JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 11, November 2007, p. 3563 - 3566

Crystallization of PLD deposited ITO thin films by thermal treating in various gaseous environments ✐

C. VIESPE*, C. GRIGORIU, M. POPESCU[a], F. SAVA[a], A. LŐRINCZI[a], A. VELEA[a], S. ZAMFIRA[b]
National Institute R&D of Lasers, Plasma and Radiation Physics, P. O. Box MG. 6, 077125 Magurele, Ilfov, Romania
[a]National Institute of Materials Physics, P. O. Box MG. 7, 077125 Magurele, Ilfov, Romania
[b]Transylvania University of Brasov, Romania

ITO films of composition $(In_2O_3)_{0.9} - (SnO_2)_{0.1}$ have been prepared by pulsed laser deposition (PLD).The films were found to be amorphous. The structure and evolution of the films during annealing in air, oxygen atmosphere and reducing atmosphere (CO_2) have been investigated by X-ray diffraction. The films annealed in ambient atmosphere start to crystallize under 250 °C annealing temperature. The films treated in oxygen atmosphere crystallize at higher temperature (~300 °C).

(Received July 1, 2007; accepted November 1, 2007)

Keywords: ITO, Pulsed laser deposition, X-ray diffraction, Amorphous, Crystallization

---

1. Introduction

Indium oxide (In_2O_3) is n-type highly degenerated, wide band gap semiconductor, which exhibits high electrical conductivity and high optical transparence in the visible region [1]. Tin oxide (SnO_2) enters into the category of trqansparent and conducting oxides, which are useful as solar windows in photovoltaic cells. Although the investigation on this oxide started in 1930s the increased performance and applications made the research on tin oxide still actual [2].

Indium tin oxide (ITO) is one of the most widely-used transparent conducting oxides for optoelectronic devices, flat panel diplays and sensors as well, as it combines good electrical conductivity with high transparency in the visible range of the electromagnetic spectrum. ITO thin films have important applications such as anode contacts in organic light-emitting diodes or coating of flexible polymer substrates used in ultra-light mobile display panels where a low processing temperature is important.

Other conductive oxides, including transition metal oxides, or doped tin oxide films have been also investigated [3-6]. Special photosensitive hetero-structures based on In_2O_3/Cd-Zn-S/Cd-Zn-Se have been prepared for solar engineering [7]. Sb_2O_3 glasses exhibit extended infrared transmission [8]. Nevertheless ITO remains the most attractive complex oxide film.

Various types of sputtering techniques were shown to allow for the deposition of good quality ITO films. Nevertheless, in many cases the surface roughness is high. The new technique of laser pulse deposition proves to be very efficient method for the deposition of many types of films with simple or complex compositions [9-15]. Moreover, during deposition the stoichiometry of the target is preserved. The films obtained by PLD show smooth surface [16, 18] without visible macroscopic defects.

ITO films can be also prepared by sol-gel method. High porosity ITO films have also been prepared [19]. Pulsed laser deposition of ITO films on plastic substrates have been performed by Izumi et al. [20].

2. Experimental

Thin ITO films of composition $(In_2O_3)_{0.9} - (SnO_2)_{0.1}$ have been prepared by pulsed laser deposition (PLD) by using an Nd:YAG laser model NL 301 Exspla in the following conditions: second harmonic with wavelength of 355 nm, pulse duration: 5 ns, profile: hat top, frequency: 10 Hz, pressure 3×10^{-2} Torr. The total number of pulses for every film was 52.000. The films were deposited on glass substrates.

The structure of the films has been investigated by X-ray diffraction.

The effect of heat treatment on the structure of ITO thin films was investigated starting from the analysis of their X-ray diffraction patterns. A TUR-M62 diffractometer provided with copper target tube has been used ($\lambda_{K\alpha}$=1.5418 Å).

Annealing has been performed in three atmospheres: a) ambient air, b) oxygen c) argon (reducing atmosphere) for two hours in every case and for several temperatures: 100 °C, 200 °C, 250 °C, 300 °C and 350 °C.

3. Results

The X-ray diffraction patterns show that the as-deposited films are amorphous.

The effect of the annealing atmosphere at various temperatures on the structure of the amorphous films was investigated (Figs. 1 and 2).

✐ presented at 3rd International Conference on Amorphous Nanostructured Chalcogenides, Brasov, 3 – 7 July, 2007

For annealing in ambient air at 200 °C temperature, the separation of a crystalline phase for the film occurs (Fig. 2 a). This phase was identified as In_2O_3 according to the Fiche # 6-0416 of the Powder Diffraction File.

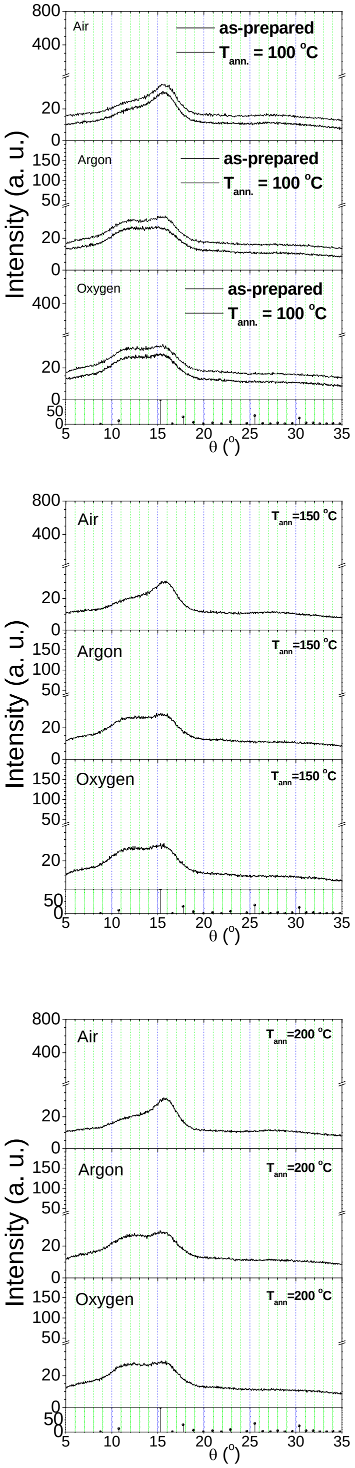

Fig. 1. The effect of the atmosphere of annealing at various temperatures on the structure of the amorphous films (the initial films, heat treated at 100 °C, and 200 °C).

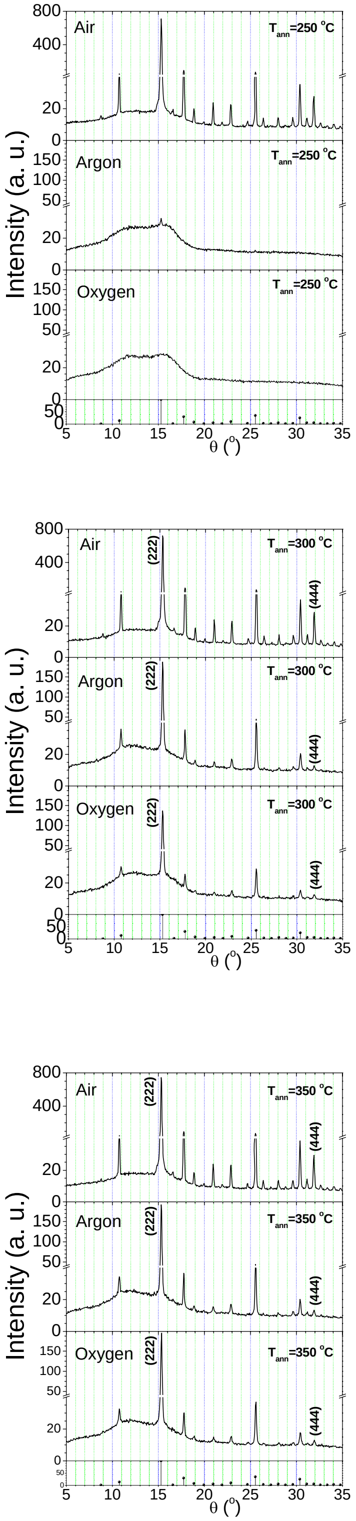

Fig. 2. The effect of the atmosphere of annealing at various temperatures on the structure of the amorphous films (heat treated at 250 °C, 300 °C, and 350 °C)

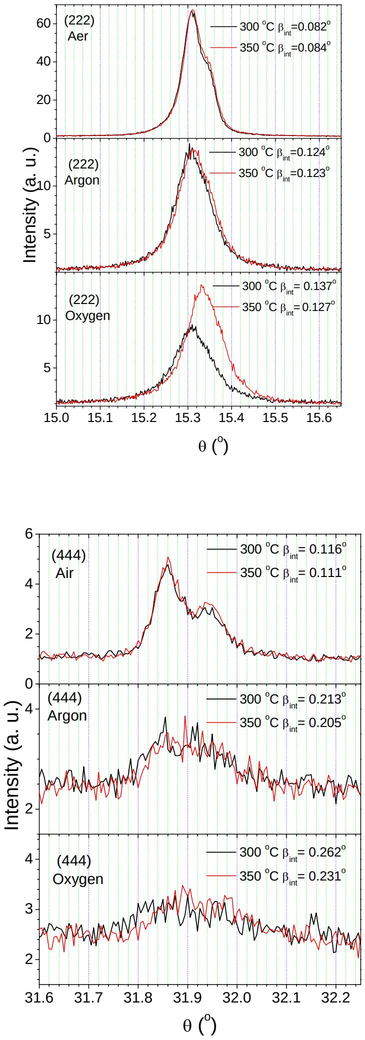

Fig. 3. X-ray diffraction peaks given by (222) and (444) ITO planes, for 350 °C annealing temperature in air, argon and oxygen fluency.

Table 1 shows the average particle size of the crystallized In_2O_3 as a function of the annealing atmosphere. The most advanced crystallization is produced in the case of films annealed in air, while the poorest crystallization is produced in the amorphous films annealed in oxygen. This is probably due to the effect of oxidation-reduction phenomena that take place during annealing. The grain size is estimated using Scherrer's formula:

$$L = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where K is the Scherrer's constant, λ is the wavelength of the radiation used in measurements, θ is the diffraction angle corresponding to the (hkl) diffraction plane and β is the pure diffraction width calculated by extracting the diffractometer breadth function from the measured width and correcting for K_α doublet splitting.

Table 1. The mean size of the In_2O_3 crystallites oriented with the plane (222) parallel to the surface of the film, measured perpendicularly to the substrate.

Atmosphere	T=300 °C		T=350 °C	
	$\Theta_{(222)}$ (°)	$D_{(222)}$ (Å)	$\Theta_{(222)}$ (°)	$D_{(222)}$ (Å)
Air	15.319	>10000	15.321	>10000
Argon	15.312	588	15.319	588
Oxygen	15.313	474	15.338	550

Fiche No. 6-416 (In_2O_3) Bragg angle $\Theta_{(222)}$ =15.302 °

4. Discussion

The X-ray diffraction results show that the crystallites formed in the films are randomly distributed. It is interesting to remark the similar results obtained by Betz et al. [21] for ITO films deposited at ambient temperature of the substrate. For 200 °C substrate temperature the ITO crystallites take a preferential orientation, either (111) for 2.0 % oxygen in the atmosphere, or (100) for 0.8 % oxygen in the atmosphere.

Regarding the structure of the as-deposited ITO films, we remark a high intensity in the diffraction pattern in the position corresponding to the diffraction peak (222) of the crystalline ITO. This feature can be ascribed to the formation of the paracrystalline structure with packing of the disordered (111) planes [22]. This paracrystalline structure is better developed in the films annealed in air (at 100 and 150 °C) than in the films annealed in oxygen atmosphere.

5. Conclusions

The crystallization of the ITO amorphous film is produced at lower annealing temperature if the film is annealed in ambient atmosphere. The average crystallite size in the crystalline phase separated by thermal annealing at 300 °C is highest for the films treated in air. The minimum crystallite size is obtained for the amorphous films treated in oxygen. The results might be of interest for the optimization of the heat treatment for tailoring the desired conduction and transparency properties of specific coatings.

Acknowledgement

The authors are thankful to CeEx-Matnantech program for financing this research in the frame of the C103/2005 project.

References

[1] J. Leong, J. H. Moon, J. H. Hong, J. S. Kang, Y. Fukuda, Y. P. Lee, J. Vacuum Sci. Technology **A14**, 293 (1996).
[2] K. Napo, F. Kadi Allah, J. C. Bernede, N. Barreau, A. Khelil, Thin Solid Films **427**, 386 (2003).
[3] K. Gesheva, A. Cziraki, T. Ivanova, A. Szekeres, J. Optoelectron. Adv. Mater. **7**(1), 557 (2005).
[4] K. A. Gesheva, T. Ivanova, G. Popkirov, F. Hamelmann, J. Optoelectron. Adv. Mater. **7**(1), 169 (2005).
[5] M. Girtan, A. Bouteville, G. G. Rusu, M. Rusu, J. Optoelectron. Adv. Mater. **8**(1), 27 (2006).
[6] D. Mardare, E. Apostol, J. Optoelectron. Adv. Mater. **8**(3), 914 (2006).
[7] H. M. Mamedov, S. I. Amirova, J. Optoelectron. Adv. Mater. **8**(4), 1852 (2006).
[8] N. Tigau, V. Ciupina, G. Prodan, J. Optoelectron. Adv. Mater. **8**(1), 37 (2006).
[9] D. Miu, J. C. Martinez, M. Maier, H. Adrian, J. Optoelectron. Adv. Mater. **8**(1), 24 (2006).
[10] L. Lanotte, G. Ausanio, A. C. Barone, C. Hison, V. Iannotti, S. Amoruso, R. Bruzzese, M. Vitiello, M. D'Incau, P. Scardi, J. Optoelectron. Adv. Mater. **8**(5), 1672 (2006).
[11] J. Ihlemann, J. Optoelectron. Adv. Mater. **7**(3), 1191 (2005).
[12] A. Og. Dikovska, P. A. Atanasov, C. Vasilev, I. G. Dimitrov, T. R. Stoyanchov, J. Optoelectron. Adv. Mater. **7**(3), 1329 (2005).
[13] P. Nemec, J. Jedelsky, M. Frumar, M. Vlcek, J. Optoelectron. Adv. Mater. **7**(5), 2635 (2005).
[14] A. Zakery, J. Optoelectron. Adv. Mater. **7**(3), 1143 (2005).
[15] T. J. Stanimirova, P. A. Atanasov, I. G. Dimitrov, A. O. Dokostovska, J. Optoelectron. Adv. Mater. **7**(3), 1335 (2005).
[16] H. Kim, J. S. Horwitz, G. P. Kushto, Z. H. Kafafi, D. B. Chrisey, Appl. Phys. Lett. **79**, 284 (1999).
[17] V. Craciun, C. Chiritescu, F. Kelly, R. K. Singh, J. Optoelectron. Adv. Mater. **4**(1), 21 (2002).
[18] A. J. Woo, G. Bourne, V. Craciun, D. Craciun, R. K. Singh, J. Optoelectron. Adv. Mater. 8(1), 20 (2006).
[19] T. F. Stoica, M. Gartner, T. Stoica, M. Losurdo, V. S. Teodorescu, M. G. Blanchin, J. Optoelectron. Adv. Mater. **7**(5), 2353 (2005).
[20] H. Izumi, T. Ishihara, H. Yoshioka, M. Motoyama, Thin Solid Films **411**, 32 (2002).
[21] U. Betz, M.K. Olson, J. Marthy, M.F. Escola, F. Atamny, Surface and Coating Technology **200**, 5751 (2006).
[22] M. Popescu, M. Leonovici, J. Optoelectron. Adv. Mater., 8 (5), 1831 (2006).

---

*Corresponding author: cviespe@inflpr.ro