Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Non-Crystalline Solids 352 (2006) 1466–1470

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Comparative study of ITO layers deposited by DC and RF magnetron sputtering at room temperature

F. Kurdesau [a,b,*], G. Khripunov [c], A.F. da Cunha [b], M. Kaelin [d], A.N. Tiwari [d,e]

[a] *Institute of Electronics of NAS of Belarus, Logoysky Tract 22, Minsk 220090, Belarus*
[b] *Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
[c] *Kharkov State Polytechnic University, UA-310002 Kharkov, Ukraine*
[d] *Thin Film Physics Group, Laboratory for Solid State Physics, ETH Zürich, Technoparkstr. 1, CH-8005 Zürich, Switzerland*
[e] *CREST (Center for Renewable Energy Systems and Technology), Department of Electronic and Electrical Engineering,*
Loughborough University, Leicestershire, LE11 3TU, UK

Abstract

Two different magnetron sputtering techniques with RF and DC plasma discharge modes were tested for room temperature deposition of ITO layers from In_2O_3:SnO_2 targets (10 wt% SnO_2). The influence of sputtering conditions (mainly the sputtering power and oxygen content in the Ar–O_2 gas mixture) on the transparency and conductivity of the formed layers was investigated. The ITO films obtained both by RF and DC magnetron sputtering at room temperature have a high transparency in the visible wavelength range (80–85%) and a low surface resistance (20–25 Ω/sq for ~300 nm thickness) but their optimized deposition conditions and structural properties are significantly different. The DC sputtering can be performed in pure Ar with a lower discharge power density (1.0 W/cm^2) and relatively high deposition rate (~60 nm/min) while the RF sputtering requires Ar–O_2 (3.0 vol.% O_2) gas mixture, higher discharge power density (1.5 W/cm^2) and yields a lower deposition rate (~20 nm/min). The RF sputtered ITO layers show a crystalline structure with strong (222), (400), (440), (622) X-ray diffraction peak intensities while the DC layers are amorphous with surface morphology formed by nano-scale grains.

PACS: 73.61.Jc; 68.55.Jk

Keywords: II–VI Semiconductors; Photovoltaics; Indium tin oxide and other transparent conductors

1. Introduction

Transparent and conductive oxide (TCO) layers are widely used for many microelectronics applications, such as transparent electrical contacts electrodes in displays, touch screens, thin film solar cells, etc. [1–4]. Tin doped indium oxide (or indium tin oxide, ITO) is one of the most investigated and used transparent conductive oxides due to the high electrical conductivity and high transparency in the visible light wavelength range [5]. Among several different methods used for ITO deposition (sputtering, evaporation, chemical vapour deposition, sol–gel method, spray pyrolysis, etc.), DC and RF magnetron sputtering are the most attractive techniques for industrial development because of high deposition rate, good reproducibility and possibility of using commercially available large area sputtering systems [6,7]. Typically, magnetron sputtering processes are performed at high substrate temperatures (⩾200 °C), as these allow the best results in terms of layer transparency and conductivity to be obtained. Nevertheless, several applications, for example solar cells and devices on plastics, require low deposition temperature,

---

[*] Corresponding author. Address: Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. Tel.: +351 234 370818; fax: +351 234 424965.
E-mail address: fiodar@fis.ua.pt (F. Kurdesau).

0022-3093/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2005.11.088

as higher temperatures would damage the underlying electronic device structure or substrate itself. Therefore process optimization for depositions at near room temperature (RT) is required. This difficult task has been investigated by several workers where the RF technique was mostly used [7,8]. The main difficulty of RF deposition at RT is due to insufficient recrystallization of ITO at low temperatures leading to the poor structural and electrical properties [9]. It is also a limiting point, and even more difficult for DC magnetron sputtering at room temperature where the formed ITO layers are usually amorphous with a high electrical resistivity [10].

High temperature ITO sputtering can be with DC as well as RF discharge plasma modes which allowing layers with similar transparency/conductivity properties to be obtained. The influence of the plasma discharge mode for the high temperature sputtering process has already been studied in several works [11,12]. Depending on the plasma mode (DC or RF), an essential difference of optimum sputtering conditions (discharge power density, pressure, oxygen concentration, etc.) was observed, as well as a difference in the crystalline structure and morphology of the formed layers.

In the present work the DC and RF sputtering deposition of ITO layers at room temperature was investigated. The sputtering conditions and their influence on optical (transparency), electrical (surface resistance, charge carrier mobility and density) and structural (surface morphology, crystalline structure) properties were studied for the DC and RF plasma discharge modes.

2. Experimental details

RF sputtering of ITO layers was performed in a commercial inline sputtering system (MRC-603) equipped with a load-lock. A 5×15 in.^{2} ITO target (10 wt% SnO_2) was used for the deposition. The base pressure of the vacuum system was 1.3×10^{-6} mbar. ITO sputtering was done in an Ar–O_2 (3.0 vol.% O_2) gas mixture at pressure of 8×10^{-3} mbar with a RF power density varying from 1.2 W/cm^2 to 3.0 W/cm^2. The sputtering time for the optimized process was about 15 min for 300 nm thick ITO layers deposition.

DC sputtering of 300–500 nm thick ITO layers was performed in a Cryolab sputtering system without load-lock. A 3 in. diameter ITO target (10 wt% SnO_2) was used for the deposition. The base pressure was 4.2×10^{-6} mbar. ITO sputtering was done either in pure Ar or in an Ar–O_2 (1.5 vol.% O_2) gas atmosphere at a working pressure of 10^{-2} mbar with a DC power density varying from 0.8 W/cm^2 up to 1.8 W/cm^2. The deposition time for the optimized process conditions was about 5 min for 300 nm thick layers preparation. Soda-lime glass substrates cleaned in the ultrasonic bath with acetone-isopraponol mixture were used for the deposition.

The spectral dependence of the transmission ($T(\lambda)$) of deposited ITO layers was measured in the visible wavelength range (300–800 nm) by a double-beam spectrophotometer. The surface resistance (R_s) was determined by the four-point probe method. The carrier concentration and mobility were calculated from Hall effect measurements using the Van-der-Paw method. The crystalline structure of deposited ITO thin films was studied by X-ray diffraction measurements (XRD) with $K_{\alpha 1}$ copper emission line ($\lambda = 1.5405$ Å). Layer morphology and cross-section (for thickness measurements) were investigated by scanning electron microscopy (SEM).

3. Results and discussion

A strong dependence of deposited layer properties on the ITO target condition was observed in the case of DC magnetron sputtering in Ar–O_2 environment. As can be seen from the layer transmission curves (R1; R3) presented in Fig. 1(a), sputtering from the ITO target after long time pre-sputtering in pure Ar (this state of target called further non-oxidized) without oxygen dilution results in the deposition of high-resistivity layers with the low transparency (Table 1). The situation is improved by adding of oxygen in a sputtering gas. However the

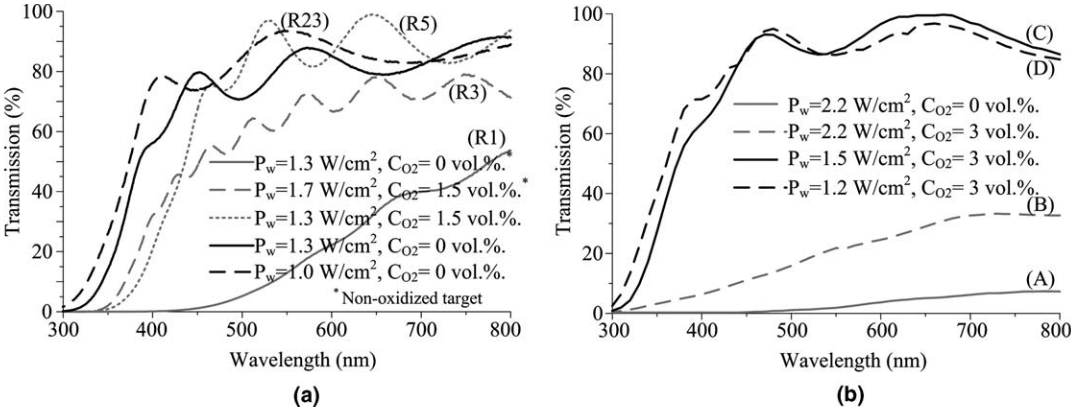

Fig. 1. Transmission spectra of ITO layers deposited by DC (a) and RF (b) magnetron sputtering at room temperature in function of the process conditions (power density and O_2 content).

Table 1
Parameters of ITO layers deposited by DC and RF magnetron sputtering

No.	P/S_{targ} (W/cm^2)	O/Ar (vol.%)	P (μBar)	*t* (min)	R_s (Ω/sq)	*T* (%)
RF samples						
A	2.2	0.0	8.0	15	9.1	3.7
B	2.2	3.0	8.0	15	15.3	23.2
C	1.5	3.0	8.0	15	20.0	88.1
D	1.2	3.0	8.0	15	475.0	88.8
DC samples						
R1	1.0	0.0[a]	10.0	10	350	23.2
R3	1.7	1.5[a]	10.0	10	7.8	65.5
R5	1.3	1.5	10.0	10	1.2×10^6	81.4
R23	1.0	0.0	10.0	5	26.0	84.6

Transmission properties are shown in Fig. 1.

[a] Non-oxidized target.

properties of the deposited ITO layers vary with sputtering time which can be associated with the degree of target oxidation. After the target reaches some constant ‘oxidation state’ when the ITO transparency is stabilized at the level 80–90% (300–800 nm) with a surface resistance in the Mega-Ohm range (see Fig. 1(a) and Table 1). Sputtering from the target in this state (called further oxidized) in pure Ar allows the layer transparency to be kept at the same level (80–85%) with a 25–30 Ω/sq surface resistance achievement (sample R23). Thus, the DC magnetron sputtering of ITO films can be performed in pure Ar if a periodical target oxidation by sputtering in an Ar–O_2 gas mixture is performed.

For RF magnetron sputtering good transparency and conductivity of ITO layers could only be obtained when oxygen containing gas (3.0 vol.% Ar–O_2) was used while the sputtering in pure Ar leads to the significant transparency degradation (Fig. 1(b)). The RF sputtering process also has a three fold lower deposition rate (∼20 nm/min) compared to DC sputtering (∼60 nm/min) for equivalent power densities (similar to what is reported in [11,12] for sputtering at high substrate temperatures).

Structural investigations of the deposited ITO layers indicate a significant difference in the crystalline structure of ITO samples sputtered by DC and RF process. XRD patterns of films prepared by RF magnetron sputtering reveal a cubic bixbyite structure with strong peaks in the crystalline directions ⟨222⟩, ⟨400⟩, ⟨440⟩ and ⟨622⟩ (see Fig. 2(a)). A correlation between transparency/conductivity and degree of orientation in the direction ⟨222⟩ is also observed. Layers with preferred orientation in the direction ⟨222⟩ (intensity ratio between (222) and (400) XRD peaks is about 1.5) obtained by RF sputtering in an Ar–O_2 gas mixture at 1.5 W/cm^2 power density, indicate the best transparency and conductivity. Meanwhile ITO films processed at higher power with and without oxygen dilution (see Fig. 2(a)) have an equal intensity of (222), (440) and (622) XRD peaks with slightly preferable orientation in the plan direction ⟨400⟩ (intensity ratios between (400) and (222) peaks are 1.07 and 1.19, respectively) when their transparency and electrical conductivity are lower (Table 1). This is in good agreement with data reported in [13].

ITO films deposited by DC magnetron sputtering at room temperature show amorphous patterns regardless of the process condition, as seen from the XRD data (Fig. 2(b)). They are characterized with a broad peak between 30° and 35° of 2Θ diffraction angle. The intensity of this peak varies slightly according to the sputtering conditions. The high resistivity samples, which yielded a dark layer when deposited from a non-oxidized target and a transparent layer when deposited in the presence of oxygen (Fig. 1, Table 1), show a higher intensity peak in the 30–35° region, with respect to the baseline level of the XRD signal. High-conductivity, transparent films deposited at optimized conditions show a less intense peak in the 30–35° 2Θ region, which decreases smoothly for smaller angles (see Fig. 2(b)).

The SEM investigation of DC sputtered layers reveals a significant difference in the function of the sputtering conditions (Fig. 3). The surface of these samples seems to be formed by small nanosized grains. The grain size is slightly increases for films sputtered from non-oxidized target and these form a relatively smooth layer surface (Fig. 3(a)). In the case of sputtering from an oxidized target with pure Ar or with an Ar–O_2 mixture, the surface morphology looks more texturized with a sporadic distribution of grain conglomerates (Fig. 3(b) and (c)). ITO layers with a similar morphology were also observed with DC processes at higher temperatures [12]. The cross-section SEM of deposited films show a compact dense structure regardless to process conditions (Fig. 3(d) and (e)) slightly depending on the layers thickness.

The carrier concentration and mobility data for the DC and RF layers shown in Figs. 2 and 3 are presented in Table 2. One can see from this table that the conductivity decrease of DC sputtered films is associated with a strong (several orders of magnitude) decrease of the carrier concentration observed for sputtering at non-optimum process conditions (non-oxidized target, oxygen presence in gas mixture) while the mobility changes are not significant. The electrical properties of RF and DC sputtered layers deposited with optimum process conditions are very similar (see Table 1). The electrical parameters for DC sputtering at room temperature are significantly better than those reported in the literature for similar processes [10]. Comparable carrier density and mobility values were reported for DC sputtering at room temperature with an Ar–H_2O gas mixture where hydrogen incorporation into the layer was also observed [14].

The detailed mechanism of electrical conductivity in amorphous ITO layers is not clear yet and needs further investigation. The comparison between the process conditions allows one to suppose that it is connected to the oxygen concentration in the layers but preliminary AES (Auger electron spectroscopy) investigations of low and high resistivity films did not show a big difference in their

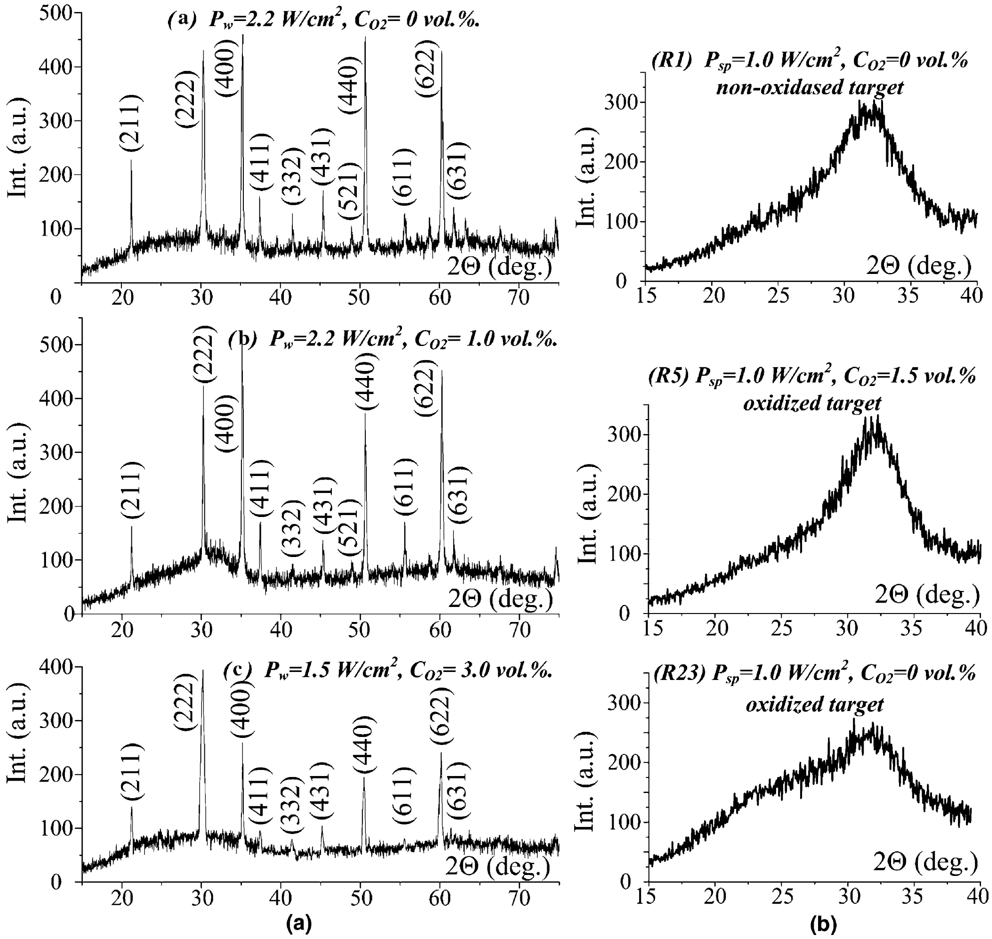

Fig. 2. XRD data for ITO layers deposited by RF (a) and DC (b) magnetron sputtering (the samples numbers are the same as in Table 1).

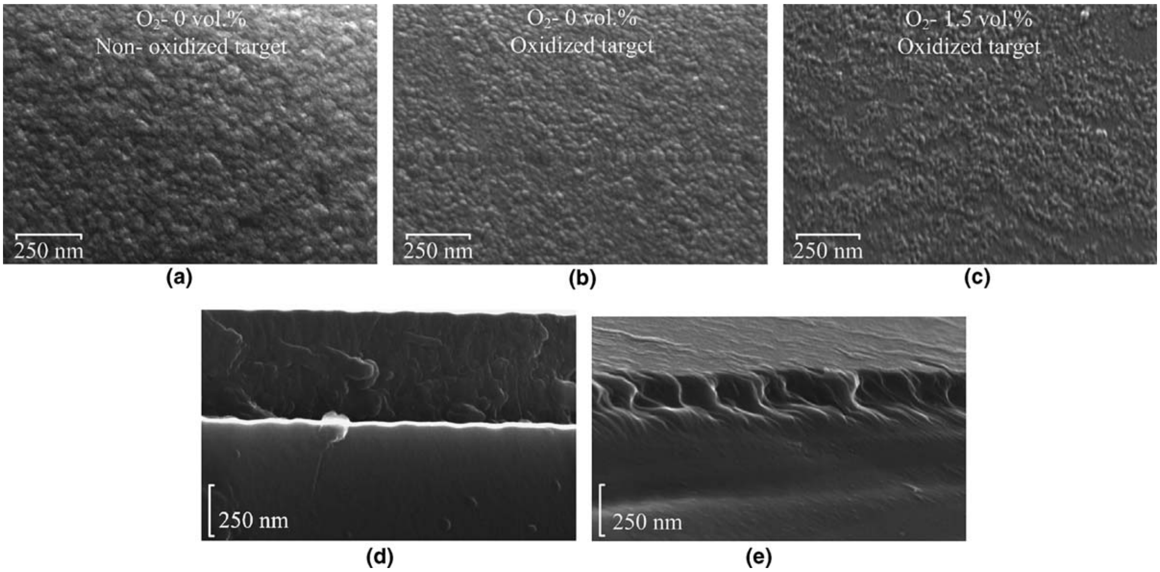

Fig. 3. SEM images of ITO layers obtained by DC magnetron sputtering at different oxygen contents in the sputtering gas: surface morphology (a)–(c) and cross-section pictures (d) and (e) used for the thickness estimation.

(In + Sn)/O atomic ratios. This should be investigated in more detail as well as the ITO layers formation kinetics according to the target/deposited film decomposing (oxygen content decreasing) [16].

Table 2
Hall mobility, carrier density and surface resistance for the ITO layers deposited at room temperature

Samples numbers (see Table 1) or references data	DC				RF	
	R1	R5	R23	[14][a]	C	[15]
Mobility (cm^2/V s)	11	30	19	16	19	29
Carrier concentration (10^{20} cm^{-3})	0.3	0.000067	6.3	7.1	5.9	4.4
Surface resistance (Ω /sq)	350	1200000	26	–	20	–

[a] Sputtering in $Ar–H_2O$.

4. Conclusions

Magnetron sputtering deposition conditions for In_2O_3:SnO_2 targets (10 wt% SnO_2) for yielding high transparency and conductive ITO layers at room temperature were studied. ITO films with a high transparency in the visible wavelength range (80–85%) and a low surface resistance (20–25 Ω/sq for ~300 nm thickness) were obtained with RF and DC magnetron sputtering but using significantly different deposition conditions. The DC sputtering for the optimum transparency/conductivity achievement was performed in pure Ar with a low discharge power density (1.0 W/cm^2) and a high deposition rate (~60 nm/min) while the RF sputtering was done in an $Ar–O_2$ (3.0 vol.% O_2) gas mixture with enhanced power density (1.5 W/cm^2) at lower deposition rates (~20 nm/min). ITO layers deposited by RF sputtering were crystalline with strong (222), (400), (440), (622) peaks in the XRD spectra and preferred orientation in the $\langle 222 \rangle$ direction for low resistance samples while all DC layers were amorphous with a small-grained (10–20 nm) surface morphology structure. The electrical properties (carrier concentration and mobility) for amorphous (DC) and crystalline (RF) ITO films are similar for optimized process condition. A strong decrease in the carrier concentration and electrical conductivity values is observed for DC deposition from non-oxidized targets and with oxygen dilution in the sputtering gas. Thus, amorphous ITO layers with good transparency and conductivity can be obtained by DC magnetron sputtering in pure Ar at room temperature when pre-sputtering in an $Ar–O_2$ gas mixture is performed in order to prevent decreasing of the oxygen concentration in the ITO target.

Acknowledgements

This work was supported by Portuguese Fundação para a Ciência e Tecnologia (FCT grant SFRH/BD/19516/2004), Swiss National Science Foundation (NF-SCOPES Project 7IP-65688), National Academy of Science of Belarus (Project 'Chalcopyrite') and Belarus Republic Foundation of Fundamental Investigations (BRFFI Project P02Y-057).

References

[1] Y. Leterrier, L. Médico, F. Demarco, J.-A.E. Månson, U. Betz, M.F. Escolà, M. Kharrazi Olsson, F. Atamny, Thin Solid Films 460 (2004) 156.
[2] N. Kikuchi, E. Kusano, E. Kishio, A. Kinbara, Vacuum 66 (2002) 365.
[3] T. Nakada, Y. Hirabayashi, T. Tokado, D. Ohmori, T. Mise, Solar Energy 77 (2004) 739.
[4] A.N. Tiwari, G. Khrypunov, F. Kurdzesau, D.L. Batzner, A. Romeo, H. Zogg, Progress in Photovoltaics: Research and Application 12 (2004) 33.
[5] I. Hamberg, C.G. Granqvist, J. Appl. Phys. 60 (1986) R123.
[6] H.-C. Lee, J.-Y. Seo, Y.-W. Choi, D.-W. Lee, Vacuum 72 (2004) 269.
[7] J.-O. Park, J.-H. Lee, J.-J. Kim, S.-H. Cho, Y.K. Cho, Thin Solid Films 474 (2005) 127.
[8] C. Guillén, J. Herrero, Thin Solid Films 480–481 (2005) 129.
[9] M. Quaas, H. Steffen, R. Hippler, H. Wulff, Surf. Sci. 540 (2003) 337.
[10] V. Teixeira, H.N. Cui, L.J. Meng, E. Fortunato, R. Martins, Thin Solid Films 420–421 (2002) 70.
[11] R. Mientus, K. Elmer, Surf. Coat. Technol. 142–144 (2001) 748.
[12] M. Bender, J. Trube, J. Stollenwerk, Thin Solid Films 354 (1999) 100.
[13] R.B.H. Tahar, T. Ban, Y. Ohya, Y. Takahashi, J. Appl. Phys. 83 (1998) 2631.
[14] Yeon Sik Jung, Thin Solid Films 467 (2004) 36.
[15] S. Ray, R. Banerjee, N. Basu, A.K. Batabyal, A.K. Barua, J. Appl. Phys. 54 (1983) 3497.
[16] S. Berg, T. Nyberg, Thin Solid Films 476 (2005) 215.