

Investigation of photovoltage generation at donor/acceptor interfaces in organic solar cells using soft X-ray photoelectron spectroscopy

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Understanding energy loss processes at organic donor-acceptor (D-A) interfaces in organic solar cells (OSCs) is an important research issue to enhance its device performance. In the past 10 years, carrier dynamics at D-A interfaces have been intensely studied using various analytical methods. Nevertheless, carrier recombination mechanisms at D-A interfaces in OSCs have not been clearly understood yet due to its complex device structures and the difficulty in the extraction of the interface information[1]. From these backgrounds, we have investigated carrier generation and recombination processes at D-A interfaces in OSCs using D-A bilayer heterojunction structure, of which structural properties (e.g., molecular orientation) were well controlled. In this manuscript, the study on the photovoltage generated at the D-A interfaces under laser irradiation using X-ray photoelectron spectroscopy is reported.

Sample preparation was done in UHV chamber using the thermal evaporation method. C₆₀ and zinc phthalocyanine (ZnPc) was chosen as acceptor and donor, respectively. A buffer layer (5 nm-thick molybdenum oxide (MoO₃) and 3 nm-thick copper iodine (CuI)) was formed on Au deposited Si wafer (Au/Si), and then 20 nm-thick ZnPc thin film was formed on it. Such a surface modification technique using a proper buffer layer is useful for controlling the molecular orientation of ZnPc (on MoO₃: edge on; on CuI: face on) [2]. Finally, C₆₀ thin film was formed on ZnPc/buffer/Au/Si to make a D-A bilayer heterojunction structure. As an exploratory experiment, we have evaluated two solar cell structures; (1) ITO/MoO₃(5 nm)/ZnPc(20 nm)/C₆₀(40 nm)/Ag (edge on orientation of ZnPc) and (2) ITO/CuI(3 nm)/ZnPc(20 nm)/C₆₀(40 nm)/Ag (face on orientation). The conversion efficiencies of the devices (1) and (2) measured under irradiation from solar simulator were 1.4 and 2.3 %, respectively. Namely, the face on orientation of ZnPc seems to be effective for suppressing the energy loss of OSCs. The X-ray photoelectron spectrum under a He-Ne laser irradiation ($\lambda = 632.8$ nm) was taken at BL07LSU. The photon energy of the incident X-ray was fixed at 520 eV. The photovoltage generation at organic layers was evaluated from the energy shift of the photoelectron spectrum by changing the laser fluence from 0 to 10 mW/mm².

Figure 1(a) shows N1s photoelectron spectra of 20 nm-thick ZnPc on MoO₃ buffer layer measured under no laser irradiation and under laser irradiation with fluence of 10 mW/mm². The energy shift of the N1s peak of ZnPc to the high binding energy (E_b) side was found in case of laser irradiation. Since the mean free path of the N1s photoelectron is estimated to be below 1 nm, this peak shift indicates the generation of the surface photovoltage. The relation of the laser fluence with the N1s peak position is summarized in Fig. 1(b). It was found that the peak position shifted toward high binding energy side with increasing the laser fluence, and the energy shift of 60 meV was found when He-Ne laser with fluence of 10 mW/mm² was irradiated. Such a large photovoltage for a single-phase organic thin film was not observed in the past reports. It maybe caused by the modification of the electrical

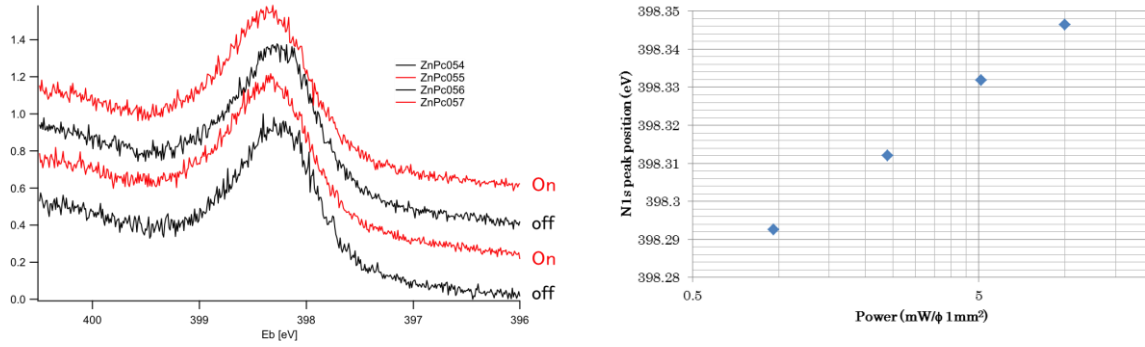


Fig.1 (a) N1s photoelectron spectra of 20 nm-thick ZnPc on MoO₃ buffer layer measured under no laser irradiation (off) and under laser irradiation (on) with fluence of 10 mW/mm². (b) Relation of the laser fluence with the N1s peak position of ZnPc formed on MoO₃.

contact (ohmic contact) at the acceptor/substrate interfaces, which promotes the extraction of the photo-generated charges from ZnPc to substrates.

Next, 3 nm-thick C₆₀ layer was deposited on the ZnPc/MoO₃ heterostructure sample shown in Fig.1, and the variation of the photoelectron spectrum was investigated. As a result, the peak shift of 80 meV was observed at 10 mW/mm² laser irradiation, as shown in Fig.2. The origin of the increase in the photovoltage for the C₆₀/ZnPc/MoO₃ heterostructure can be considered as the generation of electric charges, which occurred according to the charge separation at the D-A interfaces.

As for 20 nm-thick ZnPc formed on CuI, on the other hand, we cannot find any spectral shift under the laser irradiation. Since the decomposition of the CuI buffer and the diffusion of Cu to the inside of ZnPc took place, this result was caused by a failure of the sample preparation.

From the above experiment, it became clear that the origin of photovoltage originates in the electric charges which occurred in the ZnPc layer at the time of light irradiation, and that the charge generation is promoted by the interface of ZnPc/C₆₀. To clarify the disappearance process of the photovoltage, which is influenced by the energy loss in D-A interfaces, now we have a plan to measure the time resolved X-ray photoelectron spectroscopy[3].

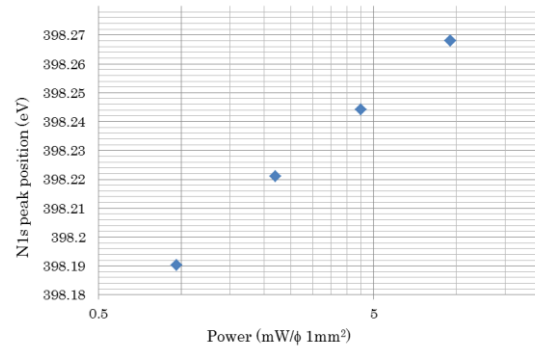


Fig.2 Relation of the laser fluence with the N1s peak position of ZnPc in C₆₀(3 nm)/ZnPc(20 nm)/MoO₃ heterostructure.

References

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