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Radio frequency sputter deposition of high-quality conductive and transparent ZnO: Al films on polymer substrates for thin film solar cells applications

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A R T I C L E I N F O

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A B S T R A C T

Thick aluminum-doped zinc oxide films were deposited at substrate temperatures from 100 °C to room temperature on polyethylene terephthalate by radio frequency magnetron sputtering, varying the deposition parameters such as radio frequency power and working pressure.
Structural, optical and electrical properties were analyzed using an x-ray diffractometer, a spectrophotometer and a four-point probe, respectively. Films were polycrystalline showing a strong preferred *c*-axis orientation (002). The best optical and electrical results were achieved using a substrate temperature of 100 °C. Furthermore, high transmittances close to 80% in the visible wavelength range were obtained for those films deposited at the lowest Argon pressure used of 0.2 Pa. In addition, resistivities as low as 1.1×10^{-3} Ω cm were reached deposited at a RF power of 75 W. Finally, a comparison of the properties of the films deposited on polymer and glass substrates was performed, obtaining values of the figure of merit for the films on polymer comparable to those obtained on glass substrates, 17,700 Ω^{-1} cm^{-1} vs 14,900 Ω^{-1} cm^{-1}, respectively.

1. Introduction

The greatly increasing use of transparent-conductive oxides (TCOs) for large area electronic applications such as solar cells and displays has promoted the study of the development of inexpensive materials that show appropriate properties [1]. In this regards, Al-doped ZnO (AZO) films have attractive much attention because of their comparable high optical transmittance and low electrical resistivity with respect to other TCOs widely used such as Tin-doped Indium Oxide (ITO) films [2]. Although probably ITO is the most successful TCO because of its optical and electronic properties, the cost for its production is very high due to the limited supply of Indium [3,4]. For this reason, AZO can be considered as a very promising candidate especially because of its low cost and wide availability of its constituent raw materials.

Many techniques have been employed in the deposition of AZO films, being the most commonly used radio frequency (RF) magnetron sputtering [5–8]. This technique is considered to be one of the most favourable deposition methods due to its high reproducibility. Besides, it permits to deposit at low temperature, leading to smooth films with a good surface uniformity. The most important sputtering parameters that should be controlled in order to achieve the films with the desired properties are the distance between the target and the substrate, the substrate temperature, the RF power, and finally the working pressure.

Nowadays, there is an increasing interest in reducing the substrate temperature for many applications in order to minimize the interdiffusion processes on previously deposited materials. Additionally, the use of flexible substrates such as plastic polymers replacing the conventional glass substrates becomes of great interest in the photovoltaic field as they contribute to cost reduction in the production processes [9]. However, the deposition on these polymer substrates presents certain challenges because of the considerably low deposition temperature needed and the rougher surfaces that they show in comparison with the glass substrates. This is because a low temperature process is not favourable to deposit high-quality AZO films required for the different solar applications. Hence, it is to know that substrate temperatures as high as 300 °C enhance the AZO thin film properties, and below it, a worsening of the electrical and optical properties is obtained [10–12]. On the other hand, due to a rough surface that may affect the electrical conductivity of the films by carrier scattering, the films deposited on the polymer substrate are more resistive than those deposited on glass.

In order to optimize the sputtering conditions of the AZO films deposited on flexible substrates, it has to be taken into account that the particles with too much energy reaching the surface of the substrate deform it due to the poor heat endurance that this substrate shows. This fact should be considered because this substrate deformation could result in a degradation of the film properties. Taking later into account, the sputter deposition of AZO films on flexible substrates should be performed at low temperature, being necessary a damage-less deposition to obtain films with low resistivity. Thus, the optimization of AZO films at

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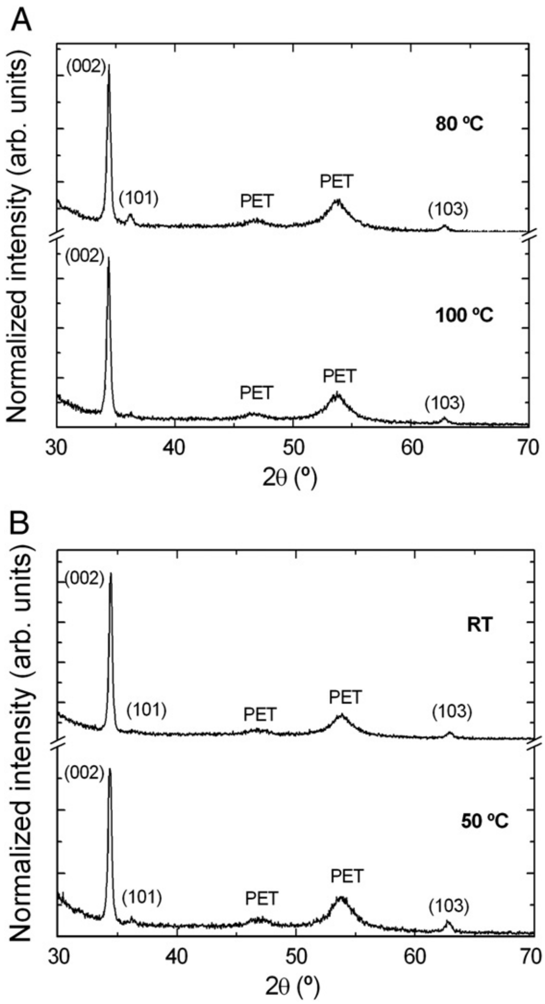

Fig. 1. XRD diffraction patterns of the AZO films deposited at 75 W and 0.67 Pa (5 mTorr) on the polymeric substrate at different temperatures (from RT to 100 °C).

low temperature is needed to develop efficient devices on flexible substrates.

In this study, we present the results concerning the optimization of the structural, optical and electrical properties of the AZO films deposited on polyethylene terephthalate (PET). The optimization process was performed varying the sputtering parameters, such as RF power and working pressure, in order to achieve the highest transparent and conducting films at a moderate substrate temperature from 100 °C to room temperature (RT). Besides, in order to analyze the feasibility of these films on PET, they were compared to AZO films with the same thickness deposited on glass substrates.

2. Experimental procedures

AZO thin films were deposited on Corning glass 7059 and PET substrates in a commercial MVSystem magnetron sputtering. In this system, there is only one cathode vertically adjustable operating by RF power, with a 3 in. diameter ceramic target ($ZnO:Al_2O_3$, 98%:2% wt). The stainless steel heater consists of two ring heating elements located on the substrate at around 5 cm, being the warming by radiation, and the control of the temperature is performed by a type K reference thermocouple. This thermocouple is mechanically placed in contact with the substrate. In all cases, the substrates were heated to the chosen temperature (100 °C) during 1 h before the deposition to guarantee the stability of the temperature and the reproducibility of the experiments.

The substrates used, both with dimensions of 10×10 cm^2, had standard thicknesses of 0.25 mm, in the case of PET, and 0.95 mm, for the glass. Before leading the substrates in the sputtering chamber, they were ultrasonically cleaned by using acetone, methanol and deionized water (D.I.W.), and then, dried by blowing nitrogen over them.

The target to substrate distance was kept at 99 mm and the base pressure was 2.7×10^{-5} Pa. The flow rate of the Argon was controlled by mass flow controller (MFC) from 30 sccm to 15 sccm, which corresponds to a working pressure varying from 1.07 Pa to 0.2 Pa, and the sputtering RF power was ranged from 25 W to 125 W.

An X-ray diffractometer (XRD) with CuKα radiation was used to identify the crystalline phase of the films. The optical transmittance and reflectance were measured with a Perkin–Elmer Lambda 950 UV/Visible/NIR spectrophotometer, while the optical parameters of the films such as refractive index and band gap energy were determined from both spectra by a computer program [13,14]. Finally, electrical sheet resistance R_s was determined from the four-point probe method, being the resistivity ρ_s obtained using $\rho_s=R_st$, where t is the film thickness estimated from optical characterization.

3. Results and discussion

3.1. Structural properties

AZO films showed in this work were physically stable and presented very good adherence to the polymeric substrate. In spite of the thickness, in the range of 600–1000 nm, no cracking or peel-off

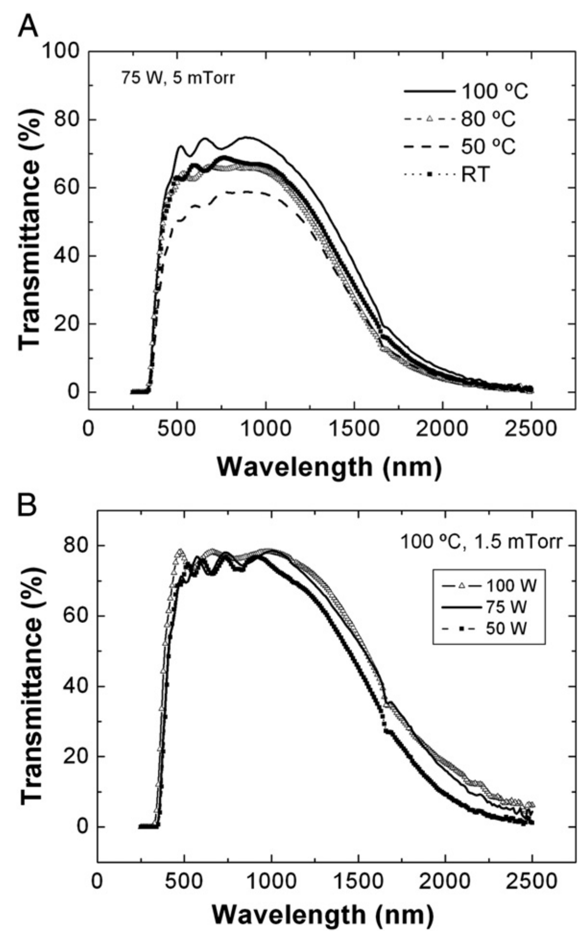

Fig. 2. Optical transmittance of AZO films deposited at (A) 75 W and 0.67 Pa (5 mTorr) on PET at different substrate temperatures, and (B) 100 °C and 0.2 Pa (1.5 mTorr) on PET at different RF powers.