Thin Solid Films xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Photoemission study of the Poly(3-hexylthiophene)/TiO2 interface and the role of 4-Mercaptopyridine

A. Calloni [a,*], G. Berti [a], A. Ferrari [a], A. Brambilla [a], G. Bussetti [a], E.V. Canesi [b], A. Petrozza [b], L. Duò [a]

[a] *CNISM and Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133 Milano, Italy*
[b] *Center for Nano Science and Technology @ Polimi, Istituto Italiano di Tecnologia, via Pascoli 70/3, 20133 Milano, Italy*

ARTICLE INFO

Available online xxxx

Keywords:
Hybrid solar cell
Titanium dioxide
Interface modifier
Band alignment
XPS
UPS

ABSTRACT

We report on a combined X-ray and UV photoemission spectroscopy study (XPS, UPS) of the interface between Poly(3-hexylthiophene) (P3HT) and mesoporous titanium dioxide (TiO_2), a key element in the development of hybrid solar cells. We employed the elemental specificity of XPS to directly probe, on the complete P3HT/TiO_2 heterostructure, the changes in the electronic levels alignment at the interface upon the addition of 4-Mercaptopyridine (4-MPy) molecules. We estimate an upper limit of 50 meV to the contribution of 4-MPy to the P3HT/TiO_2 interfacial dipole. In addition, UPS was used to provide a quantitative estimate of the relevant parameters controlling the transfer of charge through the hybrid interface, such as the binding energy of the TiO_2 valence and conduction bands and of the P3HT highest occupied/lowest unoccupied molecular orbitals. In both cases, we confirm that the alignment of P3HT energy levels to those of the substrate is not influenced by the position of the Fermi level inside the TiO_2 band gap.

1. Introduction

Many efforts have been made with the aim of developing efficient solar cells with substantially lower realization costs than those based on silicon technology. Among the proposed alternatives, dye sensitized solar cells (DSSC) have reported relatively high power conversion efficiencies, on the order of 11% [1,2], but still with some shortcomings, like for instance the use of liquid electrolytes and expensive dye molecules (i.e. ruthenium-based dyes). Concurrently with the development of fully organic devices [3,4], which make use of conjugated polymers sensitive to visible light, hybrid devices have been proposed, which are based on the junction between a porous network of titanium dioxide (TiO_2) nanoparticles (also present in DSSC), and a polymer, such as poly(3-hexylthiophene) (P3HT). Both materials are low cost, easy to synthesize and environment-friendly. Moreover, the use of a TiO_2 scaffold allows a good control on the morphology of the junction and on the phase separation between the electron acceptor (TiO_2) and donor (P3HT) materials.

The authors of Ref. [5] have demonstrated a P3HT/TiO_2 solar cell with an efficiency exceeding 1%, i.e. more than a factor of two with respect to contemporary devices based on the same materials. The key improvement was the addition of a layer of 4-mercaptopyridine (4-MPy) molecules at the P3HT/TiO_2 interface. Under illumination, the "modified" device showed improvements both in the short circuit current and in the open circuit voltage (V_{OC}), which together concur in determining its power conversion efficiency.

The role of interface modifiers, in the form of small molecules which are not directly involved in the light absorption process, has been investigated. Refs. [6,7], focused on the effect of interface modifiers bonded to the TiO_2 surface through carboxylic groups. In those studies, the changes observed in the *I*–*V* characteristic of the hybrid devices upon modification have been directly correlated with the build-up of an electric field induced by the modifiers and directly affecting the band alignment at the hetero junction. In particular, it was shown that V_{OC} scales with the energy difference between the TiO_2 conduction band minimum (CBM) and the polymer highest occupied molecular orbital (HOMO).

An abrupt change in the vacuum potential at the interface with the oxide is indeed observed whenever any sort of interaction with the organic layer takes place, in the form of simple charge transfer or chemical bonding [8]. Those works [6,7] demonstrated the feasibility of an "artificial" control over the interface electronic structure via the insertion of ordered arrays of molecules with an engineered dipole moment.

4-MPy molecules are able to strongly bond to the anatase TiO_2 surface via the nitrogen atom [5,9], and a value of 2.3 D has been calculated for the dipole moment in this bonding configuration [10], which is close to the dipole moment of the pyridine molecule (2.25 D [11]) and of the same magnitude of the dipole moments reported for the interface modifiers used in previous studies [6].

Changes in the energy level alignment at the interface must be apparent in the valence electronic levels, as well as in the core levels, probed by X-ray photoemission spectroscopy (XPS). It has been demonstrated [12] that XPS is able to yield quantitative information

---

* Corresponding author. Tel.: +39 0223996566; fax: +39 0223996126.
E-mail address: alberto1.calloni@mail.polimi.it (A. Calloni).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.11.045

on the effect of dipole layers (created by benzoic and nitrobenzoic acid molecules) at the P3HT/TiO_2 interface by the simultaneous detection of the photoemission signal coming both from the titanium substrate and the polymer overlayer. By following the same methodology, in the first part of this work we will show that the presence of 4-MPy does not induce any observable shift of the P3HT/TiO_2 interface energy levels (i.e. >0.05 eV) which would justify the performance improvement observed in the related device [5].

In the second part of this work, we will retrieve quantitative information on the electronic level alignment at the P3HT/TiO_2 interface by means of UV photoemission spectroscopy (UPS), which allows for an estimate of the surface workfunction. By combining the experimental results obtained from the P3HT/TiO_2 heterostructure, and from a clean TiO_2 substrate it is found that the P3HT energy levels are aligned to those of the substrate and only a small potential drop in the vacuum potential is observed at the interface between the two layers.

2. Experimental details

Three samples were produced and analyzed by means of photoelectron spectroscopy. In the following, they will be referred as: the P3HT/TiO_2 heterostructure (sample A), the P3HT/TiO_2 heterostructure modified with 4-MPy (sample B), the bare TiO_2 substrate (sample C). The structural formulas of 4-MPy and P3HT are shown in Figs. 1a and 1b, respectively.

The samples were prepared on commercial glass substrates coated with fluorine-doped tin oxide (8 Ω/sq from Pilkington). The substrates were covered with a compact TiO_2 layer (150–200 nm thick) obtained by spray pyrolisis of a 1:10 titanium diisopropoxide bis(acetylacetonate):ethanol solution in oxygen at 500 °C. A porous layer, with a thickness of about 1.5 μm, was obtained by doctor blading a commercial Dyesol TiO_2 paste (DSL 18NR-T) on top of the compact layer. The substrates were then fired at 550 °C in air for several minutes in order to promote the partial sintering of TiO_2 nanoparticles. After cooling, substrates were soaked in $TiCl_4$ 15 mM solution in water and oven-baked for 1 h at 70 °C. Following oven-baking, substrates were then rinsed with bidistilled water, dried in air and baked again at 550 °C for 45′. After these steps, sample C was directly analyzed, while the surface of sample B was modified by immersion in a saturated chlorobenzene solution of 4-MPy for several hours (~20 h).

P3HT (purchased by Merck and used without further purification) was then spin coated on samples A and B from a 30 mg/ml chlorobenzene solution. The deposited P3HT material had an average molecular weight (M_w) of 33,500. The low Mw guarantees a good polymer infiltration and a thin P3HT overlayer (few nm thick) left on top of the porous TiO_2 layer.

The samples were analyzed in a dedicated ultra high vacuum system with a base pressure in the low 10^{-8} Pa range by X-ray and UV photoelectron spectroscopy (XPS and UPS). Ultraviolet and X-ray radiations were obtained from a He discharge lamp (HeI line at 21.2 eV) and a Mg anode (Kα line at 1253.6 eV), respectively. Photoelectrons were collected by a 150 mm hemispherical electron analyzer with a pass energy of 25 eV (7 eV) for XPS (UPS). The binding energy (BE) scale for XPS was calibrated using Ag $3d_{5/2}$ (368.1 eV), Au $4f_{7/2}$ (84.9 eV) peaks; an overall full width at half maximum (FWHM) resolution of about 0.9 eV was estimated by fitting a Voigt lineshape to the Au $4f_{7/2}$ peak, taking into account an intrinsic linewidth of about 0.4 eV [13]. For UPS, both the energy scale and resolution (0.3 eV FWHM) were calibrated by fitting a complementary error function to the Fermi edge of a polycrystalline Au specimen. All XPS-UPS spectra were acquired at normal emission.

3. Results

We will focus first on the X-ray photoemission results. We observed sample dependent differences in the BE of the XPS features related to the TiO_2 substrate; in particular, we found that a shift of +0.33 eV was needed to align the spectra acquired from the Ti 2*p* and O 1*s* regions in sample B to those of sample A. The same analysis, performed on the spectra from samples A and C, yielded a negligible shift in the BE scale. We exclude that those differences were related to sample charging effects, given the absence of typical artifacts like unusually broad lineshapes, or changes in the spectra during the measurements. We also verified that the BE of the XPS features was not modified by changing the intensity of the excitation source. Following the method of Ref. [12], we therefore aligned the position of the Ti $2p_{3/2}$ peak in sample B to that of sample A (and therefore also of sample C) by rigidly shifting the BE scale, and then applied the same shift to all the investigated spectral regions.

Fig. 2 shows the results of photoemission from Ti 2*p* and O 1*s* orbitals in samples A and B, i.e. the heterostructures. The accuracy of our alignment procedure (about 0.05 eV) can be appreciated in the insets of Fig. 2, showing a detailed investigation of the Ti $2p_{3/2}$ and O 1*s* peak region.

The Ti 2*p* spectra (panel a) show a clearly resolved doublet, due to the spin orbit splitting of the 2*p* core orbital. The measured BE of the Ti $2p_{3/2}$ peak is 459.1 eV and the spin orbit splitting is 5.8 eV, in good agreement with the results reported in the literature for the Ti^{4+} oxidation state [14,15] and consistent with a fourfold coordination of titanium atoms in anatase TiO_2. We could not detect any signature of reduced (Ti^{3+}) species, usually considered as an indication of the presence of defects, and giving rise to additional photoemission signal at the lower BE side of the main peaks. This implies that a very low, if any, concentration of defects (typically in the form of oxygen vacancies or Ti interstitials) is present in the TiO_2 layer.

The O 1*s* spectra (panel b) show a main peak at 530.5 eV, related to photoemission from O^{2-} atoms in the TiO_2 matrix, and a shoulder extending towards higher BE (up to 3 eV from the main line) attributed to photoemission from hydroxyl (–OH) groups and water molecules, as well as from most of the oxygen functional groups found in airborne contaminants [16,17]. As expected, the alignment procedure devised for the Ti 2*p* spectra also superimposes the other features characteristic of the TiO_2 substrate, such as the O^{2-} peak.

We now move to the photoemission results from the C 1*s* and S 2*p* regions (Fig. 3, panels a and b, respectively).

The C 1*s* lineshape is dominated by photoemission from the alkyl chains in P3HT and by those C atoms in the thiophene ring not directly bound to S, giving rise to a clear peak at 285.2 eV (C–C bonds). The S 2*p* signal is composed by a spin orbit split doublet, and is related to photoemission from the S atom in the thiophene ring. The S 2*p* doublet could be modeled by a sum of two symmetric lineshapes, spaced by 1.2 eV, with the same FWHM and with a fixed 1:2 area ratio. The BE of the S $2p_{3/2}$ peak is 164.3 eV. The C 1*s* to S 2*p* BE difference is 120.9 eV, in close agreement with the literature (see e.g. Ref. [18], dealing with P3HT on Au). The C to S intensity ratio (corrected for the appropriate photoemission cross sections [19]) is about 9.8, in fair agreement with the value expected from the nominal concentration of C and S atoms (10:1) in the P3HT monomeric unit. It is therefore reasonable to assign the observed C 1*s* features mainly to P3HT atoms, with a negligible contribution from contaminants. Given an attenuation length (λ_{Ti}) of Ti 2*p* photoelectrons through the P3HT layer of 2.3 nm (estimated according to the Tanuma Powell and Penn model [20]), and considering the intensity ratio between the P3HT and the TiO_2 XPS signals, we can estimate a P3HT overlayer thickness of few nanometers (≈5 nm). No

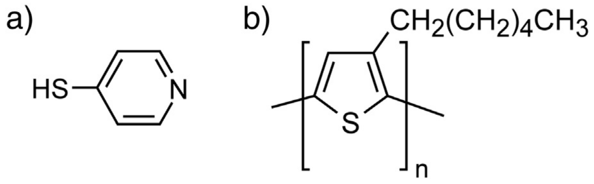

Fig. 1. Structural formulas of a) 4-Mercaptopyridine (4-MPy) and b) Poly(3-hexylthiophene) (P3HT).