

# Optical and transport properties of Ti-doped $\text{In}_2\text{O}_3$ thin films prepared by electron beam physical vapour deposition

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Ti-doped  $\text{In}_2\text{O}_3$  (ITiO) thin films have been prepared by electron beam physical vapour deposition (EB-PVD). Their optical and electrical properties are studied for the obtained compositions. After oxygen annealing all samples show excellent optical transparency; additionally, maximum values

for conductivity are obtained for samples with titanium contents near 6 at.%, with typical resistivity values of  $4 \times 10^{-5} \Omega \text{ cm}$ . Finally, the band-gap energy evolution is studied for the set of samples.

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**1 Introduction** Transparent conducting oxides (TCO) are very interesting materials for a large number of applications such as panel displays, electroluminescent devices, photovoltaic cells or light-emitting diodes [1]. For these conductor materials, attention should be paid to both transparency and electrical parameters, for that reason, tin doped indium oxide (ITO) has received much attention due to its high transparency and high electrical conductivity. Even if ITO is the most commonly used TCO, research on related materials is of fundamental importance in order to prepare transparent oxides for instance to improve anode contact for organic light-emitting diodes or windows layers for photovoltaic devices. In that sense, based on cation doping of indium oxide, several systems as Zn-doped  $\text{In}_2\text{O}_3$  [2], Mo-doped  $\text{In}_2\text{O}_3$  [3] or Ti-doped  $\text{In}_2\text{O}_3$  [4], or even In doped CdO [5] have been investigated to optimize the optical and electrical properties for the desired application.

The transparency and electrical properties of the Ti-doped  $\text{In}_2\text{O}_3$  system have been reported for films prepared by sputtering [4], by pulsed laser deposition [6] or by magnetic null discharge sputter source [7], resulting in an excellent transparent conductive oxide with good electrical conductivity and high mobility work function tenability properties.

In this work, we report on the preparation process of Ti-doped  $\text{In}_2\text{O}_3$  thin films by electron beam physical vapour deposition (EB-PVD), on the precise atomic compositional

content film and on their optical and electrical properties to account for the transparency and resistivity ( $\rho$ ) characterization.

**2 Experimental**  $\text{In}_2\text{O}_3$ :Ti (ITiO) films have been deposited by using a 6 kW electron beam source EVM-6 from Ferrotec GmbH., operated with a GENIUS evaporation controller with a CARRERA high voltage power supply. The source was located in a standard PLS-500 Pfeiffer chamber equipped with a secondary load-lock chamber. The vacuum system provides a residual pressure of  $1 \times 10^{-7}$  mbar and the typical pressure during deposition was about under  $1 \times 10^{-5}$  mbar. Low density ceramics pellets were used as EB-PVD starting material by mixing  $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$  with different titanium contents. The starting material was prepared by uniaxial pressing (near 10 Pa) at room temperature and sintering in a furnace at 1200 °C for 2 h a blend of the two oxides powders (from Aldrich) without any additive. Main parameters for EB-PVD preparation have been 6 kV for the electron-beam acceleration voltage and 20 mA for the electron-beam current intensity, which allow typical deposition rates of  $\sim 100$  nm/min for  $\text{In}_2\text{O}_3$  film deposition and 1 nm/min for  $\text{TiO}_2$ . For this study, films with thickness in the 20–400 nm range were deposited on non-intentionally heated Si(100) as well as on fused quartz substrates.

After film evaporation, as-prepared samples have been annealed for 2 h at 500 °C in a vacuum furnace. For that process, sample chamber is evacuated to a residual vacuum of  $1 \times 10^{-6}$  mbar and later an oxygen flow pass through the samples at a pressure of  $1 \times 10^{-2}$  mbar during the heating, the annealing at constant temperature and the cooling steps.

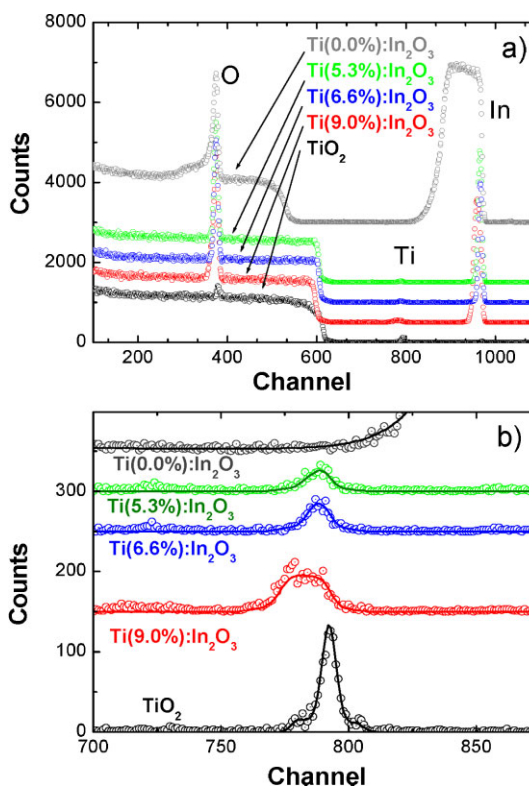
Rutherford backscattering spectroscopy (RBS) experiments were carried out at the Centro de Microanálisis de Materiales de Madrid [8]. The helium beam was obtained from a 5 MV Cockcroft–Walton tandem accelerator. RBS experiments have been performed at a backscattering angle of 170° with an ion dose of 10  $\mu\text{C}$ . In order to have a proper sensitivity to the oxygen present at the film, resonant RBS (or non-RBS, n-RBS) spectra were taken using a He beam with an energy of 3.035 MeV, allowing us to observe the resonance in the cross section for  $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ , for oxygen atoms at the film surface. Implanted Si detectors were used, with an energy resolution of 17 keV. n-RBS data were simulated using the RBX and SIMRA codes [9, 10] in order to obtain the composition profiles using the cross section reported by Cheng et al. [11] for  $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$  reaction.

Optical absorption has been characterized with a Cary 4000 UV–Vis spectrophotometer in the 190–900 nm ultra-violet–visible (UV–Vis) range. A homemade computer program has been used to manage a Keithley 224 current source and a Keithley 182 digital voltmeter to measure  $I$ – $V$  curves. The samples were contacted by sputtered platinum electrodes placed on the film surface; for that purpose four lined up platinum electrodes were deposited by sputtering and the four contact method was used to inject current and measure voltage.

**3 Results and discussion** In order to study the Ti-doped  $\text{In}_2\text{O}_3$  preparation process, we have grown a set of films by EB-PVD from pellets made of mixed  $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$  powders with compositions covering the whole range of Ti/In ratio contents. Due to the very different deposition rates obtained for the two pure oxides, a strong variation may be expected for the Ti concentration respect to the starting blend. In fact, X-ray diffraction only allows characteristic peaks corresponding to the  $\text{In}_2\text{O}_3$  phase, which suggest a low Ti content for the whole set of samples. For that reason, it is of particular importance to determine the Ti and In content at the film. Therefore, RBS has been preferred because it allows an independent determination with similar uncertainty for the three expected atomic species.

‘As-grown’ samples have metallic brightness aspect, which indicates their reduction during the deposition process. Having this in mind, samples have been annealed for 2 h at 500 °C under oxygen flux. At first glance, after that annealing process, all the samples have become transparent films (optical characterization is given below). Content characterization has been performed on annealed samples because this is the important information for this transparent conductive oxide system.

Figure 1(a) shows the whole RBS spectra corresponding to several samples prepared with different starting materials,



**Figure 1** (online colour at: [www.pss-a.com](http://www.pss-a.com)) (a) Rutherford backscattering experiments of deposited films obtained with a 3.035 MeV He beam to observe the oxygen resonance spectra. (b) Detail of experimental data corresponding to titanium signal and simulation (continuous line) obtained by the RBX code.

while in Fig. 1(b) the titanium contribution as measured by RBS can be observed in a proper zoom plot. As a first approximation, it can be concluded that no appreciable Ti content is obtained in the films when the starting material has been made from blends having  $\text{TiO}_2$  concentration smaller than 80 wt.%. The simulation of RBS data (given at the figure as continuous lines) allows an accurate evaluation of titanium, indium and oxygen contents. Table 1 summarizes RBS analysis, oxygen concentration corresponds to slightly over-stoichiometric oxides that seems reasonable after the oxygen annealing and Ti-concentration present in the films ranges from 5 to 9 at.% independently from the starting blend composition. From these results, it can be concluded that films prepared by EB-PVD from starting  $\text{TiO}_2$ – $\text{In}_2\text{O}_3$  blends with titanium oxide concentration lower than 80 wt.% have no titanium content and, otherwise, titanium oxide rich starting blends provide films with atomic titanium concentration (defined as  $[\text{Ti}]/([\text{Ti}] + [\text{In}])$ ) within the 5–9% range.

The optical characterization is presented in Fig. 2, optical absorption coming from fused quartz substrates has been removed to obtain the film absorption. For the sake of comparison, the absorption coefficient has been calculated after measuring the film thickness by an accurate determination by low angle X-ray reflectivity.

**Table 1** Characterization summary of studied films. From RBS: (i) areal density, (ii) indium, titanium and oxygen contents and (iii) Ti-concentration defined by  $[\text{Ti}]/([\text{Ti}] + [\text{In}])$ . Resistivity ( $\rho$ ), band-gap energy ( $E_g$ ) and  $n$  exponent from Eq. (1).

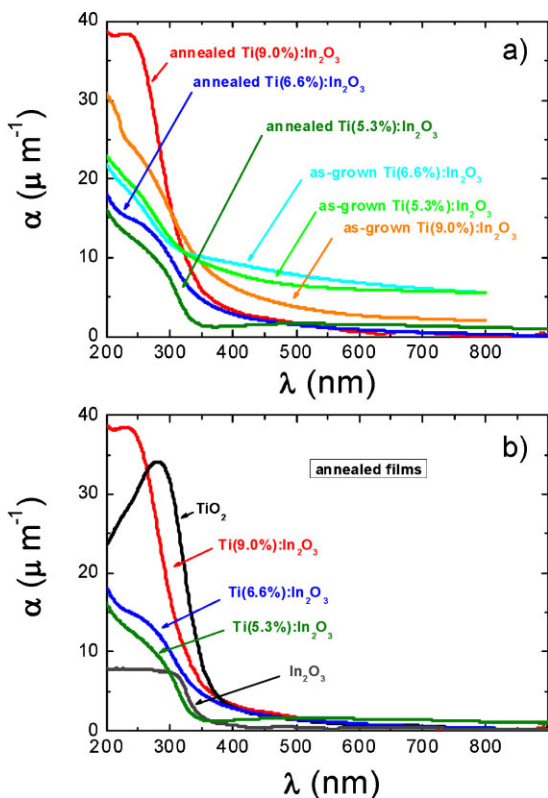
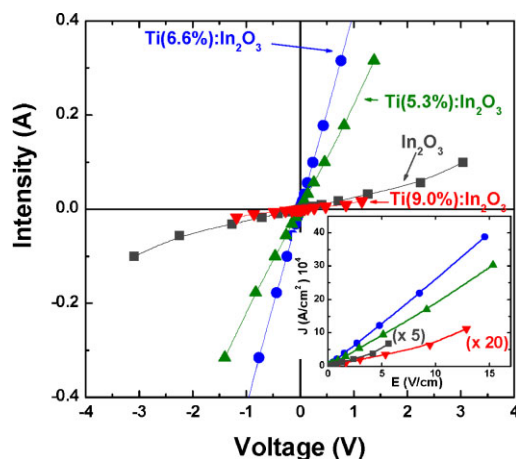
sample	areal density ( $\times 10^{15}$ at./cm <sup>2</sup> )	Content			Ti- concentration (at.%)	$\rho$ ( $\Omega$ cm)	$E_g$ (eV)
		[In]	[Ti]	[O]			
TiO <sub>2</sub>	56	0	30.6	69.4	100	–	3.05 ( $n = 2$ )
Ti(9.0%):In <sub>2</sub> O <sub>3</sub>	562	25.3	2.5	72.2	9.0	$3.1 \times 10^{-3}$	3.35 ( $n = 3/2$ )
Ti(6.6%):In <sub>2</sub> O <sub>3</sub>	322	29.7	2.1	68.2	6.6	$3.9 \times 10^{-5}$	2.95 ( $n = 3/2$ )
Ti(5.3%):In <sub>2</sub> O <sub>3</sub>	273	30.6	1.7	67.7	5.3	$5.2 \times 10^{-5}$	–
Ti(0.0%):In <sub>2</sub> O <sub>3</sub>	2710	35.0	0	65.0	0	–	–
In <sub>2</sub> O <sub>3</sub>	1512	35.9	0	64.1	0	$5.2 \times 10^{-4}$	3.4 ( $n = 3/2$ )

Figure 2(a) depicts the effect of the annealing on the transparency of samples. ‘As-grown’ films have an absorption behaviour typical from a heterogeneous media formed by a metallic phase with non-zero absorption at the whole range of visible wavelengths and at the near infrared region. On the other hand, annealed films present a transparent behaviour up to the energy corresponding to the optical band-gap, being typical from semiconductors.

Figure 2(b) shows the optical absorption characterization of annealed Ti:In<sub>2</sub>O<sub>3</sub> films deposited on fused quartz substrates, showing an excellent transparency, higher than 75%, at light wavelength of 350 nm for film thickness of

50 nm. Comparison between samples in Fig. 2(b) allows observing the behaviour of the optical gap, which moves monotonously from TiO<sub>2</sub> to In<sub>2</sub>O<sub>3</sub>. It should be noted that spectra corresponding to the Ti(5.3%):In<sub>2</sub>O<sub>3</sub> sample presents the well-known finite size oscillations, which in that particular case modifies the measured curve in such a way that decreases the absorption between 300 and 350 nm and increases from 400 to 900 nm.

The electrical resistance has been determined by measuring  $I$ – $V$  curves. Figure 3 shows raw  $I$ – $V$  measurements obtained for several Ti:In<sub>2</sub>O<sub>3</sub> samples with different titanium content (including a pure In<sub>2</sub>O<sub>3</sub> film). For all samples, an Ohmic behaviour can be clearly observed for the studied ranges of intensity and voltage; it is worth to note that no asymmetrical diode effect has been observed. The inset shows a comparison between the current density ( $J$ ) as a function of the applied electric field ( $E$ ), whose slope measures directly the inverse of the resistivity. The obtained resistivity values are given in Table 1, respect to the In<sub>2</sub>O<sub>3</sub> film, it can be observed a conductivity increase in samples with titanium content of  $\sim 6$  at.%, which decreases for the highest Ti content Ti(9.0%):In<sub>2</sub>O<sub>3</sub> film. Those values are in agreement with those already reported for films prepared by several techniques. Typical resistivities in the  $10^{-4}$   $\Omega$  cm

**Figure 2** (online colour at: www.pss-a.com) (a) Comparison of the optical absorption for as-grown and annealed films. (b) After annealing absorption coefficient of Ti:In<sub>2</sub>O<sub>3</sub> samples including TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> films prepared also by EB-PVD.**Figure 3** (online colour at: www.pss-a.com)  $I$ – $V$  curves of studied samples. The inset shows the current density dependence on the electric field to obtain the intrinsic resistivity values.

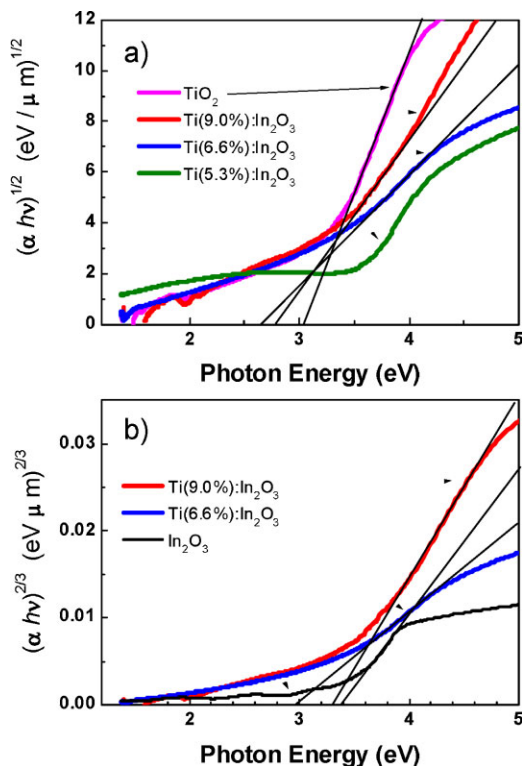
range have been obtained by Gupta et al. [6] for film deposited by PLD from 5 wt.% Ti targets; Sung and Han [7] have reported a resistivity of  $1.4 \times 10^{-3} \Omega \text{ cm}$  for films prepared by magnetic null discharge sputtering using a target sintered with 90 wt.% In<sub>2</sub>O<sub>3</sub> and 10 wt.% TiO<sub>2</sub> concentration and, on the other hand, van Hest et al. [4] and Abe and Ishiyama [12] have given an account of a minimum of the resistivity depending on the actual film Ti content, being  $\sim 1 \times 10^{-4} \Omega \text{ cm}$  for films with 3 at.% Ti content. Regarding the limit of resistivity pointed out by Bellingham et al. [13], it should be noted that in the hypothesis that a carrier concentration of  $2.1 \times 10^{-27} \text{ m}^{-3}$  is obtained by the whole In<sup>3+</sup> substitution by Ti<sup>4+</sup> in the Ti(6.6%):In<sub>2</sub>O<sub>3</sub> sample, resistivity values show excellent results.

Comparing with other TCO systems, it is clear that Ti:In<sub>2</sub>O<sub>3</sub> presents resistivity values smaller than those reported for Mo(1.2 at.%) -doped In<sub>2</sub>O<sub>3</sub> ( $1.8 \times 10^{-3} \Omega \text{ cm}$  [3]) and ITO ( $2 \times 10^{-4} \Omega \text{ cm}$  [4]) and of the same order as the reported for Zn(15 wt.%) -doped In<sub>2</sub>O<sub>3</sub> ( $3.4 \times 10^{-5} \Omega \text{ cm}$  [2]) and for low In content In:CdO ( $6 \times 10^{-5} \Omega \text{ cm}$  [5]).

Finally, the optical band-gap was calculated with the Tauc method [14] using the well-known equation,

$$\alpha E_{\text{phot}} = (E_{\text{phot}} - E_g)^n, \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $E_{\text{phot}}$  the excitation energy ( $h\nu$ ) and  $E_g$  the band-gap energy.  $n$  is a parameter



**Figure 4** (online colour at: www.pss-a.com) Determination of the band-gap energy. (a) Representation of  $(\alpha E_{\text{phot}})^{1/2}$  versus excitation energy (straight lines correspond to extrapolations). (b) Representation of  $(\alpha E_{\text{phot}})^{2/3}$  versus energy.

accounting for the different band-gap transition modes, being  $n = 1/2$  for direct allowed transition,  $n = 3/2$  for direct forbidden,  $n = 2$  for indirect allowed and  $n = 3$  for indirect forbidden. In the case of TiO<sub>2</sub>, the fundamental absorption has an indirect transition ( $n = 2$ ) and the corresponding plot [Fig. 4(a)] allows a band-gap energy of 3.05 eV which is in agreement with reported values for TiO<sub>2</sub> films prepared by sputtering [15, 16]. Absorption data corresponding to other samples are given also in this plot, where band-gap energies can be seen. Nevertheless, since In<sub>2</sub>O<sub>3</sub> is the main component, its corresponding direct forbidden transition ( $n = 3/2$ ) have to be considered. For that purpose,  $(\alpha E_{\text{phot}})^{2/3}$  versus the excitation energy has been represented in Fig. 4(b). Extrapolation of absorption curves in Fig. 4(b) gives a band-gap of 3.4 eV for In<sub>2</sub>O<sub>3</sub>, slightly higher but in good agreement with the reported [17] and calculated direct gap [18]. Ti(8.2%):In<sub>2</sub>O<sub>3</sub> and Ti(7.0%):In<sub>2</sub>O<sub>3</sub> samples show a decrease for the observed direct gap, with values of 3.35 and 2.95 eV, respectively. It is interesting to note that the sample with the smaller gap value has one of the higher conductivity. Moreover, the decrease in the band-gap energy for Ti-doped In<sub>2</sub>O<sub>3</sub> may be explained in terms of the deformation of band structure caused by the substitution of In by Ti in the In<sub>2</sub>O<sub>3</sub> lattice with an effect of shrinking the separation between the valence and conduction bands and providing carriers at the conduction band.

**4 Conclusions** Ti-doped In<sub>2</sub>O<sub>3</sub> thin films have been prepared by electron beam physical vapour deposition to study the transparent conductor oxide ITiO system. Preparation by this technique followed by oxygen thermal annealing allows excellent transparency and low resistivity values, obtaining  $\rho = 4 \times 10^{-5} \Omega \text{ cm}$  for Ti(6.6%):In<sub>2</sub>O<sub>3</sub> films, which confirms this TCO system as one of the best resistivity characteristics, having values smaller than ITO and of the same order as Zn:In<sub>2</sub>O<sub>3</sub> and In:CdO.

Additionally, it is observed a correlation between the band-gap energy and resistivity pointing out the Ti substitution at the indium oxide lattice.

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