



## Deposition of ITO films on SiO<sub>2</sub> substrates

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### Abstract

Pulsed ablation deposition (PAD) has been used to deposit indium tin oxide (ITO) films on SiO<sub>2</sub> substrates at room temperature using an ArF excimer laser. High optical transmission above 88% occurred in the visible region, the refractive index (2.0 at 540 nm) was observed to be very close to the one of the bulk target; the extinction coefficient was low and almost constant ( $6 \times 10^{-3}$ ) through the visible range. An energy gap of about 3.6 eV has been calculated for the deposited films. The film thickness profilometer (FTP) and simulations using a computer code (refractor) give approximately the same result for the film thickness ( $\approx 370$  nm). The electrical resistivity was as low as  $4 \times 10^{-6}$  Ωm. From the atomic force microscopy (AFM) observations, the films had a rough surface with average roughness  $\approx 20$  nm. Pores were observed with a density of  $\sim 150$  pores/ $\mu\text{m}^2$  and average size of 250 nm. Therefore films exhibited large surface area, which suggest applications in dye solar cells (DSC).

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### 1. Introduction

Indium tin oxide (ITO) films became of great interest in the last years because of their applications in the field of optoelectronic devices. ITO possesses a multitude of properties, including a degenerated

semiconductor (n-type) behaviour with a controllable resistivity ( $\sim 2 \times 10^{-6}$  Ωm) and a high optical gap (3.6 eV) [1–3]. These properties make the ITO to be transparent ( $\sim 80\%$ ) in the visible region and to have a plasma frequency in the NIR region [3–7]. Therefore, it is successfully used to form conductive electrodes in liquid crystal displays (LCDs), plasma display panels (PDPs), flat panel displays (FPDs), thermal control windows (TCWs) and Solar cells [1–5,7–9]. ITO has recently been also applied to automobile windows for thermal control. It has also been used to improve environmental energy efficiency in winter and summer

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as it transmits light in the visible but reflects in the infrared region [10].

Several techniques for depositing ITO films are used, among them chemical vapour deposition (CVD) [11], spray pyrolysis [12], electron beam evaporation [13,14], sputtering [15,16] and pulsed laser ablation deposition [7,17–20]. Among all these deposition methods, the best one appears to be the pulsed ablation deposition (PAD) being a versatile technique capable of producing high quality thin films for consistent optical and electrical properties in a simple and reliable way at room temperature (RT) and higher temperatures [21,22]. Since the stoichiometry and defect density of the films determine the transport of the carriers and conduction mechanism, the performance and properties of the films strongly depend on the method of preparation [3,18,23–25]. The PAD technique works particularly well for complex materials such as  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [26],  $\text{CdMnS}$  [27],  $\text{ZnO}$  [28]: thin films with almost the same stoichiometry of the target can be deposited in one step.

In this work we have deposited HO films to be used as electrodes in dye solar cells (DSC) [29,30]. Optical, electrical and morphological properties of the films have been investigated.

## 2. Experimental procedure

Several samples of ITO films were prepared in one-step pulsed ablation deposition. They were deposited at room temperature on  $\text{SiO}_2$  fused-quartz glass from a sintered ITO disk (5 cm diameter, 90 wt.%  $\text{In}_2\text{O}_3$  and 10 wt.%  $\text{SnO}_2$ ). Before clamping onto its holders in the deposition chamber, the substrates were cleaned with acetone and alcohol in an ultrasonic bath for 10 min, then rinsed in deionised water. The holders were also cleaned with alcohol in an ultrasonic bath for 10 min. The deposition took place in a stainless-steel chamber evacuated down to a base pressure of  $5 \times 10^{-5}$  Pa. The target and substrate were placed parallel at a distance of about 5.5 cm. Before starting die deposition, the target surface was cleaned with 1500 laser pulses. The ITO films were deposited using an ArF ( $\lambda = 193$  nm) excimer laser (Lambda Physik, LPX 305 i), operated with an energy of about 150 mJ/pulse, a repetition rate of 10 Hz and a pulse length of  $\tau = 30$  ns (FWHM). The laser beam was focused onto

the target to a spot area of  $1.3 \text{ mm}^2$ , using a spherical lens with focal length of 35 cm at an incident angle of  $45^\circ$  through a quartz glass window, thus producing a laser fluence at the target of  $4 \text{ J cm}^{-2}$ . The lens was placed 30 cm in front of the target. The target was rotated and spanned to avoid drilling and defect creation such as droplets and craters on the surface layer of the growing film. During deposition, pure oxygen gas was introduced into the chamber, by adjusting the oxygen inlet to maintain an oxygen pressure of 1 Pa. These deposition conditions provided growth rates of about 0.018 nm/s. The thickness of the ITO films was fixed by setting a proper number of laser pulses. After the deposition, the transmittance of the films was measured with a double beam spectrophotometer Perkin-Elmer Lambda 900 in the UV–NIR region. The thickness was measured using a Sentech FTP 500 optical profilometer. A homemade computer program named ‘Refractor’ [31] was used to confirm the measured thickness value, and calculate die optical constant i.e. refractive index ( $n$ ) and extinction coefficient ( $k$ ). The electrical resistivity was measured at RT using a Jandel four-point resistive probe. An NT-MDT AFM was used to analyse the surface morphology of the obtained films at a resolution of 5 nm.

## 3. Optical and electrical properties

The transmission spectra were measured with a double beam spectrophotometer Perkin-Elmer Lambda 900 in the UV–NIR region (Fig. 1). The optical transmittance of a typical ITO film grown an oxygen pressure of 1 Pa is displayed in Fig. 1. A high optical transmission, above 88%, was found in the visible region. The transmittance of the  $\text{SiO}_2$  glass substrate is also shown. The optical constant refractive index, extinction coefficient and thickness of the film were calculated using die refractor program, where the measured optical transmission spectra data are the main input. The model is suitable for dielectric films deposited onto weakly absorbing substrates with known refractive index. The refractive index shown in Fig. 3 is 2.0 throughout the visible region and corresponds well to that of the bulk material. Thus the stoichiometry is preserved while the extinction coefficient (Fig. 3) remains low and almost constant  $6 \times 10^{-3}$ . The simulated transmittance curve is shown

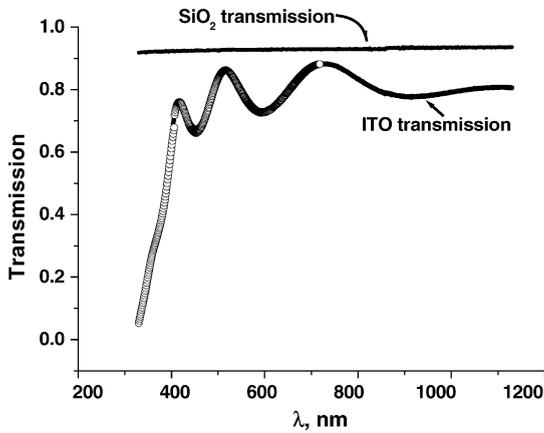


Fig. 1. Measured (black line) and calculated (circle line) transmittance spectra. The fit between the two spectra is regular. The top spectrum represents transmittance of die substrate SiO<sub>2</sub>.

in Fig. 1. As seen, the experimental transmission spectrum and the calculated transmission curve are in good agreement. The film thickness profilometer (FTP) at a resolution of about 1 nm was used to investigate the surface profile of the ITO films (Fig. 2). The thickness was uniform over an area of 1 cm<sup>2</sup> with an average value of 375 ± 22 nm, close to the result obtained from the home program which gave 370 ± 25 nm. From the solid-state band theory, the absorption coefficient for the direct allowed transition can be described as a function of incident photon energy

$$(\alpha h\nu)^2 = (h\nu - E_g) \quad (1)$$

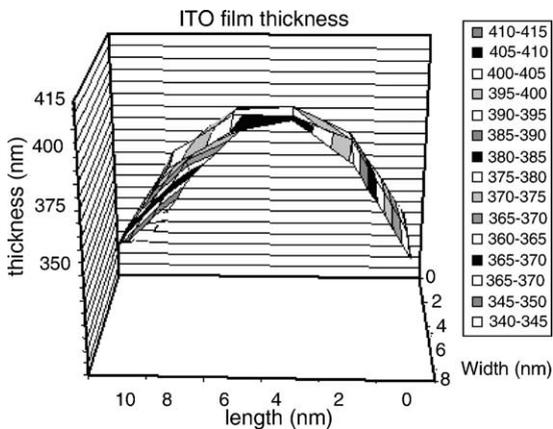


Fig. 2. Thickness profile of ITO films showing the thickness uniformity.

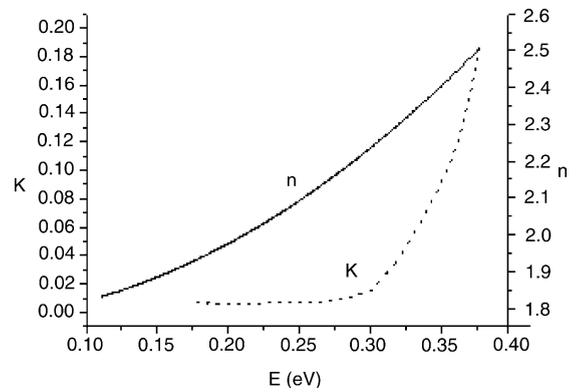


Fig. 3. Evaluated refractive index and extinction coefficient of ITO films. The values are consistent with bulk.

where  $a$  the absorption coefficient and  $E_g$  the band gap energy. By using Eq. (1),  $a$  was calculated as a function of photon energy and plotted in Fig. 4. The linear extrapolation in the transition region using Tauc's plot [32] on the photon energy-axis gives the value of the direct band gap of 3.6 eV which is in good agreement with values quoted in the literature for ITO films [1–3]. The electrical resistivity measurements were carried out by a four point resistive probe (Jandel). Using the thickness given by the FTP and computer program, the resistivity was evaluated by using the Van Der Pauw relation [33].

$$\rho = \frac{\pi d}{\ln 2} R \quad (2)$$

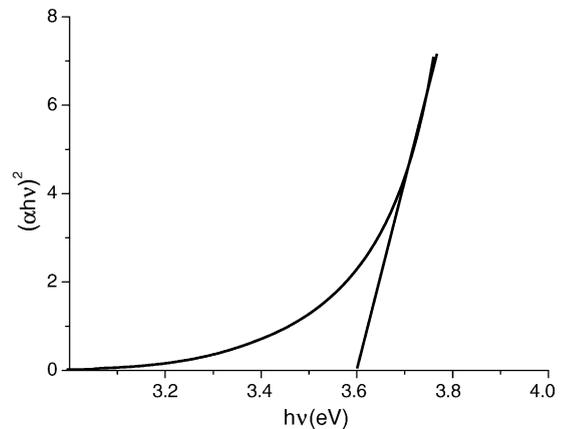


Fig. 4. The  $(\alpha h\nu)^2$  vs.  $(h\nu)$  spectrum of ITO films, the extrapolation of the straight line of the curve gives the value of the gap 3.6 eV (film thickness 370 nm).

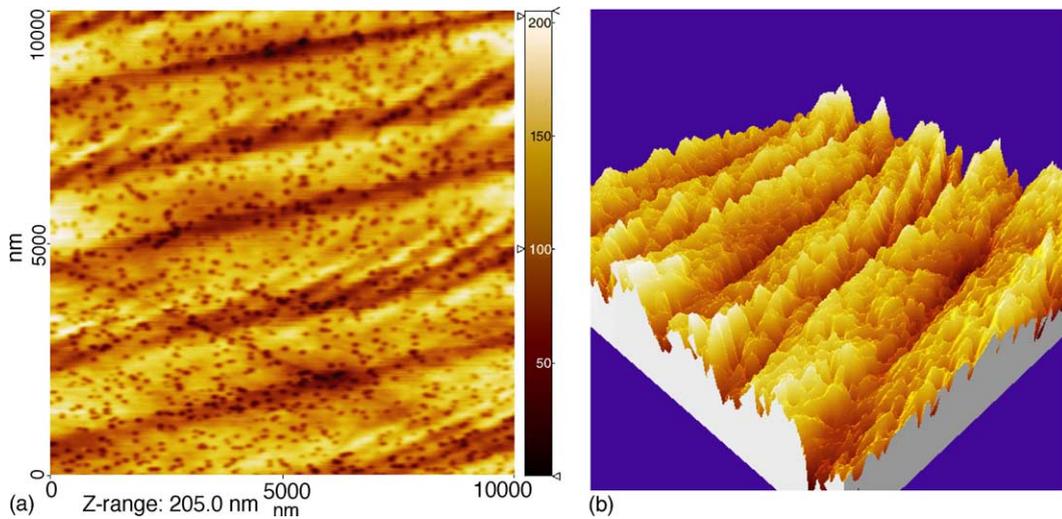


Fig. 5. (a) 2D in top view AFM image of ITO films. (b) Typical 3D AFM image of an ITO film.

where  $d$  is the thickness and  $R$  the resistance of the film. The resistivity of the film deposited at room temperature found was about  $4 \times 10^{-6} \Omega\text{m}$  in agreement to values reported in the literature for ITO films deposited at higher temperatures ( $200^\circ$ ) [1,3–5].

#### 4. Structural properties

The morphology of the laser deposited films was investigated by AFM. Typical images of an ITO film surface are shown in Fig. 5a. The surface shows a rough surface with trenches, better seen Fig. 5b 3-D plot. The root mean square (RMS) roughness of the films is  $R_a = 26 \text{ nm}$ . Holes with an average size of  $250 \text{ nm}$  are also present. The density of the holes was about  $154 \text{ holes}/\mu\text{m}^2$ . Therefore the films exhibit a large surface area, which is required for applications in dye solar cells (DSC). No crystallites or grains were observed, as well as any grain boundaries, which may induce a detrimental high resistivity.

#### 5. Conclusions

Pulsed ablation deposition has produced highly transparent and conducting ITO films at RT. AFM studies revealed trenches in the surface of the ITO films with a mean roughness of about  $26 \text{ nm}$  and high

density of large pores ( $250 \text{ nm}$ ). This is required in DSC, where a high surface area is important. An optical transmission higher than  $88\%$  has been measured in the visible region. The optical constants have been determined, as well as the film thickness using a home developed computer code. The numerically simulated results in good agreement with the experimental ones. The specific resistivity of  $4 \times 10^{-6} \Omega\text{m}$  was obtained without annealing or post treatments.

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#### References

- [1] A. Ambrosini, A. Duarte, K.R. Poepelmeier, M. Lane, C.R. Kaimewurf, T.O. Mason, J. Solid State Chem. 153 (2000) 41.
- [2] I. Hamberg, C.G. Granqvist, J. Appl. Phys. 60 (1986) 123.
- [3] S.H. Brewer, S. Franzen, Chem. Phys. 300 (2004) 285.
- [4] I. Hamberg, A. Hjortsberg, C. Gninqvist, Appl. Phys. Lett. 40 (1982) 362.
- [5] I. Hamberg, C.G. Granqvist, K.F. Berggren, B.E. Semehus, L. Engstrom, Phys. Rev. B 30 (1984) 3240.

- [6] S.H. Brewer, S. Franzen, *J. Phys. Chem. B* 106 (2002) 12986.
- [7] M. Martino, A. Luches, M. Fernandez, P. Anobile, V. Petniz-zelii, *J. Phys. D: Appl. Phys.* 34 (2001) 2606.
- [8] S. Ishibashi, Y. Higuchio, Y. Ota, K. Nakamura, *J. Vac. Sci. Technol. A* 8 (1990) 1403.
- [9] A. Hjortsberg, L. Hamberg, C. Granqvist, *Thin Solid Films* 90 (1982) 323.
- [10] R. Delong, *Coat. Mater. News* 10 (2000) 3.
- [11] K. Maki, N. Komiyu, A. Suzuki, *Thin Solid Films* 445 (2003) 224.
- [12] E. Benamar, M. Rami, C. Messaoudi, D. Sayan, A. Ennaoui, *Solar Energy Mater. Solar Cells* 56 (1999) 125.
- [13] J. George, C.S. Mourn, *Surf. Coat. Technol.* 132 (2000) 45.
- [14] M. Yamaguchi, A. Ide-Ekessabi, H. Nomura, N. Yasui, *Thin Solid Films* 447–448 (2004) 115.
- [15] T.C. Gorjanc, D. Lemig, C. Py, D. Roth, *Thin Solid Films* 413 (2002) 181.
- [16] Y. Han, D. Kim, J.S. Cho, S.K. Koh, Y.S. Song, *Solar Energy Mater. Solar Cells* 65 (2001) 211.
- [17] A.P. Caricato, M. De Sario, M. Fernandez, G. Leggieri, A. Luches, M. Martino, F. Pnidenzano, *Appl. Surf. Sci.* 197–198 (2002) 458.
- [18] J.B. Choi, J.H. Kim, K. Ah-Jeon, S.Y. Lee, *Mater. Sci. Eng. B* 102 (2003) 376.
- [19] F. Hanus, A. Jadin, L.D. Laude, *Appl. Surf. Sci.* 96–98 (1996) 807.
- [20] J.P. Zheng, H.S. Kwok, *Thin Solid Films* 232 (1993) 99.
- [21] H. Izumi, T. Ishihara, R. Yoshioka, M. Motoyama, *Thin Solid Films* 411 (2002) 32.
- [22] B. Thestrup, J. Schou, A. Nordskov, N.B. Larsen, *Appl. Surf. Sci.* 142 (1999) 248.
- [23] H.S. Kwoka, X.W. Suna, D.H. Kimb, *Thin Solid Films* 335 (1998) 299.
- [24] F.O. Adurodija, H. Izumi, T. Ishihara, H. Yoshioka, K. Yamada, H. Matsui, M. Motoyama, *Thin Solid Films* 350 (1999) 79.
- [25] R. Teghil, V. Marotta, A.G. Guidoni, T.M. Di-Paima, C. Flamini, *Appl. Surf. Sci.* 138–139 (1999) 522.
- [26] R.K. Singh, D. Kumar, *Mater. Sci. Eng.* 22 (1998) 114.
- [27] D.S. Chuu, Y.C. Chang, C.Y. Hsieh, *Thin Solid Films* 304 (1997) 29.
- [28] O. Masayuki, H. Kouji, H. Mitsugu, *Appl. Surf. Sci.* 154–155 (2000) 425.
- [29] S. Toshiyuki, S. Masakazu, S. Yutaka, M. Jun-ichi, *Thermo-chim. Acta* 352–353 (2000) 88.
- [30] K. Takuya, E. Tetsaiya, O. Kenichi, M. Hiroshi, G. Kenji, T. Nobuo, *J. Photochem. Photobiol. A: Chem.* 164 (2004) 200.
- [31] A.P. Caricato, A. Fazaa, G. Leggieri, *Appl. Surf. Sci.* (2004).
- [32] G. Tamizhmani, M. Cocivera, R.T. Oakley, C. Fischer, M. Fujimoto, *J. Phys. D: Appl. Phys.* 24 (1991) 1015.
- [33] S. Yicai, S. Junsheng, M. Qinghao, *Semicon. Sci. Technol.* 11 (1996) 806.