

Observation of transient photo-voltage at donor/acceptor interfaces in organic solar cells using time resolved X-ray photoelectron spectroscopy

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Organic thin film solar cells have attracted considerable attentions due to their low cost and flexible usages. Nevertheless, the mechanism of the device operation has not completely understood yet due to its complex device structures and the difficulty in the extraction of the interface information. As a factor of the energy loss in organic thin film solar cells, it is considered that the energy loss accompanying the exciton recombination, which happens at donor/acceptor (D-A) interfaces, is regarded as an important research subject in order to compete with a carrier generation reaction. In this manuscript, the study on the transient photovoltage generated at the D-A interfaces under pulsed laser irradiation using time resolved X-ray photoelectron spectroscopy (TRPES) is reported. In order to simplify the analysis of the carrier generation and recombination mechanism, we introduced D-A bilayer heterojunction structure, of which structural properties were well controlled.

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 an Indium Tin Oxide (ITO) substrate, 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) [1]. Finally, C₆₀ thin film was formed on ZnPc/buffer/ITO 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. TRPES utilizing a laser-pump synchrotron-radiation (SR)-probe method was taken at BL07LSU[2]. The photon energies of pump laser (pulse duration ~35 fs) and probe SR light (pulse duration ~ 50 ps) were fixed at 3.06 eV and 400 eV, respectively. Surface photovoltage (SPV) at organic layers was evaluated from the energy shift of the photoelectron spectra.

Figure 1 shows C1s spectra of C₆₀(3 nm)/ZnPc(20 nm) heterostructure formed on CuI buffer layer measured at delay times of (a) 100 ps, (b) 300 ps, and (c) 1 ns. Since mean free path of the C1s photoelectron is estimated to be below 1 nm, this peak indicates the signal of C₆₀. Upon laser pulse irradiation, C1s spectra are shifted towards the lower binding energy side by the SPV effect. The origin of the SPV for the C₆₀/ZnPc/CuI heterostructure can be considered as generation of electric charges, which occurred according to the charge separation at the D-A interfaces. The SPV is diminished with the delay time evolution. The relaxation time of the SPV of the C₆₀/ZnPc interface is roughly estimated as 1 ns, which is almost coincident with the extinction time of photo-generated cation and anion observed by transient absorption measurements[3]; therefore, the reduction of the SPV relaxation can be explained by the charge recombination at the C₆₀/ZnPc interface. Figure 2 shows C1s

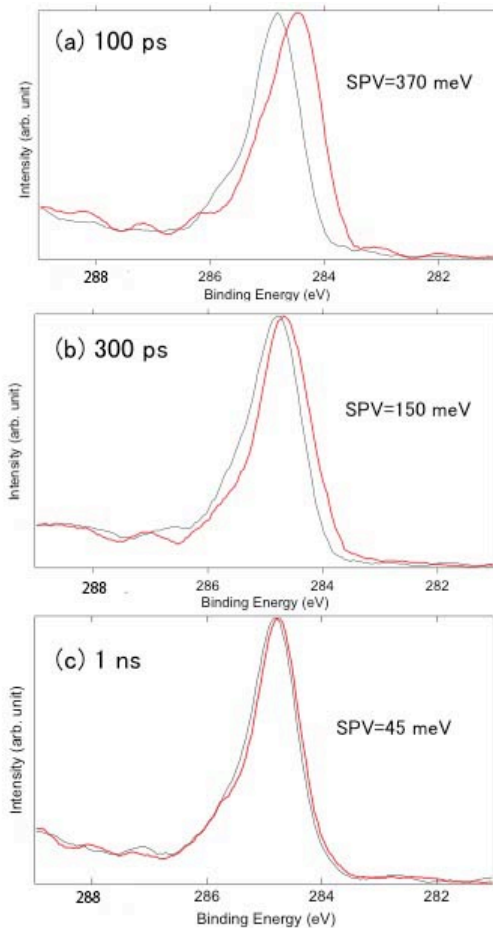


Fig.1 (red) C1s spectra of $C_{60}(3 \text{ nm})/\text{ZnPc}(20 \text{ nm})$ heterostructure formed on CuI buffer layer measured at delay times of (a) 100 ps, (b) 300 ps, and (c) 1 ns. (black) C1s spectra measured before irradiation.

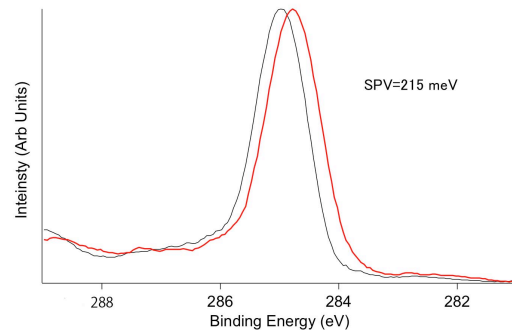


Fig.2 (red) C1s spectrum of $C_{60}(3 \text{ nm})/\text{ZnPc}(20 \text{ nm})$ heterostructure formed on MoO_3 buffer layer measured at delay time of 100 ps. (black) C1s spectrum measured before irradiation.

spectra of $C_{60}(3 \text{ nm})/\text{ZnPc}(20 \text{ nm})$ heterostructure formed on MoO_3 buffer layer measured at delay time of 100 ps. The SPV value of 215 meV is 1.7 times smaller than that observed for $C_{60}/\text{ZnPc}/\text{CuI}$. The variation of SPV might be explained by the intensity of optical absorption of oriented ZnPc films [4]. The relaxation time of the SPV for $C_{60}/\text{ZnPc}/\text{MoO}_3$ is still under investigation. To clarify the disappearance process of SPV, which is influenced by the energy loss in D-A interfaces, now we have a plan to compare the SPV decay process for both samples.

References

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