Physica B 495 (2016) 76–81

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Influence of low sputtering pressure on structural, electrical and optical properties of Al-doped zinc oxide thin films

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ARTICLE INFO

Article history:
Received 28 January 2016
Received in revised form
6 May 2016
Accepted 12 May 2016
Available online 13 May 2016

Keywords:
Al-doped zinc oxide
Sputtering pressure
Resistivity
Optical property

ABSTRACT

Aluminum-doped zinc oxide thin films were deposited without intentional heating by radio-frequency magnetron sputtering. The sputtering pressure varied from 0.02 Pa to 0.32 Pa while the deposition power was kept at 240 W for all depositions. The structural properties of as-deposited films were analyzed by X-ray diffraction and scanning electron microscopy, indicating that the deposited films have a strong preferred *c*-axis (002) orientation perpendicular to the substrate regardless of sputtering pressure. The minimum resistivity of $6.4 \times 10^{-4}\ \Omega$ cm is obtained at 0.05 Pa, which is mainly influenced by the hall mobility, rather than carrier concentration. The highest transmittance could be ~80% on average in the visible range under various working pressures, and the largest bandgap achieved is about 3.82 eV. The ultraviolet emission peaks in photoluminescence spectra are centered at about 360 nm. A new mechanism is proposed to explain the dependence of the electrical and optical properties on structural evolution of deposited films.

1. Introduction

Transparent conducting oxide (TCO) films have shown wide applications in microelectronic devices such as gas sensors, solar cells and light emitting diodes due to their high visible transmittance and low electrical resistivity [1–3]. Although indium tin oxide (ITO) is currently used for most of the above devices, the low-cost and In-free aims always encourage many researchers to search for next generation of TCO films. Aluminum-doped zinc oxide (AZO), one of the substitutions for ITO, is especially attractive due to its good electrical property with high optical transparency comparable to ITO [4]. In addition, AZO is an economical, abundant and nontoxic material with higher thermal stability. Many deposition techniques have been used for investigating the relationship between properties of AZO films and the technological parameters including magnetron sputtering [5], electron beam evaporation [6], chemical vapor deposition [7], atomic layer deposition [8], pulsed laser deposition [9], spray pyrolysis [10], sol-gel [11] and so on. Among these growth techniques, radio frequency (RF) magnetron sputtering is considered as a preferred deposition method because of its simplicity, low thermal budget, high deposition rate and its ability to be applied on large areas [12].

One of the main research topics in the development of high quality TCO films is that the minimization of resistivity is achieved by increasing the mobility rather than carrier concentration [13]. After all, high carrier concentration considerably increases the free carrier adsorption in the near-infrared (NIR) range, adversely affecting its application. Recent efforts to improve carrier mobility of sputtered AZO films have been conducted by several researchers including applying different doping concentrations, adjusting the deposition parameters and post-treatment [13–15]. Although the effects of deposition parameters in RF magnetron sputtering upon film properties have been intensively analyzed, little studies have focused on the properties of AZO thin films deposited at low sputtering pressures below 0.3 Pa, which foster good photoelectric properties and high damp heat stability due to the highly compact film structure [14,16]. Here based on the experimental results in this study, it was found that the mobility of AZO films varied almost by a factor of five in the pressure range of 0.02–0.32 Pa. So it is necessary for us to analyze the properties of the deposited AZO layers in this pressure range.

The purpose of this contribution is to investigate the influence of low deposition pressure on the structural and morphological characteristics of AZO thin films deposited at room temperature, further exploring the electrical and optical properties of films, such as mobility, transmission and so on. We used a deposition configuration in which the target was fixed under the substrate and found that the evolution of the film properties depended on working pressure.

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http://dx.doi.org/10.1016/j.physb.2016.05.015
0921-4526/

2. Experimental details

AZO thin films were deposited on the soda-lime glass (SLG) substrate at 13.56 MHz using a SKY JGP-560 RF magnetron sputtering system. A planar 4-inch-diameter ceramic target (GfE, 2 wt% Al_2O_3) with a purity of 99.95% and a density of 5.3 g/cm^3, was loaded on the vertically adjustable cathode with a ~14 cm distance from the substrate stage, which was used for all the sputtering depositions. The substrate of 6 in. were cleaned in an ultrasonic bath for ~30 min with acetone, alcohol and ultrapure water in sequence, and then blown dry with nitrogen before being loaded into the sputtering chamber. A base pressure of the sputtering chamber was obtained below $\sim 5 \times 10^{-4}$ Pa using a turbo-molecular pump, and subsequently high-purity argon gas (Ar, 99.9999%) was introduced into the sputtering system. A pre-sputtering process was employed to clean the target surface, followed by the sputtering performed in a constant power mode at 240 W since moderate power is used for the deposition to gain better electrical properties [17]. The substrate holder was rotated at 14 rpm during sputtering in order to improve the thickness uniformity. The deposition process was performed using an Ar mass flow controller from 8 sccm to 30 sccm corresponding to the working pressure in the range between 0.02 Pa and 0.32 Pa. During the sputtering of layers without intentional heating, the temperature of the substrate depended on RF power and the film thickness, which varied between 271 and 365 nm, depended on the deposition rate correlated with the working pressure.

Structural properties such as grain orientation and crystal structure were investigated for characteristic films using X-ray diffraction (XRD, Rigaku, D/max-2600/PC) with θ–2θ geometry in the range of 10°–80°. The surface morphology of the AZO thin films and energy dispersive X-ray (EDX) analysis was measured by field-emission scanning electron microscopy (FE-SEM, FEI, Nova Nano-SEM 450). The sheet resistance, carrier concentrations and mobility of the AZO films were obtained using a four point probe measurement system (JANDEL, RM3000) and van der Pauw Hall measurement at room temperature, respectively. The film thickness was analyzed using a surface profilometer (Bruker, Dektak-XT). The optical transmittance was measured with an ultraviolet (UV) /visible (Vis)/NIR spectrophotometer (SHIMADZU, UV3600) with an integrating sphere. Photoluminescence (PL, HORIBA JOBIN YVON, LabRam HR800) spectra were collected at room temperature under normal incidence using a 325 nm He-Cd laser as excitation source.

3. Results and discussions

The crystallinity of all the deposited AZO thin films was investigated by XRD studies shown in Fig. 1. As it can be observed, all these patterns have a strong (002) peak and a weak (004) peak showing the polycrystalline and hexagonal wurtzite structure of the deposited AZO layers. It has been reported that the location of the (002) peaks did not shift significantly with the changes of sputtering pressure between 0.2 Pa and 1.1 Pa [16,18], which is similar to the results in this work. To evaluate the preferential crystal orientation of AZO layers a texture coefficient (TC) was calculated according to the equation [19]: $TC_{(hkl)}=[I_{hkl}/I^0_{(hkl)}]/[(1/n)\sum(I_{hkl}/I^0_{(hkl)})]$ where $I_{(hkl)}$ and $I^0_{(hkl)}$ are the diffraction intensities of the (hkl) plane measured in the diffraction profiles for the deposited thin film and the standard ZnO power sample, respectively and n is the number of reflection faces used in the diffraction pattern. A preferred orientation occurs when the texture coefficient is above 1.0. The results of texture coefficient are listed in Table 1 and confirm that all AZO samples have an obvious preferred c-axis (002) orientation perpendicular to the substrate surface. The (002) peak clearly dominates, which could be attributed to the lowest surface free energy of (002) orientation. Meanwhile, this preferential orientation is also favorable for improving the conductivity of AZO thin film. In addition, the grain size of different samples was calculated from the corresponding full width at half maximum (FWHM) of the (002) diffraction peak based on the Scherrer formula and listed in Table 1. According to the obtained results, the grain size is estimated in the range from 26.2 to 36.3 nm when the working pressure increases. The Al concentrations of sputtered layers with different pressures were analyzed by EDX spectroscopy (Fig. S1) and given in Table 1. The measured Al content generally shows a monotonic decrease regardless of the increase of sputtering pressure, which may be due to the multiple collisions decreasing the energy and deposited probability of Al-containing species at higher Ar flow rate. It is notable that no Al_2O_3 phase has been found from the XRD patterns, which imply that Al atoms are substituted in the hexagonal lattice or segregated to the non-crystalline area in grain boundary.

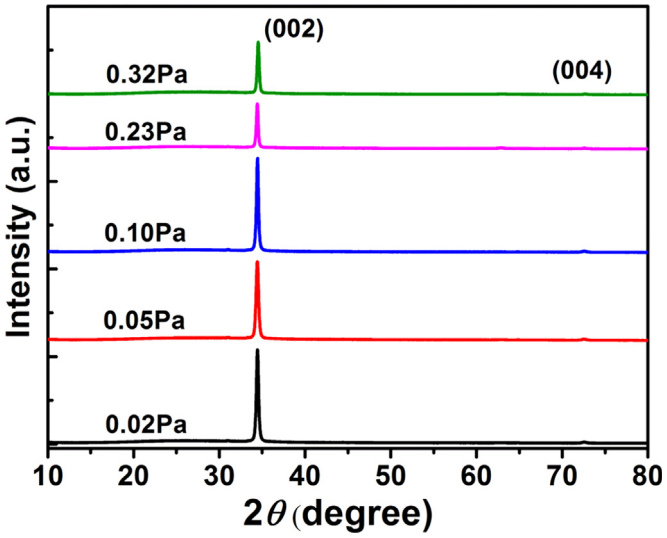

Fig. 1. XRD profiles of AZO films deposited at different working pressures.

Table 1
Grain size and texture coefficient calculated and Al concentration in AZO films measured by EDX spectroscopy.

Pressure (Pa)	Grain size (nm)	Texture coefficient		Al concentration (atomic %)
		(002)	(004)	
0.02	29.6	1.28	0.72	1.47
0.05	26.2	1.23	0.77	1.45
0.10	32.5	1.29	0.71	1.41
0.23	36.3	1.07	0.93	1.13
0.32	33.5	1.18	0.82	1.09

To obtain information about the surface morphology and the bulk structure, SEM measurements were performed on the top view and the cross-section of the AZO films prepared at different sputtering pressures and given in Fig. 2. The AZO layer deposited at 0.02 Pa consists of the closed-packed and hexagonally shaped micro-crystals with the irregularly dark zone, i.e. some defects. When Ar flow rate increases, the grain size decreases slightly and then increases at the higher pressure than 0.05 Pa. The observed evolution of grain size in the top views of AZO films is generally consistent with the variation of theoretical grain size from the FWHM value except the case of 0.32 Pa, which might be attributed to the calculated results neglecting the effect of stress in the deposited films. Furthermore, based on the XRD patterns, c-axis of AZO sample is predominantly oriented parallel to the substrate