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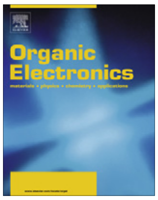

Ultrathin polythiophene films on an intrinsically conducting polymer electrode: Charge transfer induced valence states and interface dipoles

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ABSTRACT

Ultraviolet photoelectron spectroscopy was used to investigate the energy level alignment at interfaces between the organic semiconductor poly(3-hexylthiophene) (P3HT) and poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDT:PSS) electrodes. The thickness of P3HT was varied between sub-monolayer and multilayer (20 nm) coverage. The work function of PEDT:PSS decreased linearly from 4.90 to 4.35 eV as function of P3HT coverage up to a full monolayer, and remained constant for larger thickness. In contrast, the low binding energy onset of the P3HT valence band shifted abruptly by 0.15 eV towards higher binding energy between monolayer and multilayer. These results evidence the formation of an interface dipole confined to the intimate P3HT/PEDT:PSS contact, in full analogy to the already established model for small molecule/electrode interfaces. It is thus necessary to account for interface dipoles at polymer/electrode interfaces, because measurements on thick films may be compromised by additional band bending throughout the semiconductor polymer bulk.

1. Introduction

The development of improved materials for the use in organic electronics relies on a comprehensive understanding of how individual materials' properties change after making contact. Interfaces between electrodes and organic semiconductors determine to a great extent the function and efficiency of many opto-electronic devices, such as light emitting diodes, thin films transistors, and photovoltaic cells [1–3]. Despite their obvious importance, many aspects related to the formation of such interfaces have not yet reached mature understanding. For instance, for organic semiconductors based on small molecules that can be vacuum-sublimed it is well established that the work function (Φ) of electrodes can change significantly due to molecular layer deposition [3]; the origin of this phenomenon is largely attributed to an "interface dipole", which can influence the interfacial energy level alignment by 1 eV or even more [3–5]. This Φ change, often measured by photoelectron spectroscopy, proceeds monotonically (often linear) with electrode coverage between zero and one full molecular monolayer, where it saturates [6]. Many years of research have led to this conclusion, finally enabled by the fact that the coverage of a substrate with sublimed molecules can be precisely adjusted with sub-monolayer accuracy. In contrast, such defined coverage-dependent experiments are difficult to perform with conjugated polymers. One might use electro-spray methods to deposit polymers in vacuum conditions [7], however, film formation proceeds under conditions quite different from those that prevail during application-relevant solution processing. Sub-monolayers of single macromolecules have also been applied from solutions, particularly with stretched-out single polymers exhibiting relatively large cross-sections, such as dendronized polymers and polymer brushes [8,9]. In order to stretch out

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single more flexible polymers such as polystyrenesulfonate, nanostructured surfaces were applied [10], since flexible polymers, including alkylated polythiophenes, tend to collapse or aggregate [11], causing significant heterogeneities in sub-monolayer films. Due to the notorious difficulty to fabricate ultrathin (sub-monolayer range) semiconducting polymer films, detailed investigations on the coverage dependent evolution of electrode Φ and valence electronic energy levels for such polymers are rare [12]. On the other hand, spin coating is a well suited method for preparing polymer films of 10 nm thickness and beyond. In principle, one could use thicker conjugated polymer films for evaluating the energy level alignment under the assumption that the energy levels throughout the semiconductor layer are constant as function film thickness, i.e., no band bending occurs. Nonetheless, clearly discriminating between these two competing effects is complicated if actual polymer film thickness and homogeneity are not well established [13]. It is thus still uncertain to what extent an interface dipole determines polymer/electrode energetics and whether it can clearly be delineated from band bending.

In the present study, we investigate the energy level alignment at a prototypical semiconductor polymer/polymer electrode interface of direct relevance for organic photovoltaics with the polymeric donor poly(3-hexylthiophene) (P3HT) and the intrinsically conductive polymer poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDT:PSS) as electrode. We focus on the initial stage of interface formation by measuring Φ and the valence electronic structure with ultraviolet photoelectron spectroscopy for defined P3HT coverage from the sub-monolayer regime to thick films. Clear evidence for the formation of an abrupt interface dipole between the P3HT monolayer and PEDT:PSS is found.

2. Experimental details

Indium-tin-oxide (ITO) coated glass (sheet resistance 15–30 Ω) was used as substrate. ITO coupons were cleaned by sonication in acetone and isopropanol, followed by 20 min UV/ozone exposure in ambient. PEDT:PSS (AI4083, H.C. Stark GmbH & Co. KG) was spin coated from aqueous dispersion at 1500 rpm and dried at 200 °C for 5 min in ambient atmosphere. P3HT (Aldrich, M_n ~64,000 g/mol) was spin coated (3000 and 1500 rpm) in inert atmosphere from chloroform solution with concentrations of 0.5, 1 and 2 mg/ml to vary film thickness. The chemical structures of the polymers are shown in Fig. 1. Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements were performed at the end station SurICat (beamline PM4) at the synchrotron light source BESSY II (Berlin, Germany). Spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) using an excitation photon energy of 30 eV for UPS and 620 eV for XPS. The secondary electron cutoff (SECO) spectra were recorded with a sample bias of −10 V to clear the analyzer work function. The error of binding energy and work function values reported below is estimated to be smaller than ±0.05 eV. After UPS and XPS measurements samples were washed in 25 ml chloroform for 10 s at ambient atmosphere to reduce the thickness of the P3HT layer to the monolayer regime. A second series of samples were annealed *in situ* at ~120 °C for 30 min. Annealed samples were also washed subsequently in order to reduce the film thickness.

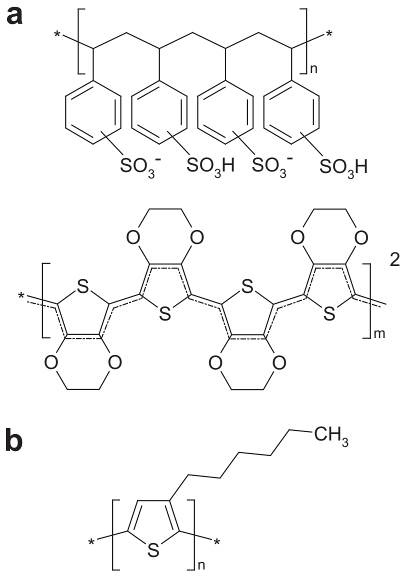

Fig. 1. Chemical structure of (a) PEDT:PSS and (b) P3HT.

To determine the thickness of P3HT films the optical absorption at 550 nm wavelength was used in conjunction with atomic force microscopy (AFM) thickness measurements. For this purpose, P3HT films were spin coated on fused silica with various thicknesses and the absorbance was measured using standard UV–vis spectroscopy (Perkin Elmer, Lambda 650). The film thickness was determined by measuring the step height across a mechanical scratch within the film with an AFM (Veeco Multimode). The slope of a linear fit of absorbance *versus* film thickness yielded a P3HT absorption coefficient at 550 nm of 0.009(4) nm^{-1}. The thickness of P3HT films used for UPS was estimated measuring the absorbance at 550 nm of control samples prepared under identical preparation conditions. The absorbance of control the samples was measured right after preparation to avoid bleaching in ambient conditions. The absorbance of the ITO/PEDT:PSS substrates was measured before spin coating P3HT for every individual sample to establish reliable background spectra for each P3HT film. The thickness of washed ultrathin films was additionally confirmed by evaluating the intensity of the S2p core level signal of the PEDT:PSS substrate in XPS. The P3HT film thickness was calculated assuming an exponential decrease of the substrate signal with increasing P3HT coverage and an elastic mean free path for photoelectrons of 2 nm [14]. The results on P3HT thickness were in good agreement with the values obtained from the absorbance measurements within a maximum error of 25% for ultrathin P3HT films. The main error cause is most likely an inhomogeneous P3HT coverage on top of PEDT:PSS in the