

Transparent Conducting Oxides on Polymer Substrates

Sharon Louch¹, Steven Edge¹, Mark Hodgson², Kevin Luxmore¹

Centre for Process Innovation, Wilton Centre, Redcar. TS10 4RF. UK

Dupont Teijin Films, Wilton centre, Middlesbrough, UK

Introduction

The transparent conducting oxides, ITO and AZO, are wide band gap ($>3.3\text{eV}$), n-type semiconducting materials. Transparent conducting oxides (TCOs) are used in many applications, including LCD flat panel displays, OLED devices, photovoltaic applications and heat mirrors [1-6]. ITO is the most widely used TCO, because of its desirable properties of high transparency and high conductivity. However, in recent years, concern about depleted indium supplies has led to an effort to find substitutes for ITO. These include indium free or reduced indium TCO materials [7, 8]. One of the most promising alternatives is aluminium doped zinc oxide (AZO). The aim of this work is to better understand the sputter deposition of ITO and AZO coatings onto polymer substrates, in order that they might be optimised for use in flexible electronic devices. The polymer substrate presents challenges for the deposition of good quality TCOs, primarily because of its low temperature resistance, thus preventing beneficial annealing processes from being used. Sputter deposition is widely used for coating of glass, but also for roll-to-roll web coating, because of the low deposition temperature and quality of the coatings thus produced.

Experimental Details

The TCO coatings were produced using an OptilabTM roll to roll web coater from General Vacuum Machines. ITO was deposited from an $\text{In}_2\text{O}_3/\text{SnO}_2$ (10%wt) 99.99% purity planar target. AZO was deposited from a ZnO/AlO (2%wt), 99.9% purity planar target. The magnetron is equipped with a 10kW Pinnacle power supply and a SparcLE-V pulsing unit from Advanced Energy. For all the samples discussed here the pulsing was activated with a frequency of 100kHz and a pulse time of $2\mu\text{s}$.

A wide variety of techniques have been used to characterise TCO thin films. Most commonly, and simply, the sheet resistance and transmission / reflection are measured. In this work transmission spectra were obtained using a Thermo Electron UV-Visible spectrophotometer in the wavelength range 200-800nm and the sheet resistance was measured using a Jandel 4

point probe or a Nagy in-line non-contact resistance monitor.

A fundamental property of semiconductor materials is the resistivity, ρ , which depends on the charge carrier concentration and the mobility of the charge carriers. This is given by $\rho = \text{sheet resistance (ohm/sq)} \times \text{thickness}$. The film thickness was determined using a Jobin Yvon MM16 ellipsometer.

For use in flexible electronic applications, such as OLED devices or flexible display panels, the atomic structure, morphology and surface properties of the TCO coatings are of particular interest, as well as the effect of these on the electrical and optical properties [3-6, 9-12]. For a selection of the polymer surfaces considered in this work, the surface roughness was measured using a Taylor Hobson CCI optical profilometer. Measurements were obtained at 10 positions and, from these an average surface roughness value was calculated. SEM images of the coating grain structure were also obtained and the grain size was determined from image analysis studies. Finally, grazing incidence x-ray diffraction (GIXRD) measurements were made to determine the crystallinity of the coatings.

Results and Discussion: ITO

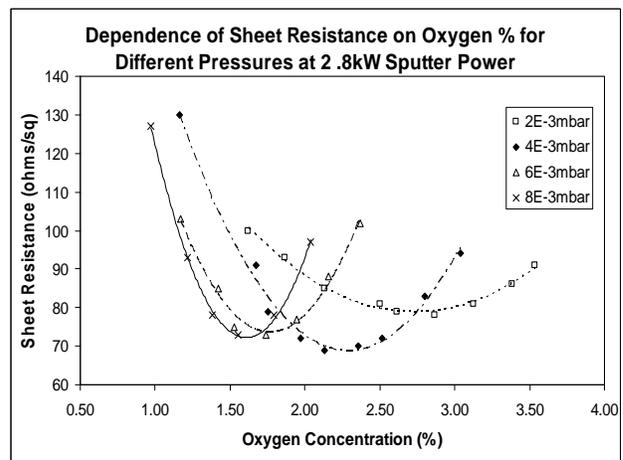


Figure 1: Resistivity minimum curves for ITO deposition at different pressures. All deposited at 2.8kW power, 0.3m/min web speed, 100mm target-web distance.

In figure 1 the ITO sheet resistance as a function of oxygen flow is plotted for samples produced at different process pressures, using a power of 2.8kW (~2.0W/mm of racetrack length), target-web distance of ~100mm, and a web speed of 0.3m/min. The well-known minimum in resistance [9, 13, 14] occurs in each case, but at 4.0×10^{-3} mbar the minimum sheet resistance is slightly lower than at the other pressures.

The optical transmission spectra for the samples produced at this pressure are shown in figure 2. The maximum transmission is reached at the point of minimum sheet resistance and, after this an increase in oxygen flow does not lead to any appreciable increase in transmission.

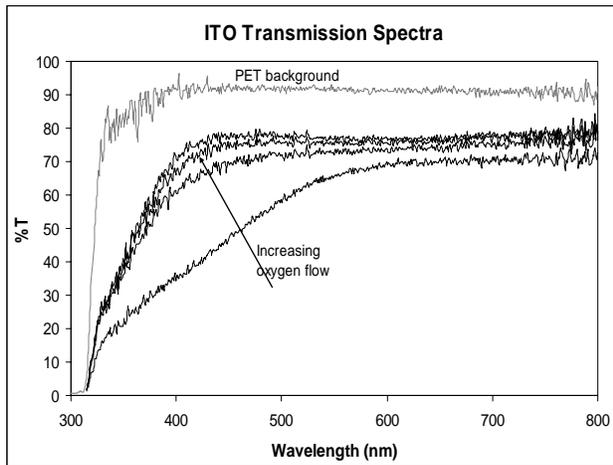


Figure 2: Transmission spectra of ITO samples deposited at 2.8kW target power, 0.3m/min web speed and 0.004mbar pressure, with increasing oxygen concentration in the sputtering gas .

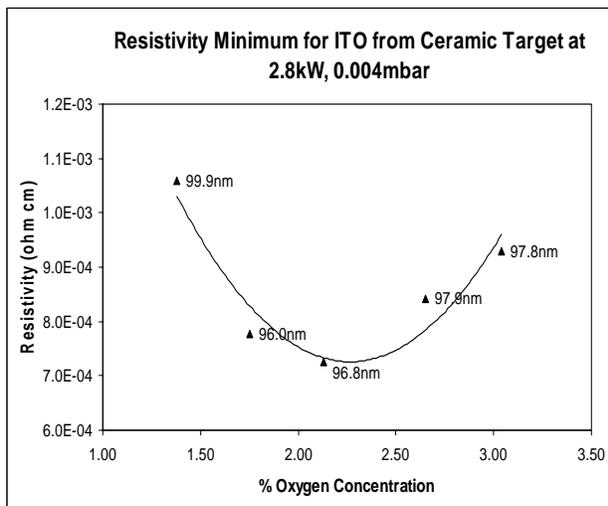


Figure 3: Resistivity of ITO coatings as a function of increasing oxygen flow at sputter power of 2.8kW and pressure of 4×10^{-3} mbar.

The experiment at 4.0×10^{-3} mbar was repeated and the curve was reproduced well. On this second occasion the film thickness was measured by ellipsometry, the calculated resistivity is plotted as a function of oxygen flow in figure 3. It is noted that the deposition rate does not change significantly with the addition of oxygen. The values of resistivity obtained, 5.5 to 7.6×10^{-4} Ω cm, are reasonable for a low temperature deposition onto polymer substrates with no subsequent annealing. (It can be problematic measuring the coating thickness on the polymer substrate by ellipsometry because it is not easy to obtain a good reference sample of the substrate. To overcome these issues, thin pieces of Si were taped to the web during deposition, and the coating thickness was then measured from these witness samples. Si is an ideal reference substrate in this regard.)

Figure 4 shows the resistivity of ITO samples prepared on different substrate surfaces, with and without ArO₂ plasma pre-treatment of the substrate. In this case the power (2.8kW) and web speed (0.3m/min) was as above, but the target-web distance was 115mm, instead of 100mm. All samples were made at a pressure of 5.4×10^{-3} mbar and oxygen concentration 2.4%. The film thickness was measured to be 65nm by ellipsometry. In all but one case, the plasma-pre treated samples had a higher sheet resistance, and consequently resistivity. The resistivity for all the non-plasma treated samples is approximately constant, within experimental error, with values in the range 5.64 to 5.95×10^{-4} Ω cm. The plasma pre-treated samples show a bigger variance in resistivity ranging between 5.5 to 7.57×10^{-4} Ω cm, indicating that the plasma pre-treatment affects each surface differently. The PET surface with adhesion promoter and the raw PEN surface were affected most by the plasma pre-treatment.

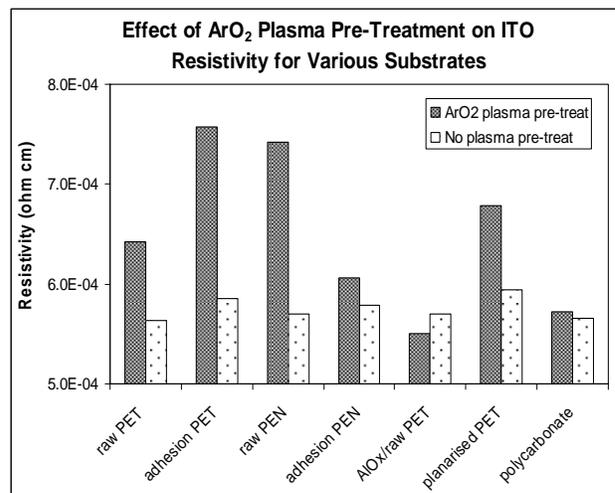


Figure 4: Effect of ArO₂ plasma pre-treatment on the sheet resistance of ITO for various different substrate surfaces.

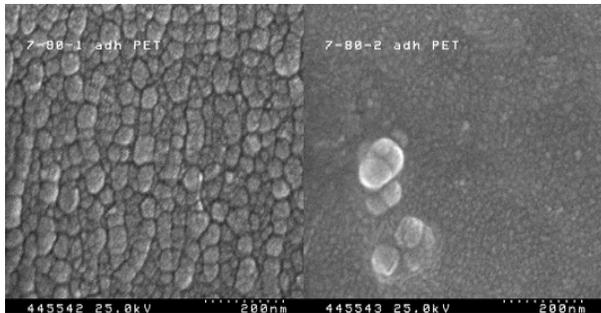


Figure 5a: SEM images of ITO grain structure on PEN with adhesion promoter layer for ArO₂ plasma pre-treated (left) and non pre-treated substrate (right).

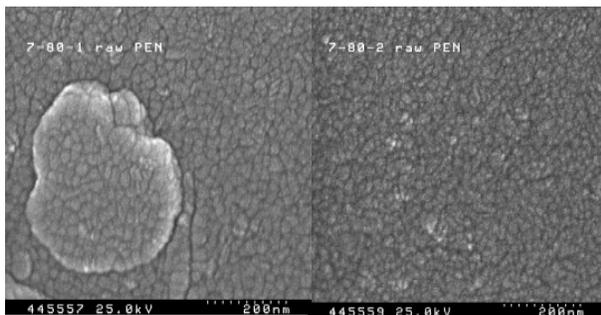


Figure 5b SEM images of ITO grain structure on raw PET for ArO₂ plasma pre-treated (left) and non pre-treated substrate (right)

In order to understand what had happened to the ITO coating on the plasma pre-treated surfaces, SEM images were obtained. The images for the adhesion PET and raw PEN surfaces, with and without plasma pre-treatment are shown in figure 5. It is evident that there is an increase in the grain size for the plasma-treated samples and this may be related to the increase in sheet resistance / resistivity. The average grain size was found to be 47 and 17nm for the adhesion promoter side of PET with and without plasma pre-treatment, respectively. The surface roughness values obtained were 5.4nm and 2.64nm for the samples with and without plasma pre-treatment, respectively. For the raw PEN surface the average grain size was measured to be 27 and 20nm for the plasma pre-treated and non pre-treated samples, respectively. It is usually found that the grain size increases with film thickness and with annealing (improved crystallinity) and that, as a consequence of the larger grain size, the resistivity decreases [6]. This does not seem to be the case here, however. It might also be expected that grain size would decrease with plasma pre-treatment as the surface energy of the substrate will be increased, leading to a higher density of nucleation sites for the growing film. At this time these observations are unexplained and further investigation will be required to understand what is happening.

A feasibility study was carried out for the possibility of using grazing incidence X-ray diffraction (GIXRD) measurements to characterise these types of samples. Three of the ITO samples were measured at an incident beam angle of 0.4° and the data is displayed in figure 6. The samples all exhibited crystalline phases. In addition, the grain size was estimated to be ~20nm from the width of the peaks.

Results and Discussion: AZO

Some preliminary studies on AZO deposition were also carried out. When using the ceramic type targets for AZO deposition, oxygen does not need to be added to the process [8]. The effect of ArN₂ plasma pre-treatment was investigated because, from the results above for ITO, it was thought that the ArO₂ plasma might be too aggressive, and hence causing some damage to the web. AZO samples were prepared at 4kW target power, at pressures of 2, 4 and 6 x 10⁻³mbar at a web speed of 0.3m/min on ArN₂ plasma pre-treated and non pre-treated raw PET substrates. The results are plotted in figure 6. The accompanying SEM images of the grain structure are shown in figure 7. It can be seen that the ArN₂ has a detrimental effect on the sheet resistance, but that this effect is largest at the lowest pressure. There is also a noticeable difference in grain size between the two samples deposited at the lowest pressure of 2x10⁻³mbar, although it has not been measured at the time of writing this paper. Once again the plasma pre-treated sample has the larger grain size and the higher sheet resistance. The samples produced at the other pressures appear to have a similar grain structure whether or not the surface is pre-treated, and the difference in sheet resistance is not as significant in these cases.

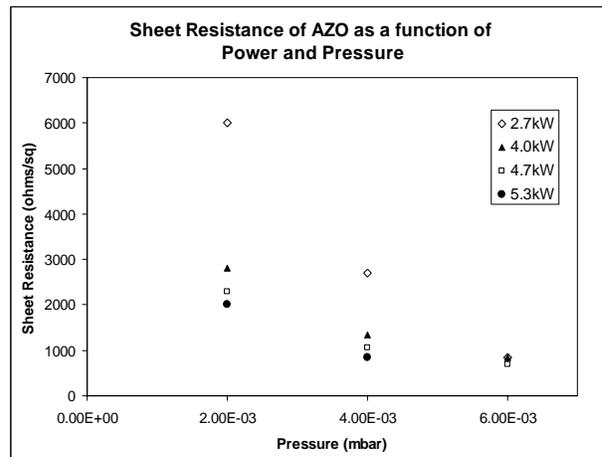


Figure 6: Effect of ArN₂ plasma pre-treatment on sheet resistance of AZO coatings deposited at various powers and pressures on raw PET substrate.

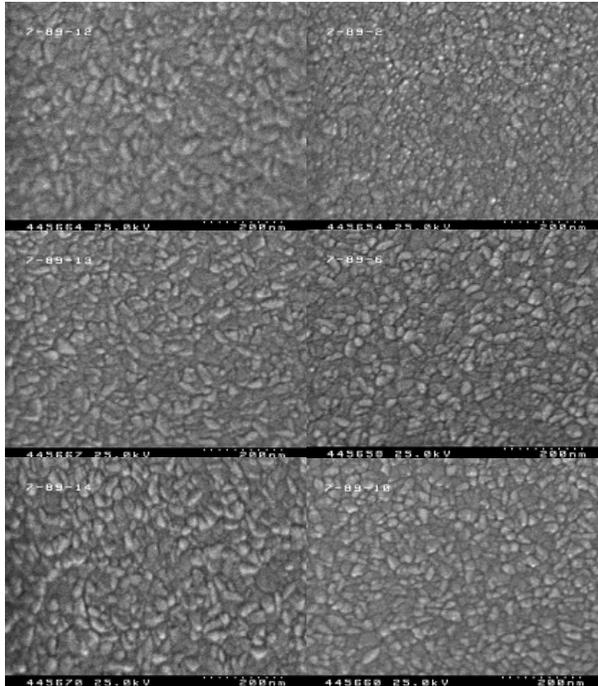


Figure 7: SEM images of AZO coatings on raw PET surface. The images on the left are for the ArN₂ plasma pre-treated samples and the images on the right are for the samples with no plasma pre-treatment. The sputtering pressure was 2, 4 and 6 x10⁻³mbar for the top, middle and bottom images, respectively.

Summary and Conclusions

ITO sheet resistance as a function of oxygen flow was plotted for different pressures at fixed power, web speed and target-film distance. The curves all exhibited a minimum resistance value, which coincided with the maximum optical transmission in the wavelength range 400-800nm. Above this optimum point the transmission did not increase significantly with increasing oxygen flow. The minimum sheet resistance value obtained was at a pressure of 4x10⁻³mbar.

ITO under the same process conditions was deposited onto seven different substrate surfaces, both with and without ArO₂ plasma pre-treatment. No significant differences in the sheet resistance were recorded across the different substrate types for the non pre-treated samples. For the ArO₂ plasma pre-treated samples the sheet resistance was higher in all cases except one. The difference was largest in the case of the raw PET surface and on the adhesion promoter side of PEN. This observation maybe related to differences in grain size which were observed in SEM images, with the plasma pre-treated samples exhibiting larger grain sizes. Further investigation is needed to fully understand this phenomenon.

AZO coatings were deposited onto a raw PET surface at different pressures, and the effect of ArN₂ plasma pre-treatment was investigated. The sheet resistance was higher for the samples that were plasma pre-treated, and the biggest difference was for the lowest pressure. SEM images of the plasma pre-treated and non pre-treated samples at the lowest pressure of 2x10⁻³mbar showed a difference in grain size, once again, with the larger grain size for the pre-treated film.

GIXRD data for both ITO and AZO samples indicated crystalline phases in the coatings.

1. K.L.Chopra, S.Major, D.K.Pandya, Thin Solid Films 102 (1983) 1
2. I. Hamburg, C.G. Granqvist. J.Appl.Phys 60 (1986) R123
3. A.Luis, C.Nunes de Carvalho, G.Lavareda, A.Ameral, P.Broguiera, M.H. Godinho, Vacuum 64 (2002) 475
4. Y.Leterrier, L.Medico, F. Demarco, J.A.E. manson, U.Betz, M.F. Escola, M. Kharrazi Olsson, F.Attamy. Thin Solid Films 460 (2004) 156
5. A.B.Chebeotereva, G.G. Untila, T.N.Kost, S.Jorgensen, A.G. Ulyashin Thin Solid Films, 515 (2007) 8505
6. U.Betz, M Kharrazi Olsson, J. Marthy, M.F. Escola. Thin Solid Films 516 (2008) 1334
7. T. Minami. Thin Solid Films 516 (2008) 1314
8. T. Minami. Thin Solid Films 516 (2008) 5822
9. M. Bender, W. Seelig, C.Daube, H.Frankenberger, B.Ocker, J. Stollenwerk. Thin Solid Films. 326 (1998) 72
10. Hai-Nang Cui, V. Texeira, Li-Jian Meng, R Martins, E. Fortunato Vacuum (2008) 1
11. C. Guillen, J. Herrero. Thin Solid films 480 (2005) 129
12. M. Boehme, C. Charton. Thin Solid Films 200 (2005) 932
13. H. Hoffmann, J. Pickl, M. Schmidt, D. Krause, J. Appl. Phys 16 (1978) 239
14. M. Buchanan, J.B. Webb, D.F. Williams, Appl. Phys. Lett 37 (1980) 213