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Photoelectron spectroscopic study on band alignment of poly(3-hexylthiophene-2,5-diyl)/polar-ZnO heterointerface

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ABSTRACT

We used hard X-ray photoelectron spectroscopy (HX-PES) to investigate the polarity effect of ZnO, which has Zn terminated (+ polar) and O terminated (− polar) surfaces, on poly(3-hexylthiophene-2,5-diyl) (P3HT)/ZnO photovoltaic structures. HX-PES, which has a longer inelastic mean free path than conventional X-ray photoelectron spectroscopy, revealed that the open circuit voltage (V_{OC}), estimated from the gap between the highest occupied molecular orbital of P3HT and the conduction band minimum of Zn-polar ZnO, was larger than that of the O-polar ZnO. Although polarity dependence was observed for the electrical structure at the P3HT/ZnO interface, the V_{OC} of the photovoltaic property of Zn-polar ZnO was almost the same as that of O-polar ZnO (~0.4 V) due to electron–hole recombination, which degrades the photovoltaic properties at the interface. The HX-PES results also suggested that the recombination could be attributed to the short depletion length of the ZnO surface.

1. Introduction

Organic/inorganic photovoltaic structures have good potential for practical devices applications owing to their cost effective and large-area fabrication techniques [1–4]. A poly(3-hexylthiophene-2,5-diyl) (P3HT)/zinc oxide (ZnO) photovoltaic structure is a promising candidate [5–9]. This is because P3HT, which is a p-type conjugated polymer, is suitable for use as the absorbing layer owing to its high hole mobility and ambient stability [10]. ZnO has attractive properties including a wide band gap, a high quantum efficiency, and the potential for application to various low temperature growth techniques [11–13]. As regards the photovoltaic performance, the interfacial band alignment of the organic/inorganic interface is especially important. In particular, the open circuit voltage (V_{OC}), which can be estimated from the gap between the highest occupied molecular orbital (HOMO) of an organic material and the conduction band minimum (CBM) of an inorganic material, is strongly dependent on the band offset at the organic/inorganic interface [14]. As regards the P3HT/ZnO interface, although the theoretical V_{OC} was 2.07 V [15], the reported experimental V_{OC} estimated by current–voltage (I–V) measurements was ~0.5 V [16,17], suggesting that the band alignment of the P3HT/ZnO interface is not yet fully understood. Furthermore, ZnO has a wurtzite crystal structure with two distinct {0001} planes. A lack of inversion symmetry and ionic bonds makes this material polar. ZnO single crystals with a Zn-terminated plane (0001) and an O-terminated plane (000–1) are denoted as Zn-ZnO and O-ZnO, respectively. These two faces have different structures, compositions, and chemical and physical properties [18–20]. The electrical interface structures at the P3HT/ZnO interface should therefore be different.

The aim of this work was to investigate the polarity effect of ZnO on a P3HT/ZnO photovoltaic structure. To probe the entire organic/inorganic interface structure and the band bending behavior in the inorganic region, we employed hard X-ray photoelectron spectroscopy (HX-PES). HX-PES is a powerful tool for investigating a heterostructure interface because it has a longer mean free path than conventional X-ray photoelectron spectroscopy using Al Kα radiation (XPS: $h\nu = 1486.6$ eV). [21,22]. Furthermore, by combining angle-resolved measurements (AR-HX-PES), HX-PES allows us to obtain rough measurements of the depth profiles at the P3HT/ZnO interface.

2. Experimental apparatus and method

The ZnO substrates were fabricated by hydrothermal synthesis (Tokyo Denpa Co., Ltd.) One side of the substrates had a Zn-terminated face and the other an O-terminated face. The substrates were annealed in an oxygen atmosphere at 950 °C for 7 h to obtain a clear step-and-terrace surface. Both substrate surfaces were spin coated with a 3 wt.% P3HT (Sigma–Aldrich, 483095) chlorobenzene aqueous solution and annealed at 180 °C for 30 min in a 1×10^{-2} Pa vacuum. 40- and 300-nm-thick P3HT films were coated on the substrates for HX-PES and electrical measurements, respectively. For the photovoltaic performance

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measurement, a bottom indium tin oxide (ITO) electrode was deposited on the reverse of the ZnO and Ag top electrodes were deposited on P3HT using DC sputtering and vacuum evaporation methods, respectively. The Ag for the HX-PES and electrical measurements was 5 and 100 nm thick, respectively. HX-PES was performed at the SPring-8 BL15XU undulator beamline [23]. The total energy resolution of HX-PES was 240 meV. To determine the absolute binding energy, the photoelectron spectra data were calibrated against the Fermi level position of Au. The sample was in contact with the system ground, whose energy was equal to the Fermi level position of Au, via a conductive copper tape. Core level spectra were fitted using the Voigt function after the background had been removed by employing the Shirley function [24]. AR-HX-PES measurements were performed at take-off angles (TOAs) of 7, 30, 50, and 60°; a TOA of 60° is surface/interface sensitive, whereas a TOA of 7° is bulk sensitive. To estimate the band bending behavior of P3HT, a detailed AR-HX-PES analysis was performed using COMPRO (Common Data Processing System) ver.11 written by Yoshihara and Yoshikawa, which simulates the potential energy distribution using the convolution of calculated peaks at several TOAs [22,25,26]. In this study, the band bending direction was denoted as downward and upward band bending. Upward and downward band bending denote the relative band bending toward the conduction and valence band, respectively. The surface morphology was observed using atomic force microscopy (AFM; SII NanoTechnology Inc., SPI4000 & E-sweep). The I–V characteristics and photovoltaic performance of these samples were evaluated using a semiconductor parameter analyzer (Agilent, B1500A) with AM1.5G solar irradiation from the bottom electrode side with a light density of 100 mW/cm^2.

3. Results and discussion

Fig. 1 shows AFM images of polar ZnO substrates and P3HT/polar ZnO stack structures. The ZnO substrates had step and terrace structures. The root mean square (RMS) roughness values of Zn-ZnO and O-ZnO were 0.29 ± 0.05 and 0.24 ± 0.05 nm, respectively. After the P3HT coating, the surfaces of P3HT on Zn-ZnO and O-ZnO had a small grained structure as shown in Fig. 1(c) and (d). The RMS roughness values of P3HT on Zn-ZnO and O-ZnO were 0.72 ± 0.05 and 0.78 ± 0.05 nm, respectively. The surface morphology and growth rate did not exhibit any polarity dependence.

Fig. 2(a) shows the valence band (HOMO state) spectra of the P3HT on Zn- and O-ZnO measured by HX-PES. The valence band spectra of Zn- and O-ZnO substrates are also shown as references. The spectra of the P3HT/ZnO consisted of the superimposed spectra of P3HT and ZnO, meaning that HX-PES probed the P3HT/ZnO interface. The difference between the shapes of the spectra of the P3HT on Zn- and O-ZnO around 5 eV originated in the difference between the O 1*s* states of the Zn- and O-ZnO substrates [27,28]. The top of the HOMO state of the P3HT exhibited no polarity dependence due to the weak signal as shown in the inset of Fig. 2(a). However, polarity dependence was observed with the core level spectra. Fig. 2(b) shows S 1*s* spectra of P3HT/Zn- and O-ZnO at a TOA of 7°. Zn-ZnO showed a clearer asymmetry property than O-ZnO, which can be speculatively attributed to the band bending

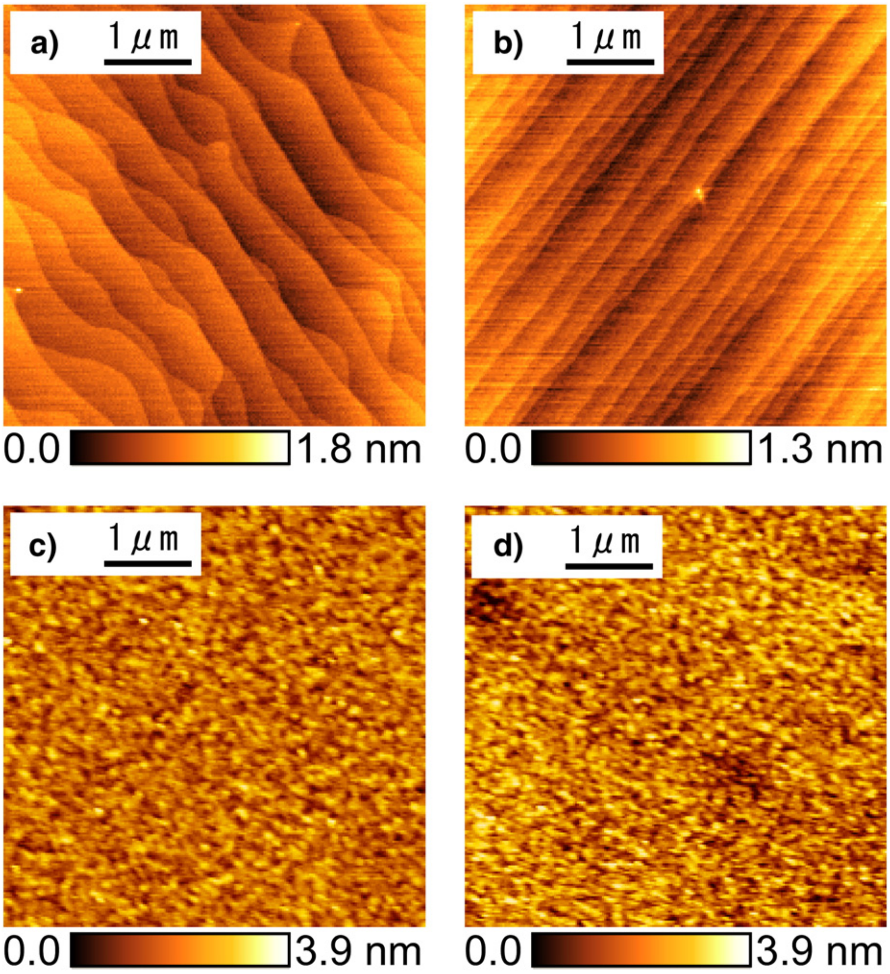

Fig. 1. AFM images of (a) Zn-ZnO substrate, (b) O-ZnO substrate, (c) P3HT/Zn-ZnO, and (d) P3HT/O-ZnO.