Comparison of RF and Pulsed Magnetron Sputtering for the Deposition of AZO Thin Films on PET

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1. Introduction

Films of Transparent Conducting Oxide (TCO) have been used, amongst others, as transparent electrodes, in photovoltaic cells, light-emitting films, and intelligent windows[1-4]. Nowadays, the most used TCO is Indium Tin Oxide (ITO). This material, however, is expensive to produce owing to the relatively low abundance of In in the Earth’s crust. Moreover, In is a toxic element, which restricts its use in the usual plasma processes used to produce electronic devices.

Consequently, alternative TCOs are being sought that could substitute ITO, especially in technologies that require large quantities of material, for example, in photovoltaic cells. Thus, zinc oxide doped with Al (AZO) is a promising TCO because of its distinct characteristics, such as being a naturally abundant, non-toxic, element, with a low production cost, and being compatible with chemical and physical processing for the production of opto-electronic devices. Regarding its electrical properties, new forms of synthesis have been studied to obtain AZO films as conductive as ITO, while maintaining its optical transparency above 80% in the visible region.

Recently, the use of polymeric substrates for the fabrication of light-emitting devices[5] and even of photovoltaic cells[6] has been consolidating scientifically and industrially. Diverse flexible polymers, such as polyamide, have been studied as substrates for the fabrication of opto-electronic devices. Polyethylene Terephthalate (PET) has received considerable attention for several reasons. First, compared to polyamide (PI), PET has greater optical transparency and mechanical resistance, and lower fabrication cost. Second, PET recycled from food packaging may be used, further reducing the production cost and contributing to environmental preservation.

Diverse methods such as sol-gel, thermal vaporization, PLD and magnetron sputtering have been employed to synthesize TCOs. In these deposition methods[7-8], desired resistivities were observed for TCOs, but required the use of temperatures greater than RT (room temperature). Owing to the degradation of the polymeric matrix above the melting point (for example, 80°C for PET and 250°C for polyamide), or by collisions with energetic species, however, there are some limitations on the choice of synthesis parameters of TCO. Thus, the synthesis of TCO films on polymeric substrates requires process parameters that do not degrade the substrate, allow good adhesion, generate little film/substrate stress, and yet maintain the desired optical and electrical properties[9-13].

In this context, magnetron sputtering, in addition to excellent reproducibility and low production cost in large scale, also allows the synthesis of thin films while maintaining the substrate at room temperature[14-16]. Even in this case, however, the deposition parameters must be finely adjusted to obtain a transparent, electrically conducting film, well-adhered to the substrate. As observed in several studies[17-19], devices containing TCO films combined with flexible substrates can be obtained by exploiting the advantages of sputtering already mentioned.

According to Shen et al.[10] and Koidis et al.[20], AZO/PET films present an electrical resistivity of $10^{-3}$ Ωcm when using higher plasma powers. However, there was a reduction in optical transparency caused mainly by the breaking of chemical bonds of the PET produced by the collision of energetic particles produced in the plasma. Other important aspects are the production of cracks and low adhesion to the...
substrate. Cracks may be generated by factors such as high deposition rates or collisions with energetic particles during the deposition as well as mechanical stress or morphological structures of the deposited film. In turn, according to Fortunato et al., cracks cause a reduction in the electrical conductivity of the TCO film.

For these reasons, the power applied to the plasma and the type of power supply are crucial factors for the successful deposition of AZO on polymeric substrates or organic devices by magnetron sputtering. Indeed, Lin et al. reported that the electrical resistivity of ITO/PES films remained at 1x10⁴ Ωcm even at low deposition powers when using a pulsed supply. The same behavior does not occur with films produced using a RF supply.

Hence this work compares the synthesis of AZO films on PET by magnetron sputtering at room temperature, using a RF supply (13.56 MHz) and a pulsed supply of frequency 15 kHz (PMS). In addition, the formation of cracks and the electrical stability with ageing were assessed for AZO films of different thicknesses deposited on PET.

Several TCO’s require high deposition temperatures, which makes their application onto polymeric substrates unfeasible. The results of the present study could help solve this problem. Deposition on polymeric substrates could expand the possibilities of new technologies such as Flexible Electronic Devices (FEDs), organic photovoltaics, organic light-emitting diodes, etc. Also, it could facilitate the production and optimize the cost on an industrial scale by using roll-to-roll manufacturing methods.

2. Experimental

Rectangular PET substrates, 35 mm x 25 mm, and 0.1 mm thickness were used. For 10 min. for each stage, substrates were cleaned in an ultrasonic bath of distilled water, and then washed in isopropanol. A conductive AZO (ZnO with 2 wt.% of Al₂O₃, 99.9%) target of 3 inches diameter was used. Film deposition was undertaken using RF (13.56 MHz) and a pulsed supply (15 kHz). The target-sample distance (d₁,₅) was 4 and 5 cm. In both cases, the argon pressure was fixed at 3 mTorr and the power maintained at 60 W for 30 min.

The thickness of the AZO/PET films was measured using a DEKTAK 150 profilometer. Electrical properties were determined using the linear four-point method. The optical transmittance and electrical resistivity of the samples studied.

| Sample | Supply  | d₁,₅ (cm) | t (nm) | T (%) | ρ (mΩ·cm) |
|--------|---------|-----------|-------|-------|-----------|
| A1     | RF      | 5         | 260   | 80    | 38        |
| A2     | RF      | 4         | 272   | 80    | 17        |
| B1     | PMS     | 5         | 193   | 81    | 7.0       |
| B2     | PMS     | 4         | 250   | 83    | 2.5       |

Figure 1. Optical transmittance and reflectance spectra of the PET substrate and the AZO/PET films described in Table 1. Above 1250 nm, the transmittance spectra exhibit a

3. Results and Discussion

Table 1 presents the thickness, mean optical transmittance in the 400 to 700 nm wavelength range and electrical resistivity of the AZO/PET films as a function of the type of supply (RF and PMS) and different target-substrate distances. The optical transmittance of the AZO/PET was greater than 80%, independent of the deposition parameters. Film electrical resistivity was around 10⁻² Ωcm with the RF supply and 10⁻¹ Ωcm with PMS. The decrease in resistivity obtained using a PMS power supply is caused by the absence of cracks (that is revealed by SEM) and to the high concentration of carbon (as revealed by EDS) compared to that of films deposited using RF. In addition, the electrical resistivity increased as the target-substrate distance increased from 4 cm to 5 cm.

Figure 1 shows the transmittance and reflectance spectra of the PET substrate and the AZO/PET films described in Table 1. Above 1250 nm, the transmittance spectra exhibit a
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Below 370 nm there is absorption owing to interband transitions in AZO. In the visible region, the transmittance remains ~80%, while the optical reflectance is around 15%. Interference fringes are present. Compared with the PET spectra, note that AZO is almost transparent in this region of the spectrum. These films have greater transmittances than similar films on polymeric substrates reported in the literature.4,10,27

**Figure 2.** X-ray diffractogram of bulk ZnO bulk and of the AZO films deposited on PET. The arrows indicate the DRX peaks of the PET substrate and the (002) and (103) planes of the AZO films.

**Figure 3.** Micrographs (obtained by SEM) of AZO/PET films deposited by RF and PMS, with target-substrate distances of 5 and 4 cm. For the films deposited using RF, the presence of cracks is evident, which affects the adhesion to the substrate and the electrical conductivity of the AZO film.
measurements were made. The 001 and 002 positions are above cracks, while position 003 is above a homogeneous region of the film.

Figure 4b shows that the 001 and 002 positions exhibit a high carbon concentration, which derives from the PET substrate. This shows that in the cracks, the film is completely separate, revealing the polymeric substrate and causing an increase in the electrical resistance of the AZO film.

At the 003 position, only Zn, Al and O are revealed, which are characteristic of the AZO. Furthermore, the composition of the AZO film is compatible with the EDS values (at.%) for the ceramic target: Zn=55.0, Al=1.7 and O=43.3. There are slight increases in the concentrations of O and Al, which are consistent with their greater bond energies.

Such results also indicate that EDS measurements may be used to quantify the presence of cracks, via de C concentration. For this, EDS area analyses were carried out with an electron beam over a typical area of 1 mm x 1 mm. The data obtained are shown in Table 3. From Figure 4, the C concentration represents an estimate of the crack density (more precisely the area of the exposed substrate) along the AZO film.

The films synthesized by PMS present a much lower density of cracks than films produced using RF. Indeed, the EDS data indicate that sample B2 is free of cracks. Moreover, this film has an optical transmittance of 83%, an electrical resistivity of $2.5 \times 10^{-3} \, \Omega \text{cm}$, and the lowest estimated residual tension ($-0.48$). Thus it may be concluded that the PMS synthesis at a target-substrate distance of 4 cm produced superior AZO/PET films both in electrical properties and in film/substrate adhesion.

Our result shows an advance in comparison with those presented by Tsay and Pai who found a resistivity of $3.7 \times 10^{-2} \, \Omega \text{cm}$ using a deposition temperature of 135°C.

To investigate the stability of the films upon ageing, films were deposited using PMS under the same conditions as those used for sample B2 ($P=60W$, $d_{TS}=4cm$ at room temperature) for deposition times of 5 min (B3) and 30 min (B4). The film thicknesses, measured using profilometry, were 51±3 nm and 200±10 nm, respectively. Figure 5 represents the optical transmittance and reflectance spectra.
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Table 3. EDS area measurements over an area of 1 mm x 1mm of the AZO/PET films. From Figure 4, the C concentration represents an estimate of the density of cracks along the AZO film.

| Sample | C   | O   | Al  | Zn  |
|--------|-----|-----|-----|-----|
| A1     | 10.9| 42.6| 1.4 | 46.2|
| A2     | 22.8| 38.9| 1.2 | 43.8|
| B1     | 2.2 | 44  | 1.5 | 52.3|
| B2     | 0   | 44.9| 1.6 | 52.4|

4. Conclusions

This study compared AZO/PET films deposited by magnetron sputtering at ambient temperature, using different plasma power supplies: RF (13.56 MHz) and pulsed at a frequency of 15 kHz (PMS). In addition, the formation of cracks was evaluated together with the electrical stability with ageing.

All of the AZO/PET samples present optical transmittances greater than 80% in the visible region. Morphological analysis revealed that all the films are polycrystalline and exhibit a wurtzite structure with preferential growth in the crystallographic direction of the (002) plane. The films produced using RF, however, show greater residual tensions, which contribute to the formation of cracks in the AZO film.

A greater density of cracks was observed for the AZO films deposited by PMS. Regarding the electrical resistivity, the AZO films synthesized by RF possess values above $1.0 \times 10^{-2} \text{Ωcm}$, while the films produced using PMS have values of about $1.0 \times 10^{-3} \text{Ωcm}$.

Finally, the film that gave the best performance was that deposited at a target-substrate distance of 4 cm, using the PMS source, for 30 min. Under this condition the film had a resistivity of $1.0 \times 10^{-3} \text{Ωcm}$, a transmittance of ~83%, presented no cracks and exhibited good stability in its properties upon ageing.

Therefore, PMS shows itself to be more adequate for the production of AZO films on PET, with potential application in the fabrication of cheap, flexible opto-electronic devices.

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6. References

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