Materials Science and Engineering B 136 (2007) 37–40

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Effect of sputtering pressure and annealing temperature on the properties of indium tin oxide thin films

A. Mohammadi Gheidari *, F. Behafarid, G. Kavei, M. Kazemzad

Material & Energy Research Center (MERC), P.O. Box 14155-4777, Tehran, Iran

Received 27 June 2006; received in revised form 13 July 2006; accepted 22 August 2006

Abstract

Indium tin oxide (ITO) thin films were deposited on glass substrates by RF sputtering system at different sputtering pressure (SP) (20–34 mTorr) and room temperature. The sputtering pressure effects on the deposition rate, electro-optical and structural properties of the as-deposited films were systematically investigated. The optimum sputtering pressure of 27 mTorr, giving a good compromise between electrical conductivity and optical transmittance was found to deposit films. The films were heat-treated in vacuum (200–450 °C) and their electro-optical and structural properties investigated with temperature. A criterion factor Q, which is the ratio between the normalized average transmission to normalized resistivity was defined. It has been observed that Q has its maximum value for heat treatment at 400 °C and the X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis proves the films have preferred crystal growth towards (2 2 2) direction and average size of grains are 35–40 nm.

Keywords: Indium tin oxide; Sputtering; Annealing; Electro-optical; Structural

1. Introduction

Indium tin oxide (ITO) thin films as transparent conductive (TCO) layers are widely used in optoelectronic and solar cell technology [1–3,5–16]. They have high electrical conductivity and transmission in visible and near-infrared (IR) spectrum [7,8]. Because of its many advantages such as high deposition rate, sputtering is the preferred technology and the electro-optical and structural characteristics of the films are strongly sputtering parameters dependent. One of these parameters is sputtering pressure (SP), which is adjustable easily in all kind of sputtering systems. Sputtering pressure can be controlled by controlling the flow of sputtering gas, and has effective influences on the structure, electrical resistivity and optical transmission of the films. Usually post heat treatment in vacuum is known to be very effective in improving characteristics of the films [9,10]. In the present work, the effect of sputtering pressure and annealing temperature, on the structural, electrical and optical properties of the ITO films will be discussed.

2. Experiment

ITO thin films were deposited onto cleaned soda lime glass substrates by RF sputtering system at room temperature. The target was a ceramic (In_2O_3; SnO_2: 90/10) with a distance of 3.5 cm from substrate holder. Prior to deposition the chamber was evacuated down to 9×10^{-6} Torr by a rotary and diffusion pump and then the Ar/O_2 (90/10, %) gas mixture was introduced to the chamber as sputtering plasma gas. For all deposition steps the target was pre-sputtered for 15 min in the chosen sputtering condition. A series of samples were prepared at different sputtering pressures ranging from 20 to 34 mTorr in a high sputtering power of 350 W. The deposition time was kept 60 min for all samples. Giving a good compromise between electrical conductivity and optical transmittance, the optimum sputtering pressure value of 27 mTorr was further used to deposit films. In order to understand the post annealing effect on the physical, structural and electro-optical properties of the films, these films were then annealed at temperatures ranging from 200 to 450 °C in vacuum. Structural properties were studied by means of the X-ray diffraction (XRD) and the scanning electron microscopy (SEM) techniques. The optical transmission and sheet resistance of the films were measured by spectrophotometer and four point probe technique, respectively. Some physical properties of the

* Corresponding author. Tel.: +98 26 16204131x4; fax: +98 26 16201888.
E-mail address: a.mohammadi@tfl.ir (A.M. Gheidari).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.08.058

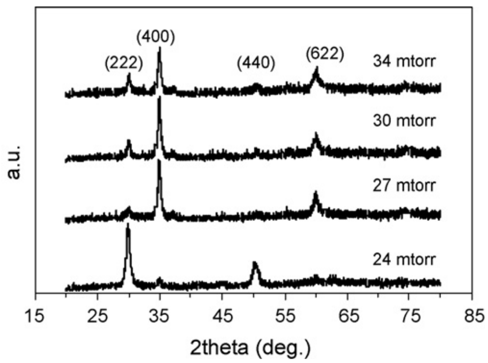

Fig. 1. XRD analysis of ITO films prepared at SP of 24, 27, 30 and 34 mTorr.

Table 1

	Sputtering pressure (mTorr)			
	24	27	30	34
Optical gap, E_g (eV)	3.65	3.69	3.54	3.85
Resistivity, ρ ($\times 10^{-4}\ \Omega$ cm)	102	65	59	147
I(2 2 2)/I(4 0 0)	4.94	0.16	0.50	0.35
Film texture	⟨1 1 1⟩	⟨1 0 0⟩	⟨1 0 0⟩	⟨1 0 0⟩
Grain[a] size$_{(222)}$ (nm)	13.84	12	19.51	16.5
Grain size$_{(400)}$ (nm)	14.65	16.45	14.74	16.1
Lattice constant (nm)	10.319	10.276	10.264	10.268
T_{ave} (400–800 nm)	76.2%	82%	80.05%	84.8%
(2 2 2) Plane distance	2.979	2.974	2.966	2.958
Deposition rate (nm/min)	7.1	7.92	10.5	2.8
Thickness (nm)	425	475	630	168

[a] Grain sizes were derived from the XRD spectra using Scherrer method [16].

films were also derived from the XRD and transmission data. The films heat treatment was carried out in vacuum furnace for 1 hour within the chamber evacuated down to 3×10^{-5} Torr and then cooled in the same condition.

3. Results and discussions

3.1. As-deposited samples

Fig. 1 shows the XRD analysis of the some selected samples prepared at sputtering pressures of 24, 27, 30 and 34 mTorr. It can be seen that the main growth directions are (2 2 2), (4 0 0), (4 4 0) and (6 2 2), which are related to the cubic structure of the In_2O_3 [10]. The ratio between the intensity of (2 2 2) peak to (4 0 0) (I_{222}/I_{400}) for the films deposited at sputtering pressure of 20–24 mTorr is 5 or even more which is much more than the standard value for ITO powder [9]. Therefore the most part of the layer parallel to surface has been textured in ⟨1 1 1⟩ direction, while for films deposited at sputtering pressure of 25–34 mTorr this ratio is much less than standard value, resulting in the ⟨1 0 0⟩ textured films. Many authors have studied the crystal growth orientation and texture of as-deposited films. It is well known that the plasma density changes with sputtering pressure and sputtering power. It was reported that the change in the plasma density during the deposition of ITO films changes the film properties by influencing the thermalization distance [11,12]. When the thermalization distance is larger than target to substrate gap, an energetic impingement of O^- ions with growing surface leads to oxygen deficient films (films prepared at SP of 25–34 mTorr), which tend to orient along (4 0 0) direction, while for low sputtering pressure of 20–24 mTorr, the thermalization distance is smaller than target to substrate gap, therefore the films have more reduced oxygen vacancies and tend to grow in (2 2 2) direction [13–15]. The lattice parameter (calculated from XRD strongest peak) and interplaner distances (d) of the film are summarized in Table 1. It can be seen that these parameters are larger than their standard values. It can be concluded that the as-grown films are under tensile stress [16]. For the films prepared at high sputtering power and room temperature the larger value of lattice parameter can fairly be attributed to the introduction of Sn atom into the crystal lattice. The lattice parameters and plane distances decrease by increasing sputtering pressure from 20 to 34 mTorr. This can be related to higher oxygen vacancies at higher sputtering pressure. Transmission spectra of the films deposited at different sputtering pressure are shown in Fig. 2. The optical absorption coefficient (α) was calculated from these spectra and energy gap (E_g) for films was determined using α^2 versus $h\nu$ plot [16]. The decrease in energy gap for the films deposited at SP of 27–34 mTorr can be attributed to the film's thickness and increasing oxygen vacancy [12,16]. This is well supported by film's resistivity variation (Table 1). The calculated average transmissions (T_{ave}) in the visible region of spectrum and films resistivity are shown in Table 1. For the samples deposited at sputtering pressure ranging from 20 to 27 mTorr, the average transmission increases by sputtering pressure increase, but any

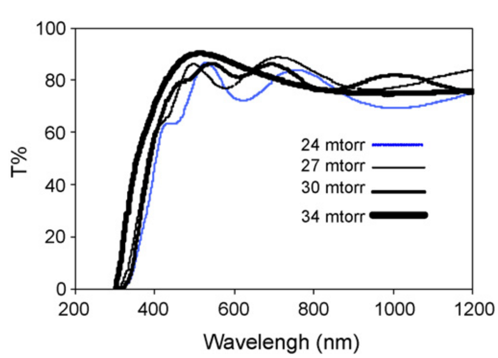

Fig. 2. Transmittance spectra of ITO films prepared at SP of 24, 27, 30 and 34 mTorr.

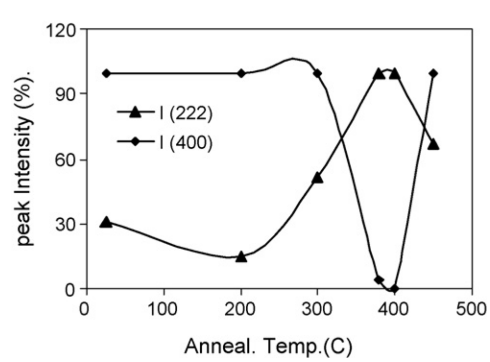

Fig. 3. Variation of the (2 2 2) and (4 0 0) peaks with temperature.

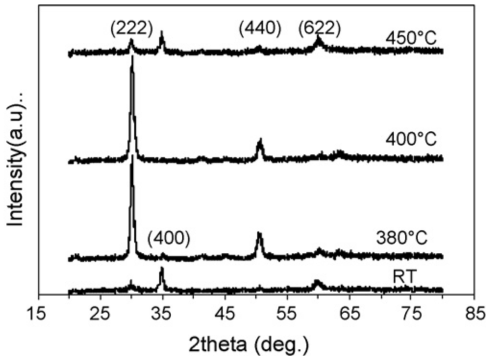

Fig. 4. XRD analysis of the films annealed at 380, 400 and 450 °C.

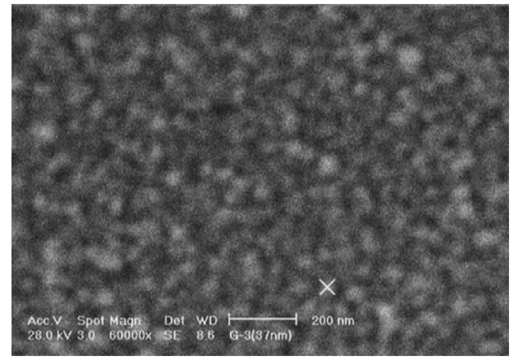

Fig. 5. SEM image of the sample annealed at 400 °C.

increase in sputtering pressure from 27 to 30 mTorr decreases the average transmission by 82% (for 27 mTorr). By increasing the sputtering pressure from 20 to 30 mTorr the film resistivity decreases. A sensible increase in T_{ave} is then observed for films deposited at 30–34 mTorr, which can be related to films reduced thickness and as a consequence less optical scattering path. In this sputtering pressure region, the higher plasma density increases the number of collisions, which causes the reduction of particles mean free path and deposition rate (Table 1).

3.2. Annealed samples

Fig. 3 shows the variation of the (2 2 2) and (4 0 0) peak intensities for the films prepared at sputtering pressure of 27 mTorr with annealing temperature. It can be seen that the intensity of (4 0 0) peak decreases with increasing annealing temperature while the intensity of (2 2 2) peak increases and at 400 °C the (4 0 0) peak disappears completely. Similarly, Holmelund et al. [17] observed a strongly preferred ⟨1 1 1⟩ textured film deposited at substrate temperature of 200 °C by pulsed laser deposition (PLD) technique. The XRD patterns of samples annealed at 380 and 450 °C are shown in Fig. 4. It can be seen at $T = 380$ °C the (4 0 0) peak is going to be disappeared and the annealing temperature of $T = 450$ °C shows that not only the (2 2 2) peak intensity decreases significantly by further annealing temperature, but also the (4 0 0) peak reappears and its intensity becomes higher. Therefore the temperature of 400 °C is most suitable annealing temperature for our samples. The variation of (2 2 2) and (4 0 0) grain sizes (from XRD data) lattice parameter and interplaner distance (d) for (2 2 2) and (4 0 0) crystal planes are presented in Table 2. It can be seen that the (4 0 0) grains are larger than those for (2 2 2) orientated films and have scattered nature with annealing temperature. The size of (2 2 2) grains increases with increasing annealing temperature and takes the maximum value of 26.2 nm at 400 °C. The interplaner distance for (2 2 2) crystal planes decreases systematically with increasing temperature to 400 °C. This means the film favors to release its stress along [1 1 1] direction by annealing and at 400 °C the film has minimum value of stress. Fig. 5 shows the SEM image of the sample annealed at 400 °C. It is clear that the films have a granular structure and the grain sizes and shapes in this image are larger than those calculated from XRD spectra (26.2 nm). In SEM analysis the size of some grains were checked by SEM and seen that they have sizes in the range of 35–40 nm.

For example, the size of one of these grains (denoted by (×) sign in Fig. 5) is about 37 nm (illustrated at bottom of SEM image by white font (G-3 (37 nm)). This difference is in agreement with Kerkach et al. report [16]. The optical transmission spectra for visible and near-IR spectrum of as-deposited and 400 °C annealed films are shown in Fig. 6. The optical band gap and resistivity of the films in various annealing temperatures are also summarized in Table 2. It can be seen that the resistivity of the films takes its lowest value at 400 °C along with transmission enhancement; this can be attributed to larger carrier mobility, film crystallite improvement and grain size enlargement at this temperature [10–16]. A criterion parameter Q, which characterizes the electro-optical properties of the films, was defined as the ratio of normalized average transmission to normalized

Table 2

	Anneal. temp. (°C)						
	RT	200	300	350	380	400	450
Optical gap (eV)	3.69	3.72	3.71	3.71	3.72	3.72	3.76
ρ ($\times 10^{-4}$ Ω cm)	65	23	17	16.2	7	2.21	18
I(2 2 2)/I(4 0 0)	0.16	0.14	0.51	0.65	22.9	Only (2 2 2)	0.66
Film texture	⟨1 0 0⟩	⟨1 0 0⟩	⟨1 0 0⟩	⟨1 0 0⟩	⟨1 1 1⟩	⟨1 1 1⟩	⟨1 0 0⟩
$G_{(222)}$ (nm)	12	10	16.44	15.8	17.1	26.2	15.9
$G_{(400)}$ (nm)	16.45	20.8	17.7	20.2	–	Only (2 2 2)	17
Lattice constant	10.276	10.302	10.264	10.256	10.263	10.232	10.252
d (2 2 2)	2.974	2.970	2.967	2.967	2.963	2.954	2.961
d (4 0 0)	2.569	2.575	2.566	2.564	2.564	–	2.563
T_{ave} (300–1200 nm) (%)	74.1	74.8	75.7	75	78.5	77.1	76.7

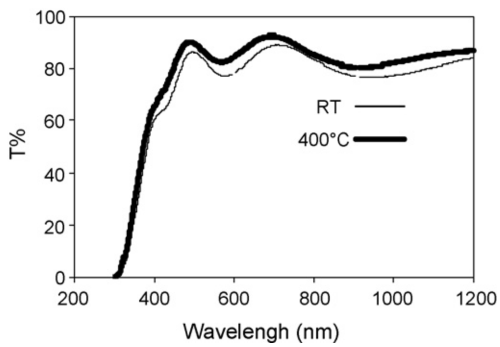

Fig. 6. Transmittance spectra for as-deposited and 400 °C annealed films.

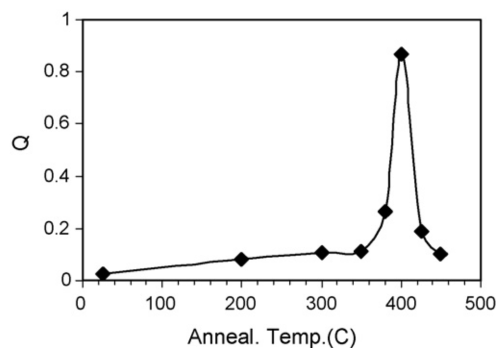

Fig. 7. Variation of Q with annealing temperature.

resistivity. In this study, the average transmission and resistivity of the films have been normalized to 90% and $2 \times 10^{-4}\,\Omega\,\text{cm}$, respectively. The variation of Q with temperature is shown in Fig. 7. It can be seen that the maximum value of Q is obtained at 400 °C. Furthermore, the parameter Q can also be specialized for solar cell application as:

$$Q = \frac{\text{Norm. }(T_{\text{ave}})}{\text{Norm. (resistivity)}}$$

where Norm. (T_{ave}) is the normalized new average transmission of the layer that is defined as:

$$T_{\text{average}} = \frac{\int_0^\infty I_{\text{AirMass 1.5}}(\lambda)T(\lambda)\text{IQE}(\lambda)\,\mathrm{d}\lambda}{\int_0^\infty I_{\text{AirMass 1.5}}(\lambda)\text{IQE}(\lambda)\,\mathrm{d}\lambda}$$

where $I_{\text{AirMass 1.5}}(\lambda)$, $T(\lambda)$ and IQE(λ) are the intensity of light arriving the earth (not the same for all over the world), optical transmission of the ITO layer measured by spectrophotometer, and internal quantum efficiency of solar cell, respectively. As a good approximation, the IQE(λ) can be assumed almost constant for the spectral range of 300–1200 nm and also equal to zero for other ranges of light spectrum. Therefore the later equation can be rewritten as:

$$T_{\text{average}} = \frac{\int_{300}^{1200} I_{\text{AirMass 1.5}}(\lambda)T(\lambda)\,\mathrm{d}\lambda}{\int_{300}^{1200} I_{\text{AirMass 1.5}}(\lambda)\,\mathrm{d}\lambda}$$

4. Conclusions

ITO thin films have been deposited onto glass substrates by RF sputtering at different sputtering pressure (20–34 mTorr). It has been observed that the deposition rate increases by increasing sputtering pressure up to 30 mTorr and decreases above 30 mTorr. The films crystal orientation changed from [1 1 1] to [1 0 0] as the sputtering pressure went over 24 mTorr. The sputtering pressure of 27 mTorr, having good combined electrical conductivity and optical transparency, has been used to deposit the films and these films were annealed at different temperatures in vacuum. The annealing temperature of 400 °C showed better conductivity and transparency, larger grain size and lower stress for the films. The defined parameter, Q, as the films figure of merit showed its the highest value at this annealing temperature too. The parameter Q specialized for solar cell application.

References

[1] T.J. Cotts, M.W. Wanlass, T.A. Gessert, X. Li, J.S. Ward, J. Vac. Sci. Technol. 6 (1991) 1722.
[2] H. Fujikawa, K. Noda, S. Tokito, Y. Taga, Appl. Phys. Lett. 70 (1997) 270.
[3] L. Davis, Thin Solid Films 236 (1993) 1.
[5] R. Scropp, A. Madam, J. Appl. Phys. 66 (1989) 2027.
[6] D. Bonnet, Thin Solid Films 361–362 (2000) 547.
[7] J.L. Vossen, Phys. Thin Films 9 (1977) 1.
[8] I. Hamberg, C.G. Granqvist, J. Appl. Phys. 60 (1986) R123.
[9] C. Guillen, J. Herrero, Thin Solid Films 510 (2006) 260.
[10] Y. Hu, X. Diao, C. Wang, W. Hao, T. Wang, Vacuum 75 (2004) 183.
[11] C.V.R. Vassant Kumar, A. Mansingh, J. Appl. Phys. 65 (1989) 1270.
[12] E. Terzini, G. Nobile, S. Loreti, C. Minarini, T. Polichetti, P. Thilakan, Jpn. J. Appl. Phys. 38 (1999) 3448.
[13] E. Terzini, P. Thilakan, C. Minarini, Mater. Sci. Eng. B 77 (2000) 110.
[14] M.P.R. Panicker, W.F. Essinger, J. Electrochem. Soc. 128 (1981) 1943.
[15] C. Guillen, J. Herrero, Thin Solid Films 431–432 (2003) 403.
[16] L. Kerkach, A. Layadi, E. Dogheche, D. Remiens, J. Phys. D: Appl. Phys. 39 (2006) 184.
[17] E. Holmelund, B. Thestrup, N.B. Larsen, M.M. Nielsen, E. Johnson, S. Tougaard, Appl. Phys. A (Mater. Sci. Process.) 74 (2002) 147.