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Surface potential measurement of organic photo-diode consisting of fullerene/copper phthalocyanine double layered device

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Abstract

We investigated the surface potential built across the electrode/fullerene (C_{60}) or copper phthalocyanine (CuPc) interface and C_{60}/CuPc interface as a function of the thickness of the semiconductor film in the dark condition and under illumination. The surface potential of C_{60} on Au, Al and Mg changes negatively with the increment of film thickness and it saturates at −0.25, −1.0 and −1.5 V within 20 nm. The Fermi level alignment at C_{60}/electrode interface is established within ∼20 nm from electrode, and very high electric field exists due to the displacement of negative electronic charges from electrode into C_{60}. On the other hand, the surface potential of CuPc on ITO changes to +0.1 V, and the work functions of C_{60} and CuPc were estimated as 5.0 eV and 4.7 eV. C_{60} film also accepts electrons from CuPc at hetero-junction interface, and the Fermi-level alignment was again obtained at C_{60}/CuPc interface under illumination. The built-in potential of ca. 0.3 V formed at C_{60}/CuPc interface was considered as the origin of the reduction of open-circuit voltage in ITO/CuPc/C_{60}/Au device compared with the optimum value of 0.6 V. On the other hand, the very high electric field formed at C_{60}/Mg contact improved the photovoltaic properties.

Keywords: Surface potential; Phthalocyanine; Fullerene; Photovoltaic device; Open circuit voltage

1. Introduction

Solid state organic photovoltaic devices have been attracting a great deal of attention recently because of their potential as very low cost, easily fabricated solar energy converters. The developments of donor–acceptor (DA) hetero-junction cell [1] and the bulk hetero junction of DA blend type photo-diodes [2,3], such as phthalocyanine/fullerene [4–6] or conducting polymer/fullerene derivatives [7–11], led to the dramatic improvement of solar power conversion efficiencies of $\eta_P \sim 5\%$. However, there are still unknown mechanisms in the photovoltaic properties, such as the origin of the open circuit voltage, band bending profiles formed at electrode interface or p–n junction and their effect on the photovoltaic properties and so on. There are three considerable origins of the open circuit voltage V_{OC} in organic photovoltaic devices; i) Firstly, the diffusion potential (or built-in potential) V_D formed at the p–n junction has been considered as the typical origin of V_{OC}. However, the concept of V_D had been established for the inorganic semiconductor physics. And it is acceptable under the assumption that the same mechanism is applicable to the organic photovoltaic devices [12]. ii) Secondly, it is relatively difficult to define Fermi level of the non-doped organic semiconductor, and it probably works as a dielectric material rather than semiconductor in the dark condition. In organic p–n junction, photo-carrier generation will mainly occur at the donor–acceptor interface. Where p-type semiconductor is electron donor and n-type semiconductor is electron acceptor. Therefore, the quasi Fermi level of p-type semiconductor locates around HOMO of electron donor (HOMO-D), whereas the quasi Fermi level of n-type semiconductor locates around LUMO of electron acceptor (LUMO-A). In this case, an optimum value of V_{OC} is often expected as the energy level difference between LUMO-A and HOMO-D [5]. iii) And thirdly, the internal electric field due to the Fermi level difference of electrode materials or the Fermi level difference between the electrode and semiconductor materials should be also the other origin of V_{OC}. The surface potential measurement, which is known as Kelvin prove technique, is widely used to determine the relative work function of metals and semiconductors as well as the surface photo-induced

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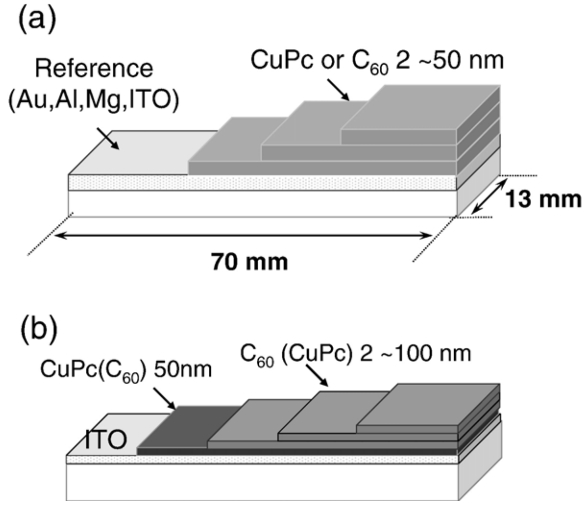

Fig. 1. (a) Sample configuration of the surface potential measurement for electrode/organic semiconductor contact, and (b) for C_{60}/CuPc hetero-junction interface.

voltage of semiconductors by measuring the contact potential difference between a reference surface and the surface of the samples. It has been therefore used to determine the band offset and energy level alignment in hetero-junction, electrode/semiconductor interfaces, and is used to measure the dipole formed on the surface of the materials [13–18]. Furthermore, the thickness dependence of the surface potential of hetero-junction or electrode/semiconductor interface will give us the very important information about the actual band bending profiles, distribution of internal electric field etc.

In this study, we investigated the surface potential profiles built across the electrode/fullerene (C_{60}), electrode/copper phthalocyanine (CuPc) and C_{60}/CuPc interface as a function of the thickness of the semiconductor film in the dark condition and under illumination. We have then discussed the photovoltaic properties of p–n junction devices consisting of phthalocyanine and fullerene double layered structure taking into account the surface potential profiles.

2. Experimental

Sublimated copper phthalocyanine (CuPc) and fullerene (C_{60}) were used as p-type (donor) and n-type (acceptor) organic semiconductors.

For the surface potential measurement, CuPc was evaporated on ITO coated glass slide as illustrated in Fig. 1(a). The solvent-cleaned ITO electrode was treated by UV-ozone for 20 min before deposition of CuPc. In a same manner, C_{60} was evaporated on Au, Al, and Mg-coated glass slide (70 mm × 13 mm). The deposition rates of CuPc and C_{60} thin films were 0.1 nm/s and 0.1–0.15 nm/s, respectively, and the substrate temperature was maintained at 30 °C. The samples for the surface potential built across CuPc/C_{60} interface was prepared on ITO electrode. A 50-nm-thick CuPc or C_{60} film was firstly deposited on ITO, the second-layer of C_{60} or CuPc was then deposited as shown in Fig. 1(b). Surface potential were measured in a conventional glove box which was filled with the nitrogen atmosphere by conventional Kelvin prove (TRECK 320C). Here, the resolution of the Kelvin prove is 0.01 V. All samples were heat-treated at a temperature of 100 °C for 30 min before the surface potential measurement to remove the adsorbates, such as water molecules, and to stabilize the surface potential. The samples were spontaneously cooled down to room temperature and then fixed on the sample folder of the surface potential equipment. The surface potential built across C_{60} and CuPc film was then measured as a function of the film thickness of organic semiconductor, assuming that the surface potential of clean base electrode (indicated as position A in Fig. 2) was zero in the dark condition and under illumination [13–15]. Similarly, the built up potential across C_{60}/CuPc hetero-junction interface were measured as a function of the

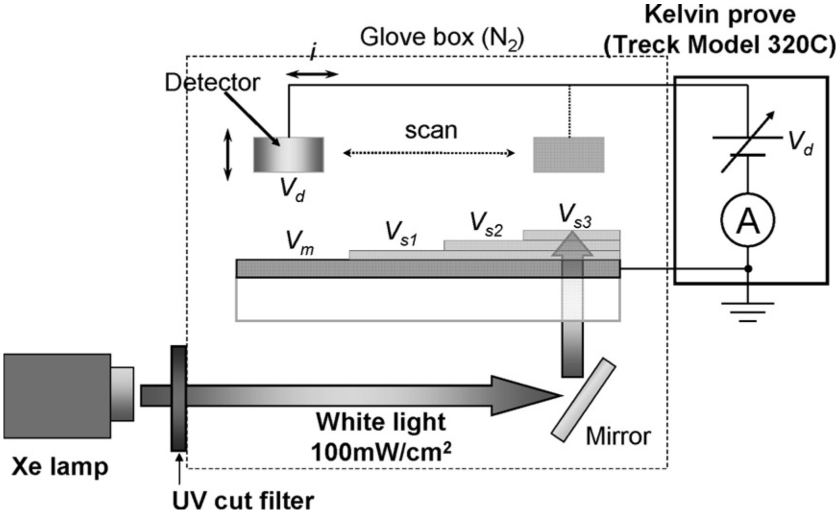

Fig. 2. Configuration of surface potential measurement. Surface potential was measured with reference to reference electrode (position A) in order to measure the charge phenomena at electrode/film interface. The potential built across C_{60}/CuPc interface was measured with reference to the potential of 50-nm-thick CuPc first layer (or C_{60}).