Electron-collecting oxide layers in inverted polymer solar cells via oxidation of thermally evaporated titanium

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Abstract

A simple and intuitive deposition technique is here discussed to obtain titanium oxide (TiO_X) used as an electron collecting layer in polymer solar cells based on the thermal evaporation of the pristine titanium (Ti) and further thermal treatment to convert the metal in oxide. Since the degradation of indium-doped tin oxide (ITO) at high temperatures is an issue, we demonstrated that the combination of glass/fluorine tin oxide (FTO) and high temperatures represents a promising approach in the fabrication of inverted polymer solar cells with such a titanium oxide electron collecting layer.

1.1 Introduction

Interface engineering is one of the most used strategies in organic photovoltaics (OPV) to fabricate high efficiency devices [1, 2]. Insertion of charge collecting buffer layers or functionalization of the interfaces between electrodes and active film permit to enhance charge collection, control of the energy level alignment, and stability of polymer solar cells (PSCs) [2-9]. Conventional PSCs are usually based on an indium-doped tin oxide (ITO) anode and a low work-function (φ) metal cathode, such as LiF/Al ($\varphi \sim 3.4$ eV) [10] and Ca/Al (~ 2.9 eV) [11]. Since the low work-function metal is vulnerable to oxidation in ambient air, electrode degradation is a major issue [12, 13]. Recently, the optimization of the inverted structure, in

which an electron-collecting/hole-blocking layer, such as titanium dioxide (TiO_2), zinc oxide (ZnO), or caesium carbonate (Cs_2CO_3) is inserted between ITO and the active layer, has been investigated to enhance stability, thanks to a more air-stable and high work-function metals used as the top electrode, like silver (Ag, $\varphi \sim 4.6\,eV$) [11] or gold (Au, from 4.6 to 5.1 eV based on deposition technique) [3, 14]. Although titanium oxide is characterized by lower electron mobility than ZnO and Cs_2CO_3, it possesses interesting optical [15] and morphological [16] properties. For example, the treatment of TiO_X at high temperatures (>400°C) converts the amorphous oxide into crystalline TiO_2 [16]. Several processes have been investigated in the literature in order to achieve thin films of titanium dioxide, these include solution processing [17, 18], spray pyrolysis [19] and atomic layer deposition (ALD) [20]. In addition, pristine titanium (Ti) was also investigated as an electron collecting layer in a cell structure. As described by Glatthaar *et al.*, 20-nm of Ti, deposited via electron beam between Al and the active layer, leads to a better interface in ITO-free solar cells [21]. 5-nm Ti deposited by radio-frequency (RF) magnetron sputtering on AZO (aluminium-doped zinc oxide) covered glass and subsequently oxidized by oxygen plasma treatment improved the stability of an organic solar cell [22]. A recent study describes a thermal oxidized TiO_2 deposited by sputtering on top of fluorine tin oxide (FTO) as compact layer in perovskite solar cells.[23] In what follows, we describe a simple and intuitive approach based thermal oxidation of Ti deposited by using a thermal evaporator which is present in the majority of laboratories involved in organic solar cell fabrication for the synthesis of an electron collecting layer for polymer solar cells. We investigate the influence of temperature on the optical and electrical properties of thermally evaporated Ti on different transparent conducting oxides (TCOs), such as ITO and fluorine tin oxide (FTO). We then incorporate these thermally oxidized Ti-TiOx layers in inverted polymer solar cell structure showing how the increasing degree of oxidation of the Ti layers improves

the performance of the solar cells, yielding a simple and effective recipe for the creation of an effective electron collecting layer.

2. Experimental Methods

Polymer solar cells were built on FTO (Pilkington, $\sim 8\Omega/\square$) and ITO (Xinyan Technology, $\sim 8\Omega/\square$) glass substrates. Titanium (Umicore) was thermally evaporated on the substrates at 0.3 Å/s in high vacuum ($1 \cdot 10^{-6}$ mbar). Subsequently, the Ti thin films were thermally oxidized in air at different temperatures: room temperature (RT), 150°, 300° and 450°C, for 30 minutes. Devices were fabricated using regioregular *poly(3-hexylthiophene)* (P3HT, Sigma-Aldrich) and *phenyl-C$_{61}$-butyric acid methyl ester* (PCBM, Solenne BV), as donor polymer and acceptor fullerene, respectively. The P3HT:PCBM blend (1:0.7) was prepared at 2%wt in *o-dichlorobenzene* (DCB) and stirred in N_2 ambient overnight ($\sim 12h$) at 70°C. The active layer was spin coated on top of TiO_X obtaining a thickness of ~ 200 nm. As hole transport layer (HTL), a formulation of *poly(3,4-ethylenedioxythiophene) polystyrene sulfonate* (PEDOT:PSS, Clevios VPAI4083) was modified with surfactant Triton-X100 (1% v/v) and spin-coated on P3HT:PCBM, depositing ~ 50 nm; the addition of surfactant in PEDOT:PSS aqueous solution allows a correct deposition of the interface layer in an inverted structure, to overcome the hydrophobic nature of the active layer surface[24]. Bi-layer electrodes of 10-nm chromium (Cr) and 90-nm gold (Au) were deposited by high vacuum thermal evaporation ($1 \cdot 10^{-6}$ mbar). The final fabricated device had an inverted cell architecture, TCO/ETL/P3HT:PCBM/PEDOT:PSS/Cr/Au.

3. Results and discussion

The influence of thermal treatments on the optical properties of the Ti film was investigated to analyse the different transmittance spectra of the treated films at room temperature, 150 °C,

300 °C and 450 °C. The transmittance curves of 10-nm thick evaporated Ti on glass substrates after half-hour treatment at different temperatures are shown in Fig. 1. The pristine titanium is characterized by a transmittance of around 54 % above 350 nm. Although the oxidation starts even at room temperature under normal environmental exposure, air oxidation at RT does not introduce significant variation in the optical properties of the film after 30 min. Increasing the temperature of the treatment to 150 °C, and then 300 °C transforms the Ti layer into a more transparent form. Finally, the thermal treatment at 450 °C strongly increases the transmittance of the layer, reaching values close to the underlying glass (~ 90 %). This is very apparent even to the naked eye from the insets of Fig. 1(a). Interestingly, a slight decrease of transmittance in the near-UV is observed which is due to high crystalline titanium dioxide [25]. In order to prove this, we calculated through the Lambert-Beer law the absorbance spectrum of TiO_2 (we considered the reflectance negligible), and plotted it in Fig. 1(b). For 10-nm Ti (red line), the peaks are weak. On the other hand, 15-nm Ti thermally treated at 450 °C shows the characteristic peak of titanium dioxide in the near UV ($\lambda \approx 370$ nm).

Initial experiments, where devices were built on ITO-coated glass, focused on the influence of the thermal treatment at different temperatures of oxidation T_{ox} (RT, 150°, 300° and 450°C) on solar cell performance as function of starting titanium film thickness (5, 10 and 15 nm). The structure was ITO/treated-Ti/P3HT:PCBM/PEDOT:PSS/Cr/Au. Fig. 2 shows the relationship between physical parameters and the efficiency of solar cells. The highest efficiency was achieved with 10-nm thick Ti treated at 300 °C. At the higher temperature (450 °C), the efficiency suffers due to degradation of ITO and its associated series resistance, which is known to occur above the 250-300°C temperature threshold [26]. Hence, we prepared a second batch of solar cells on FTO conducting substrates, since they exhibit a stable sheet resistance up to 450°C (and even up to 600 °C [26]), a temperature threshold at which we have noted good conversion of the Ti layer into TiOx. Compared to ITO-based devices, those on FTO show

higher efficiencies (~ 1.4 %) even at room temperature. From Fig.2, the average PCE achieved with the Ti layer treated at 450°C is 2.2 ± 0.20 %, a considerable increase (~ 60 %) compared to the cells with the untreated Ti layer. Fig. 3 shows the best photovoltaic devices fabricated on FTO-coated glass substrates with the Ti layer treated at room temperature and 450 °C, respectively. The efficient improvement in FTO-based solar cells is due mainly to the increase in J_{SC} (from 5.5 ± 0.89 mA/cm^2 at RT to 8.26 ± 0.39 mA/cm^2 at 450 °C), but also of V_{OC} (from 528 ± 7 mV at RT to 540 ± 1 mV at 450 °C).

As can be noted, the FTO/TiO$_X$ substrates deliver higher efficiency solar cells after treatment at both RT and 450 °C, compared to the same devices prepared over ITO. The causes for the difference in behaviour are essentially twofold. However, although the efficiencies are lower than those usually achieved with recent low band-copolymers, this comparison clarifies that the higher temperature annealing treatments enabled by the FTO use conducts to a better oxidation of the Ti layer, as shown in figure 1, neglecting the limit due to the ITO degradation.[27]

TiO$_2$ is known to be a very efficient electron extractor for polymer solar cells. FTO substrates provide a better collecting contact (in terms of J_{SC} and V_{OC}) than ITO. This is likely due to the morphology, chemical composition and work function of the TCO, which leads to a different growth of Ti/TiO$_2$. Fig. 4 shows the absorbance of 10-nm Ti evaporated and progressively thermal treated on top of different substrates: glass, glass/ITO and glass/FTO. The absorbance spectra of Ti on top glass and glass/ITO exhibit a significant decrease significantly (~ 100 %) over 320 nm after the thermal treatment at 450 °C. Such decrease is entirely expect as a result of the thermal oxidation of Ti. Contrary, for Ti on top of glass ITO, the absorbance spectrum increases (almost up to two times) from 320 and 350 nm with a minimum peak at 400 nm compared to that measured with not-treated Ti. This behaviour is comparable to that observed for Ti-doped ITO suggesting that this is the result of an indium diffusion into titanium oxide

triggered by ITO degradation at the high temperatures [28, 29]. Furthermore, Ti is been also shown to form small Ti crystallites ($\sim$ 8–10 nm) at the surface of thicker Ti ($\sim$ 150 nm) that aggregate into separated clusters [30] comparable with the thickness here discussed. And, 15-nm Ti is necessary to obtain a completely coverage of TCO substrate, in particular for FTO [23]. Therefore, the FTO work function ($\sim$4.4 eV) [6] lower compared to ITO (4.7eV) [3] can contribute to improve electron extraction, which is further enhanced after oxidizing the layer at 450 °C, even for a non-fully-converted and clustered thin Ti.

4. Conclusion

We discussed the development of a simple deposition and processing technique for titanium oxide and its incorporation of an electron collecting layer in an inverted polymer solar cell with the structure TCO/TiO$_X$/P3HT:PCBM/PEDOT:PSS/Cr/Au. It is based on the deposition of the pristine metal (Ti), then its oxidation in air environment via thermal treatment. Since the degradation of ITO for temperature > 250/300°C is an issue in organic photovoltaics, combining glass/FTO and high temperatures represents a promising approach in fabrication process of inverted polymer solar cells. This method (metal deposition and thermal treatment in air for its oxidation) can be extended to other metal oxides often used in polymer solar cell fabrication.

Acknoledgments

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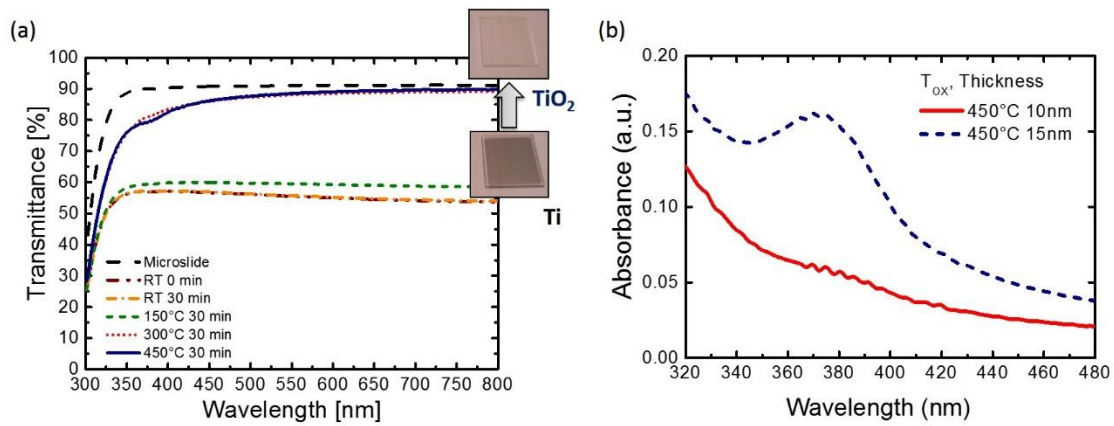
Figure 1 (a) Transmittance of the microslide used as substrate for every measurements (black dashed line), 10-nm pristine Ti (brown dash-dot-dotted line), Ti left 30 min at room temperature (RT, orange dash-dot-dashed line), and at 150°C (green short-dashed line), 300°C (red dotted line) and 450°C (blue solid line). The photographs show titanium before (bottom) and after (top) thermal treatment at 450°C. (b) Absorbance spectra (extrapolated by the Lambert-Beer law) the absorbance spectrum of TiOx of both 10-nm (red solid line) and 15-nm Ti (blue dashed line) thermally treated at 450 °C (we considered the reflectance negligible).
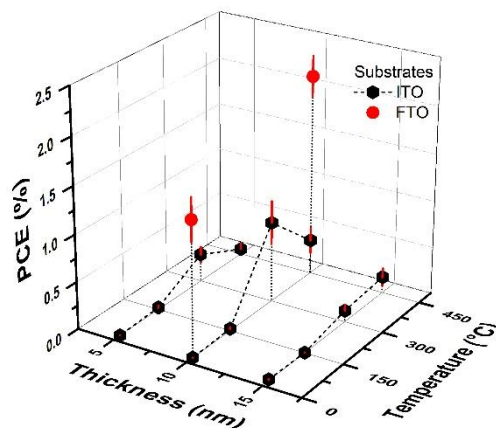
Figure 2 Mean and standard deviation (red line) of solar cell power conversion efficiencies (PCE) characterised by different initial thickness (5, 10 and 15 nm) of Ti, thermally treated at different T_{OX} (RT, 150, 300 and 450°C) for 30 min. The structure of the devices is ITO/treated Ti /P3HT:PCBM/PEDOT:PSS/Cr/Au.

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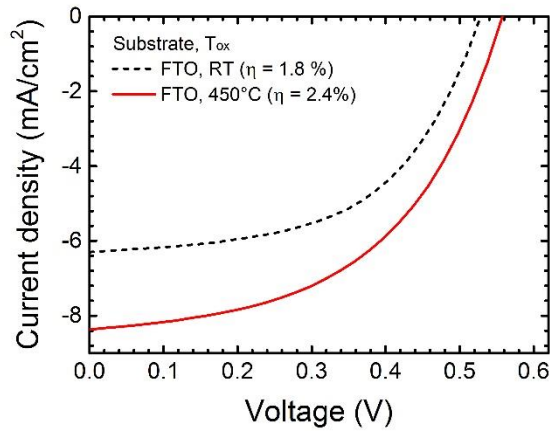
Figure 3 Photovoltaic J-V curves of highest efficient cells incorporating Ti on glass/FTO at different temperatures of Ti oxidation , RT (black dashed line) and 450°C (red solid line), respectively.
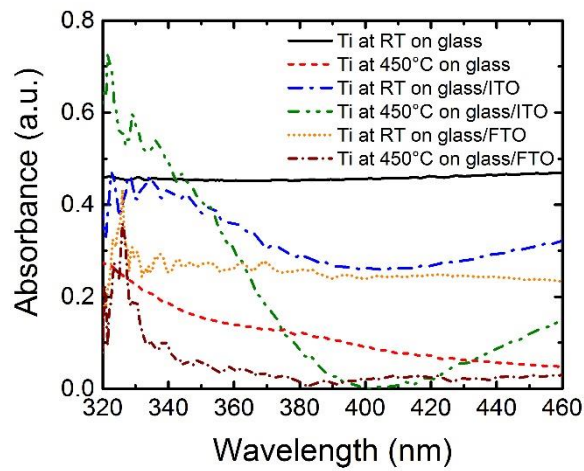
Figure 4 Absorbance spectra of 10-nm Ti evaporated on glass (black solid line), on glass/ITO (blue dash-dotted line) and on glass/FTO (orange dotted line), and the related samples treated at 450 °C on glass (red dashed line), on glass/ITO (green dash-dot-dotted line) and on glass/FTO (brown dash-dot-dashed line).