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On the properties of aluminium doped zinc oxide thin films deposited on plastic substrates from ceramic targets

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ABSTRACT

We report on the deposition of Al doped ZnO (AZO) thin films on unheated polyethylene terephthalate (PET) substrates by pulsed laser deposition technique using a UV excimer laser and Al_2O_3:ZnO ceramic targets (1.5 and 2 wt% Al_2O_3). The deposited AZO films have been investigated by atomic force microscopy, scanning electron microscopy, X-ray diffraction, and optical spectrophotometry. Films present excellent optical and electrical properties (transmission in the visible range $T > 85\%$; resistivity at room temperature $\rho = 1.3 \times 10^{-3}\ \Omega$ cm) as electrodes for plastic solar cells. A good correlation was found between deposition conditions (laser fluence) and structural, morphological, optical and electrical properties.

1. Introduction

The new advancements in organic solar cells performance with a certified conversion efficiency of 9.2% achieved in 2012 [1], comparable to commercial amorphous silicon solar cells (8–11%), confirm that plastic solar cells will become one of the future solutions in energy conversion. Besides the increase of efficiency [2–6], other problems to solve are the improvement of devices stability [7–10] and the reduction of fabrication cost. Indium tin oxide (ITO) thin films deposited on rigid glass substrates have been extensively studied [11–15] and are widely used as transparent conducting electrodes in many optoelectronic devices [16–20]. However, the price and the limited resources of indium and the fragility of films deposited on glass indicate that is necessary to look for alternative solutions. Another transparent conducting oxide (TCO) is doped zinc oxide (ZnO). The main advantages of ZnO are that it is a non-toxic, inexpensive, and abundant semiconducting material with wide band gap energy $E_g = 3.3$ eV. During the past years there have been many reports on doping of ZnO with different elements such as Ga, In, Al, F, N, Mg, and Cr [21–26] using various techniques for deposition such as sputtering [27–29], spin coating [30–33], thermal oxidation [34–36], chemical vapor deposition, spray [37–41], and pulsed laser deposition (PLD) [42–58]. Most of these studies are focused on films deposited on fragile substrates such as glass that cannot be deformed easily. For novel technical applications, e.g. in plastic solar cells and plastic electronic devices, the deposition of films on flexible and light-weight substrate materials is required.

The TCO thin films are usually deposited at high substrate temperature (400–550 °C) which is not compatible with plastic substrates. The growth of good quality TCO films at room temperature is difficult and may require adequate deposition techniques. Since now, most of the reports on ZnO films on polymer substrates are dealing with sputter deposition processes and only few papers report on films deposited by PLD [52–56]. The process parameters (laser fluence Φ, gas background, substrate temperature, etc.) can be controlled independently in PLD. This enables to tune the chemical composition and the crystalline texture of films. The deposition rate in PLD is high compared to other vapor deposition techniques. Due to the high kinetic energy of species in the laser-induced plasma plume the films may be crystallized at lower substrate temperature [42,43].

The type of substrate material influences strongly the morphology of deposited films. The roughness of transparent electrodes is an important characteristics in the fabrication of organic solar cells due to short-circuits and/or leakage currents which can rise.

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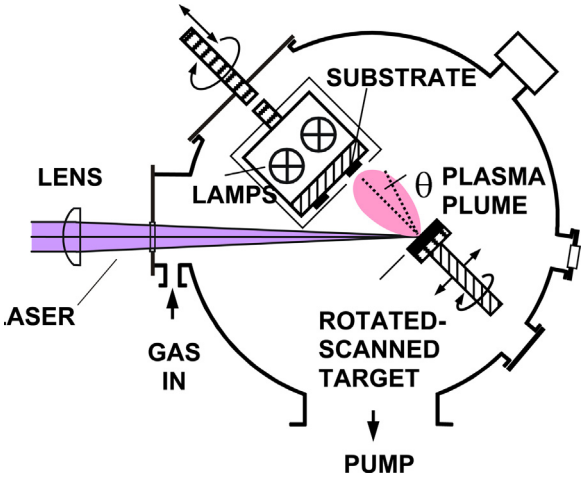

Fig. 1. Pulsed laser deposition setup.

In the present paper we study the structural, morphological, electrical, and optical properties of aluminium doped ZnO films prepared on unheated polyethylene terephthalate (PET) substrates by reactive PLD using ceramic Al doped ZnO targets (1.5 and 2 wt% Al_2O_3). The AZO films on PET are of good quality and it is shown that the optical band gap and the roughness of films can be controlled by the laser fluence employed during deposition.

2. Experimental

The Al doped ZnO thin films were deposited on PET substrates (HIFI PMX739, 175 μm) at room temperature using an KrF excimer laser (wavelength ($_L$ = 248 nm, pulse length (∼ ns). The target–substrate distance was kept at 4 cm and the target was rotated and translated during the deposition. The number of laser pulses was 18,000 for all samples and the pressure of reactive O_2 gas background was 0.05 mbar. Two series of films were deposited using two different ZnO ceramic targets that were doped with 1.5 and 2.0 wt% Al_2O_3. The laser fluence was varied between 1.0 and 3.4 J/cm^2. The experimental set-up is schematically represented in Fig. 1 [58].

The thickness of deposited AZO films was measured by profilometry using a Dektak profilometer. The structural characteristics were studied by Cu Kα (λ = 1.5418 Å) X-ray diffractometry (XRD) and the film surface morphology was determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optical transmittance and reflectance spectra were recorded in the wavelength range 300–1100 nm at room temperature using a Hitachi UV-4001 spectrophotometer. The electrical resistivity at room temperature was measured by the four point method.

3. Results and discussion

The AFM and SEM micrographs of the AZO thin films on PET substrates revealed a strong dependence of film morphology on the deposition parameters. Figs. 2 and 3 show the AFM and SEM pictures for the two series of films that were deposited at various fluences Φ from both targets. The first series of films is obtained using the 98.5 wt% ZnO:1.5 wt% Al_2O_3 target (Fig. 2) and the second series if for films produced from the 98 wt% ZnO:2 wt% Al_2O_3 target (Fig. 3). The AFM and SEM images indicate that the roughness of films and the grain size increase at higher Φ for both types of targets used. The measured thickness of AZO films showed a clear trend to larger values for higher Φ (Table 1). With nanosecond laser pulses of wavelength $\lambda_L < hc/E_g$ the ablation rate increases with increasing fluence (for $\Phi > \Phi_{th}$, the threshold fluence) [58]. The growth kinetics, the thickness, and the structural and physical properties of PLD films are therefore depending on Φ. The larger grain size and film roughness may hence be explained by the increased deposition rate. Further processes associated to thermal effects at higher fluences may influence the film growth also.

The variation of AFM surface roughness with laser fluence for both series of films is represented in Fig. 4. The roughness is systematically higher for films obtained from targets having higher Al doping concentration. This result is in agreement with the observation of Venkatachalam et al. [51]. For both types of targets the measured film roughness monotonously increases with Φ. This suggests that the film morphology may be controlled by the fluence level.

Figs. 5 and 6 show XRD diffraction patterns of AZO films on PET deposited using the ZnO target doped with 1.5 wt% and 2 wt% Al_2O_3, respectively. The measurements have been done for a 2θ diffraction angle scan between 5° and 75°. The diffraction peaks of PET are very pronounced (Fig. 6). In order to select the zinc oxide films response, the diffraction pattern for angle scan between 32° and 39° are presented in Fig. 5 and in the inset of Fig. 6. The observed (0 0 2) peak for ZnO indicates that the microcrystallites in AZO films grow predominantly with the (0 0 2) plane oriented parallel to the substrate surface. The small variations in peak position for films produced at different fluences might be due to a strained crystalline structure. The crystallite sizes corresponding to this preferential orientation were calculated by using Debye–Scherrer's formula [59]

$$D_m = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

where D_m is the crystallite size in the direction perpendicular to the substrate surface, β the full-width at half maximum of a distinctive peak, θ the Bragg angle and λ the wavelength of X-rays. The calculated crystallite size varies slightly with laser fluence. The obtained values for D_m together with grain sizes obtained from SEM analysis are given in Table 1.

The optical transmission and reflection spectra of the AZO films on PET substrates were recorded between 300 nm and 1100 nm. Fig. 7 depicts the spectra of films that were prepared from the targets containing 1.5 wt% Al_2O_3 (Fig. 7a) and 2 wt% Al_2O_3 (Fig. 7b). From the measured transmission $T(\lambda)$ and reflection $R(\lambda)$ data, the absorption coefficient $\alpha(\lambda)$ was calculated using the formula

$$\alpha(\lambda) = \frac{1}{t} \ln\left[\frac{(1 - R(\lambda))^2}{T(\lambda)}\right], \tag{2}$$

where t is the film thickness. For direct band gap semiconductors the absorption near the absorption edge follows the formula

$$\alpha \sim A(h\nu - E_g)^{1/2}, \tag{3}$$

where $h\nu$ is the photon energy. The dependence of $(\alpha)^2$ on photon energy is represented in Fig. 8 for films grown in different conditions. The optical band gap values (listed in Table 1) were determined from linear fits to the data and the intercept with x-axis. The obtained values are higher than that of bulk material (3.3 eV) and undoped ZnO thin films (3.25–3.27 eV) [46]. The shift in the absorption edge is a result of Burstein–Moss effect [60,61]. According to this, the optical band gap increases with the charge carrier concentration

$$\Delta E_g = \left(\frac{\hbar^2}{2m^*_{vc}}\right)(3\pi^2 n)^{2/3}, \tag{4}$$

where ΔE_g is the band gap shift for the doped semiconductor with respect to the undoped semiconductor, m^*_{vc} is the reduced effective mass, and $\hbar$ the Planck's constant and n the carrier concentration. Fig. 9 shows the dependence of the optical band gap of AZO films on the laser fluence for the two types of targets. The slight increase