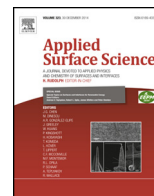




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Engineering of the energetic structure of the anode of organic photovoltaic devices utilizing hot-wire deposited transition metal oxide layers

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ABSTRACT

In this work we use hydrogen deposited molybdenum and tungsten oxides (chemically described as $H:MO_x$, $x \leq 3$ where $M = Mo$ or W) to control the energetics at the anode of bulk heterojunction (BHJ) organic photovoltaics (OPVs) based on poly(3-hexylthiophene):[6,6]-phenyl butyric acid methyl ester (P3HT:PC₇₁BM) blends. Significantly improved current densities and open circuit voltages were achieved as a result of improved hole transport from the P3HT highest occupied molecular orbital (HOMO) toward indium tin oxide (ITO) anode. This was attributed to the formation of shallow gap states in these oxides which are located just below the Fermi level and above the polymer HOMO and thus may act as a barrier-free path for the extraction of holes. Consequently, these states can be used for controlling the energetic structure of the anode of OPVs. By using ultraviolet photoelectron spectroscopy it was found that dependent on the deposition conditions these gap states and work function of the metal oxides may be tailored to contribute to the precise alignment of the HOMO of the organic semiconductor (OSC) with the Fermi level of the anode electrode resulting in further enhancement of the device performance.

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1. Introduction

During the last three decades the use of organic semiconductors (OSCs) [1] for the fabrication of various electronic devices such as field-effect transistors (OFETs) [2], light emitting diodes (OLEDs) [3] and photovoltaics (OPVs) [4], is intensively investigated. In all these devices the charge carriers are injected in (or extracted from) the OSC through inorganic (metallic) contacts. The electric contacts between organic and inorganic materials though, are substantially different from those between inorganics only, because the junctions are usually formed with weak Van-der-Waals forces as opposed to the inorganics where they are made by sharing electrons of the atoms of the two materials that form the junction [5]. Under such conditions the simple model introduced by Bloch to explain the movement of electrons through a periodic crystal

(based on the delocalization of electrons shared between atoms throughout the entire crystal) cannot be applied. The above model becomes even more inapplicable for holes, which are the dominant carriers in most OSCs, the propagation of which pre-supposes the continuity of the material and, therefore, of the wave functions at the top of the valence band. When a carrier is forced to cross an organic–inorganic material junction, even if this passage is energetically favored, in the best case will be delayed and thus create an additional barrier thus blocking the other carriers, while in the worst case it will be completely localized by the random potential created at the interface due to the Van-der-Waals potential. Consequently, when designing the contacts of OPVs several requirements must be fulfilled. The first problem which must be faced is the narrowness of the molecular energy levels of OSCs [1,5]. While in inorganic materials valence and conduction bands are several eVs wide, in OSCs the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) are of the order of a few hundreds of meVs wide only [1,5]. To facilitate charge extraction in OPVs it is therefore necessary to incorporate inorganic materials between the metal contacts and OSC (the so-called charge interfacial layers, CILs) exhibiting energy levels near those of the

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HOMO and/or LUMO levels of the OSC. Moreover, because of the softness of organic molecules, after losing or gaining an electron by a molecule of OSCs, polarons (or bi-polarons) are formed and transfer electric charge, whose electronic levels are different than those of the HOMO and LUMO levels of the neutral atom [6,7]. Such differentiations of the energetic levels of carriers must be taken into consideration for the design of contacts. Finally, a difference between the work function (defined as the energy distance between the Fermi level and the vacuum) of the material of the electrode and HOMO or the LUMO of the semiconductor implies the formation of an electrostatic field (interfacial dipole, ID) at the interface, which in correctly designed contacts, is oriented so as to push the carriers toward the electrodes.

In practice few materials can be used as contacts in OPVs. The anode must be formed from a transparent-conductive material (such as fluorine doped tin oxide, indium–tin oxide and doped zinc oxide) the most common of which exhibit work functions within the range 4.3–4.8 eV, dependent on the treatment of their surface. The work functions of the various metals vary within broader limits, between approximately 3 and 6 eV [8], but excluding metals unstable in air, highly hygroscopic and reactive toward the various layers involved in OSC-based devices, this range is limited to metals with work function between 4.5 and 6 eV. Given then that the ionization potential (energy distance between the HOMO and the vacuum level) of most OSCs lies near 5.5–6.0 eV while their HOMO–LUMO distance is of the order of ~ 2 eV to be useful in OPVs, it is evident that the choice of the appropriate materials for the formation of contacts is seriously limited. For instance, for the case of bulk heterojunction (BHJ) OPV cells based on the well-known poly(3-hexylthiophene):[6,6]-phenyl butyric acid methyl ester (P3HT:PCBM) blend with HOMO and LUMO levels of 3.2 and 5.3/3.9 and 6.1 eV respectively, a material with states between the Fermi level of the ITO (4.7 eV) and the HOMO of P3HT is needed for an efficient collection of holes. In addition, a material with states between the LUMO of PCBM and the Fermi level of Al (4.3 eV) is needed to facilitate the collection of electrons.

In this work we use hydrogen doped molybdenum (MoO_x with $x \leq 3$) and tungsten (and WO_x) oxides (chemically described also as H:MO_x where $M = \text{Mo}$ or W) to engineer the anode of OPVs based on P3HT:PC₇₁BM blends according to the basic rules described above. As shown previously [9], in stoichiometric forms ($x = 3$) these oxide films, deposited by heating a filament of the corresponding metal at pressures of 0.1 Torr in environments of nitrogen, exhibit a band gap of approximately 3.0 eV, which is free of states. By introducing hydrogen in the deposition environment the oxygen stoichiometry of these layers decreases and a band is created deep in the gap (intermediate band, IB) at approximately 2 eV below the edge of the conduction band (CB) [10–13]. Finally, by injecting hydrogen pulses during deposition using an atomic layer deposition (ALD) valve, atomic hydrogen is formed in the deposition chamber that dopes films creating another IB, shallower than before, at approximately 1 eV below the CB [12,13]. These IBs can be used to control the energetic structure of the anode of OPVs [14]. Also, dependent on the deposition conditions the work function of these oxides may be “tailored” to contribute to the precise alignment of the HOMO and LUMO states of the OSC with the Fermi levels of the electrodes. As a result, highly efficient OPVs based on the P3HT/PC₇₁BM blend with the aid of these H:MO_x layers are demonstrated.

2. Experimental

2.1. Metal oxides deposition

The deposition system used in this study was described before [11,14]. It consisted of a stainless steel reactor in which the sample

was positioned on an aluminum susceptor 2 cm below a tungsten filament heated by an (AC) current lead by two Cu leads. All depositions in this work were made with a filament temperature of 660 °C chosen because it was found to allow for the rapid superficial oxidation of the filament and, at the same time, for the deposition of high quality films. The base pressure was set at 0.1 Torr by a commercial system containing a diaphragm pressure gage (Baratron) and a PC-driven needle valve allowing for the flow of (one of) various gases such as O_2 , N_2 , H_2 or forming gas (FG, a mixture of H_2 – N_2 , 10% in H_2) through the reactor thus setting the deposition environment. The same PC was also used for driving the ALD and the various shut-off valves. The ALD valves and the associated gas lines were heated allowing for the injection of a variety of precursors into the reactor. However, in this work the filament played the role of the precursor [11], the deposition ambient was set by a gas flow (either of N_2 or FG) and H_2 was injected during deposition through an ALD valve. For the deposition, after loading the substrate, the system was evacuated down to 10^{-2} Torr. Then, the base pressure (deposition ambient) was set to 0.1 Torr by the flow of either N_2 or of FG through the PC driven needle valve and then the metallic wire (W or Mo, Aldrich +99.99 pure) was turned on. Depositions were also carried out with simultaneous injection of H_2 pulses leading to peak pressures of 0.8 Torr lasting for approximately 1 s. Due to the relatively short deposition times and the high thermal mass of the aluminum susceptor, the substrate temperature was remaining near room temperature during deposition. After turning-off the filament, the system was left to cool down to room temperature while the base pressure (deposition ambient) was maintained. The cooling down was enduring several minutes.

2.2. Device fabrication and characterization

The OPV devices were fabricated on ITO-coated glass substrates (2×2 cm) with a sheet resistance $20 \Omega/\text{sq}$, which served as the anode electrode. Substrates were ultrasonically cleaned with a standard solvent regiment (15 min in acetone and isopropyl alcohol). The Mo or W oxide layer was then deposited followed by the deposition of the 100 nm thick active layer, which was a blend (1:0.8 wt%) of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), spin-coated from a 10 mg/mL chloroform solution. After deposition the active layer was annealed at 125 °C for 10 min. A thin polyoxometalate (POM) layer was deposited from a solution in methanol, on top of the active to serve as an electron injection/transport layer [15,16]. The devices were completed with a 150 nm thick aluminum cathode, deposited in a dedicated chamber.

2.3. Characterization methods

Current density–voltage characteristics of the fabricated solar cells were measured with a Keithley 2400 source-measure unit. For V_{oc} and photocurrent measurements, devices were illuminated with a Xenon lamp and an AM1.5G filter to simulate solar light illumination conditions with an intensity of 100 mW cm^{-2} . Film thickness was estimated with ellipsometry. The position of the valence band maximum of different metal oxides was extracted from the near-Fermi level region of ultraviolet photoelectron spectroscopy (UPS) spectra of 10 nm thick films while their work function (WF) was extracted from the secondary electron cut-off of the same spectra. Measurements were made in a Leybold/Specs MAX 200 spectrometer under ultra-high vacuum UHV ($\approx 10^{-10}$ Torr) equipped with a Leybold EA-11 analyzer and using the HeI (21.22 eV) excitation line. The analyzer resolution was determined from the width of the Au Fermi edge to be 0.16 eV.

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