Organic Semiconductor Valence Band Alignment Determined By Internal Photoemission Spectroscopy

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We report the determination of the valence band (VB) alignment for the polymer semiconductors Poly(3-hexylthiophene) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM) by using internal photoemission (IPE) spectroscopy. IPE is a mature and robust measurement technique for determining the band off-set at metal-oxide-semiconductor (MOS) interfaces in advanced CMOS devices and at semiconductor:semiconductor interfaces in advanced heterostructures. We report here on the successful use of this technique in determining the band off-set between the P3HT VB or PCBM VB and the conduction band (CB) of silicon dioxide (SiO_2) from which we are able to determine the VB position of P3HT or PCBM relative to the vacuum level. Solutions of each organic semiconductor were spin coated onto 280 nm thick SiO_2 on heavily doped P-type silicon. A 10 nm thick semitransparent aluminum (Al) electrode with adjoining 70 nm thick Al contact pad were deposited onto the organic semiconductor films through aligned shadow masks. The schematic of the completed IPE test structure is shown in Fig. 1. All processing was done in an argon filled glove box. IPE measurements were made in air. Spectroscopic Ellipsometry was used to determine the SiO_2 bandgap and thickness, and the average organic semiconductor film thickness.

Photocurrent in the IPE measurement was generated by using a monochromator with photon energy ranging from 1.5eV to 6.0eV (0.05 eV steps) and with a DC voltage which ranged from 20V to -20V (-2V steps) applied between the silicon backside and the thick Al contact. Both positive photocurrent (electrons excited from the P3HT VB or PCBM VB to the SiO_2 CB and collected by the Si substrate contact) and negative photocurrent (electrons excited from the Si valence band to the SiO_2 CB) were observed. The latter provides greater accuracy in determining the relative position of the SiO_2 CB. For the IPE measurement, the yield (Y) is defined as the ratio of the carriers contributing to the photocurrent to the incident photon flux, and the threshold at each applied voltage is obtained by extrapolating $Y^{1/3}(h\nu)$ to zero according to Fowler coordinates [1]. The barrier height is determined from Schottky plots extrapolated to zero field. By using this established method we extract a barrier height of 4.2 eV ± 0.1 eV for the Si:SiO_2 interface, 4.0 eV ± 0.1 eV for the P3HT:SiO_2 interface, and 4.5 eV ± 0.1 eV from preliminary results for the PCBM:SiO_2 interface. No photocurrent was observed at photon energy near 3.3 eV, indicating thtat photoexcitation from the Al contact did not contribute to the measured positive photocurrent. The CB of SiO_2 is known to reside 0.9 eV below the vacuum level [2], thus yielding a P3HT VB position of 4.9 eV ± 0.1 eV and a PCBM VB position of 5.4 eV ± 0.1 eV relative to the vacuum level. Reported values from Ultraviolet Photoelectron Spectroscopy studies are closer to 4.6 eV for ordered P3HT [3,4] and 5.8 eV for PCBM [3]. Work is in progress to extend this study to other donor and acceptor-like organic semiconductors.

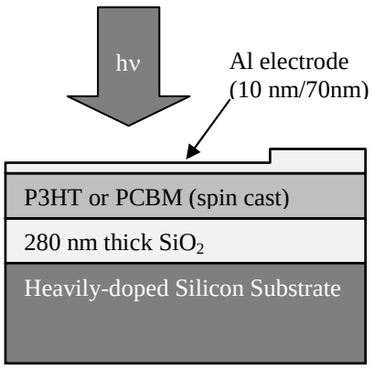

Figure 1. Schematic cross-section of the IPE test structure

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