickness increasing.

AZO is a direct *n*-type semiconductor and the optical band gap (E_g) of the films can be determined by extrapolation methods from the absorption edge. The absorption edge for direct interband transition is given by:

$$\alpha^2 = hv - E_g \qquad (1)$$

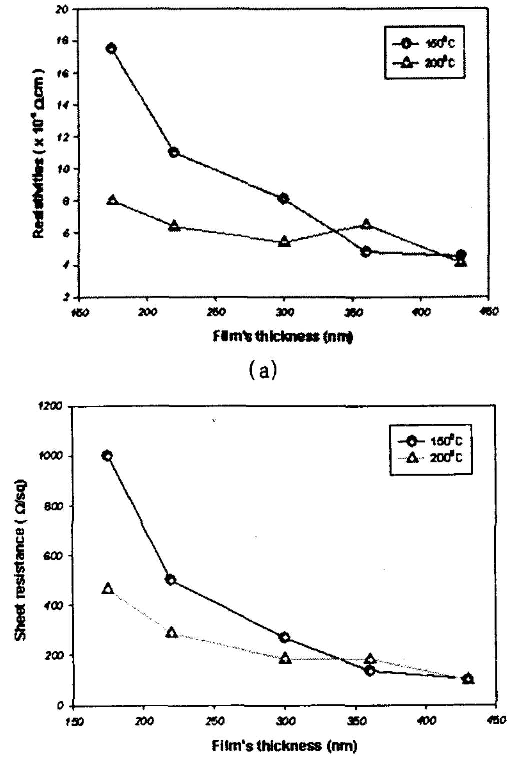
where h is Planck' s constant, and v is the frequency of the incident photon. The coefficient of absorption is defined as



(a)

(b)

Fig. 4. (a) Optical transmittance of AZO films deposited in various temperature and thickness, (b) AZO film's optical band gap



(a)

(b)

Fig. 5. (a) resistivity of AZO films deposited in various temperature and thickness, (b) Sheet resistance

$$I = I_o e^{-\alpha t} \qquad (2)$$

where I is the intensity of transmitted light, I_o is the intensity of incident light, and t is the thickness of Al-doped ZnO. Since the transmittance is defined as I/I_o, we obtain from Eq. (2). Fig. 4.b is the plot of α^2 vs $h\nu$ indicates that AZO film is direct transition semiconductor. The energy gap can then be obtained from the intercept of α^2 vs $h\nu$.

AZO films showed Burstein-Moss shift, i.e. shifted of optical band gap between 3.3 to 3.45 eV. Here, at film with thickness 150 nm, incorporated hydrogen into sputtering gas has increased optical band gap, whereas the increasing substrate temperature at 430 nm, has reduced optical band gap.

3.3. Electrical Properties

Films' resistivity and sheet resistance of AZO films in mixture Ar+3% H_2 as a function of thickness is given in Fig. 5 We observed 150 nm thick AZO film deposited with pure argon at optimum working pressure and 200^0C substrate temperature had resistivity 5.1 x 10^{-2} Ω.cm and sheet resistance 3.3.kΩ/□. The presence of hydrogen in sputtering gas has reduced film's resistivity and sheet resistance to 8 x 10^{-3} Ω.cm and 463 Ω/□ at the same film's thickness.

Based on film's structural analysis transformation films columnar structure into spherical shape due to presence of hydrogen in sputtering gas has effected the reduction of films' resistivity and sheet resistance. From the theoretical background, reduction of film' s resistivity and sheet resistance were most probably caused by hydrogen which acts as a source of conductivity for ZnO. Addonizo *et.al.* [20] stated that hydrogen in sputtering gas is able to enhance the Al doping effectiveness by destabilizing Al_2O_3 formation at the growing surface.

As film' s thickness approached 430 nm, resistivity and sheet resistance decreased until lowest value at $4.1\ \mathrm{x}10^{-3}$ Ω.cm and 97 Ω/□. These phenomena resulted from increasing the films' thickness which improved films' crystal quality indicated by higher intensity of (100) and (101) peak orientations.

4. Conclusion

We investigated deposition of sputtered AZO films by low RF power density on Corning glass 1737. New preferential peaks orientation of (100) and (101) was formed in AZO films deposited with incorporating 3% H_2 in Ar sputtering gas and produced dominated spherical shape of film' s structure. This new preferential orientation indicated that the *c*-axis of AZO films was parallel to the substrate or in other way, *a*-axis was perpendicular to the substrate. From UV-VIS-NIR Spectrophotometer analysis, it further showed high optical transmittance at about ~ 90% at visible light spectra (400 - 700 nm) and Burstein-Moss shift from 3.3 - 3.45 eV. As film' s thickness increased to 430 nm, there was *improvement* in resistivity and sheet resistance as low as 4.1×10^{-3} Ω.cm.

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