Characterization of Zn coated Radio Frequency sputtered AZO thin films

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Abstract

Transparent conducting oxides (TCOs) have become an essential part of today's life through their application in touch screen technology. The growing interest for superior and cheap transparent conducting films, primarily driven by the smart televisions and phones market, has led to renewed efforts to develop novel TCOs. Currently, the most widely used material for transparent conducting applications is Sn-doped indium oxide (ITO), but this material is expensive. Al-Doped zinc oxide (AZO) is among the few metal oxides which can replace costly tin doped indium oxide (ITO) due to many properties similar to it. Thin films of AZO of different thickness 100 nm, 200 nm, 300 nm were deposited on glass substrates using Al doped ZnO target by RF magnetron sputtering system and 15 nm Zn layer on top of it by DC magnetron sputtering system and annealed in inert environment. These films show a carrier concentration of 2.28×10^{21} cm^{-3}, mobility of 27 cm^2/V-s and resistivity of 10^{-4} Ω-cm. Such a low value of resistivity is attributed to a dense compact columnar morphology of the sputtered films as evident from FESEM micrograph. The nanocolumns of such close proximity with higher surface related defects increase the carrier concentration enormously. As a result, compact columnar structure improves conduction process and increases electrical conductivity which is comparable to the standard TCO characteristics used in the optoelectronic devices.

Keywords: Al-doped, ZnO Thin films, AZO, Sputtered.

1. Introduction

A growing demand in realizing low-cost conducting transparent films exists for large production of optoelectronic devices, for example light emitting diodes, sensor devices, solar cells and many modern display applications including plasma display panels and liquid crystal [1, 2]. Sn-doped indium oxide (ITO) and F-doped SnO_2 (FTO) exhibits extraordinary combination of electrical and optical properties: (i) more than 82 % optical transparent in the visible region and (ii) very low resistivity of around 10^{-4} Ω-cm [3], that's why it is mostly used as transparent conducting oxide (TCO). But, there are concerns regarding its future availability and price of FTO and ITO due to the inadequate availability of the metal In as the production of optoelectronic devices using ITO expands rapidly. Alternatively, positive ion doped ZnO is supposed to be the best material which can be used as TCO [4-8]. The properties of ZnO are the wide band gap of 3.3 eV [5-8], and high transparency in the visible range [5-8], easy wet chemical etaching for device fabrication, high UV light trapping characteristics, low resistivity, and low preparation costs. The trivalent dopants used in ZnO to obtain TCO are mainly Al^{3+}, In^{3+}, B^{3+}, Ga^{3+} [5–8]. It should be mentioned [5-8] that Al is not only abundant and non-toxic, but also a relatively cheaper material. Therefore, for all TCO related applications, instead of using high cost FTO or ITO films, alternative low-cost Al-doped ZnO (AZO) films can be successfully used. Now a day, for manufacturing TCO for flat panel displays, solar cells, organic light emitting diodes etc., AZO films are being considered. A number

of literatures [9-15] have been reported that, the AZO films grown by different methods such as DC or RF sputtering, vapor arc plasma evaporation, ALD, CVD, PLD, sol–gel spin cast techniques, the resistivity values obtained in the range of 10^{-2}–10^{-4} Ω-cm and carrier concentration values is ranging from 10^{19} to 10^{20} cm^{-3}. It has been reported that, the free carriers can be increased by different post-growth treatments [4, 9, 16-17]. The film resistivity has been reduced by post-growth annealing in air or H_2 [4], vacuum [9, 16], or inert gases [17]. The mobility values are relatively lower in most of the reports, though; the carrier concentration is in the order of 10^{20}–10^{21} cm^{-3}. Similar observation has been also reported by Li et al. [18] and Shin et al. [19] that, AZO based TCO film showed carrier concentration of 2 x 10^{21} cm^{-3} though; the mobility value was only 5 cm^2/Vs. To obtain a higher mobility value, the Zn interstitial defects should be increased besides Al doping. The extra defects contributed to extra electrons near the conduction band which increases carrier concentration at room temperature; as a result, higher mobility value will be obtained. It has been already reported by our group [20] that, the electrical properties of AZO films has been improved by coating with a thin Zn layer and annealed in a face-to- face position at higher temperature in inert atmosphere. During annealing, diffusion to the next immediate layer is forced to occur due to the mechanically holding of two films in a face-to-face condition, as the exposure of the top layer to the ambient is restricted. The best Zn layer thickness was obtained at 15 nm [21]. Keeping the Zn coating layer fixed, varied the underlying AZO layer thickness and same post growth annealing treatment studied the best electrical and optical properties. Wang et al. [22] reported that, two films grown on quartz plates are placed in a face-to-face condition during annealing enhance the near band edge emission in ZnO films. This paper reported that, sputtered AZO films of different thickness have been annealed in a face-to-face post-growth annealing technique to study its structural, electrical and optical properties, so as to obtain the best thickness for underlying AZO layer to be used as a TCO in optoelectronic devices.

2. Experimental details

Al doped (1%) zinc oxide target (99.999%, MTI corp.) was used to deposit AZO thin films on clean glass substrates using radio frequency magnetron sputtering system (RMVT, model: RMS T-4065). Deposition parameters and the other details have been reported elsewhere [23, 24]. In brief, the growth parameters are substrate temperature, RF power, and Ar gas flow rate were maintained as 773 K, 150 W, and 15 SCCM, respectively. Three sets of films with thicknesses of about 100 nm, 200 nm, and 300 nm were grown to study its characteristics as TCO. The thickness of the film was confirmed by using profilometer (Dektak) and atomic force microscopy (AFM) technique. DC magnetron sputtering was used to grow a thin Zn metal layer of thickness about 15 nm at 773 K temperature on all the AZO films. For the post-growth treatment, two pieces of same thickness Zn coated AZO films were held in a face-to-face condition, and annealed at 823 K in pure Ar atmosphere for an hour.

UV–VIS-NIR spectrophotometer (Perkin Elmer, Lambda-35) were used to obtain transmittance data of the films in the wavelength range 300–800 nm. AZO films crystalline phase were confirmed by X-ray diffractometer using Cu K_α radiation operated at 30 mA, 35 kV (Seifert XDAL 3000). Energy dispersive spectroscopy (EDS) was employed for the elemental analyses of the films. The morphology of the films was investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-6700). The room temperature mobility, carrier concentration and resistivity, values of the films were measured by using van der Pauw geometry in a Hall measurement system under the application of 1 T magnetic field (Ecopia, HMS-3000).

3. Results and discussion

First, the optical properties of the films were studied. Transmittance characteristics of Zn coated AZO films shown in Fig. 1. Optical transmittance spectra of annealed AZO films 15 nm Zn coated different thicknesses of 100 nm, 200 nm and 300 nm in the wavelength range 325–800 nm. All the films are more than 85% transparent but the transmittance decreases a little with the thickness of the films in the 400–800 nm range as reported earlier [25]. Below 390 nm, all the films have sharp band-edge absorption and transmittance falls of below 4%. The thin metal coating blocks some light, so the transparency decreases in Zn coated films. But after face-to-face annealing improvement in the transparency can be seen as all the films are more than 85% transparent in the visible region. The average transmittance data for few of the films in the range 400-800 nm are given in Table 1. The transmittance data indicate that the annealed AZO films are highly transparent for its potential application in the devices.

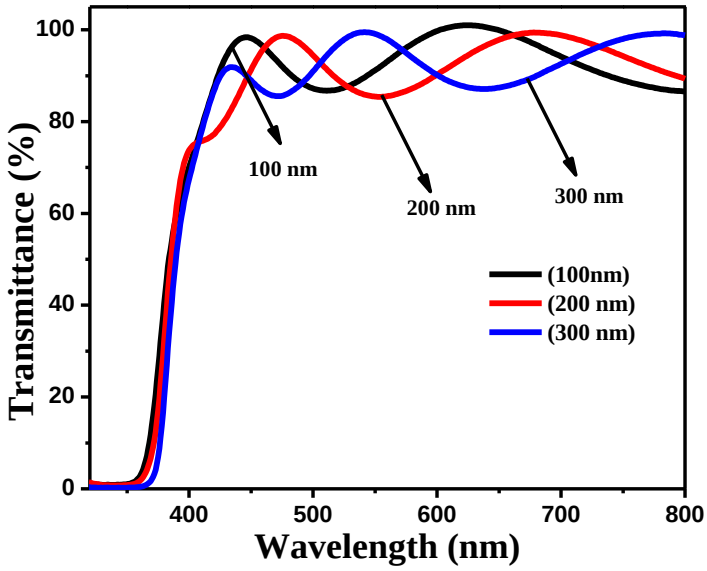


FIG 1. Transmittance of 100 nm, 200 nm and 300 nm underlying AZO layer with 15 nm Zn coating annealed films.

Fig. 2 presents the XRD patterns of all the AZO films which show the presence of only (002) peak at 2θ value of 34.421^{o}, which is in well agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card no JCPDS PDF no 36-1451. This indicates that all the films preferentially grown along [0002] direction. This growth along [0002] direction can be explained in terms of surface free energy consideration as explained by Nistor et al. [26]. In wurtzite ZnO structure, the (002) plane is a polar plane (alternate stacking of O (-) and Zn (+) planes), and therefore the surface free energy of such polar plane is very high. The non-polar planes have a relatively lower surface free energy in contrast to the polar planes. Thus the crystallites preferably grow along [0002] planes to attain minimum surface free energy. Absence of any Zn related peak confirms that Zn coatings are indeed very thin to produce any diffraction pattern. So any island formed due to Zn atoms may be ruled out from this result. Fig. 3 shows the EDS result of 300 nm AZO layer annealed thin film which confirms the presence of Al in the AZO films.

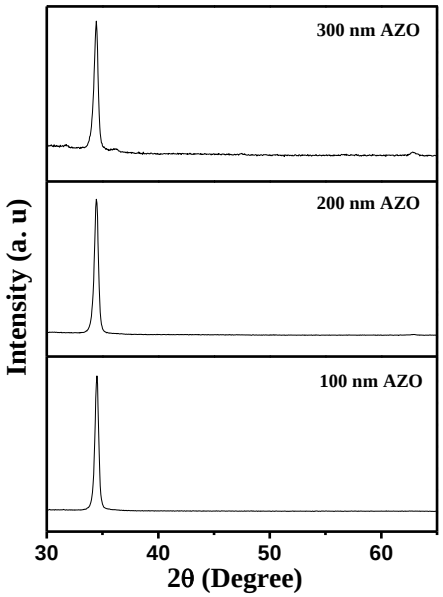
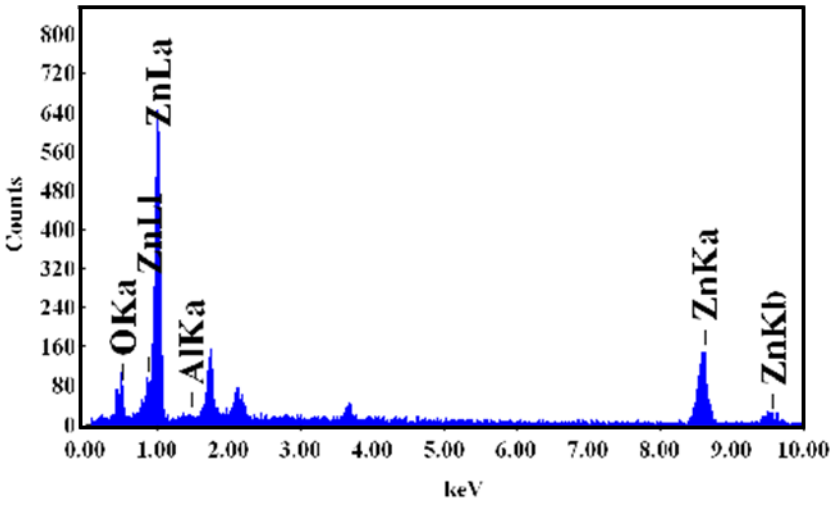


FIG 2. XRD patterns of 15 nm Zn coated 100 nm, 200 nm and 300 nm underlying AZO layered annealed films.



Ele...	Cl...	(keV)	mass%	Error%	At%
O K		0.525	16.37	0.70	44.35
Al K		1.486	0.23	0.71	0.37
Zn K		8.630	83.40	2.01	55.29
Total			100.00		100.00

FIG 3: EDS image of 15 nm Zn coated 300 nm underlying AZO layered annealed film.

The morphology of the Zn coated AZO films are revealed in Fig 4. As evidence from XRD result, the cross-section views of one of the film of underlying 300 nm AZO layer in Fig. 4 (a) show a perfect nanocolumnar growth along the c-axis where the nanocolumns are very closely spaced with a homogeneous packing density. Top view Fig 4 (b) also suggest that after face-to-face annealing top Zn layer diffuses in the underlying AZO layer [27] which increases the free carrier concentration and have continuous and uniform packing density. As a result, the density of the nanocolumns in the sputtered film is high enough which may increase the electrical conductivity or decrease the resistivity value.

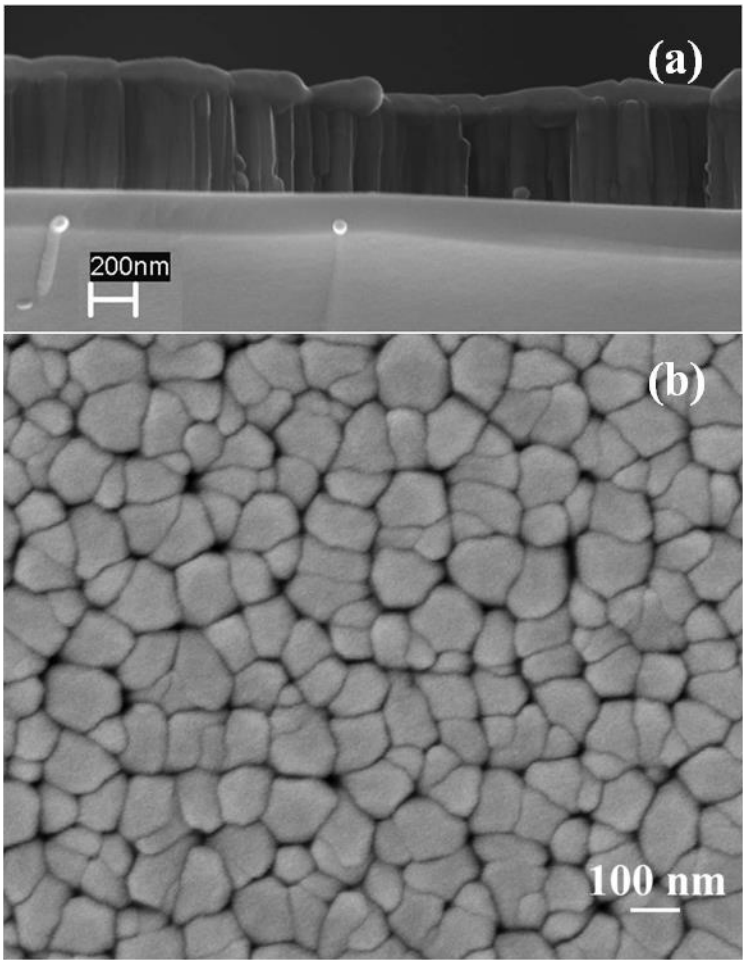


FIG 4. FESEM images of AZO films: (a) Cross-sectional view of the 300 nm underlying AZO layer with 15 nm Zn coated annealed film, (b) Top view of the same film.

The electrical results were also investigated. The results of room temperature Hall measurements are illustrated in the Table 1. The carrier concentration, resistivity, and mobility values are 4.93 $x10^{20}$ cm^{-3}, 3.84 x 10^{-3} **Ω**-cm, and 3.30 cm^2/Vs respectively for uncoated as-grown AZO film of 200 nm thickness. The mobility and carrier concentration values are increased for all the 15 nm Zn coated without annealed different thickness AZO films. As the underlying AZO thickness increases carrier concentration and mobility values increases but resistivity value decreases which is desired for TCO application. After 15 nm Zn coating, in 100 nm AZO film the carrier concentration, resistivity and mobility values are 7.04 $x10^{20}$ cm^{-3}, 9.49 x 10^{-4} **Ω**-cm and 9.35 cm^2/Vs respectively changes to 2.02 $x10^{21}$ cm^{-3}, 1.78 x 10^{-4} **Ω**-cm

and 17.41 cm^2/Vs respectively for 300 nm AZO coated film. It indicates that the resistivity and carrier concentration values have been decreased and increased, respectively, almost by an order of magnitude when the underlying AZO layer thickness increases from 100 nm to 300 nm before annealing. After face-to-face annealing for 100 nm AZO film carrier concentration, resistivity and mobility values are 2.01 $x10^{21}$ cm^{-3}, 2.08 x 10^{-4} Ω-cm and 14.95 cm^2/Vs respectively changes to carrier concentration, resistivity and mobility values 2.28 $x10^{21}$ cm^{-3}, 1.01 x 10^{-4} Ω-cm and 27.12 cm^2/Vs respectively for 300 nm AZO coated film. So the carrier concentration values increases slightly with the improvement in the mobility values and resistivity values decreases by half in 300 nm AZO coated film with respect to 100 nm film. Thus with increase of underlying AZO layer and face-to-face annealing, electrical results show much improvement which is desirable for TCO applications. This improvement may be attributed to the compact nanocolumnar structure and uniform density films as evidenced from FESEM image. The number of free carriers increases due to surface defect in nanocolumns [24] with diffusion of top Zn layer. Compact structure may decrease the resistivity value. Thus the electrical result is supported by morphology and structural data.

Table 1. Carrier concentration, mobility, resistivity, and transmittance values of different AZO films.

Sample	Carrier concentration (cm^{-3})	Resistivity (Ω-cm)	Mobility (cm^2/Vs)	Transmittance (%) in 400-800 nm range
200 nm AZO	4.93×10^{20}	3.84×10^{-3}	3.30	92
100 nm AZO & Zn-coated	7.04×10^{20}	9.49×10^{-4}	9.35	89
200 nm AZO & Zn-coated	1.09×10^{21}	6.26×10^{-4}	9.16	87
300 nm AZO & Zn-coated	2.02×10^{21}	1.78×10^{-4}	17.41	87
100 nm AZO & annealed	2.01×10^{21}	2.08×10^{-4}	14.95	91
200 nm AZO & annealed	2.17×10^{21}	1.19×10^{-4}	24.22	89
300 nm AZO & annealed	2.28×10^{21}	1.01×10^{-4}	27.12	88

4. Conclusion

Face-to-face annealing process in pure Ar ambient has been employed after depositing 15 nm thin Zn metal layer on top AZO films of different thicknesses to investrigate the optical, structural, morphological and electrical results. All the results were analysed keeping in mind its potential application in devices. Underlying AZO film of 300 nm shows the highest carrier concentration and mobility values with lowest resistivity values which are quite comparable to the standard TCO value of resistivity of around 10^{-4} Ω-cm with very high optical transmittance value in visible region. The nanocolumns structure and close proximity with higher surface related defects increase the carrier concentration enormously and compact columnar structure increases conductivity. Finding novel low cost TCO material and methods for fabricating and post-sintering doped metal oxide thin films has become an increasingly interesting area of research as current market demand. This study on coating of metal layer on top of AZO and annealing, would help to investigate and understand, underlying mechanism of different metal layers and annealing techniques to be employed to obtain best properties as TCO.

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