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Research Article

Airbrush Spray Coating of Amorphous Titanium Dioxide for Inverted Polymer Solar Cells

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One of the main topics of organic photovoltaics manufacturing is the need for simple, low cost, and large area compatible techniques. Solution-based processes are the best candidates to achieve this aim. Among these, airbrush spray coating has successfully applied to deposit both active and PEDOT layers of bulk-heterojunction solar cells. However, this technique is not yet sufficiently studied for interfacial layers (electron and hole transporting layers or optical spacers). In this paper, we show that amorphous titanium dioxide (TiO_x) films, obtained with an airbrush from a solution of titanium (IV) isopropoxide diluted in isopropanol, are successfully deposited on glass and PET substrates. Good surface covering results from the coalescence of droplets after optimizing the spray coating system. Simple inverted polymer solar cells are fabricated using TiO_x as electron transporting layer obtaining encouraging electrical performances ($\eta = 1.54\%$ on glass/FTO and 0.7% on PET/ITO substrates).

1. Introduction

During the last years, much efforts have been spent in the field of organic photovoltaics (OPV), the most promising technology for solar energy harvesting with reduced energy payback time [1] and high power to weight ratio [2], which is able to ensure large-scale manufacture at low cost. In particular, polymer solar cells (PSCs) are extensively studied for the simplicity of processing and the opportunity to realize lightweight and flexible devices. As reported in the literature, an inverted architecture of PSCs facilitates the realization of semitransparent devices [3, 4], with higher photocurrent [5], reaching good operational stability [6], and overcoming some problems of the conventional structure, like detrimental interaction at ITO/PEDOT interface [7] or rapid oxidation of the low-work-function metal of the electrode [8]. Inorganic *n*-type semiconductors, such as titanium dioxide (TiO_2), zinc oxide (ZnO), and cesium carbonate (Cs_2CO_3), are usually used as electron transporting layer (ETL) in inverted PSCs, due to their large band gaps and the good electron extraction property. Although Cs_2CO_3 has demonstrated to be a valid ETL for high efficiency devices [9, 10], its use involves the handling of hazardous solvents. In this work, we, therefore, prefer TiO_2 whose preparation is simpler and safer. TiO_2 films can be deposited by different techniques [11–13], but very few of them allow to process films at low temperatures (<150°C), compatible with plastic substrates. At this condition, titanium dioxide is generally in amorphous phase (TiO_x), and it can be realized by solution methodologies as spin coating [14], electrodeposition [15, 16], and chemical bath [17]. Spray deposition is a simple, low cost, and large area compatible technique that is already successfully applied to PSCs to realize the active layer [18, 19], PEDOT [20, 21], and some ETLs [10, 22], but not yet applied to TiO_x for low temperature processing over plastic substrates. We investigate the use of airbrushing in order to realize amorphous titanium dioxide thin film as electron transporting layer for inverted polymer solar cells on glass and plastic substrates.

2. Experimental Details

The photovoltaic devices were realized on FTO-coated glass substrate (Pilkington, ~8 Ω/□) and on PET foils coated with a transparent conductive ITO/Ag/ITO multilayer (PET/DMD, Solutia, ~8 Ω/□). Glass/FTO substrates were patterned by wet etching using chloridric acid (3 M) and zinc powder [23] and cleaned by ultrasonic bath with acetone and isopropyl alcohol (15 min each step); PET/DMD foils were etched by immersion in bromidric acid and then cleaned by ultrasonic bath with isopropyl alcohol for 15 min.

Amorphous titanium dioxide (TiO_x) was deposited by spraying a solution of the precursor titanium (IV) isopropoxide 5% (v/v) (Sigma-Aldrich) in isopropyl alcohol by a dual action commercial airbrush (Mecafer) supplied by compressed air. The process was carried out in conventional environment (air) under chemical hood. The active layer is a P3HT (Rieke Metal) and PCBM (Solenne BV) blend (1 : 0.7) dissolved in *ortho*-dichlorobenzene (*o*-DCB) at 2 wt% and stirred on a hot plate at 70°C for 24 h. It was spin coated in a glove box at 900 rpm for 60 s and then dried by slow evaporation in nitrogen atmosphere.

Two materials were used as hole transporting layer (HTL): (i) PEDOT (VPAI4083, Clevios) mixed with Triton-X surfactant at 1 wt% (to improve the wettability on hydrophobic layers), was spin coated at 3000 rpm for 60 s and annealed at 140°C for 10 min and (ii) molybdenum oxide (MoO_3) was evaporated on active layer in high vacuum (10^{-6} m bar) at 0.2 Å/s. Finally, a silver layer of 100 nm was thermally evaporated as electrode in high vacuum at 1 Å/s. A shadow mask was used in order to define the active area of the solar cells, equal to $7*7\ \mathrm{mm}^2$.

The thickness of the as-deposited films was measured with a profilometer (Dektak 150); optical images and transmittances of TiO_x films were acquired by a microscope (LEXT OLS4000) and a UV-VIS-NIR spectrophotometer (Shimadzu UV2550), respectively.

The morphology of TiO_x surface was analyzed by scanning electron microscopy (SEM, JEOL JSM-6010LA) and the crystalline phase of the layers was investigated using a HORIBA micro-Raman system (LabRAM ARAMIS) equipped with Ar^+ ion laser (514.5 nm) as excitation source.

Electrical performance of the devices was evaluated outside the glove box under a solar simulator KHS Solar Constant 1200 AM1.5 Class B ($100\ \mathrm{mW/cm^2}$) with a parameter analyzer (Agilent E5291A); for the measurements, we used a shadow mask to avoid performance contributions outside the active area [24]. Before each measurement, the irradiation level at the quote and position of the solar cell was verified by a means of a calibrated pyranometer (Skye SKS1110). All the samples were measured unsealed.

3. Results and Discussion

A preliminary investigation was carried out in order to find the highest possible temperature to hold plastic substrates during the spray deposition. According to our previous work [25], mechanical and optical characteristics of PET foils are preserved until ~150°C; therefore, this temperature was chosen and applied to our process as not damaging for PET substrates.

Different parameters of the airbrush spray process were varied in specific ranges to find the optimized conditions for a uniform and homogeneous deposition of TiO_x films on glass/FTO substrates: air compressed pressure (1-2 bar), precursor solution concentration (1%–5%), airbrush distance from substrate (10–30 cm), and spray nozzle outlet. Uniformity of TiO_x deposition was checked by optical microscopy. The optical images in Figure 1 represent the effect of precursor concentration (1, 2, and 5% v/v), the parameter that most affects the TiO_x droplets deposition. The solid content of TiO_x is limited to ring-shaped droplets for low concentrations (1 and 2% v/v) and fills the entire droplet areas for 5% v/v concentration, allowing a better surface covering; larger concentrations make the process difficult because of the hydrolysis and polycondensation of precursor which occur directly in the solution phase.

Figure 1(c) is an example of good uniformity; although uncovered areas are evident, the deposition is an acceptable compromise because further sprays cause the generation of TiO_x white powder (Figure 1(d)). The image also reveals the possible mechanisms of TiO_x formation; sprayed droplets reach the heated substrate where they undergo solvent evaporation and solute hydrolysis, so that the surface is covered by condensed TiO_x droplets.

A deeper structural and optical investigation was performed on the sample shown in Figure 1(c). Scanning Electron Microscope (SEM) analysis of the surface (Figure 2) confirms the results obtained by optical microscopy; TiO_x is made of droplets of various dimensions, not uniformly distributed on the substrate which superimpose and coalesce, leaving some areas uncovered.

Moreover, Raman spectroscopy reveals the amorphous nature of the film (Figure 3), as expected for the low operational temperature (150°C), not sufficient for the crystallization of the material. For comparison, a titanium dioxide film was deposited at 450°C in the same conditions and the typical peaks associated to anatase phase (142, 400, 514, and 635 cm^{-1}) are observed in the corresponding spectrum.

Figure 4 shows the transmittance of TiO_x film deposited on glass/FTO. The layer does not seem to influence the transmittance of the pristine substrate; a slight mismatch is evident only at high wavelengths because of the major absorption of TiO_x [26]. The thickness of TiO_x layer results to be ~50 nm as measured at the profilometer.

Inverted solar cells were fabricated on glass/FTO substrates (inset of Figure 5). Optimized parameters were used for the realization of TiO_x layer: air compressed pressure (1.5 bar), precursor solution concentration (5% v/v), airbrush-substrate distance (20 cm), temperature substrate (150°C) and intermediate spray nozzle outlet. The devices were completed with P3HT : PCBM active layer, PEDOT/ Triton-X as hole transporting layer, and silver anode. As a reference, a sample with a TiO_x layer spin-coated from the precursor and annealed at 150°C was also realized [27]. The *I*-*V* curves of the solar cells are shown in Figure 5. The device behavior exhibits a strong dependence from the number of sprays in TiO_x deposition. The best results

Table 1: Photovoltaic parameters of the device fabricated on glass/FTO and PET/DMD.

Technique	Substrate	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
Airbrush 4 sprays	glass/FTO	568	6.3	42.9	1.54
Airbrush 6 sprays	glass/FTO	522	6.7	33.5	1.17
Spin coating	glass/FTO	505	6.7	37.9	1.28
Airbrush 4 sprays	PET/DMD	491	3.6	35.8	0.63

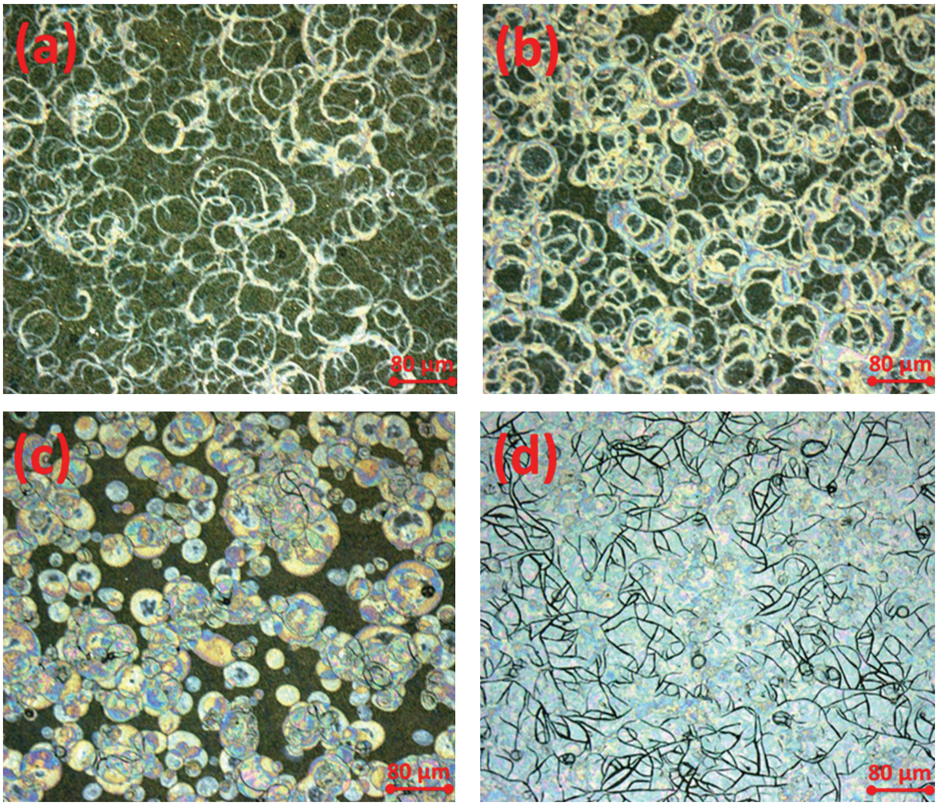

Figure 1: Optical images of TiO_x realized on glass/FTO substrate with 4 sprays at different TTIP concentration in 2-isopropanol: (a) 1%, (b) 2%, and (c) 5%. In case of (d), that corresponds to a 5% concentration with 8 sprays, white powder formation is observed.

are reached with four and six sprays, demonstrating the feasibility of the spray deposition of TiO_x even at low temperatures. Relatively high values of V_{OC} prove the validity of the sprayed TiO_x film in terms of work function for a good electron injection; in addition, it has already been demonstrated that, in spite of its amorphous nature, TiO_x has an acceptable electron mobility, a well-defined energy gap (3.7 eV), and a good charge selectivity [28, 29]. Six sprays are enough to reproduce the results of the spin-coated sol-gel film. Moreover, with four sprays, we obtain an increase in the V_{OC} and FF, probably due to the reduced thickness of the TiO_x film that decreases the internal series resistance of the cell.

The detailed electrical characterization of the devices is summarized in Table 1. For samples realized with a number of TiO_x sprays out of the range 4–6, we did not observe any measurable photovoltaic activity.

The encouraging results obtained from devices on glass substrates suggested us to transfer the same process on plastic. Inverted solar cells were fabricated on PET/DMD foils spraying TiO_x at the conditions previously described. During the process, the foils were held on glass support by means of a repositionable adhesive (3 M spray mount). The cells were completed with P3HT : PCBM active layer, MoO_3 thin film (3 nm), and silver anode (100 nm). We chose to deposit evaporated MoO_3 as a hole transporting layer to ensure a better conformation on the underlying blend and to prevent problems due to the hygroscopic nature of the PEDOT [27]. The preliminary results are reported on Table 1. Even if the photocurrent measured on plastic substrate is lower with respect to glass/FTO, we believe that these results demonstrate that it is worthy to focus on further optimization for possible upscale of the technique to large-area deposition of polymer solar cells.

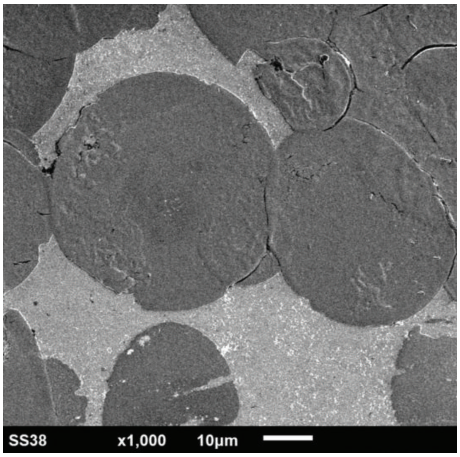

FIGURE 2: SEM surface image of sprayed TiO_x droplets on glass/FTO substrate.

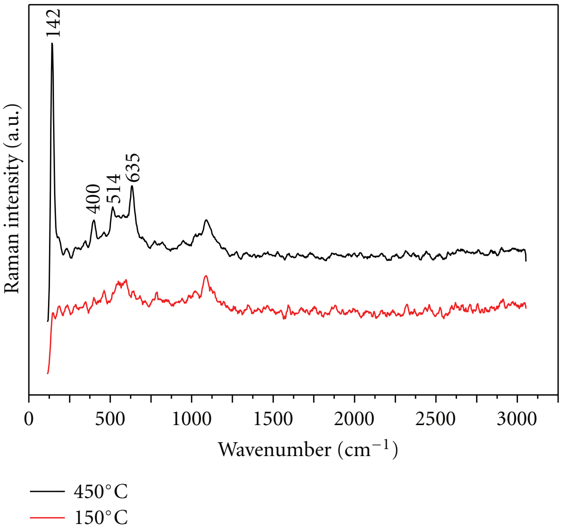

FIGURE 3: Raman spectra of titanium dioxide deposited on glass/FTO substrate at 150°C (amorphous phase) and 450°C (anatase phase). The peak at 1090 cm^{-1} (not indicated) identifies the substrate.

4. Conclusions

Airbrush spray coating was employed and optimized to deposit amorphous titanium dioxide (TiO_x) at low temperatures (<150°C), compatible with plastic PET substrate. Optical and structural characterizations show a layer realized by overlap and coalescence of TiO_x droplets, with suitable features to be applied as electron transporting layer in inverted polymer solar cells. Glass/FTO/TiO_x/PCBM : P3HT/PEDOT/Ag devices were fabricated, and interesting results were obtained in terms of V_{OC} (568 mV) and overall efficiency (1.54%). At the same spraying conditions, PET/DMD/TiO_x/PCBM : P3HT/MoO_3/Ag devices were also realized; V_{OC} (491 mV) and efficiency (0.63%) values are encouraging. We will perform further investigation to improve the electrical performance and achieve semitransparency. A sprayed TiO_x layer could be a boost in the perspective of the fabrication of a "fully sprayed" solar cell.

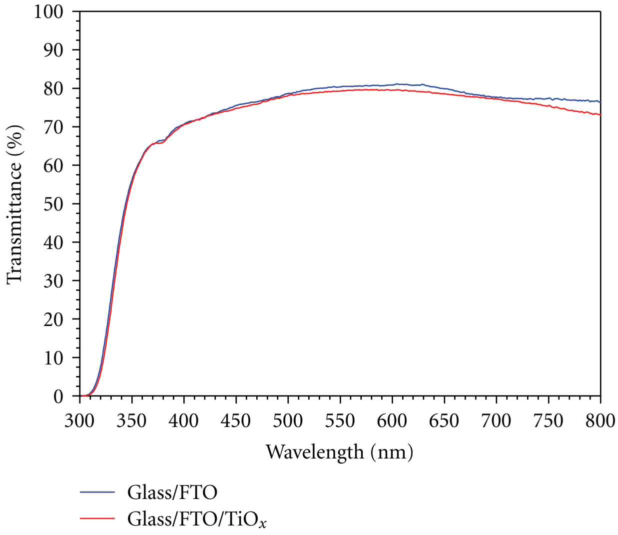

FIGURE 4: Transmittance of pristine glass/FTO (blue curve) and glass/FTO with the deposited TiO_x (red curve).

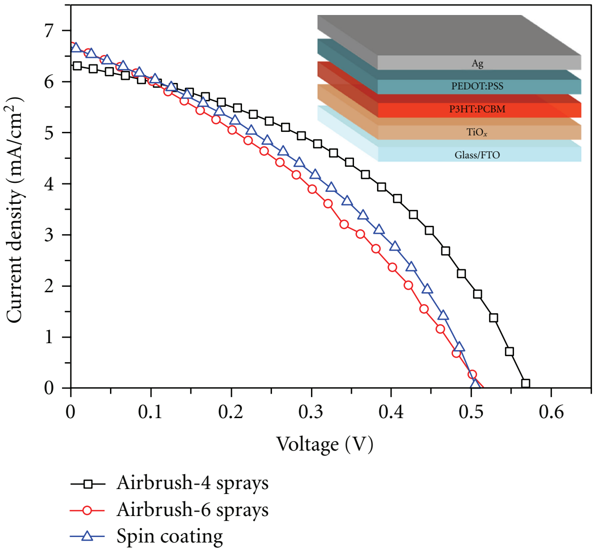

FIGURE 5: J-V characteristics of a device with TiO_x deposited by airbrush 4 sprays (□) and airbrush 6 sprays (◯) compared with a device with TiO_x realized by spin coating (△).

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