

Investigation of photo-carrier generation processes of organic solar cells using time resolved X-ray photoelectron spectroscopy

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Abstract

To investigate the carrier dynamics at donor/acceptor (D-A) interfaces in Organic thin film solar cells (OSCs), we measured the surface potential after pulsed laser irradiation using time resolved X-ray photoelectron spectroscopy (TRPES). By analyzing the photoelectron energy shifts after irradiation, we found that surface photo-voltage (SPV) was not much generated at the D-A interface, even under high irradiation flux. The lack of an internal electric field at D-A interfaces may cause the absence of SPV. Controlling the electrostatic potential gradient at D-A interfaces is therefore important for effective carrier generation in OSCs.

1. Introduction

Organic thin film solar cells have attracted considerable attentions due to their low cost and flexible usages. The mechanism of the device operation, however, has not completely understood yet. The energy loss accompanying the exciton decay, which occurs at the donor/acceptor (D-A) interfaces, is regarded as an important research subject in order to compete with the carrier generation and to enhance the energy conversion efficiency. In this manuscript, we report our study of transient photovoltage generated at D-A interfaces under pulsed laser irradiation using time resolved X-ray photoelectron spectroscopy (TRPES).

2. Experiments

Sample preparation was done using the thermal evaporation method. C₆₀ and zinc phthalocyanine (ZnPc) were chosen as acceptor and donor molecules, respectively. A buffer layer of 3 nm-thick copper iodine (CuI) was formed on an Indium Tin Oxide (ITO) substrate for controlling the molecular orientation of ZnPc (face on orientation). C₆₀ thin films were formed on ZnPc/CuI/ITO to make a D-A bilayer heterojunction. TRPES, utilizing the laser-pump synchrotron-radiation (SR)-probe method, was taken at BL07LSU at SPring-8 [1]. Pump laser (pulse duration ~35 fs; photon energy 3.06 eV) and probe SR light (pulse duration ~50 ps; photon energy 400 and 600 eV) were used during the measurements. The absorption coefficient of ZnPc and C₆₀ at 3.06 eV are 4×10^4 and 8×10^4 cm⁻¹, respectively. Therefore, the decay length of the photon is fairly long as compared with the thickness of the specimen,

and the pump laser was absorbed for both layers. Amount of the surface photovoltage (SPV) at organic layers was evaluated from the core-level energy shift in the photoelectron spectra.

3. Results and Discussion

Fig.1 shows C1s spectra of C₆₀(3 nm)/ZnPc(20 nm) heterostructure formed on CuI buffer layer measured at the probe delay times of 100, 300, 500 ps, and 1 ns. Since mean free path of the C1s photoelectron, under the present measurement condition, is estimated to be below 1 nm, the peak corresponded to the signal of C₆₀. Upon laser pulse irradiation, the C1s peaks were shifted towards the lower binding energy, and the shift was diminished with the delay time evolution. The relaxation time of the spectral shift of the C1s photoelectron is roughly estimated as ~1 ns.

To understand the nature of the spectral shift after irradiation of the pump laser, we investigated TRPES spectra using different probe SR light. In these measurements, the 3.06 eV pump laser with a power density of 50 mJ/cm²/pulse was used, and the probe delay time was fixed to 100 ps. The change

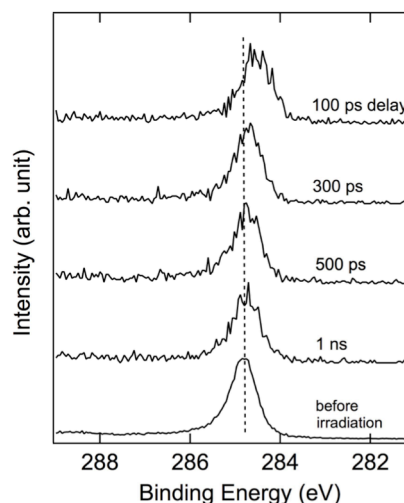


Fig.1 Change in C1s spectra of C₆₀(3 nm)/ZnPc (20 nm) heterostructure formed on CuI buffer layer as a function of delay times. The 3.06 eV laser with a power density of 6.7 mJ/cm²/pulse and the 400 eV SR light were used.

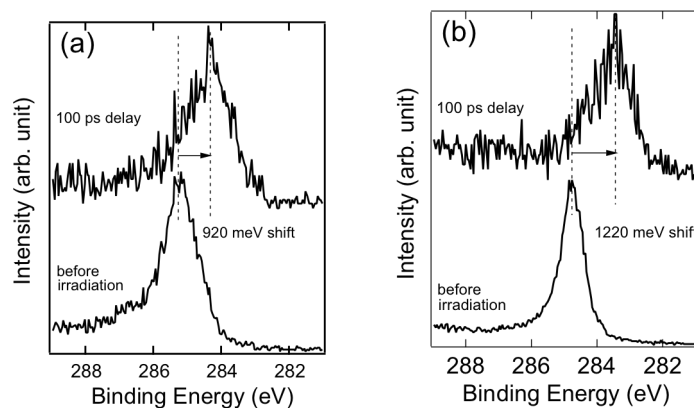


Fig. 2 C1s photoelectron spectra taken with (a) 600 eV and (b) 400 eV probe SR light. The 3.06 eV pump laser with a power density of 50 mJ/cm²/pulse was used. The delay time was fixed to 100 ps.

in the spectral shift of the C1s photoelectron upon the laser irradiation was found when changing the photon energy of the SR light from 400 to 600 eV, as shown in Fig. 2. If the spectral shift upon the laser irradiation was originated from SPV, the shift of the C1s peak must be constant regardless of the probe SR light. Thus, the spectral shift was not mainly caused by SPV and the other reason has to be considered.

Fig. 3 shows spectral shift of C1s photoelectron as a function of the intensity of the excitation laser in double logarithmic plot. The carrier generation at organic D-A interfaces is known to be proportional to the incident light power. In contrast, the energy shift with TRPES increased in proportion to the square of the excitation laser intensity, as illustrated by slope of the fitted line in Fig. 3. Such a nonlinear increase in the energy shift was observed in case that space charges were induced at the surface by pump laser[2].

Multi-photon electron emission, in which an electron absorbs multiple photons simultaneously, takes place when intense ultrashort laser pulses are irradiated to specimens. Since the ionization energies of ZnPc and C₆₀ are 5.2 and 6.2 eV respectively, two-photon emission, of which probability depends on the square of the excitation light intensity, was probably induced before probe SR light irradiation. The electron cloud emitted along the normal direction by the pump laser influences the distribution of the electric potential on the specimen surface, causing the spectral shift of C1s photoelectrons. The power dependency and the relaxation time of the spectral shift correspond to the trend in the previous report [2], our model may explain the experimental results.

The injection level of photons by the pump laser is several orders of magnitude higher than that of the sunlight [1]. The absence of the SPV upon pump laser irradiation is likely due to the flat potential in organic layers. Namely, spatial separation of the photo-generated electron-hole pairs hardly occurs due to the lack of the internal electric field. Therefore,

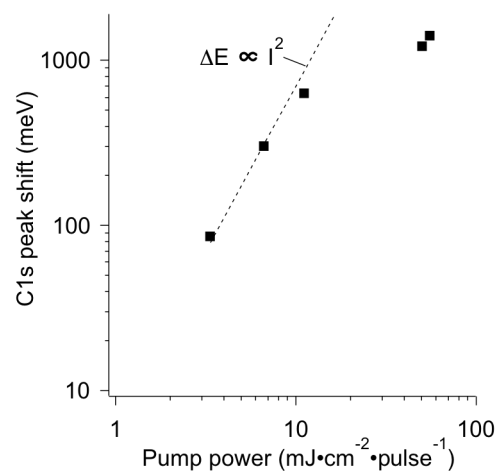


Fig. 3 Spectral shift of C1s photoelectron (ΔE) as a function of the power of the excitation laser in double logarithmic plot. The dashed lines are linear fits to the experimental results. Power law dependencies on the pump pulse power (I) are indicated.

one needs to consider the optimal electric control at D-A interface for the effective carrier separation.

4. Conclusion

We have measured the time evolution potential shift caused by photo-carrier generation using TRPES. The SPV was not observed at the D-A interfaces. The electric field at D-A interfaces may cause the absence of a SPV. Thus, local electric field at D-A interfaces is a key for effective carrier generation in OSCs.

References

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- [2] L-P Oloff et al., *New J. Phys.* **16**, Art.123045, 2014.