

Enhancement of the Electrical Properties of ITO Deposited on Polymeric Substrates by Using a ZnO Buffer Layer

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ABSTRACT

In this paper we present the effect of the insertion of a non-doped nanocrystalline zinc oxide/buffer layer on the electrical, optical and structural properties of indium tin oxide produced at room temperature by radio frequency plasma enhanced reactive thermal evaporation on polymeric substrates. The electrical resistivity of the ITO films is reduced by more than two orders of magnitude (4.5×10^{-1} to $2.9 \times 10^{-3} \Omega \text{cm}$). From the Hall effect measurements it is observed that the large decrease associated to the electrical resistivity, is due to the increase associated to the Hall mobility. Concerning the optical properties no effect was observed, being the transmittance in the visible and near the infra red region always higher than 80%.

INTRODUCTION

Nowadays flexible electronics is an emerging and multidisciplinary research topic in several areas including for example flat panel displays and organic electronics [1]. Polymer substrates suitable for these applications are being developed. However, polymers are very sensitive, to moisture and oxygen and some of them are even chemically unstable when used with thin film technologies. Transparent diffusion barrier coatings have been extensively researched in order to provide a smooth surface and reduce the diffusion of water vapour and oxygen into displays laid down on polymer substrates. However, defects on the relatively rough surface of polymers, can cause pinholes in the final coating and lead to catastrophic failure of barrier properties. For this work, thin ZnO barrier coatings were deposited by rf magnetron sputtering on PEN substrates (included in the group of semi-crystalline polymers), at room temperature, to protect the substrates surface of contamination from water and moisture diffusion [2]. The strong preferred orientation (002) of the ZnO films is also an advantage in order to induce an increase of ITO films grain size, reducing electron scattering. ITO thin films were deposited on those PEN substrates with and without a ZnO barrier at room temperature by rf plasma enhanced reactive thermal evaporation. High quality ITO films at lower deposition temperatures are essential to substitute glass substrates for polymer foils. In this paper a detailed description of the preparation conditions as well as on the electrical (Hall effect), optical (transmittance), structural (X-ray diffraction) and morphological (FE SEM) properties will be presented.

EXPERIMENTAL DETAILS

ITO thin films were deposited on polyethylene naphthalate – PEN substrates coated with ZnO layers by an improved radio frequency plasma enhanced reactive thermal evaporation (rf-PERTE) of a 85%In-15%Sn alloy in the presence of oxygen at room temperature, using the conventional evaporation arrangement. A Balzers tungsten crucible (ref. BD.482 200) is used for the alloys evaporation and the source-substrate distance was kept at 30 cm approximately. The oxygen is introduced into the deposition system from a steel tube through a calibrated leak valve. In order to enhance the reaction of the In/In-Sn evaporating species and the oxygen, an oxygen plasma is generated by a radio frequency electrode ($16 \times 16 \text{ cm}^2$) placed into the deposition chamber, between the resistance-heated crucible and the substrate holder, 10 cm from the substrates. Two types of substrates were used: window glass and PEN with a thickness of 75 μm , previously cleaned with washing agents (commercial detergent and deionized water) before loading. The evaporation chamber is initially evacuated to a base pressure of 8×10^{-6} mbar. The evaporation of the alloy is performed steadily and the time of evaporation recorded in order to calculate the evaporation rate. In the beginning, a shutter between the substrates and the crucible is used to prevent contaminants from the heated crucible to reach the substrates. ITO thin films deposition parameters were the following: rf power of 50 W, deposition rate 0.1-0.2 nm/s and oxygen partial pressure in the range of $6\text{-}6.5 \times 10^{-4}$ mbar. The concentration of tin in the In-Sn alloy was 10 wt%. The ZnO buffer layer was deposited by rf (13.56 MHz) magnetron sputtering using a ceramic oxide target ZnO with 5 cm diameter, from Super Conductor Materials, Inc. with a purity of 99.99%. The sputtering was carried out under room temperature and the argon deposition pressure was 0.15 Pa. In order to avoid the undesirable heating of the substrate due to the ion bombardment the films were grown by steps (maximum of three) keeping the substrate temperature below 40 °C (313 K). The distance between the substrate and the target was 10 cm and the rf power was 100 W. The film thickness of the buffer layer was varied between 50 nm and 175 nm.

The film thickness (d) was measured using a surface profilometer (Dektak 3D from Sloan Tech.). The electrical resistivity (ρ), free carrier concentration (n) and Hall mobility (μ) were determined from Hall effect measurements using the Van der Pauw geometry (Biorad HL5500) at a constant magnetic field of 0.5 T. The optical transmittance was measured using a UV-VIS-NIR double beam spectrophotometer (UV-3100 PC, Shimadzu) in the wavelength range from 300 nm to 2500 nm. The structural properties of the films were determined using X-ray diffraction measurements with Cu- K_α radiation (Rigaku DMAX III-C series). The surface morphologies were analyzed using a Field Effect Scanning Electron Microscope (FE-SEM, S-1400 Hitachi).

DISCUSSION

ZnO buffer layer

The main objective of the insertion of the ZnO buffer layer is to improve the electrical properties of the ITO films deposited by an improved thermal evaporation technique (usually to get ITO films with high conductivities, using this technique, the substrate should be heated during deposition [3], which is not compatible to polymeric substrates) simultaneously increase the crystallinity and prevent interface reactions between the ITO and the polymeric substrate.

Figure 1 shows the produced at $P = 100$ W, observed, revealing preferred orientation reveal a limited crystallinity, the maximum of the peaks is at $2\theta \approx 35^\circ$, average crystallite size is ~ 10 nm, obtained by scanning electron microscopy films [4]. The low crystallinity at room temperature was observed, this film is $\sim 10^8 \Omega \text{cm}$.

Figure 1. Typical XRD pattern of ITO film produced at an rf power of 100 W. The film thickness is 100 nm.

ITO films

The dependence of the electrical properties of the ZnO buffer layer on the thickness of the ZnO buffer layer is shown in Figure 2. The resistivity of the ZnO buffer layer decreases with the thickness of the ZnO buffer layer. The Hall mobility of the ZnO buffer layer is also dependent on the thickness of the ZnO buffer layer. The Hall mobility of the ZnO buffer layer increases with the thickness of the ZnO buffer layer. The Hall mobility of the ZnO buffer layer is slightly increased with the thickness of the ZnO buffer layer. The ITO films deposited on the ZnO buffer layer show a slightly increased Hall mobility. The SEM images of the ITO films deposited on the ZnO buffer layer show a slightly increased crystallinity of the ITO film. The ITO film deposited on the ZnO buffer layer shows a slightly increased crystallinity of the ITO film since no peaks were observed. The only observation is

Figure 1 shows the X-ray diffraction pattern for a typical ZnO film used as buffer layer, produced at $P = 100$ W, deposited on soda lime substrate. Only the ZnO (002) peak at $2\theta \approx 34^\circ$ is observed, revealing that the film is nano/polycrystalline with a strong hexagonal structure and a preferred orientation with the c-axis perpendicular to the substrate. The large width of the peak reveal a limited crystalline domain. For the film produced at 100 W, using the full-width at half-maximum of the peak at an angle of 34.1° , we calculated by using the Scherrer formulation, an average crystallite size of the order of 10 ± 1 nm, which is also consistent with the results obtained by scanning electron microscopy and atomic force microscopy performed on similar films [4]. The low crystallite size is also associated with the fact that the films were processed at room temperature without any type of post thermal annealing. The typical electrical resistivity of this film is $\sim 10^8 \Omega\text{cm}$.

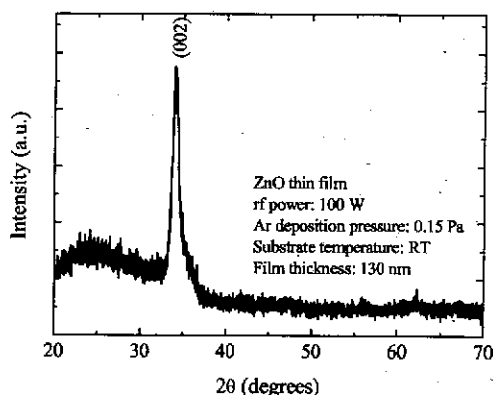


Figure 1. Typical x-ray diffractogram of a ZnO film produced by rf magnetron sputtering, with an rf power of 100 W and an argon pressure of 0.15 Pa at room temperature on glass substrate. The film thickness is 130 nm.

ITO films

The dependence of the electrical properties (ρ , n and μ_H) of the ITO films as a function of the ZnO buffer layer thickness is presented in figures 2a) and b). From figure 2a) it can be seen that the resistivity of the ITO film shows a remarkable decrease from 4.5×10^{-1} to $2.9 \times 10^{-3} \Omega\text{cm}$, for a ZnO buffer layer thickness of 100 nm. This improvement is accomplished by the increase of the Hall mobility and the carrier concentration, as it is indicated in figure 2b). By using a ZnO buffer layer it is possible to reduce the grain boundary scattering which is related to the increase of the Hall mobility as well as to increase the tin solubility inside the In_2O_3 matrix, proved also by a slightly increase on the carrier concentration. Similar results have already been obtained for ITO films deposited on ZnO buffered glass substrates [5]. These results are also correlated with the SEM images presented in figures 3 a) and b). The surface of the ITO film deposited onto the PEN substrate covered by 100 nm ZnO (b) presents a higher roughness, than that one of the same ITO film deposited onto bare PEN (a). This is indicative of an increase associated to the crystallinity of the film. Nevertheless the X-ray measurements performed are not conclusive, since no peaks were detected for the ITO films deposited onto the ZnO buffered substrates. The only observation is related to the highly textured ZnO film, as it is indicated in figure 4.

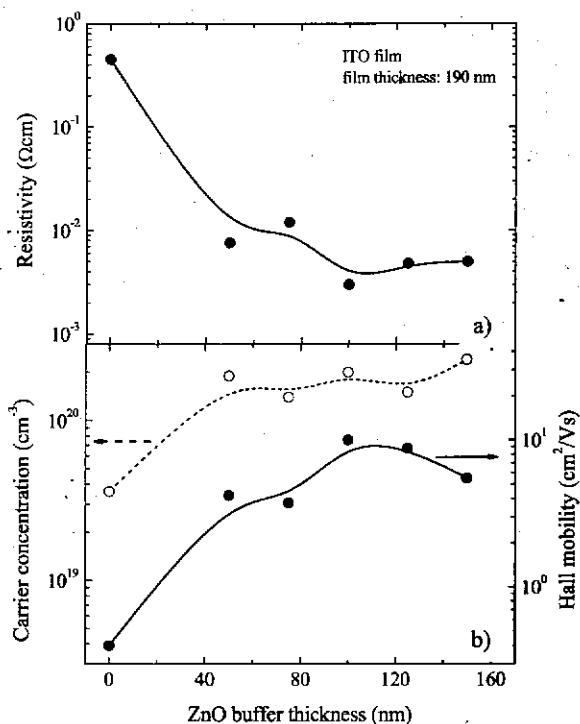


Figure 2. Dependence of electrical resistivity (a), carrier concentration and Hall mobility (b) on the ZnO buffer layer thickness.

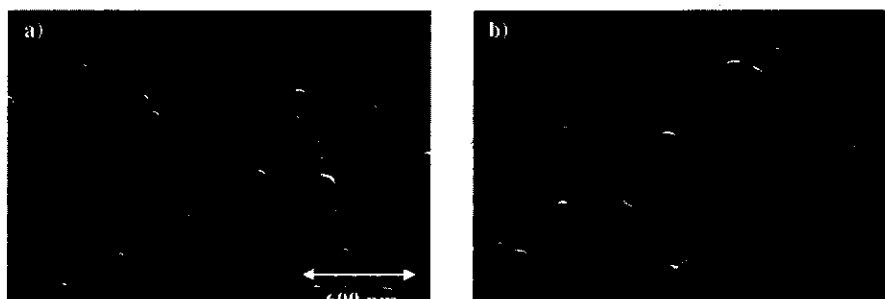


Figure 3. Scanning electron micrographs for ITO film deposited on (a) PEN and (b) PEN/ZnO substrates.

Figure 5 presents the optical transmittance in the wavelength range 300-1600 nm for ITO films deposited on PEN substrate without and with the ZnO buffer layer, using air as reference.

Figure 4. X-ray

The average transmittance is 80 %, for both samples at the same wavelength. The transmittance decreases substantially

Figure 5. Optical transmittance

Usually the carrier concentration and mobility. Nevertheless, the carrier concentration near the infra red region is preserved. The properties preservation is done in this work. The insertion of the ZnO buffer layer increases the carrier concentration orders of magnitude.

For comparison, the ITO film deposited onto soda-lime glass substrate

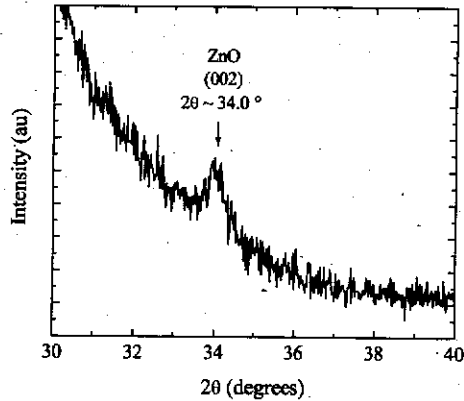


Figure 4. X-ray diffraction pattern for ITO film, deposited on SiO_2/PEN and PEN substrates.

The average transmittance in the visible and infra red part of the spectra is on the average 80 %, for both samples. The transmittance of the PEN substrate with $75\ \mu\text{m}$ thickness, for the same wavelength range, is around 85 %. We would like to point out that, it was possible to decrease substantially the electrical properties without any deterioration of the optical properties.

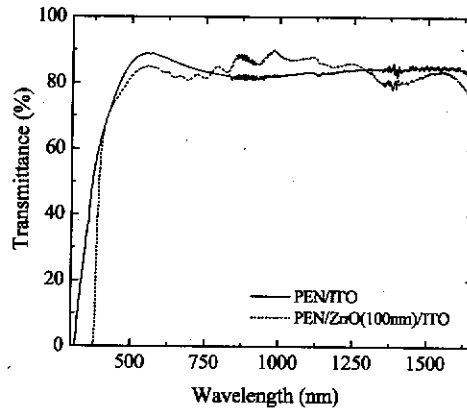


Figure 5. Optical transmittance versus wavelength for IZO films produced at room temperature.

Usually the conductivity could be improved by increasing the carrier concentration or the mobility. Nevertheless by increasing the carrier concentration we start to loose transmittance near the infra red region due to the plasma frequency [6]. The only way to increase the electrical properties preserving the optical ones is by reducing the scattering of electrons. This is what was done in this work. As we can see at figure 5 the optical properties were not affecting by the insertion of the ZnO buffer layer, while the electrical ones were improved by more than two orders of magnitude.

For comparison purposes we present in Table I the electrical properties for the same ITO film deposited onto soda lime glass. The results clearly show that the electrical resistivity of the ITO

film was improved on the PEN substrate with the ZnO buffer layer. Nevertheless, the optimum values for the electrical properties of ITO deposited onto soda lime glass were not yet reached. The main reason is related to the lower value obtained for the Hall mobility. In opposition to glass substrates, the polymers have a low thermal resistance, weak mechanical properties and a high thermal expansion coefficient ($20 \times 10^{-6}/K$ [7]). The different values of the thermal expansion coefficient of the polymer and that of oxide semiconductors induce defects (for example residual thermal micro-stresses) and consequently deteriorate (mainly) the electrical properties of the conducting film. Nevertheless the films were physically stable and present very good adherence to the polymer substrates. No crack or peel off of the films was observed after deposition.

Table I. Electrical properties exhibited by the ITO thin film deposited on different substrates with an average thickness of 190 nm.

Sample	$\rho_s (\Omega/sq)$	$\rho (\Omega cm)$	$\mu_H (cm^2/Vs)$	$n (cm^{-3})$
ITO/PEN	2400	4.5×10^{-1}	0.4	3.6×10^{19}
ITO/ZnO/PEN	161	3.0×10^{-3}	10.0	2.0×10^{20}
ITO/glass	49	5.9×10^{-4}	25.9	4.0×10^{20}

CONCLUSIONS

Finally, we can conclude that the electrical properties of ITO thin films deposited by radio-frequency plasma enhanced reactive thermal evaporation at room temperature on PEN substrates, could be improved by more than two orders of magnitude by using a ZnO buffer layer produced by rf magnetron sputtering at room temperature, with a thickness of 100 nm. Concerning the optical transmittance no effect was observed, keeping both films an average transmittance of the order of 80%. The obtained results are in accordance with the specifications required for TCO coated flexible substrates having potential applications in high resolution flat panel displays.

ACKNOWLEDGEMENTS

The authors would like to acknowledge A. Lopes for the SEM analysis. This work is partially financed by the Portuguese Science Foundation (FCT-MCES) through the POCTI projects: ESE/35578, CTM/35440 and CTM/38924. One of the authors (EF) gratefully acknowledges the grant from Fundação Luso Americana.

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