Structural and electrical properties of Al doped ZnO thin films deposited at room temperature on poly(vinilidene fluoride) substrates

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Abstract.

Transparent, conducting, Al-doped ZnO films have been deposited, by dc and pulsed dc magnetron sputtering, on glass and electroactive polymer (poly (vinylidene fluoride)-PVDF) substrates. Samples have been prepared at room temperature varying the argon sputtering pressure, after optimizing other processing conditions. All ZnO:Al films are polycrystalline and preferentially oriented along the [002] axis. Electrical resistivity around $3.3x10^{-3}$ Ω.cm and optical transmittance of ~85% at 550 nm have been obtained for AZOY films deposited on glass, while a resistivity of $1.7x10^{-2}$ Ω.cm and transmittance of ~70% at 550 nm have been attained in similar coatings on PVDF. One of the main parameters affecting film resistivity seems to be the roughness of the substrate.

Introduction

Thin films of transparent conductive oxides (TCO) deposited by several techniques have a broad range of applications in optoelectronics, piezoelectric transducers and gas sensors, amongst others. For this reason TCO coatings have been the target of exhaustive studies [1-5] for the past decade. ZnO thin films doped with Al, Ga or In have low electrical resistivity and high optical transmittance [4-7] and have been used as an alternative to ITO (indium tin oxide), the most commonly studied TCO material, yet more expensive and much less abundant.

This work reports on the deposition and characterisation of transparent conducting oxide films on electroactive polymers, in order to develop applications such as flexible touch screens and keyboards. The main role of TCO films in such applications is the reading of the electrical signals generated by the electroactive polymer, though keeping the transparency of the piezoactive ensemble. The electroactive polymer used as substrate for this investigation is poly(vinilidene fluoride), (PVDF). The electroactive properties of the polymer suffer some degradation at

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temperatures higher than 70ºC, which requests the deposition of the TCO films at room temperature.

Experimental Details

ZnO:Al films have been deposited under a mixed Ar/O_2 atmosphere with a base pressure of $2x10^{-4}$ Pa. From a 10 cm diameter AZOY target, which contains a very small amount of Y_2O_3 in addition to ZnO and Al_2O_3 (2 at %), dc and pulsed dc magnetron sputtering have been used to produce the films. Glass and PVDF (28 μm thick), have been used as substrates. A target current of 0.2 A has been used during depositions, which corresponds to a current density of 2.5 mA cm^{-2}. The target-to-substrate distance was kept constant at 8 cm in all runs and the substrate was not heated. In case of pulsed magnetron sputtering, a frequency of 140 kHz and a duty cycle of 0.7 has been employed. The duty cycle of the power supply was optimised in the range of 0.25 to 0.7 to achieve the best transport properties. X-ray diffraction (XRD) has been used to examine the crystallinity and crystal orientation using Cu K_α radiation. (Philips PW 1710 apparatus). Spectral transmittance of the films has been measured by UV-Vis-NIR Spectrophotometer (Shimadzu UV 3101 PC) in the spectral range from 200 nm to 900 nm. These results have also been used to calculate the thickness of the coatings using the Swanepoel method [8].

The roughness of the samples has been evaluated using an Atomic Force Microscope (AFM) - multimode SPM of Digital Instruments. Electrical resistivity, carrier concentration and Hall mobility in the coatings on glass substrate have been measured using the Van der Pawn geometry, under a magnetic field of 1 T. In the films over PVDF substrates, two aluminium contacts (8 mm x 2 mm) separated by 1 mm have been deposited in order to measure the sheet resistance Agilent 34401A digital multimeter.

Results and Discussion

Deposition Rate

In order to study the effect of the working pressure and to measure the deposition rate, several films have been deposited on glass, by varying only the Ar flow. Two series of coatings have been deposited: in one series the target has been dc powered and in the other a dc pulsed power has been used. In both series, a current of 0.2 A has been applied to the target. The deposition rate, as a function of the working pressure, is displayed in Fig.1, for both film series. A similar behaviour has been found on both cases. Deposition rate has ranged from 76 nm/min, at a working pressure of 0.14 Pa, to 29 nm/min, at 0.36 Pa. An increase of the working pressure decreases the mean free path of the sputtered atoms leading to a decrease of the number of atoms reaching the substrate, which in turn reduces the deposition rate.

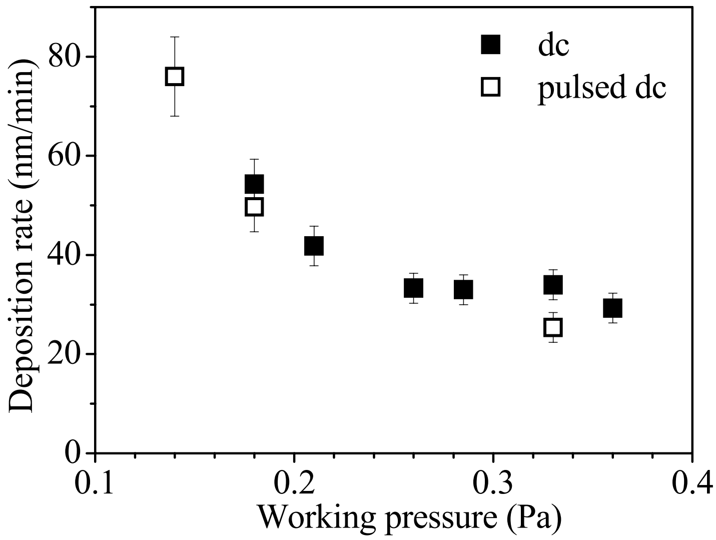

Fig. 1 – Deposition rate as a function of the working pressure for dc powered and pulsed dc powered coating depositions.

The ZnO:Al films are textured, with the c-axis perpendicular to the substrate surface, as evidenced by Fig.2. In this picture, the X-Ray diffraction patterns of ~ 1 μm-thick films prepared under working pressures of 0.21, 0.26 and 0.36 Pa are displayed. The intensity of the (002) diffraction peak increases with the working pressure and a shifts to higher angles, from 33.95º to 34.16º. A similar behaviour has already been observed previously [9, 10]. The intensity increase

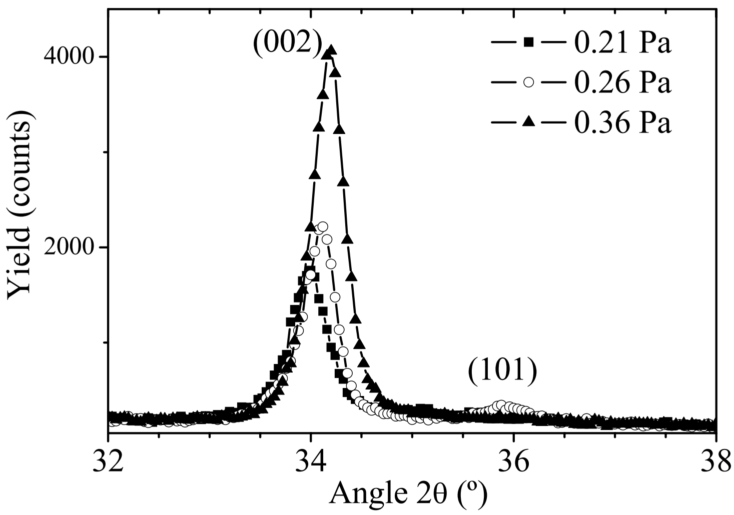

Fig. 2 – XRD pattern of samples prepared under different working pressure.

associated with a slight decrease of peak width indicates an improvement of the crystallographic quality of the final film with increasing working pressure. The peak shift should be related to the decrease of the residual stress within the film. At low pressure a higher bombardment of the growing film with energetic particles may induce crystallographic defects, creating residual stress.

Higher argon pressure leads to lower mean free path of impinging particles, which reduces their energy when they impinge the growing film. The average crystallite size has been estimated by means of Fourier analysis [11] and ranged from 16 to 22 nm as the working pressure increased from 0.21 to 0.36 Pa.

Electrical resistivity and optical transmittance of films deposited on glass

The balance between UV-visible transmittance and electrical resistivity of the films has been tentatively optimised varying the polarization and working pressure. Fig. 3 exhibits the visible optical transmittance of two representative AZOY coatings deposited both on glass and on PVDF. For comparison the optical transmittance of the substrates -glass and PVDF- are also depicted. The lower transparency of PVDF relatively to the glass one (except for low wavelengths as glass absorbs radiation under λ <~300 nm, PVDF only absorbs under λ <250 nm), is maintained in the samples with AZOY coatings. A set of dc tension values, from -80 V to 0 V, have tentatively been applied to the substrate as a form of bias polarization. To promote the grain growth and crystallinity of the final films, a small negative bias of -30 V/-40 V has finally been chosen to be applied to the substrate since it favours the low-energy-ion bombardment during the film formation and avoids high residual stress.

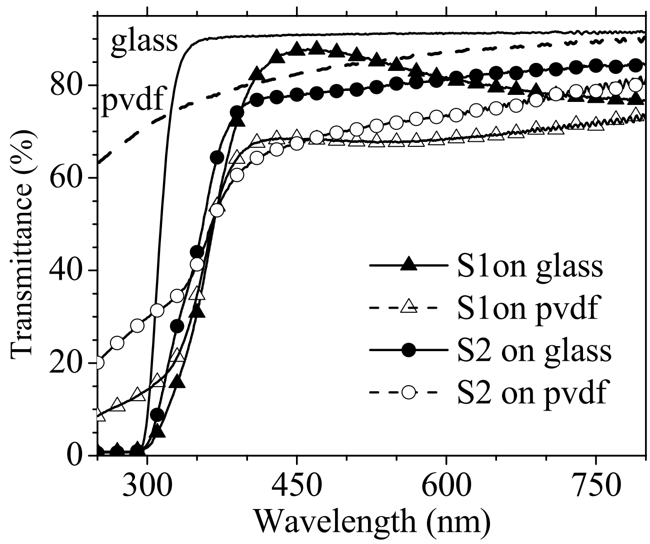

Fig. 3 – Optical transmittance as a function of the wavelength, sampling the substrates - glass and PVDF - and two representative AZOY coatings deposited on both glass and PVDF substrates.

Two sets of sub-conditions have then been prepared: either dc power supply plus dc bias (-30 V) or dc pulsed power supply (140 kHz/0.7 duty cycle) plus dc pulsed bias (-40 V/90 kHz). The results obtained for the optical transmittance at 550 nm and the electrical resistivity are shown in Fig. 4 as a function of the Ar/working pressure. The parameter leading to the best balanced transmittance-resistivity has been a working pressure of ~0.33 Pa, using dc power/dc substrate bias. The decrease

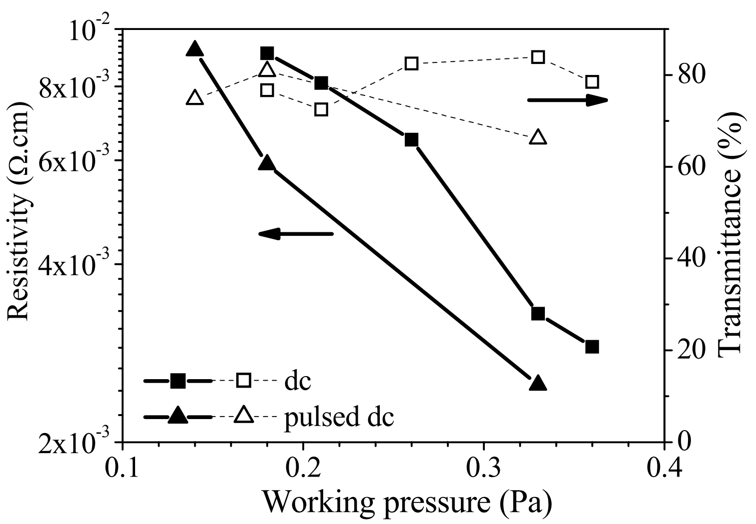

Fig. 4 – Evolution of the resistivity (solid symbols) and average transmittance at 550 nm (open symbols) of AZOY coatings on glass as a function of the working pressure, using either dc powered or pulsed dc powered magnetron.

of the electrical resistivity with increasing working pressure follows the crystallographic quality improvement discussed in the previous paragraph. A similar dependence -a slight decrease of resistivity with increasing working pressure (for pressures below ~0.3 Pa)- has already been reported previously [12, 13]. However, for higher pressure values it was observed a strong increase of electrical resistivity, the threshold being in the range 0.2 Pa – 0.4 Pa, depending on other deposition parameters. As expected, these films present n-type conduction, as deduced from Hall-effect measurements. The charge carrier concentration and Hall mobility have also been calculated and are shown in Fig. 5. Again, the pulsed-dc-power/pulsed-dc-substrate-bias deposition condition does not seem to bring great advantage to the final relation between these characteristics and the

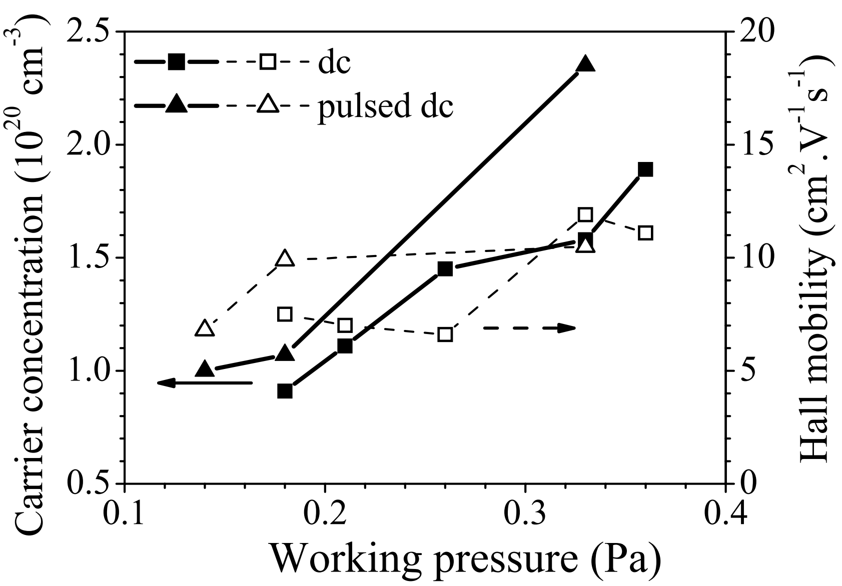

Fig. 5 – Evolution of the carrier concentration (solid symbols) and Hall mobility (open symbols) of AZOY coatings on glass as a function of the working pressure, using dc powered and pulsed dc powered magnetron.

working pressure: although in these samples the carrier concentration increases faster with the deposition working pressure, their Hall mobility does not step by. Again, the increase of carrier mobility follows the crystallographic quality improvement. The increase in carrier density can be related to a slight decrease of oxygen content in the film (not measured) and/or to the amount of Al atoms in the crystalline regions. In fact samples prepared introducing oxygen in the working atmosphere always display an increase of the resistivity. Once again, better performing ZnO final coatings seem to have been produced under a working pressure of ~0.33 Pa with dc power and substrate bias.

Electrical resistivity and optical transmittance of films deposited on PVDF

Excluding the sensitive working pressure, the deposition conditions that have led to the best balance between transmittance and electrical resistivity, carrier concentration and mobility, have thus been used hence forth as standard for all deposition on the polymeric substrate PVDF. Therefore, AZOY films have been deposited on PVDF under working pressures ranging from 0.23 to 0.39 Pa. Under 0.33 Pa, coatings of different thicknesses have been deposited. Resulting data are depicted in Fig. 6 where electrical resistivity and the optical transmittance at λ = 550 nm are shown as function of the working pressure used during deposition (a) and of the ZnO film thickness (b). According to previous results (showed in Fig. 1), in this range of working pressures the deposition rate is almost constant. The thickness of all the samples, whose results are depicted in Fig. 6a, is about 68 nm. No considerable differences have been obtained among the XRD patterns from these samples (not shown here), where only the (002) peak of ZnO, located at $2\theta \sim 34.2^{\circ}$, appears with lower intensity. These AZOY films deposited on PVDF exhibit electric and optical performances significantly worse than those deposited on glass substrates. The increase in working pressure resulted in higher resistivity, which is in opposition to the behaviour obtained on films deposited on glass. It has also been observed that the resistivity has been affected by the number of PVDF substrates present in the substrate holder during deposition, which indicates that the main reason for this behaviour may be the polymer degasification.

The optical transmittance of these coatings is usually 10% to 20% lower than that of those coatings deposited on glass, as already shown in Fig. 3. This reduction relatively to the glass-substrate films is not entirely due to the lower substrate transmittance of PVDF in relation to glass. There is strong evidence that the substrate surface plays an important role in this behaviour.

As shown in Fig. 6b, the film thickness has influence on both resistivity and transmittance. Increasing film thickness yields a reduction in the film resistivity. This phenomenon is associated

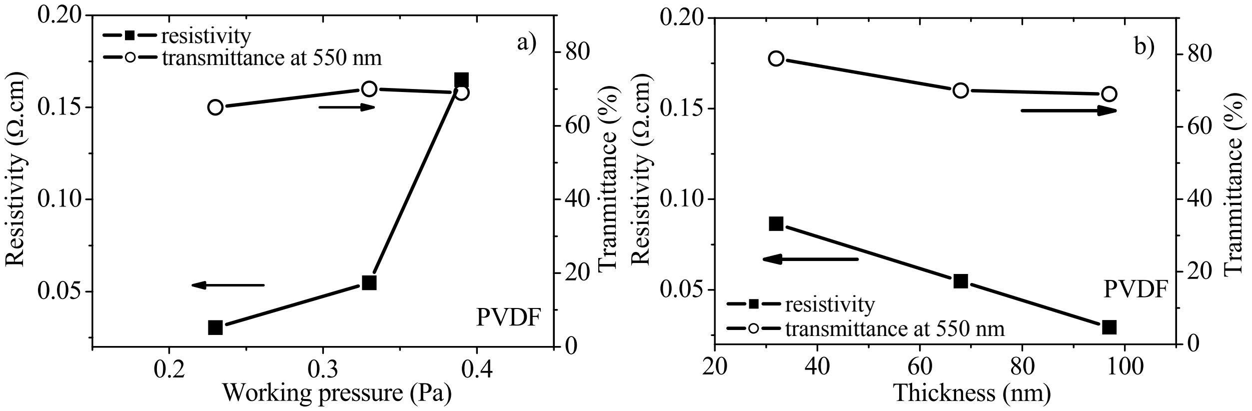

Fig. 6 – Electrical resistivity (■) and average optical transmittance at 550 nm (○) of AZOY coatings on PVDF as a function of the: a) working pressure and b) film thickness.

with the crystallinity improvement as thickness increases, the concomitant increase of carrier mobility [12] and with the increase of film thickness itself. As reported by other authors, the resistivity of thin films is affected by surface roughness of the substrate, since the high roughness of the substrate leads to a non uniform morphology of the film [14]. Likewise, high surface roughness increases the multiple reflections, leading to a reduction of the overall transmittance. Results from AFM (see Fig. 7) lead us to conclude that the relatively low transmittance of PVDF-based films is mostly due to the high value of the diffuse reflective on PVDF rough surface. In fact, the high surface roughness of PVDF substrates (28 μm thick) is intrinsic to its processing method. In order to improve its electroactive properties, PVDF substrate is usually stretched, which results in an average rms roughness of about 20 nm. PVD technique replicates the surface topography, which means that the roughness of the films is usually higher than that of the substrate. Fig. 7 shows a representative AFM image of two AZOY films with same thickness (68 nm) that have been

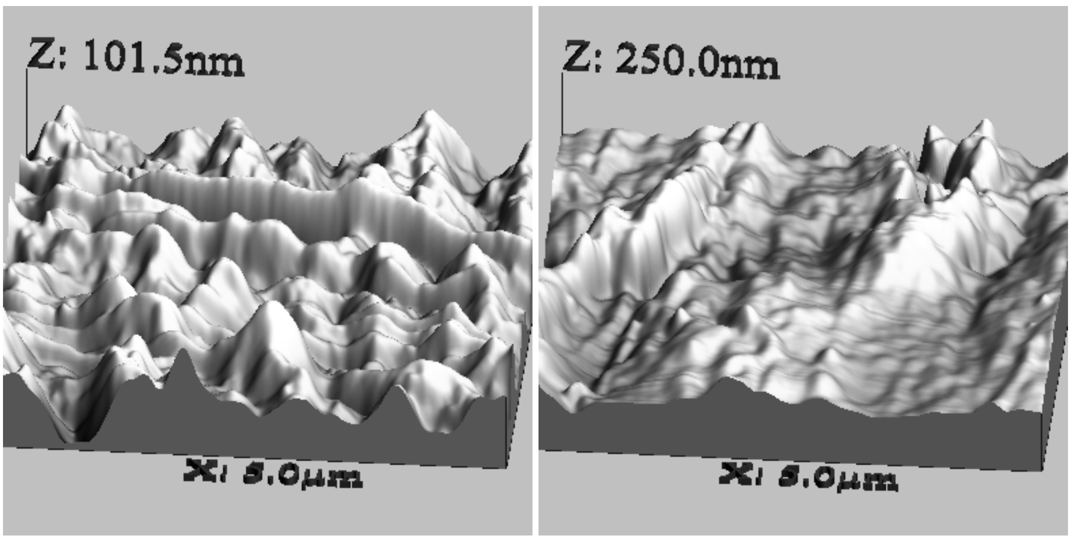

Fig. 7 - AFM images of two AZOY films with the same thickness (68 nm) on PVDF substrates prepared under different working pressure: a) 0.23 Pa and b) 0.33 Pa.

prepared under working pressures of 0.33 Pa (a) and 0.23 Pa (b), which revealed rms roughness of 23 and 19 nm, respectively. A roughness of about 0.2 nm was measured with the glass substrates, and the roughness of the AZOY coatings deposited on glass was lower than 1.5 nm.

Summary

AZOY thin films have been prepared at room temperature on glass and PVDF substrates. Increasing working pressure, the crystallographic quality of the AZOY films deposited on glass increases. The improvement structural quality led to a decrease of electrical resistivity Resistivity, as low as $3.3x10^{-3}$ Ω.cm and transmittance of ~85% at 550 nm have been obtained in AZOY films on glass. However, the performance of similar coatings deposited on PVDF is weaker than those deposited on glass. The optical transmittance of these coatings on PVDF is usually 10% to 20% lower than that of related coatings on glass. Resistivity is also significantly higher. A resistivity of $1.7x10^{-2}$ Ω.cm and transmittance of ~70% at 550 nm has been obtained on AZOY coatings deposited on PVDF. The former fact is mainly ascribed to increased substrate roughness.

Acknowledgements

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