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Systematic variation of the stabilizer to reduce the annealing temperature of sol–gel derived titanium oxide in inverted organic solar cells

M. Seßler [a,b,*], A. Saeed [a], M. Kohlstädt [a,b], U. Würfel [a,b]

[a] Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstraße 2, 79110 Freiburg, Germany
[b] Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany

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ABSTRACT

Solution-processed titanium oxide is used as an electron selective window layer in inverted organic solar cells. For the goal of roll-to-roll processed organic photovoltaics annealing temperatures of 150 °C and above have to be avoided. Therefore the influence of different stabilizers (complexing agents) on the required annealing temperature for the TiO_x layers is investigated. A clear connection between the boiling points of the different complexing agents and the annealing temperature is observed. In total a series of four different stabilizers with boiling points ranging from 55 °C to 140 °C have been studied. By applying a low boiling complexing agent in the synthesis of the TiO_x-nanoparticles the required annealing temperature could be brought down from 150 °C to 85 °C while maintaining a power conversion efficiency of 3.4% using a mixture of Poly(3-hexylthiophene-2,5-diyl) and [6,6]-phenyl-C_{61}-butyric acid methyl ester as the photoactive layer.

1. Introduction

Research on organic photovoltaics (OPV) has been a rising field in the last 20 years. Most recent power conversion efficiency records of above 10% [1–4] show the potential of the OPV technology and encourage further research in this field. The advantages of OPV are mainly believed to be low production cost, light weight products and applicability on flexible foil substrates. In organic solar cells thin films of large bandgap semiconductors as charge carrier selective window layers are often implemented between the photoactive material and the electrodes. They ensure selective charge carrier extraction at the contacts leading to a decrease in surface recombination and hence to an increase in power conversion efficiency of the solar cell. Examples in literature are zinc oxide, cesium carbonate, molybdenum oxide and titanium oxide [5–12]. In this study we investigate the electron selective behaviour of TiO_x in inverted organic solar cells (see Fig. 1). In the inverted setup, the commonly used transparent Indium Tin Oxide electrode is acting as the electron contact which means high work function metals can be applied as the hole contact on top of the solar cell. Because of the higher work function, these metals are less prone to oxidation and are reported to increase the lifetime of the solar cells [13]. With its LUMO level in the range of 4 eV, TiO_x enables a good electron transfer from the commonly used acceptor material [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) while providing a energy barrier of roughly 1 eV for the hole transport. Furthermore, because of its large bandgap of 3.2 eV, TiO_x does hardly absorb photons in the spectral range of the photoactive material.

* Corresponding author at: Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany. Tel.: +49 (0)761 2034799.
E-mail address: martin.sessler@ise.fraunhofer.de (M. Seßler).

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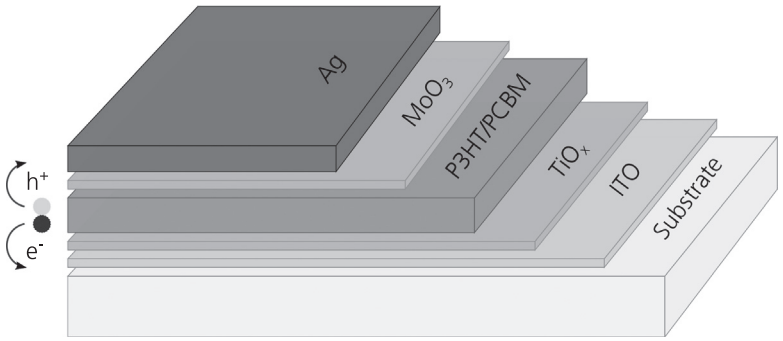

Fig. 1. Schematic of an inverted organic solar cell using TiO_x as an electron selective window layer.

To fully exploit the above mentioned advantages of organic photovoltaics the solar cells have to be produced in a continuous roll-to-roll process on flexible substrates. To realize a low production cost of OPV devices the substrates have to be cost efficient as well. However these substrates usually can not withstand temperatures above 150 °C. As a consequence the annealing temperature of the individual layers of the organic solar cells is a crucial parameter. In this work we present a way to influence the required annealing temperature for TiO_x window layers by varying the stabilizer in the synthesis. This correlation has been observed previously by Sasajima et al. [14]. It is the intention of this work to extend the investigations of Sasajima et al. by focussing on the influence of the stabilizer on sol–gel processed TiO_x nanoparticles. For this reason, four TiO_x solutions containing different stabilizers have been synthesized and successfully applied in inverted organic solar cells.

2. Experimental

2.1. Synthesis of the TiO_x nanoparticle solutions

The titanium oxide nanoparticle solutions were prepared based on a synthesis route by Kim et al. [11]. Titanium (IV) isopropoxid (8.44 mmol, 97%, Sigma–Aldrich) is slowly added to a cooled flask containing 1-Methoxy-2-propanol (0.159 mol, >99.0%, Fluka) in N_2 atmosphere. The mixture is then refluxed for 1 h. Afterwards 20.7 mmol (2.45 equivalents of the titanium (IV) isopropoxid) of the complexing agent is added to the mixture. Four different stabilizers were used: Acetylacetone (AA, Sigma–Aldrich), dipropylamine (DPA, Merck), *n*-ethylpropylamine (NEP, Alfa Aesar) and diethylamine (DEA, Sigma–Aldrich). The mixture is again refluxed for one hour. The resulting TiO_x nanoparticle solutions are transparent, colourless solutions.

2.2. Fabrication of the inverted organic solar cells

The organic solar cells investigated in this study are based on a bulk-heterojunction of Poly(3-hexylthiophene-2,5-diyl) (P3HT) and $PC_{61}BM$. The following layer stack was used: ITO/TiO_x/P3HT–PCBM/MoO_3/Ag. For the fabrication of the inverted organic solar cells, ITO structured glass substrates were successively cleaned in acetone, isopropanol and deionized water in an ultrasonic bath followed by an UV-ozone treatment for 20 min. The TiO_x window layers were prepared by spin coating at 3000 rpm for 30 s under ambient conditions. Depending on the applied stabilizer, the TiO_x layer is annealed in ambient air for 1 h and then transferred to a nitrogen glovebox for further processing. A P3HT/PCBM solution in ortho-dichlorobenzene is spin-casted at 720 rpm for 4 min and successively annealed at 150 °C for 15 min. After annealing the top electrode consisting of 10 nm of MoO_3 and 100 nm of Ag is thermally evaporated under a high vacuum (10^{-6} mbar) through a shadow mask.

2.3. Measurements

Scanning electron microscopy (SEM) measurements were carried out on an Hitachi S-4700 microscope. Current density–voltage (*JV*) curves were recorded using a Keithley2400 source meter under a simulated AM1.5G illumination at 1000 W/m^2. The spectral mismatch of the solar simulator (Steuernagel SolarCelltest 575) was corrected using a calibrated silicon reference cell.

Thermogravimetric analysis (TGA) was conducted on a thermobalance from Netzsch (STA 409). The measurements were performed in the range of 30–180 °C at a speed of 1 K/min in ambient air.

3. Results and discussion

SEM measurements were carried out to investigate the influence of the different stabilizers on the morphology of the TiO_x layers. Since the recorded pictures of the TiO_x layers showed no visible difference for the different stabilizers, Fig. 2 exemplarily shows the SEM pictures of a NEP-stabilized TiO_x layer.

Concluding from Fig. 2 the TiO_x nanoparticle solutions form a very smooth layer with a thickness of roughly 80 nm independent of the utilized stabilizer.

Table 1 shows the solar cell characteristics of an inverted organic solar cell using TiO_x as an electron selective window layer. In this case a nanoparticle solution containing acetylacetone (AA) as complexing agent was used. Concluding from the data shown in Table 1, an increase in J_{SC} and especially in the fill factor with rising

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