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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 3.3×10^{-3} Ω cm and optical transmittance of ~85% at 550 nm have been obtained for AZOY films deposited on glass, while a resistivity of 1.7×10^{-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.

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

2. Experimental details

ZnO:Al films have been deposited under a mixed Ar/O_2 atmosphere with a base pressure of 2×10^{-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×2 mm) separated by 1 mm have been deposited in order to measure the sheet resistance using an Agilent 34401A digital multimeter.

3. Results and discussion

3.1. 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

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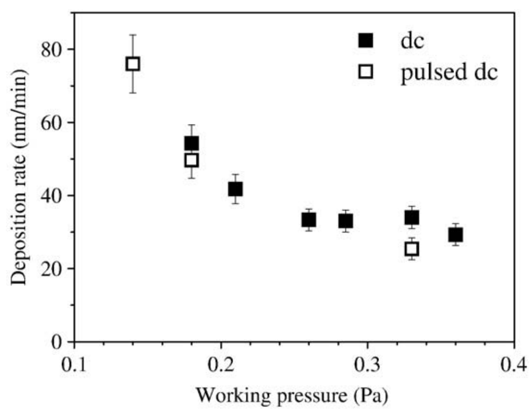

Fig. 1. Deposition rate as a function of the working pressure for dc powered and pulsed dc powered coating depositions.

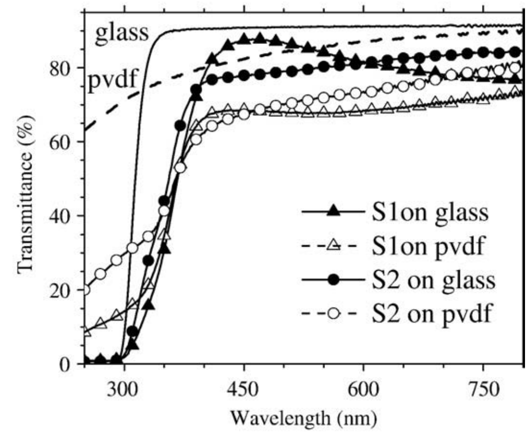

Fig. 3. Optical transmittance as a function of the wavelength, sampling the substrates – glass and PVDF – and two representative AZOY coatings deposited on both glass and PVDF substrates.

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.

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 33.95° to 34.16°. A similar behaviour has already been observed previously [9,10]. The intensity increase 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.

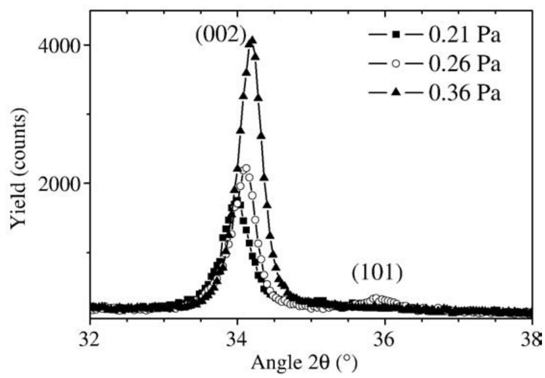

Fig. 2. XRD pattern of samples prepared under different working pressure.

3.2. 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 $\lambda<\sim300$ nm, PVDF only absorbs under $\lambda<250$ 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.

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 of the electrical resistivity with increasing

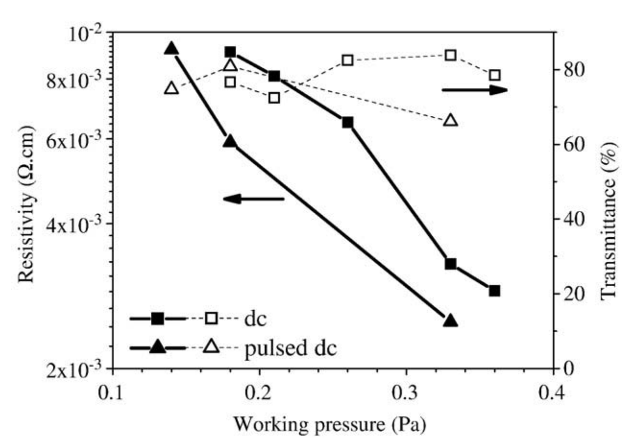

Fig. 4. Evolution of the resistivity (solid symbols) and average transmittance at 550 nm (open symbols) of AZOY coatings on glass as a function of the working pressure, using either dc powered or pulsed dc powered magnetron.