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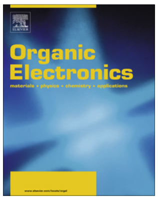

Band bending at the P3HT/ITO interface studied by photoelectron spectroscopy

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ABSTRACT

The electronic structure of poly (3-hexylthiophene) (P3HT)/indium tin oxide interfaces was studied by photoelectron spectroscopy (PES). In the thickness dependent core and valence PES data we observe a significant band bending of about (0.8 ± 0.1) eV within 40 nm distance of the interface. The thickness dependence of the polaronic state follows an exponential law, thus indicating a Schottky–Mott-like behaviour due to trap states. From a drift-diffusion simulation we can determine a p-type doping concentration of $C = \left(5^{+5}_{-4}\right) \cdot 10^{15}\ \mathrm{cm}^{-3}$ and a width of the Gaussian density of states of $\sigma = 155$ meV for a vanishing injection barrier.

1. Introduction

Poly (3-hexylthiophene) (P3HT) is one of the most important polymer materials used as organic semiconductor in electronic devices [1,2]. One of the key issues for the device function and performance is the charge transfer across the interface between the organic semiconductor and the electrodes [3,4]. This charge injection or extraction, respectively, is determined by the electronic structure in the interfacial regime [5] which thus demands particular attention.

Charge extraction barriers can lead to s-shaped current–voltage characteristics [6] and thus reduce the fill factor and consequently the power conversion efficiency of SCs. Moreover, injection barriers can substantially reduce the open circuit voltage in case of solar cells (SCs) [7–9]. Common electrode materials are metals (such as silver, gold, and aluminum) and in case of optoelectronic devices transparent conductive oxides such as indium tin oxide (ITO) are used to establish an optically transparent contact. P3HT/ITO contacts are hence relevant model systems to study the particularities of the energy level alignment between the organic semiconductor and the contact in the interfacial region.

In this paper, we performed PES on P3HT/ITO contacts, varying the polymer thickness to investigate the impact of the electrode on the organic semiconductor energy levels.

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2. Experimental

All X-ray and UV photoelectron spectroscopy measurements (XPS and UPS, respectively) were performed in a UHV system, described in detail elsewhere [10]. The base pressure was below $2 \cdot 10^{-10}$ mbar and the samples were at room temperature ($T = 300$ K). For XPS the Mg K_a anode of a twin-anode source was used, while the He-I excitation line of a gas discharge lamp was applied for UPS. For work function measurements the sample was biased by −9 V.

After rinsing with acetone, the ITO coated glass substrates were oxygen plasma-treated resulting in surfaces with low contamination as verified by XPS. The surface roughness was determined to 2.8–4.7 nm from X-ray diffraction scans and surface profiler measurements (Veeco Dektak 150). The plasma-treatment resulted in a very reproducible sample work function of $\phi = (4.78 \pm 0.05)$ eV in accordance with literature [11,12]. A representative work-function measurement on a plasma-treated ITO sample is displayed in Fig. 1. Note that the work function after plasma treatment is significantly larger than reported for non-plasma-treated samples [13,12,14,15] and is furthermore stable under X-ray and UV-illumination on the experimental time scale of several minutes.

In order to access the properties of the P3HT/ITO interfacial regime with surface sensitive techniques such as PES the preparation of ultra-thin P3HT films is required. The generally applied spin-coating, however, implies a lower limit of the film thickness of a few nm. For lower coverages films become inhomogenous. As a consequence other preparation routes have been applied, such as thermal evaporation [16] or electrospray deposition in UHV [17], or post-preparation thinning out by solvents [18]. Although these approaches allow performing experiments with P3HT samples down to sub-monolayer coverages, we utilized spin-coating in this work in order to grant film structures and morphologies comparable to those used in various other experiments and in applications.

The spin-coating was performed at 1500 rpm from solutions between 20 mg/ml and 25 mg/ml of regioregular P3HT (purchased from Rieke Metals) in chlorobenzene onto the ITO substrates. The resulting layer thickness was between 5 nm and 152 nm, as determined by a surface profiler for samples thicker than 25 nm and by optical absorption for the ultra-thin films. The P3HT film preparation and sample mounting was performed in a glove box. The transfer time into the UHV system was kept below 10 s in order to minimize contamination.

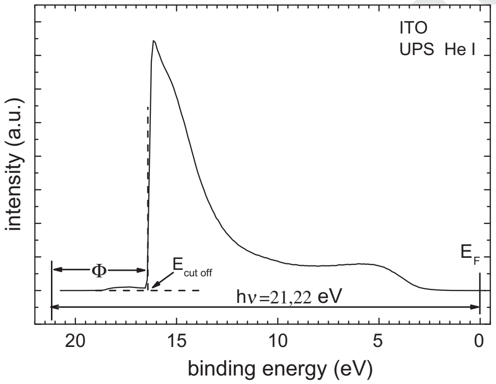

Fig. 1. UPS scan of an oxygen plasma-treated ITO sample. The determination of the work function from the secondary electron cut off is illustrated. The sample was biased by −9 V and the energy scale is referenced to the Fermi energy E_F.

3. Experimental results

Fig. 2 displays the result of thickness dependent PES measurements on P3HT thin films prepared on ITO/glass substrates. The film thickness variation allows us to access the evolution of the electronic structure in the interface regime. The C 1s (Fig. 2a) and S 2p (Fig. 2b) data consistently show a shift of the core level positions towards lower binding energy in the vicinity of the P3HT/ITO interface. The same shift is observed for the P3HT HOMO band in Fig. 2c. Here, the delocalized π-band results in the broad feature which spreads over 1.5 eV, followed by a sharper peak at around 3.5 eV, which can be attributed to a localized P3HT π-band [19].

Fig. 3 summarizes the thickness dependent energy shift of the C 1s (Fig. 3a), S $2p_{3/2}$ (Fig. 3b), and HOMO level (Fig. 3c) derived from Fig. 2. While the energetic positions were straightforwardly derived from the maxima of the C 1s peaks in Fig. 2a, the HOMO onset was used as a reference in the valence spectra (Fig. 2c). The position of the S $2p_{3/2}$ level was determined from a fit to the experimental data by three Gaussian functions. One Gaussian each was used for the S $2p_{3/2}$ and S $2p_{1/2}$ signals utilizing constraints for the area ($A_{3/2} = 2 \cdot A_{1/2}$), width ($w_{3/2} = w_{1/2}$) and spin–orbit splitting ($\Delta E = 1.1$ eV). An additional Gaussian was allowed to model the high energy background from satellites. The fit results are plotted in Fig. 2b as solid lines. In addition, the results of work function measurements on the same samples are plotted in Fig. 3d. The comparison shows that the energetic position of the P3HT core and valence levels in the interface regime immediately follow the sample work function.

4. Discussion

The energy level alignment at the P3HT/ITO interface clearly shows a behaviour reminiscent of band bending.[20,4] For contacts between inorganic semiconductors and metals this is a well-known effect and is generally described by the Schottky–Mott model. According to this model, a band bending is observed due to the smaller work function of the semiconductor, which leads to a transfer of electrons to the metal and thus to a positive space charge in the semiconductor interface region. The resulting electrostatic potential "bends" the electronic levels of the semiconductor upwards in the vicinity of the metal contact. The magnitude of this built-in potential can be quantified from the difference of the energy position of the valence levels at and far away from the interface. In our case it can be estimated to more than 0.7 eV from the binding energy of the P3HT HOMO in thick films and an extrapolation of the HOMO position for very thin samples (see Fig. 2c).

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