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Influence of equilibrium charge reservoir formation on photo generated charge transport in TiO_2/organic devices

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ABSTRACT

Charge transport measurements have been performed using the photo induced charge extraction by linearly increasing voltage (photo-CELIV) technique on indium tin oxide/titanium dioxide/poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester/copper (ITO/TiO_2/P3HT:PCBM/Cu) devices. By adjusting the offset voltage such that holes are accumulated at the ITO/TiO_2 contact we obtain space charge limited current (SCLC) extraction in the dark. Using photo-generation the current response is limited by SCLC extraction at low carrier concentrations but becomes purely recombination limited at high photo-generated carrier concentration. A 1-D drift diffusion model has been developed to simulate our results and we show that the hole blocking ITO/TiO_2 contact is responsible for the SCLC behavior. The highly reduced recombination of charges seen in P3HT:PCBM devices is necessary to obtain the large extraction current transients that are seen in the experimental measurements. By comparing the simulated dark CELIV and photo-CELIV we show that photo-generated extraction is more sensitive towards changes in the surface recombination velocity.

1. Introduction

Bulk-hetero junction (BHJ) and dye-sensitized solar cells (DSSC) are promising candidates for achieving cheap, renewable energy production. The present state of the art efficiencies of these types of solar cells are 12.3% for DSSC [1], 10.7% for BHJ [2] and 10.6% in the case of BHJ in tandem configuration [3]. Clarification of the charge transport properties of materials which are used in these types of solar cells are of vital importance for achieving higher power conversion efficiencies.

Conjugated polymers have been widely used in solar cell applications. In BHJ solar cells polymers are typically used as the donor with a fullerene derivative (such as PCBM) as the acceptor. These two materials are blended to achieve an interpenetrating structure where the nano-domains of the materials should be around 10–20 nm [4] for efficient exciton dissociation [5,6]. Conjugated polymers have also been used in DSSC applications to replace the liquid electrolyte, however, with lower efficiencies [7–9] compared to state of the art liquid electrolyte DSSCs.

One way of improving BHJ solar cells is to use charge blocking layers [10–12] to prevent electrons (holes) from reaching the anode (cathode). Metal oxides such as titanium dioxide [10,11] (TiO_2) and zinc oxide [13] (ZnO) are

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typically used as a hole blocking layers in BHJ applications as well as optical spacers. In addition to their use as blocking layers and optical spacers, these materials have also found use in inverted type of solar cells, where their high lying conduction band serves as electron extracting pathways. Clarifying how charge blocking layers affect the charge transport in these devices is of great importance when designing solar cells with higher power conversion efficiencies.

The charge extraction by linearly increasing voltage (CELIV) technique [14] is a useful tool for characterizing charge transport and recombination in low mobility materials such as organic semiconductors. The technique can be used to study equilibrium (dark) or photo generated charge carriers (photo-CELIV) [15]. To obtain the mobility of photo generated charge carriers using photo-CELIV Juška et al. showed that the absorption profile must be taken into account otherwise one risks making large errors in the mobility of the charge carriers [16]. The mobility measured using the CELIV technique is an average of both charge carriers thus, separation of the fast and slower carriers using this technique is difficult. To obtain both mobilities Juška et al. have developed the metal–insulator–semiconductor CELIV (MIS–CELIV) [17] technique where a linearly increasing voltage pulse is applied on a device with a metal/insulator/semiconductor/metal structure in the dark. In this way charges are injected into the semiconductor and accumulated at the insulator/semiconductor interface by an applied offset voltage and subsequently extracted by a linearly increasing voltage pulse. By choosing different polarities of the offset voltage either electrons or holes are accumulated at the insulator/semiconductor interface. The amount of charges extracted can be varied by adjusting the magnitude of the offset voltage. Using this technique space charge limited current (SCLC) extraction is observed at large offsets. The same type of SCLC extraction can also be seen in devices using a charge blocking layer instead of an insulator.

In this work we have used the model system P3HT:PCBM to clarify how a hole blocking layer affects the photo-generated charge transport and recombination in solar cell applications. Here we have placed a thin (~7 nm) TiO_2 layer between the ITO contact and the active layer where the complete device has the structure: ITO/TiO_2/P3HT:PCBM/Cu. The charge transport behavior in these devices has been characterized using the photo induced charge extraction by linearly increasing voltage (photo-CELIV) technique. The experimental photo-CELIV transients have been modeled using a 1-D drift diffusion model to give insight to the charge transport and recombination behavior in these devices.

2. Experimental

The thin titanium dioxide layers were made by dip coating the ITO substrates (Bruker) in a titanium chloride ($TiCl_4$) solution. The titania precursor solution was made by dissolving $TiCl_4$ in a mixture of ethanol (EtOH), deionized water (H_2O), tetrahydrofuran (THF) and Pluronic 127 in a molar ratio of ($TiCl_4$:EtOH:H_2O:THF:Pluronic 127) 1:250:10:20:0.001. The coating was performed using a dip coater (KSV Instruments Ltd., Helsinki, Finland), by which the substrates were immersed into the precursor solution, at room temperature and at constant humidity (25%). After immersion, the substrates were then withdrawn from the $TiCl_4$ solution at a constant rate of 1.2 mm/s. After the dipping procedure, the TiO_2 films were sintered at 500 °C for 10 min to form the anatase layer. The crystallinity and the thickness of the TiO_2 films was clarified using a Bruker D8 Discover instrument in X-ray diffraction or X-ray reflection mode, respectively and the homogeneity of the films was checked by atomic force microscopy.

The active materials used in this work was a 1:1, by weight, blend of P3HT (OS2100, Plextronics) and PCBM (Solenne BV) in a chlorobenzene solution. The blend layer was deposited by spin-coating and the thicknesses obtained, as determined by the CELIV technique [14], was d = 600–900 nm. A 30 nm thick copper electrode was evaporated on top of the organic layer and the complete device was heat treated at 120 °C for 15 min. Copper was used in this work due to its work function (4.7 eV) being close to that of ITO (4.8 eV), leading to a small built in field in these kinds of devices, which is beneficial to charge transport and recombination measurements. The device configuration and the energy levels of the materials used in this work are shown in Fig. 1a and b, respectively.

The photo-CELIV technique has been used in this work to clarify the charge transport behavior; a schematic of

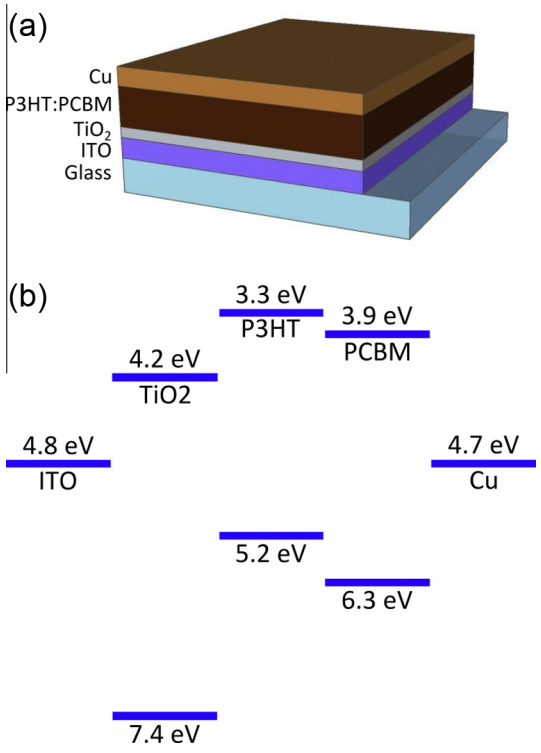

Fig. 1. (a) Configuration of the device used in this work and (b) energy levels of the materials used here.