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Effect of argon plasma-treated polyethylene terepthalate on ZnO:Al properties for flexible thin film silicon solar cells applications

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ABSTRACT

The 0.4 μm-thick Aluminum-doped Zinc Oxide (ZnO:Al) films were deposited at 100 °C on polyethylene terephthalate (PET) substrates by Radio Frequency (RF) magnetron sputtering. Prior to the AZO deposition, an Argon plasma treatment on the substrate surface was carried out by applying a RF bias power on it without intentional heating. The parameters varied in the etching process were the plasma etching time from 0 to 360 s, the RF bias power from 50 to 250 W, and the gas flux from 3 to 5 sccm. The effect of the substrate surface treatment on the mechanical stability, crystallinity and the optoelectronic properties of ZnO:Al thin films were evaluated. The results showed physically stable ZnO:Al films with good adherence to the substrate using appropriated plasma treatment parameters. This fact was attributed to physico/chemical PET surface modifications on the first few molecular layers after the plasma irradiation. The performance of flexible solar devices fabricated on optimized ZnO:Al thin films with adequate adhesion and optoelectronic properties was analysed.

1. Introduction

In the photovoltaic market, the new open field of low cost, light weight, flexible and unbreakable large area photovoltaic devices implies the use of plastic substrates as an available cheap solution [1]. The substrate flexibility allows continuous roll to roll, increasing considerably the production rate and the reproducibility in the panel fabrication process; and besides, opening up new solar applications such as integration into buildings and into small portable devices. However, it is well-know that almost all plastic substrates are polymeric materials with glass transition temperatures not high enough to be used in conventional device fabrication processes. Thus, how decreasing the substrate temperature without losing thin film qualities becomes a key issue. In this sense, numerous efforts have been focused on the determination of proper growth parameters for thin films when using plastic substrates [2,3]. Moreover, the difference existing in thermal expansion coefficients and lattice mismatch between films and substrates result in brittle functional layers when grown on flexible substrates, inducing cracking and/or peeling off the film [4]. This fact should account for the device design because it may influence the mechanical stability of the structure and affect negatively its performance, leading to short-circuit devices [5].

ZnO:Al (AZO) is a transparent conductive oxide (TCO) widely used and considered as an important component in flexible devices applications [6] such as displays [7], thin film transistors, solar cells [8–10] and sensors [11]. AZO thin films can be prepared by various deposition techniques [12–14], being magnetron sputtering deposition particularly attractive for low temperature large area fabrication processes on transparent, flexible, and plastic substrates. This technique is used most often for high deposition rates, process stability and process reliability [15]. Several groups have investigated the effect of deposited parameters on structural and optoelectronic properties of AZO films on many flexible substrates [2,16,17]. Taking into account that flexible devices would need to remain functional after repeated flexing, the evaluation of the AZO residual stress emerged during deposition becomes an important issue. Because most flexible substrates are easily degraded at temperatures as low as 150 °C, it is difficult to achieve flexible crack-free AZO films at those conditions [18].

On the other hand, the surface characteristics of polymers are one of the important factors to determine the interfacial properties and consequently, to define the thin film technological performance. The low surface free energy that most of polymers present, results in poor adhesion of additional coating, leading to technical challenges [19–21]. To solve this problem, plasma-surface modification (PSM) is widely used as effective and cheap

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surface treatment technique [22]. Changes in the physico/chemical properties of the polymer film induced by a plasma exposure may also cause chemical and/or structural changes in the interface surface/film region that would affect the thin film structure and its electrical properties. To modify the polymer surfaces, low temperature and low-pressure plasma are commonly used [23,24]. The plasma exposure can cause effects such as surface cleaning, surface ablation or etching, cross-linking and modification of chemical properties [25]. The effect of the plasma treatment depends basically on several parameters like the type of plasma (DC, RF or microwave), the discharge power density, the process pressure, the gas flow rate and the exposure time. Depending on the gas used, the surface of the polymer can be activated during the plasma treatment, which would bring about the chain scission of the existing groups on the surface and/or create new functional groups [26–28]. Among the polymer substrates, polyethylene terephtalate (PET) is one of the most important thermoplastic used in several industries because of its excellent mechanical properties due to the presence of the aromatic ring in the polymer structure. This fact combined with its processing tolerance, its low cost and its high transmittance in a wide spectral range make it a good choice as substrate for a wide range of applications in the photovoltaic field [29,30].

In this work, the main objective is focused on investigating the feasibility of PET surface modifications using different Argon (Ar) plasma treatments. This process is considered as an alternative approach to influence and modify suitably the functional properties of AZO thin films deposited on top. Appropriated plasma treatment conditions are established in terms of achieving suitable AZO thin films with mechanical stability and good adhesion. Finally, a-Si solar cells are prepared to demonstrate the potential applications of the optimized Ar plasma treatment and ZnO:Al films showed in this work.

2. Experimental

2.1. Substrate preparation

The 250 μm-thick and biaxially oriented polyethylene terephthalate (PET) substrates with density of 1.3–1.4 g/cm^3 used in this work originally from a sheet of Goodfellow were cut into 10×10 cm^2 pieces. Before loading into the sputtering chamber, the substrates were ultrasonically cleaned firstly with ultrapure water ($\rho > 18$ MΩ cm) from a Direct Q-3 water purification system from Millipore and secondly, with isopropanol for 2 min at room temperature (RT). Finally, they were dried by blowing nitrogen over them.

Prior to AZO deposition, an Argon plasma etching on the substrate surface was carried out using a commercial UNIVEX 450B magnetron sputtering equipment from Oerlikon Leybold Vacuum. This system is equipped with four magnetron sources operating by RF/DC power placed in a confocal configuration and a rotated, heated and a RF biased substrate holder that permits to realize the substrate etching. In our case, the RF bias process was carried out without intentional heating, with a radio-frequency of 13.56 MHz, and with a base pressure of 1.5×10^{-5} Pa. The purity of the Ar gas used for the etching process was 99.999%, and the plasma etching conditions were as follow: an exposure plasma time varying from 0 to 360 s, a RF substrate bias power applied, from 0 to 250 W and an Ar flux controlled by mass flow controller (MFC), from 3 to 5 sccm, that corresponds to a working pressure of 0.1 Pa and 0.3 Pa, respectively. After plasma irradiation, the chamber was evacuated down to base pressure.

Next, the substrate temperature was increased progressively up to 100 °C and maintained it for 15 min before depositing the AZO thin films. This pre-heating process was performed to guarantee both the stability of the temperature and its reproducibility.

2.2. AZO thin film deposition

The 0.4 μm-thick AZO thin films were deposited at 100 °C on the Ar-treated PET substrates by RF magnetron sputtering. The 4 in. diameter ZnO:Al_2O_3 (98/2 wt%) ceramic target used in this work comes from Tosoh Corporation. The base pressure was 1.5×10^{-5} Pa and the deposition parameters were extrapolated from the optimized AZO thin films deposited onto glass substrates (not shown), being a RF power (RFP) ranged from 200 to 250 W, basically to minimize the possible damage on the polymer substrate [2], and a working Ar pressure of 0.1 Pa.

2.3. Characterization techniques

The deposited AZO films and the Ar-treated polymers were characterized by X-ray diffraction (XRD) using a commercial Panalytical X'Pert MPD X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.542$ Å). In the particular case of AZO films, the average grain size G was estimated from the Scherrer formula

$$G = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ, θ, and β are the X-ray wavelength, the Bragg diffraction angle, and the full width at half maximum (FWHM) of the 2θ peak in radians, respectively. A Gaussian fit was applied to the curves to extract both the peak position and FWHM values, presenting an error bar of about 5%.

The residual stresses can be calculated using the biaxial strain model [31]. The strain along the c-axis ε_{zz} can be estimated by the relation

$$\varepsilon_{zz} = \frac{(c - c_o)}{c_o} \quad (2)$$

being c_o the strain-free lattice constant of bulk AZO (5.206 Å) and c, the lattice constant of AZO films measured by XRD. Further, the biaxial film stress σ is related to the measured c-axis strain by the relation

$$\sigma = \left[2C_{13} - (C_{11} + C_{12})\left(\frac{C_{33}}{C_{13}}\right)\right]\varepsilon_{zz} \quad (3)$$

being C_{ij} the elastic stiffness constants with values for ZnO of $C_{11} = 208.8$ GPa, $C_{33} = 213.8$ GPa, $C_{12} = 119.7$ GPa and $C_{13} = 104.2$ GPa [32]. A negative value denotes a compressive stress of the film. The error bar estimated for the grain size and residual stress calculation was about 10%.

The possible changes in the chemical composition of the Ar-treated PET surfaces were analysed using a Fourier transform infrared (FTIR) spectroscopy in transmission mode using a commercial Perkin Elmer Spectrum 100. The number of scans was maintained to 32 for all samples.

The surface morphology of both PET and AZO films was evaluated by a standard atomic force microscope (AFM) Multimode SPM from Veeco-Digital Instruments operated in tapping mode and using antimony-doped silicon AFM tips (TESPSS tips from Veeco). The roughness was quantified by the average value of the Root Mean Square (RMS) deviation of the AFM measured height from the mean data plane in AFM 10×10 μm^2 images. The error bar in this parameter due to the roughness variation across the surface was about 20%.

Moreover, the micro-composition of the AZO films deposited were investigated using an Oxford Instrument X-Max energy dispersive X-ray (EDX) analysis with a resolution of 127 eV at 5.9 keV in a commercial JEOL JS6335 scanning electron microscopy (SEM) equipped with field a emission gun operated at 20 keV.