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Study of multiple photovoltaic processes in stacked organic active layers

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ABSTRACT

By using optical electric-field-induced second-harmonic generation (EFISHG) measurement, we studied multiple photovoltaic (PV) effects which exist in multi-layer devices consisting of multiple pentacene and C_{60} layers stacked together in various sequence. Results verified that the photovoltaic effects happen on every donor–acceptor (DA) interface and induce multiple electric fields inside the devices. Meanwhile, the light degradation in film thickness direction changes the intensity and the relaxation time of the established internal electric fields. For the multi-layer devices with more than one DA interface, the internal electric fields with opposite directions always co-exist, which leads to suppress the total photovoltaic effect. Finally, we showed that the interaction between different internal electric fields is inhibited by decreasing the charge accumulation inside the organic active layer and thus the total PV effect of the device can be enhanced.

1. Introduction

Recently organic solar cells (OSCs) have received significant attention all over the world as a promising source of renewable energy because of its fabrication possibility by using low-cost and large-area roll-to-roll manufacturing technologies [1–4]. Tremendous success has been achieved to increase the power conversion efficiency of OSCs by developing more efficient organic materials and by designing novel device structures [5–7]. In addition to such lots of efforts on the improvement of the efficiency of OSCs, the study of carrier mechanisms in OSCs is also helpful to promote the application of OSCs as a low-cost and sustainable device [8–10]. For double active layer OSCs with single pn-junction, the carrier behavior is rather easy to be analyzed because there is only one donor–acceptor (DA) interface. In our previous studies, by using optical electric-field-induced second-harmonic generation (EFISHG) measurement, we analyzed photo-induced interfacial carrier behaviors of OSCs under various external conditions on the basis of the Maxwell–Wagner model, and clarified the contribution of interfacial charging to the performance of OSCs [11–13]. However, in actual OSCs, this double-layer structure cannot be further popularized, owing to the significant loss of the incident light, the limited absorption width, short exciton diffusion length and so forth. In order to gain a high efficiency, the tandem structure or bulk-heterojunction (BHJs) structure OSCs, consisting of multiple DA interfaces, can overcome the limitations arisen from the double layer OSCs [5,14]. Hence, it is necessary for us to further analyze the carrier behavior in more complex OSCs structures, such as tandem or BHJs OSCs.

It is instructive to note that for both tandem and BHJs OSCs, more than one DA interfaces co-exist in the devices, which results in multiple photovoltaic (PV) processes. Therefore, the detailed study of these multiple PV processes and their interaction is necessary for clarifying the working principle of both tandem and BHJs OSCs. On the other hand, the optical EFISHG measurement is capable

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of directly catching carrier motions, and thus is very useful to investigate fundamental processes such as carrier injection, accumulation, transport, and recombination [11,12]. Very recently, we have shown that the EFISHG measurement is available as a tool for probing photo-voltage generation process in BHJs OSCs [15]. Hence, real-time EFISHG observation of the potential profiles as well as of internal electric fields in stacked organic multi-layer devices will be helpful to elucidate the interaction between different PV effects. In this study, we fabricated organic multi-layer samples with several donor and acceptor layers stacked together in a variety of combinations. The samples were all triggered by illumination pulse under open-circuit condition, and investigated by using the EFISHG measurement. Results showed that the PV effects happen on each DA interface, while the established internal electric fields have different strength and relaxation time constants. We also prepared the BHJs OSCs and studied the multiple PV effect in such structures. It has been found that photo-induced PV electric fields with different direction interact with each other and suppress the open-circuit voltage (V_{oc}). This problem can be solved by enhancing the charge collection near the electrode region.

2. Experimental

2.1. Sample preparation

Multi-layer OSCs samples with pentacene and C_{60} as donor and acceptor materials were prepared (device A, B and C), as portrayed in Fig. 1(a–c), respectively. The glass substrates were UV/ozone treated, and nearly free from organic residuals. Al electrode with a thickness of 100 nm was firstly evaporated on the top of glass substrate. Here the Al electrode was used as the reflective background for the generation of EFISHG signal. The stacked organic active layers (pentacene or C_{60}) with different thickness and different sequence combination were successively deposited onto the Al electrode, as shown in Fig. 1(a–c). In order to directly study the carrier behavior near the interface, the thickness of the each organic active layer was chosen to be ≈15 nm, which is close to the reported diffusion length of the exciton [16,17]. In this case, the deposition of metal electrode on the top of the sample may lead to the damage and contamination of the organic thin films. Therefore we applied no top electrode to the sample and the samples can all be considered being under open-circuit condition. Meanwhile, the lacking of top electrode does not allow common electrical methods to be used, while optical measurement such as EFISHG can be employed. We also prepared the OSCs sample with BHJs structure (device D and E), as shown in Fig. 1(d and e). The co-deposition was performed using two spatially separated sources from the different directions, where the deposition rate was kept to be 1:1 (pentacene:C_{60}). The deposited film thickness was monitored with a quartz crystal microbalance. For device E, two buffer layers of pentacene and C_{60} with a thickness of 15 nm were deposited on the top and bottom part of the sample and the total thickness of the sample is kept to be the same as that for device D (60 nm).

2.2. EFISHG measurement

Fig. 1(f) portrays the experimental arrangement used for the EFISHG measurements. Two kinds of optical signal were applied to the device, a probing signal and an illumination source as the trigger signal. A *p*-polarized pulsed laser was focused onto the sample surface at an incident angle of 45° as the probing light (repetition rate 10 Hz, average power 1 mW, duration 4 ns), which was generated from an optical parametric oscillator pumped with the third-harmonic light of *Q*-switched Nd:YAG laser. A red light from a light-emitting diode (wavelength 630 nm, intensity 1 mW/cm^2) was used as a light source to provide illumination pulse (repetition rate 10 Hz, duration 50 ms, switching on and off times within 50 ns) to trigger the devices. The working area of the multi-layer sample was corresponding to the size of the illumination spot (A = 3.1 mm^2). Note that pentacene and C_{60} layers absorb light at a wavelength of 630 nm [15], and excitons are mostly generated inside the pentacene layers [11]. The time delay of applied laser pulse corresponds to the initial time, i.e., t = 0, of illumination pulse. The EFISHG light generated by the pulsed laser was detected using the photomultiplier tube, and its intensity was recorded with a digital multimeter. We used a laser beam with a wavelength of λ_ω = 1000 nm, and recorded the generated EFISHG signal at a wavelength of $\lambda_{2\omega}$ = 500 nm to selectively measure the electric field in C_{60} layer [15,18]. The generated EFISHG signal was due to the coupling of electrons in C_{60} molecules and incident laser beam $E(\omega)$ in the presence of local electrostatic field $E(0)$ in the C_{60}-layer, and the square-root of the SHG signal was in proportion to the electric field $E(0)$ with the relation $I_{SHG} \propto |E(0)|^2$ [11,19].

The results of EFISHG are interpreted using a theoretical model based on dielectric physics [10,11]. Noteworthy that for the photovoltaic model based on semiconductor physics [20,21], the internal electric field of OSCs is governed by the depletion layer of so-called PN junction. The charge redistribution happens in the depletion region and the electric field outside the depletion region vanishes and energy band shows flat structure in the middle part of semiconductor. On the other hand, for the OSCs, charge redistribution and built-in potential do not only concentrate in the depletion region, and the electric field is non zero and may cross the whole organic layer, which suggests that dielectric model is more suitable [13,20]. In this case, the EFISHG signal, which reflects the changing of the average electric field across the organic layer, can precisely depict the electric field distribution of the OSCs sample [13–15].

2.3. Photovoltaic effect and EFISHG observation

Under the illumination, exciton dissociation leads to the separation of carriers at the DA interface. The photo-generated free charge carriers are highly localized, which results in a high interfacial concentration gradient of the carriers [22,23]. Hence, the photo current inside the OSCs will have a contribution from diffusion (J_F) and drift (J_d) forces. The current density equation is given as $J = qn E\mu + qD\nabla n$,