

TRANSPARENT AND CONDUCTING INDIUM TIN OXIDE THIN FILMS GROWN BY PULSED LASER DEPOSITION AT LOW TEMPERATURES

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Thin films of indium tin oxide (ITO) were grown by conventional and ultraviolet-assisted pulsed laser deposition technique (PLD and UVPLD) on Si and Corning glass substrates at substrate temperatures from 40 to 180 °C. X-ray diffraction investigations showed that films deposited at substrate temperatures up to 70 °C were amorphous, whereas those deposited at temperatures of 120 °C and higher showed good crystallinity, with a (222) texture. A splitting of the (222) diffraction peaks indicated that the films contain a two layer structure possessing different lattice parameters. The ratio of these two peaks intensity strongly depended on the nature of the substrates in spite the fact that their thermal expansion coefficients were very similar, indicating that thermal stress is not very important during growth of ITO thin films. X-ray reflectivity studies showed that the films surface morphology was very smooth with root-mean-square roughness values below 0.5 nm and densities values around 7.20 g/cm³, the tabulated value of ITO. Spectroscopic ellipsometry measurements indicated that the films were very transparent, exhibiting extinction coefficient values below 0.1 in the visible region and refractive index values close to those measured for reference ITO films. X-ray photoelectron spectroscopy investigations showed homogeneous bulk chemical composition with fully oxidized In and Sn atoms and a very small Sn enrichment of the composition in the surface region. The carriers mobility, measured in a van der Pauw configuration by the Hall effect, was rather high for films deposited at 40 and 70 °C and then decreased with the increased of the substrate temperature, because the onset of crystallization at such low temperatures produces a rather defective structure.

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1. Introduction

Many high-tech applications of transparent conducting oxides (TCO) using plastic substrates or solar cells with multiple junctions that can not withstand the usual deposition temperatures of several hundreds degrees centigrade, have spurred a renewed interest in low temperature processing techniques for ITO deposition. Although sputtering techniques were shown to allow the deposition of good quality ITO films even at room temperature [1-4], their surface roughness was too high for some of these applications [3-5]. It was reported that much smoother ITO films that also exhibited good electrical and optical properties were obtained by using the pulsed laser deposition (PLD) technique [5-7]. We have shown recently that the surface morphology of ITO thin films can be further improved by using an *in situ* ultraviolet-assisted PLD technique (UVPLD) [8, 9]. In this paper we present results about the effect of UV irradiation on the structural and electrical properties of ITO films deposited at low temperatures.

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2. Experiment

The films were grown in a typical PLD system that uses an excimer laser (KrF, $\lambda = 248$ nm, fluence ~ 2 J/cm², repetition rate 5 Hz) to ablate ITO targets (99.99% purity, 10 % by weight SnO₂). The oxygen pressure during deposition was set at 10 mTorr, the optimum value for our setup [8, 9]. Low pressure Hg lamps that emit 185 nm radiation which photodissociates molecular oxygen and provides more reactive oxygen containing species, were fitted into the deposition system to irradiate the substrate during the laser ablation-growth process. Films were deposited onto (100) Si wafers that had their native oxide removed by a dip in diluted HF and on corning glass substrates. The thickness and optical properties of films deposited on Si were investigated by variable angle spectroscopic ellipsometry (VASE, Woollam Co.) at 70° incidence. The films surface and interfacial morphology, thickness and density were investigated by x-ray reflectivity (XRR) using an X'Pert MRD instrument (Panalytical). The same instrument was used to analyze the crystalline structure of the films in grazing angle incidence (GIXD, $\Omega = 1^\circ$) and θ -2 θ geometry (XRD). XPS investigations were performed with a Perkin Elmer instrument using Mg K α radiation. Data were acquired at 45 and 90° takeoff angles to investigate the depth dependence of the surface region composition. Binding energies were referenced with respect to the position of adventitious C1s at 284.6 eV. The resistivity, carrier density, and Hall mobility of the films were determined by Hall effect measurement.

3. Results

Films deposited up to a substrate temperature of 70 °C were amorphous, while those deposited at 120 °C were crystalline, more so for those grown by UVPLD. The use of GIXD technique, which is more appropriate for thin films, revealed the presence of several crystalline orientations in the grown films as one can see in Fig. 1. It is worth noting that the diffraction peaks corresponding to the (222) planes were, as expected, the most intense ones.

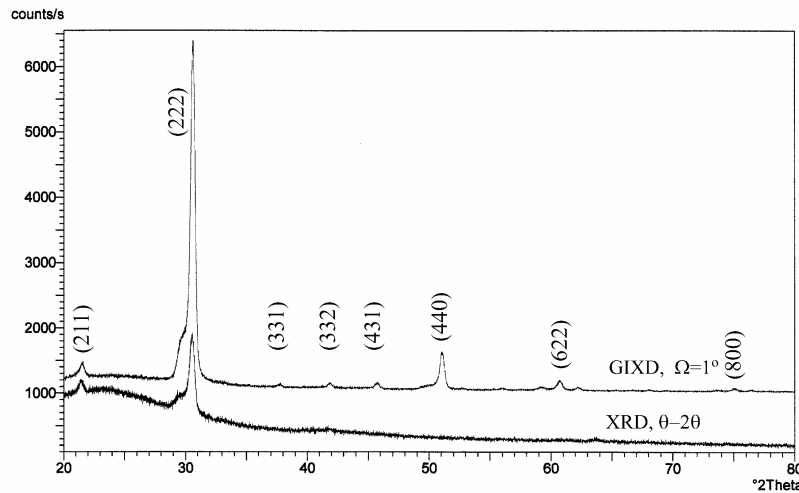


Fig. 1. GIXD and XRD spectra of ITO films deposited at 120 °C on glass by UVPLD.

These (222) peaks, as well as several other more intense peaks such as (440) and (211) exhibited a very visible shoulder towards lower diffraction angle. The relative intensity of this shoulder was noted to decrease with the increase of the substrate temperature or film thickness. For spectra acquired in the usual θ -2 θ geometry these shoulders were more pronounced. This fact indicates that the layers which produced this diffraction peak are located near the interface with the substrate. One can clearly observe from Fig. 2, where the GIXD spectra of ITO films deposited on glass at various temperatures are displayed, that the UVPLD films exhibited lower intensity shoulders than the PLD grown films. There have been several studies that showed that the diffraction peak

splitting phenomenon in the case of ITO thin films is caused by the presence of a two layer structure [10-13]. During the initial growth stage a rather defective structure that is stressed is formed at the interface with the substrate. As growth continues and the films becomes thicker than 100 nm, a new layer with a lower defect density and therefore less stressed is observed. The fact that it was possible to observe this peak splitting for ITO film thicknesses below 100 nm indicates that the transition from the first and defective layer towards the higher crystallinity layer started earlier during the growth than in other deposition techniques. Furthermore, it started even earlier during UVPLD process than in the case of conventional PLD.

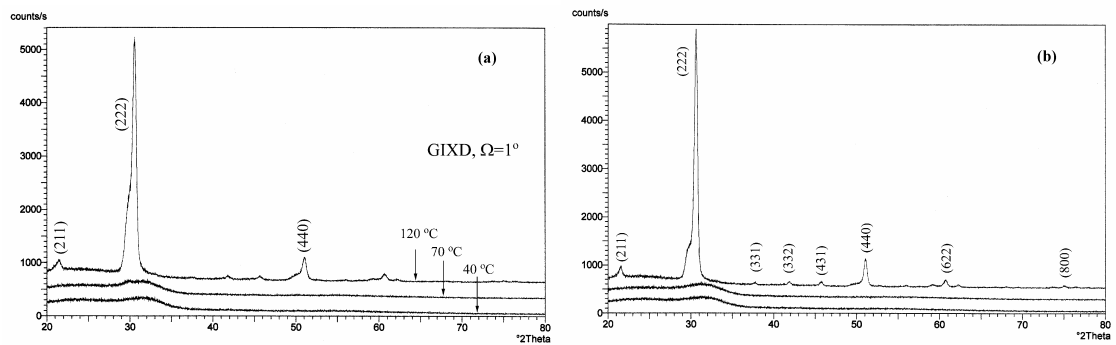


Fig. 2. GIXD ($\Omega=1^\circ$) spectra of ITO films deposited on glass at different temperatures by PLD (a) and UVPLD (b).

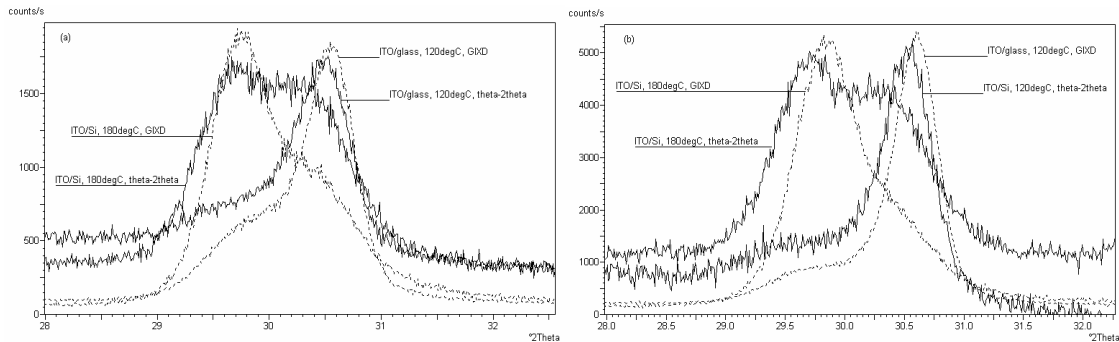


Fig. 3. XRD and GIXD spectra of the (222) peak from ITO films deposited on glass and Si by PLD (a) and UVPLD (b).

It is interesting to note that for films grown on Si substrates this shoulder appeared to the right hand of the (222) peak as one can see in Fig. 3. It was argued [13] that the stress which causes the peak splitting was mainly due to intrinsic defects and chemical inhomogeneities, and that the thermal stress effects should be negligible. The thermal expansion coefficient of Si and Corning glass are 2.7 and $3.7 \times 10^{-6} \text{ K}^{-1}$, respectively [14], while ITO has a significantly larger value [7,15] of $8.5\text{-}10.2 \times 10^{-6} \text{ K}^{-1}$. Therefore, the deposited ITO films experienced similar thermal stress levels on these two substrates and, in agreement with the previous investigations, this should not play an important role in the peak splitting. Another interesting observation from Fig. 3 is that the thickness of the defective layer is larger for the films grown on Si. During laser-ablation deposition the substrate is bombarded by energetic species. The kinetic energy of the incoming species colliding with the substrate is transformed into heat and conducted away through the substrate. Since glass has a much poorer thermal conductivity than Si this might result in a localized heating which will improve crystallinity and thus explain the observed results. However, why the peak position shifts is still puzzling and requires further studies.

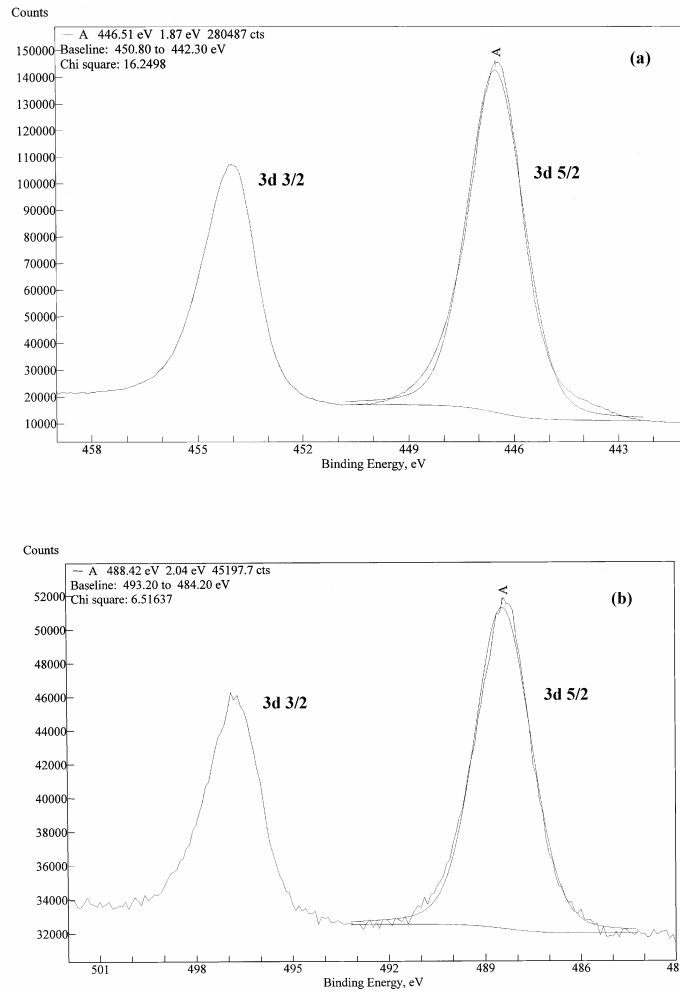


Fig. 4. Typical high resolution XPS spectra of the In 3d (a) and Sn 3d (b) regions acquired from an ITO film deposited on Si at 180 °C by UVPLD. The fitting of the 3d_{5/2} peaks is also shown.

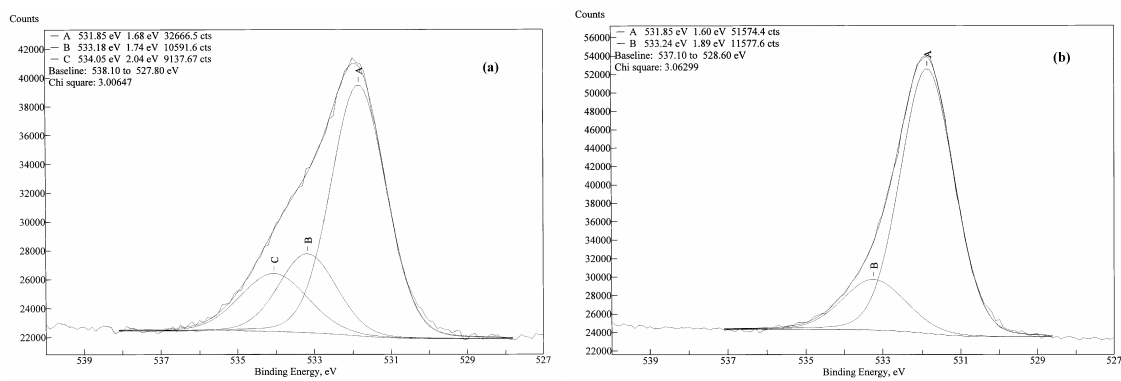


Fig. 5. Typical high resolution XPS spectra of the O 1s region acquired from an ITO film deposited on Si at 180 °C by UVPLD: as-received surface (a) and after 5 min Ar⁺ sputtering. The fitting of the peaks is also shown.

Table 1. XPS calculated stoichiometry of as-received and Ar⁺ sputtered ITO films grown on Si at 180 °C. The takeoff angle used to acquire the XPS spectra is also indicated.

UVPLD	Oxygen-A	Oxygen-B	In	Sn
as-re_45°	0.42	0.14	0.37	0.07
as-re_90°	0.42	0.15	0.37	0.07
5min_45°	0.45	0.10	0.40	0.06
10min_45°	0.47	0.07	0.40	0.06
10min_90°	0.47	0.07	0.40	0.06
PLD				
as-re_45°	0.40	0.15	0.40	0.06
as-re_90°	0.43	0.12	0.39	0.06
5min_45°	0.48	0.05	0.41	0.05
10min_45°	0.46	0.08	0.41	0.05
10min_90°	0.48	0.06	0.41	0.05

XPS survey-type spectra showed only the presence of In, Sn, O, and adventitious C characteristic lines. High resolution spectra of In 3d and Sn 3d peaks, displayed in Fig. 4, showed the presence of symmetric peaks, an indication of single oxidation states, which were identified from the binding energy position as corresponding to In³⁺ and Sn⁴⁺ [16-18]. The oxygen peak acquired from the as-received surface exhibited a more complicated shape that required, as shown in Fig. 5, three peaks for a good fitting. After sputtering for 5 min with Ar⁺ the O1s peak was deconvoluted in only two peaks.

There is an ongoing debate whether the peak denoted B in Figs. 5a and b corresponds to O atoms bonded to Sn or to a substoichiometric In oxide [18]. A very clear assignment of this oxygen peak is complicated by the fact that during laser ablation under high oxygen pressures some oxygen atoms are trapped inside the growing films and appear as a shoulder towards higher binding energies. Also, the surface of oxide films some time contains hydroxide compounds which also exhibit higher BE oxygen than the non-hydrated oxides. However, as one can see in Table 1, which presents the composition of the ITO films at the surface and after 5 and 10 min of Ar⁺ sputtering for two takeoff angles to have a depth-dependence indication, there isn't any correlation between the area of this peak and that of Sn peak. Thus, the only conclusion one can draw from this study is that this peak is not due to oxygen atoms bonded to Sn atoms. Also from Table 1 one can note a small Sn segregation at the surface. Similar Sn segregation phenomena, both at the surface and grain boundaries, were previously reported for ITO films. However, it should be mentioned that the Sn segregation observed in this study for PLD and UVPLD grown films is much smaller than the values usually reported [19].

The thickness of the films was obtained by fitting acquired XRR spectra, as that shown in Fig. 6, with a 3 layer structure (interfacial layer, ITO film and surface contamination layer) using the Wingixa™ software. It is clear from Fig. 6 that the use of this three-layer model allowed a very good fitting of the acquired spectra. The complete results of the modeling are shown in Table 2. First, one can note the high density values, very close to the theoretical ITO density [1,12,20]. Secondly, the surface roughness values (rms) were very low, the films being very smooth.

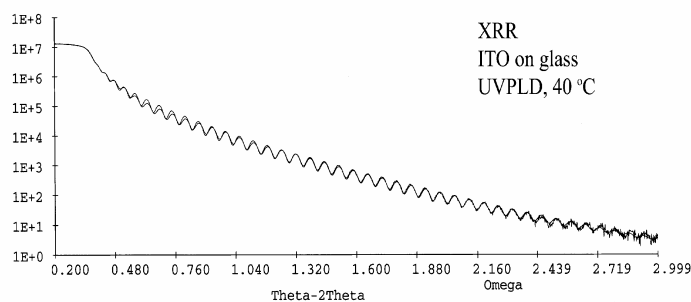


Fig. 6. XRR spectrum of an of ITO film grown at 40 °C by UVPLD and its simulation with the Wingixa™ software.

Table 2. XRR simulation results for ITO films deposited on glass and Si.

	T _s (°C)/substrate	Structure	Thickness (nm)	Density (g/cm ³)	Roughness (nm)
PLD #79	40 glass	Interfacial layer	0.4	3.05	1.3
		ITO layer	59.7	7.02	0.7
		Surface layer	1.0	5.01	0.4
#78	70 glass	Interfacial layer	0.5	3.02	1.3
		ITO layer	63.1	7.04	0.6
		Surface layer	0.9	5.13	0.4
#77	120 glass	Interfacial layer	2.1	4.76	1.0
		ITO layer	58.4	7.11	0.5
		Surface layer	1.4	5.94	0.4
#73	180 Si	Interfacial layer	0.7	5.32	1.0
		ITO layer	50.4	7.20	0.4
		Surface layer	1.0	7.06	0.5
UVPLD #80	40 glass	Interfacial layer	1.6	3.69	0.7
		ITO layer	63.3	7.14	0.6
		Surface layer	1.2	6.01	0.5
#82	70 glass	Interfacial layer	1.4	4.58	1.0
		ITO layer	64.2	7.13	0.5
		Surface layer	1.1	5.99	0.5
#81	120 glass	Interfacial layer	1.6	4.42	1.2
		ITO layer	61.5	7.20	0.6
		Surface layer	0.6	5.62	0.4
#83	180 on Si	Interfacial layer	0.8	3.62	0.8
		ITO layer	64.2	7.20	0.3
		Surface layer	1.0	6.28	0.4

Table 3. Comparison of VASE and XRR simulation results for film thickness.

	T _s (°C)	Structure	Thickness (nm)		Composition
			VASE	XRR	
PLD #76	180	Interfacial layer	1.0	0.7	SiO ₂
		ITO layer	55.8	50.4	ITO
		Surface layer	2.0	1.0	ema(ITO+40% void)
UVPLD #83	180	Interfacial layer	1.0	0.8	SiO ₂
		ITO layer	66.7	64.2	ITO
		Surface layer	1.7	1.0	ema(ITO+37% void)

VASE measurements showed that the refractive index coefficients were quite close to the reference values previously reported for high quality ITO films and that the extinction coefficients of the deposited films were below 0.1 in the visible region, a characteristic of very transparent films. The high transparency in the visible region was also confirmed by spectrophotometry measurements that will be presented elsewhere. Since the thickness values were very important for correct calculations of the electrical resistivity, mobility and carriers density values from the Hall measurements, we compared in Table 3 the results of XRR modeling with those from VASE for films deposited on Si substrates. A similar 3 layer model was used for VASE simulations. The surface contaminant layer was modeled like a mixture between ITO and voids and the refractive index and extinction coefficient values were calculated using the effective medium approximation (ema). As one can note from the values displayed in Table 3, where the thicknesses of two ITO samples deposited on Si are displayed, that the agreement was quite good.

Table 4 shows the results of the electrical measurements. ITO films deposited at 40 °C and 70 °C exhibited rather high mobility values. The onset of crystallization, which resulted in a rather defective structure as already evidenced by XRD investigations, could explain the observed decrease of the mobility values for films deposited at 120 °C. However, this decrease was partially compensated for PLD grown films by an increase in carrier concentrations that still resulted in a rather low resistivity value.

Table 4. Electrical properties of ITO films deposited on glass.

	Substrate temperature (°C)	Thickness XRR (nm)	Resistivity vdP (10^{-4} , Ω .cm)	Carrier concentration ($10^{20} \times \text{cm}^{-3}$)	Mobility Hall ($\text{cm}^2/\text{V.s}$)
PLD #79	40	60	4.10	5.50	27
#78	70	64	3.75	3.46	48
#77	120	63	4.95	9.11	14
UVPLD #80	40	64	3.34	7.29	26
#82	70	65	3.36	5.63	33
#81	120	62	11.0	3.84	13

4. Conclusions

Good quality ITO films have been grown from 40 °C up to 180 °C on glass and Si substrates using an *in situ* ultraviolet-assisted pulsed laser deposition technique. The films exhibited density values around 7.2 g/cm^3 , the theoretical density of ITO and very smooth surfaces. X-ray photoelectron spectroscopy showed uniform bulk composition and minimal Sn segregation at the surface. Spectroscopic ellipsometry measurements showed refractive index and extinction coefficient values close to reference values measured for high quality transparent films. Films deposited at temperatures lower than 70 °C were amorphous and exhibited high carrier mobility and low resistivity values. The onset of crystallization resulted in the formation of a two layer structure containing a defective layer that decreased the carrier mobility.

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