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# Electronic properties of a perylene bisimide interfaced with gold or aluminum: The influence of the substrate

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ABSTRACT

The interfaces between perylene bisimide with 4–t–butylphenyl N-substituents (an organic semiconductor) and gold or aluminum were studied by Ultraviolet and X-ray photoelectron spectroscopies (UPS and XPS). Neither of the substrates reacts with the organic semiconductor. An interfacial dipole of 0.5 eV is found at the interface with gold, whereas with aluminum a vacuum level alignment is observed. The onset of the highest occupied molecular orbital (HOMO) was determined at 2.3 eV below the Fermi level. An electron injection barrier of 0.6 eV was found for aluminum and 0.9 eV for gold, which indicates that the interface with aluminum seems more promising for organic field effect applications.

## 1. Introduction

Over the past few years organic semiconductors have attracted an increasing technological interest which is accompanied by a significant progress in fundamental research related to these materials [1]. Among many promising organic semiconductor materials, suitable for organic electronics applications, arylene bisimide derivatives deserve special attention. Their synthesis is relatively facile [2], they combine solution processibility with good n-type semiconducting properties. Moreover, they exhibit air-operating stability in such devices as organic field effect transistors (OFETs) and organic solar cells (OSCs) [3]. N,N′–bis(4–t–butylphenyl)–3,4,9,10–perylene tetracarboxylic–3,4:9,10–bisimide, $C_{44}H_{34}N_2O_4$ (PBI-4-t-BuPh) studied in this research is a member of this family of semiconductors [2].

In this work the interfaces of Au and Al with PBI-4-t-BuPh were studied with the goal to compare the effect of the substrates on the interface energetics. Gold and aluminum are two different work function ($\Phi$) metals commonly used as electrodes in organic electronic devices [4]. The electronic properties and the chemical composition of the interfaces were investigated by X-ray and Ultraviolet Photoelectron Spectroscopies (XPS and UPS).

## 2. Experimental details

Detailed description of the synthesis of PBI-4-t-BuPh and cyclic voltammetry measurements on it can be found in reference [2]. All spectroscopic experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure during measurements lower than $3 \times 10^{-9}$ mbar. For XPS, a non-monochromatized MgK$\alpha$ X-ray source (1253.6 eV) was used. Photoemission spectra were collected with a Leybold-Heraeus EA11 hemispherical energy analyzer operating at constant pass energy of 100 eV for XPS. Ultraviolet Photoemission Spectroscopy (UPS) measurements were performed using the He I line (21.2 eV). In both XPS and UPS the photoelectrons were collected at normal emission with respect to the substrate. For UPS the samples were biased at $-12.22$ V. The analyzer resolution for XPS was measured by the full width at half maximum (FWHM) of the Au4$f_{7/2}$ photoelectron peak of an atomically clean polycrystalline Au foil and was determined to be 1.37 eV at 100 eV pass energy, while for UPS the resolution was 0.21 eV, as determined by the width of the Fermi edge of the same Au foil.

For the XPS quantitative analysis the relative sensitivity factors (RSFs) of Wagner et al. [5] were used after correction for the EA11 spectrometer operating conditions and the analyzer transmission characteristics [6]. In order to calculate the XPS equivalent thickness, the Ladas et al. method [7] was used taking the inelastic mean free path (IMFP) $\lambda_i$ equal to 2.77 nm for C 1s and 3.22 nm for Au4f electrons passing through PBI-4-t-BuPh and 1.87 nm for Au4f electrons moving through gold. The density $\rho$ was taken equal to 1352 kg/m$^3$ and 19300 kg/m$^3$ for the perylene for the gold respectively, the organic semiconductor band gap $E_g = 3$ eV. Wherever thickness is quoted in the subsequent text, the XPS equivalent thickness as calculated above is implied.

Cleaning of the substrate surfaces from adventitious carbon and oxygen due to atmospheric exposure was done under UHV by Ar$^+$

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ion sputtering cycles, at room temperature for Au and at 300 °C for Al. The organic semiconductor was evaporated in situ from a home-made pinhole evaporation source, after careful outgassing, at 380 °C in a stepwise fashion. The pressure during the evaporation steps was less than $5 \times 10^{-9}$ mbar while the substrate was at room temperature. After each deposition step, the surface was characterized by XPS and UPS.

## 3. Results and discussion

No carbon or other contaminants remained on the Au foil after cleaning. On Al surface no carbon could be detected by XPS after cleaning, but a small amount of residual oxygen is always present. XPS was calibrated using the Au4f peak of a clean Au foil at 84.0 eV binding energy (BE).

Fig. 1 below shows the deconvolution of the Al2p peak of the substrate prior to any organic deposition. The peak is resolved into the main metallic Al2p peak at a binding energy of 73.0 eV and a secondary peak at 74.4 eV attributed to the native oxide [8]. The calculated XPS equivalent thickness of the remaining Al native oxide layer after the $Ar^+$ sputtering cleaning cycles was estimated to be 0.4 ± 0.1 nm. This was calculated from the ratio of two Al peaks (Fig. 1) using the method described above.

Upon the deposition of the organic material the substrate metal core level peaks attenuate as new peaks (initially C1s and later O1s and N1s) related to the PBI-4-t-BuPh (not shown). The C1s peak attributed to the studied perylene bisimide starts to appear after the first deposition step corresponding to a thickness of 0.1 nm for both substrates and its intensity increases as the organic film thickness increases.

Fig. 2 presents the C1s core level binding energy as a function of PBI-4-t-BuPh layer thickness. In the case of Au the total change in binding energies can be split into two parts: the first corresponding to a deposition thickness up to 1.7 nm, where the binding energy increases quickly by 0.5 eV and then with further deposition its increase is smaller (0.2 eV), until it reaches the final value of C1s at 285.2 eV BE. This behavior can be explained by polarization screening for the observed increase in the binding energy of the C1s peak during the initial deposition on the clean Au surface. The changes observed for the organic layer thickness exceeding 1.7 nm can be explained by the organic's energy level band bending that occurs at thicker depositions. The energy levels are bent by the charge redistribution in the organic layer to achieve the electrical equilibrium with the alignment of the Fermi levels of the two materials. In the case of Al substrate no change is observed in the core level binding energy within experimental error during the organic deposition which implies that no band bending occurs between the organic semiconductor and $AlO_x$.

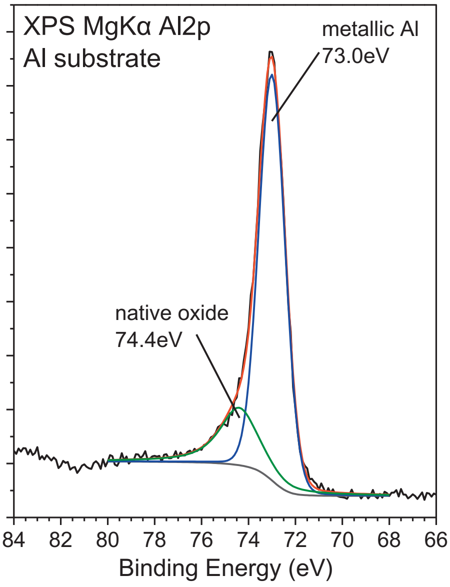

**Fig. 1.** The Al2p XPS peak of the Al pristine substrate.

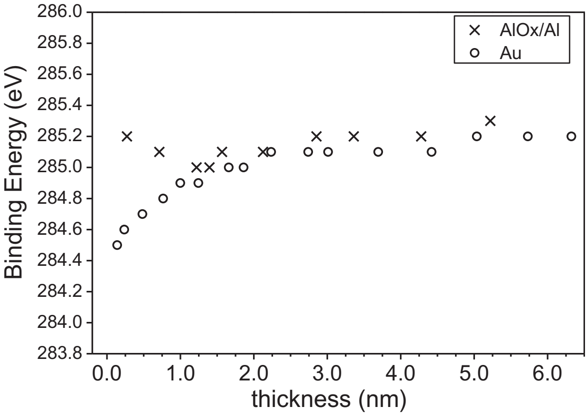

**Fig. 2.** The C1s XPS peak binding energy as a function of PBI-4-t-BuPh thickness on Al (×) and Au (○).

Gaussian–Lorentzian sum peaks were used to fit the C1s core level spectra peaks after the subtraction of a Shirley-type background [9]. The C1s peak for a 6 nm thick organic film on Au was resolved into three components, reflecting photoemission from multiple carbon bonds within the molecule (Fig. 3). The binding energies of the XPS C1s components for the organic overlayer are: 285.2 eV for the aromatic and methyl carbon–carbon bonds, 288.5 eV for the carbon bonds present in the imide parts of the bisimide derivative and 290.9 eV which is a π → π* shake-up satellite of the main peak [10]. The area ratios of the aromatic and methyl to imide carbon peaks are in agreement with the stoichiometry of the PBI-4-t-BuPh molecule. Similar results were found for Al (not shown).

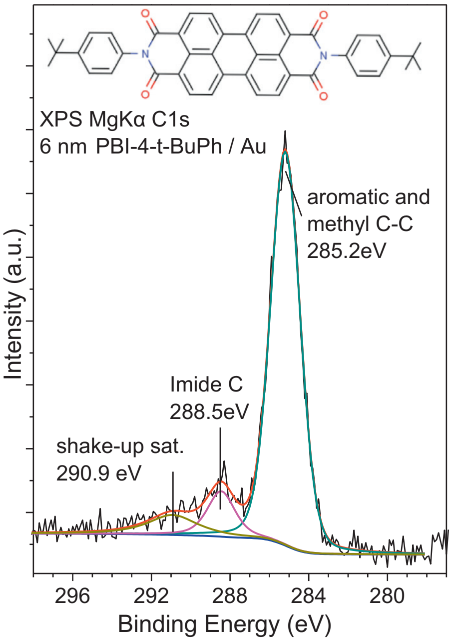

**Fig. 3.** The molecular structure of PBI-4-t-BuPh (insert) and the C1s XPS peak of a 6 nm perylene bisimide thick film deposited on Au.