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# Transparent films on polymers for photovoltaic applications

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## Abstract

Highly conductive and transparent tin-doped indium oxide (ITO) films have been prepared by RF sputtering processes on polymer substrates, polyethylene terephthalate (PET) and polyimide (Kapton KJ<sup>®</sup>), and onto glass as reference. The utilisation of a RF plasma pre-treatment of the organic substrate surface leads to the realisation of adherent films on unheated substrates with good optoelectronic properties and without damage to the polymers. High transparency, near 80% on the 400–1100 nm spectra range, and conductivity,  $\sigma > 10^3 (\Omega \text{ cm})^{-1}$ , have been achieved for ITO films deposited onto PET and Kapton KJ<sup>®</sup> substrates. These are adequate values for the utilisation of these modified polymer samples as substrates for photovoltaic solar cells. Better optical and electrical properties of the ITO films have been observed when deposited on polymer foils if compared with those deposited on glass. Improved quality of ITO samples have been correlated with the growth of more oriented and crystalline ITO films along the preferred orientation  $\langle 100 \rangle$ . The ITO films fabricated on polymers by the method proposed do not require substrate heating during the film preparation or any post-deposition annealing treatment in order to achieve the optoelectronic quality required. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* ITO; Polymer substrates; Sputtering; Transparent conducting films

## 1. Introduction

The main properties that transparent conductive oxide (TCO) layers (such as  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$  or  $\text{SnO}_2$  films) for solar cells generally need to possess are high values of both transparency and conductivity [1]. These layers deposited onto glass are used as substrates for different photovoltaic technologies [2–3]. The utilisation of glass substrates on the production of photovoltaic modules has the inconvenience of the relative high cost of glass, the fragility and the handling problems, which

during the production steps can determine the final yield of the process owing to the glass cutting, breaking, cleaning, etc. One alternative concept is based on the introduction of polymer foils as substrates instead of glass. Recently, solar cells with high efficiency, 12.8%, have been reported [4] on a 20  $\mu\text{m}$  thin polyimide film. The utilisation of these flexible polymer foils as substrates for solar cells open the way to roll-to-roll production, and additionally to interesting and novel applications for these kind of thin and bendable photovoltaic modules.

Concerning tin-doped indium oxide (ITO) films many works have been published on the preparation of this material by RF-sputtering on glass as substrate, while few reports treated the polymer

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substrates [5–7]. The ITO films made by DC/RF-sputtering method often require substrate heating or post-preparation annealing at temperatures over 150°C in order to improve the film properties, mainly conductivity. ITO films on polymer substrates can offer many advantages. However, it is necessary, their preparation at low substrate temperature due to the poor thermal endurance of the organic substrate [6]. Another problem that arises on the preparation of ITO films on polymers is the adhesion between both films. Usually, for glass substrates, plasma etching with Ar or Ar/O<sub>2</sub> mixture is accomplished [7] in order to promote the adhesion. The utilisation of polymer substrates make this point a key issue owing to the possible damage of the sensitive polymer surface by the plasma etching. For polymer substrates, acceptable adhesion of coatings can be obtained only by surface modification, creation of peroxide centres, radicals, etc. [8–10].

In this paper a first study of the deposition of ITO films on polymers foils, PET and Kapton KJ<sup>®</sup>, having in mind the obtention of coatings with adequate properties for photovoltaics application, conductivity and transparency, is presented.

## 2. Experimental details

Details of the RF-sputtering process and equipment preparation have been given elsewhere [7], only remarks on the preparation and characterisation of the films are given here. A water-cooled target In<sub>2</sub>O<sub>3</sub>:Sn (99.99% purity, Ø75 × 3 mm) with a composition 95:5 (wt%, Cerac Inc. (USA)) was used. Substrates were soda-lime glass (1 mm thick) and thermoplastic foils, PET (0.013 mm thick) and Kapton KJ<sup>®</sup> (0.025 mm thick) from Goodfellow (UK).

Before the deposition process various pre-treatments of the substrates surface were tested in order to obtain improved adherence of the ITO films onto the polymers foils. Application of plasma etching over the substrates using Ar and Ar/O<sub>2</sub> gases, 0.8 Pa process pressure, during 0.5–5 min under plasma power 3 W/cm<sup>2</sup> was accomplished. All the ITO films deposited after these

pre-treatments flake out from the substrates or even in extreme conditions lead to the substrate degradation by carbonisation. It has been shown [10] that the bombardment of PET surfaces with ions is responsible for carbon-rich surface layers, owing to decreases of the atomic ratio O1s/C1s and the loosing of C=O polar bonding that promote the adhesion of ITO/PET interfaces. In order to avoid the undesired effect observed by the use of the Ar and/or O<sub>2</sub> ions, they were substituted by low nitrogen flows, 0.01 Pa, and lower plasma power, 1 W/cm<sup>2</sup> during 30 s for substrate plasma-treated. Following this new process adherent ITO films were obtained without degradation of the polymer surface, naked eyed observation.

Sputter deposition was carried out under a total gas pressure of 0.8 Pa with the introduction of O<sub>2</sub>, partial pressure  $5 \times 10^{-3}$  Pa. The deposition process was carried out at room temperature, i.e. the substrate was not heated during or after the film deposition, and water-cooled substrate holder was employed.

Under above conditions, and after 7 min deposition time, the film thickness of the ITO films was 0.5 μm, was measured on glass substrates as reference by a Dektak 3030 profilometer. The growth rate of ITO films has been 12 nm/s independent on the substrate. The sheet resistance of the films was determined using both a four-point probe apparatus, Veeco FPP5000, and by two-point probe method after evaporation of Al contact.

Optical transmission measurements of the samples referred to the air have been done with unpolarised light at normal incidence in the wavelength range from 300 to 1500 nm, with a double beam spectrophotometer Perkin Elmer Lambda 9. Film structure has been analysed by X-ray diffraction (XRD) to investigate the present phases and to evaluate their degree of crystallinity. XRD measurements were accomplished by using the nickel-filtered Kα1 emission line of copper ( $\lambda = 1.5405 \text{ \AA}$ ). Peak diffraction angles ( $2\theta$ ) in the XRD patterns were converted to interplanar d-spacing and thus, phase identification has been carried out by comparison of the observed d-spacing with the powder diffraction standards card files.

Chemical studies by X-ray photoelectron spectroscopy (XPS) have been accomplished with a Perkin Elmer Phi 5400 ESCA system. Samples were excited with a Mg K $\alpha$  X-ray source ( $h\nu = 1253.6\text{ eV}$ ) operated at 300 W input. Superficial analyses have been carried out at  $10^{-9}\text{ Pa}$  base pressure and  $1\text{ mm}^2$  spot size. Peaks deconvolution and assignation have been established according to the data accessible in Perkin Elmer XPS-Handbook [11] and referenced bibliography. Atomic composition has been determined from the typical XPS peaks by evaluating the corresponding peak areas weighted by the element sensitivity factors.

### 3. Results and discussion

XRD patterns corresponding with the ITO thin films as grown by sputtering onto various substrates are shown in Fig. 1. All diffraction peaks are related to the  $\text{In}_2\text{O}_3$  crystalline phase according to the ASTM diffraction card no. 6–416. PET substrate shows also a broad diffraction peak at  $2\theta$  angle about  $26^\circ$ . From Fig. 1 it has been observed that ITO polycrystalline layers are grown with (222) preferred orientation, as indicated by the higher intensity of the corresponding diffraction peak detected at  $30.4^\circ$  angle. The ITO films

show very high (222) orientation when sputtered onto glass substrate, but such preferential orientation decrease when sputtering is made onto Kapton or PET substrates. Thus polycrystalline ITO films can be deposited on PET and Kapton KJ<sup>®</sup> without heating of the polymer foil substrates. It has been pointed out that ITO films on the investigated polymers present a preferential orientation on the (222) axis but show diffraction patterns with significant contributions of the (211), (400), (440) and (622) peaks. From Fig. 1, it is observed that the utilisation of polymers foils lead to ITO films with different crystallinity that on glass and with evolution of their orientation to the (400) axis. Some authors [12] have suggested the importance of oriented growth of the ITO films in order to improve the conductivity of the layers. The increase of the integrated peaks ratio (400)/(222) favoured the preferential orientation  $\langle 100 \rangle$ , which is correlated with a decrease of the donor sites trapped at dislocations or point defect aggregates and the increase of the ITO films conductivity [12]. From the XRD patterns of the ITO films deposited glass, Kapton KJ<sup>®</sup> and PET the ratio (400)/(222) has been calculated, Table 1, observing that this ratio becomes increasingly prominent when polymer foils are used instead of glass.

Along the characterisation of the ITO films deposited onto different substrates optical films transmittance over the wavelength range 300–1500 nm was measured with respect to the air. Fig. 2(a) shows the wavelength-dependent transmittance of the bared substrates, where the most remarkable point is the visible cut-off of the Kapton KJ<sup>®</sup> film owing to its yellowish semitransparent appearance. Fig. 2(b) shows the spectra obtained for ITO films over the different substrates. Fig. 2(b) reveals that transparency of the ITO layers is higher on polymer substrates especially in the infrared region mainly due to the better  $\langle 100 \rangle$  crystallisation and the reduction of absorbing structural defects in the ITO films grown on polymers. In order to better understand the improvement of the optical properties of ITO films on polymer substrates, the average transparency for the different samples has been calculated on the spectra range 400–1100 nm (usual range of

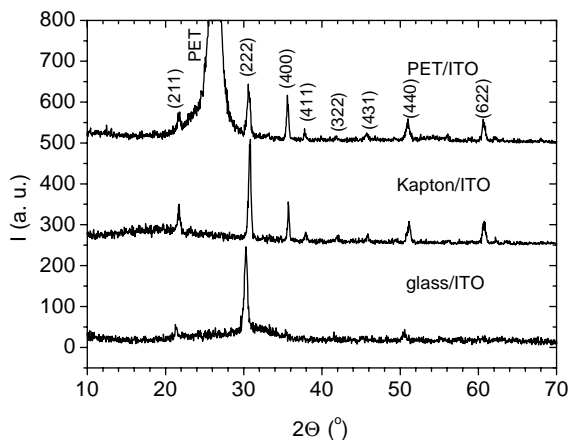


Fig. 1. XRD patterns of ITO thin films grown by sputtering onto various substrates: soda lime glass, Kapton KJ<sup>®</sup> and PET.

Table 1  
Structural, optical and electrical data for ITO films deposited on glass and polymer foils

Substrate	XRD intensity ratio of (400)/(222) peaks	Transparency wavelength range 400–1100 nm			Sheet resistance ( $\Omega/\text{sq.}$ )	Conductivity ( $\Omega\text{cm}^{-1}$ )
		Average (%)	Max. (%)	Min. (%)		
Glass	0.03	69.3	79.3	37.3	40	$4.0 \times 10^2$
Kapton KJ <sup>®</sup>	0.37	72.5	85.4	3.5	14	$1.2 \times 10^3$
PET	0.83	77.8	84.3	47.7	4	$4.1 \times 10^3$

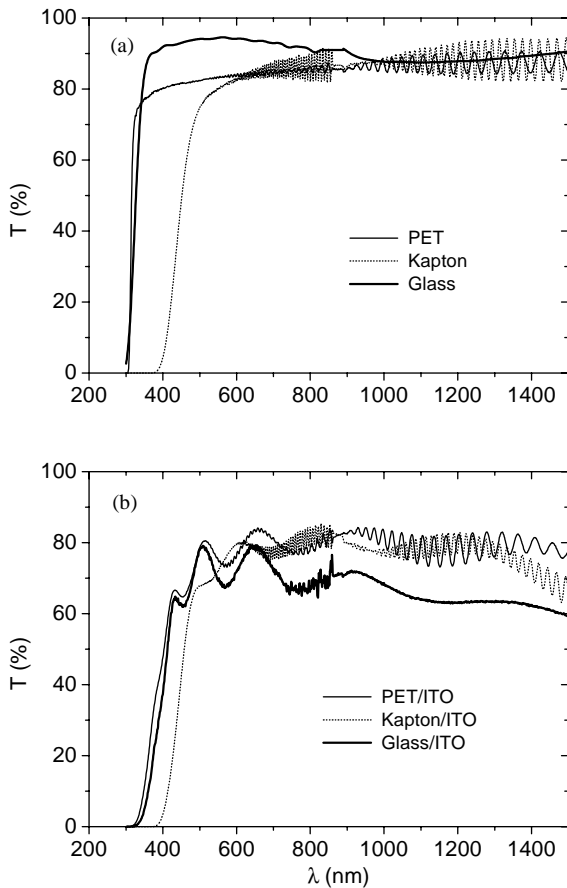


Fig. 2. Optical transmission spectra on PET, Kapton KJ<sup>®</sup>, and soda lime glass bare substrates (a) and of ITO films deposited on the same substrates (b).

photovoltaic solar cells operation), Table 1. Interesting observation is the increasing of the amount of light that through the polymer samples if compared with glass, even for Kapton KJ<sup>®</sup> substrates, that have to produce increasing of the

final photocurrent when these structures will be used as substrates for photovoltaic solar cell devices.

Table 1 also shows the dependence of the electrical properties, sheet resistance and conductivity, of ITO films on the substrate used. It can be seen that the sheet resistance of the ITO films changes considerably when polymer foils are used as substrates. The lowest value is obtained on PET films,  $4\ \Omega/\text{sq.}$ , which is considerable lower than other previously reported for ITO films on PET substrates,  $250\ \Omega/\text{sq.}$  [13]. Until our knowledge, conductive ITO films have not been reported on Kapton. Reason of the low sheet resistance for the PET films is the high textured surface and high value of the ratio of the XRD peaks (400)/(200), if it is compared with values obtained on glass, such as was discussed above.

XPS analysis of signals detected on the ITO films grown by sputtering onto glass and PET substrates are summarised in Table 2. C 1s signals are showed in Fig. 3, where the main peak detected at a binding energy of 284.8 eV is due to C–C and C–H species, which are typical from air contamination. Whereas another small peak at 288.9 eV is attributed to C=O. From O 1s signals depicted also in Fig. 3, two components have been identified as oxygen in the form of  $\text{O}^-$  at 529.9 eV and of C=O/OH<sup>-</sup> at 531.7 eV. Finally, the rather broad and asymmetric In 3d5/2 peaks showed in Fig. 3 consist mainly of  $\text{In}_2\text{O}_3$  contribution with an energy about 444.3 eV and a small proportion of  $\text{In}(\text{OH})_3$  at 445.5 eV. From the deconvolution and quantification data of Table 2, it has been found that glass/ITO surface seems more affected by air contamination, meanwhile the ratio Sn/In remains constant in both substrates. Main differences between both substrates can be determined in the

Table 2

Summary of deconvolution and quantification data corresponding with the XPS spectra of ITO thin films grown by sputtering onto glass and PET substrates

Sample	XPS chemical analysis						
Glass/ITO	55 at% C		26 at% O		18 at% In		1 at% Sn
	97% C–C/C–H	3% C=O	64% O <sup>=</sup>	36% C=O/OH <sup>-</sup>	92% In <sub>2</sub> O <sub>3</sub>	8% In(OH) <sub>3</sub>	100% SnO <sub>2</sub>
PET/ITO	18 at% C		44 at% O		36 at% In		2 at% Sn
	91% C–C/C–H	9% C=O	73% O <sup>=</sup>	27% C=O/OH <sup>-</sup>	95% In <sub>2</sub> O <sub>3</sub>	5% In(OH) <sub>3</sub>	100% SnO <sub>2</sub>

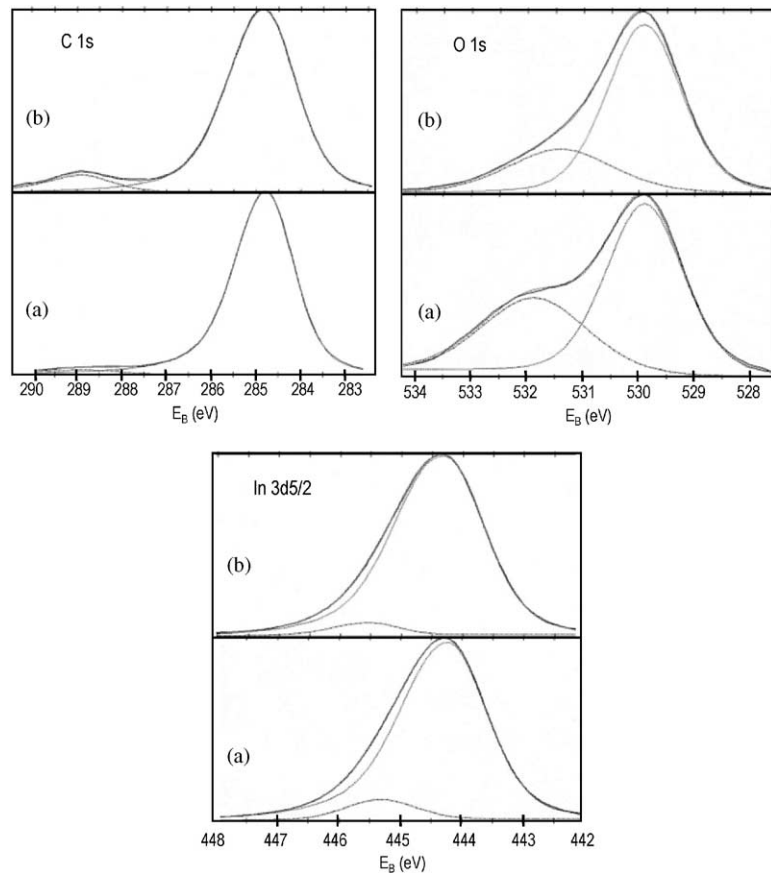


Fig. 3. XPS signals corresponding with C 1s, O 1s, and In 3d5/2 on the ITO films grown by sputtering onto glass substrate (a) and onto PET substrate (b).

presence of more amount of In(OH)<sub>3</sub>, probably as amorphous specie, on glass samples and the major relative strength of the O<sup>=</sup> peak on PET substrates.

It is well known that tin impurities and ionised oxygen vacancy donors govern the charge carrier density in an ITO film. On the case of PET films, XPS spectra indicate more oxygen-deficient ions

[14] on the ITO films. This increase on the number of oxygen vacancies promotes the increase of charge carriers on PET/ITO samples and hence an increase on the ITO films conductivity. On another side, it seems that the slight high value of the ratio  $\text{SnO}_2/\text{In}_2\text{O}_3$  on glass samples is not enough to compensate the doping level established by the oxygen ions on the PET/ITO films.

#### 4. Conclusions

ITO films have been deposited without substrate heating on two polymer materials PET and Kapton KJ<sup>®</sup>. Films on polymers have shown better electrical and optical properties than the equivalent processed films on glass. Excellent quality on both transparency and conductivity make this kind of ITO samples supported on polymers extremely appropriate as substrates for photovoltaic solar cells. Better optical and electrical properties of ITO films are correlated to the growth of more oriented and crystalline ITO layers, along the preferred orientation  $\langle 100 \rangle$ . XPS analysis of ITO samples on PET showed a high presence of oxygen vacancy ions, which are responsible of better conductivity on ITO substrates.

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