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The roles of traps in the energy loss for aged organic solar cells: A transient photovoltage study

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ABSTRACT

By investigating the turn-on and turn-off photovoltage dynamics as a function of aging time, we reported the roles of traps on the energy loss in organic solar cells composing of copper phthalocyanine (CuPc)/fullerene (C60). Illuminating the device with square pulses of light, a peak of transient photovoltage after turn-on was observed after device degradation. After turn-off, the transient photovoltage first goes to the negative before settling back to zero, which is the result of electron trapping in the C60 layer before being neutralized by re-injected holes. Furthermore, by adding a tris (8-hydroxyquinolinato) aluminum buffer to prevent the traps from propagating into C60 layer, the peak after turn-on is greatly suppressed and the negative peak after turn-off vanishes, supporting the trapped electrons in the C60 layer play the critical role in the appearance of peak of the transient photovoltage.

1. Introduction

Despite the significant efforts on the development of the organic solar cells (OSCs), both power conversion efficiency [1–6] and environmental stability [7–10] are still needed to be improved for practical device applications. Traps are formed fast, especially in ambient air condition without encapsulation, and cause the instability of device [9]. Though it reaches a general consensus that the buildup of traps during the aging process is responsible for the degradation of performance of OSCs [9–12], the roles of the traps are still not well identified. This is because the traps have complicated pathways causing the energy loss in OSCs, for example, (i) traps may quench the excitons very fast through energy transfer from exciton to defective molecules [11], (ii) the traps could capture free photo-carriers forming trapped charges which may reduce the net internal electric field, and result in the decrease of charge separation efficiency [13–15], or (iii) the trapped charges could involve in trap-assisted recombination with the counter part of free photo-carriers causing loss of both photo-carriers [16,17]. However, for continuous illumination measurements, it is hard to distinguish these roles because any of them would lead to the loss of device efficiency, in particular, the decrease of short-circuit current (I_{sc}), open- circuit voltage (V_{oc}) or the fill factor (*FF*).

Fortunately, transient techniques such as charge extraction by linearly increasing voltage (CELIV) [18], ultra-fast transient photovoltage [19,20], time of flight (TOF) [21–23] and transient absorption spectroscopy (TAS) [24,25] can provide direct information regarding the charge transport and recombination dynamics, so they can be useful tools to understand the operation of OSCs and help distinguish the energy loss mechanisms. However, in these approaches the device was excited by nanosecond laser pulse, which is not representative of real operating conditions where the device is under continuous illumination.

A new class of transient measurements called step function excitation where the square pulses of light as the source was used, allows the time required for the device to reach the steady state to be investigated [13–

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15,26,27]. Trapping and detrapping of charges were found in different structures of polymer/fullerene, polymer/nanocrystal, and polymer/polymer by McNeill et al. [13–15]. They indicated in the trap-limited device, the trap-reduced separation efficiency due to the reduced internal electric field was the major cause for the decay of transient photocurrent after turn-on. However, other effects from traps such as trap-assisted recombination should not be overlooked, and what we observed is principally a comprehensive result of these effects. Therefore, to distinguish overall roles of traps, further experiments are needed.

In this paper, by employing the square pulse of illumination proposed by McNeill et al. we report the transient photovoltage as a function of aging time to reveal the roles of trap in the energy loss in OSCs composing of copper phthalocyanine (CuPc)/fullerence (C60). After device degradation, besides the decrease of magnitude of transient photovoltage, a peak after turn-on companied by a negative peak after turn-off was observed on a timescale of hundreds of microseconds. By varying pulse light intensity, constant background illumination, and pulse width, we found the buildup of traps, especially the trapped electrons within the C60 layer, plays the most important role in the appearances of peaks after turn-on and turn-off. Finally, we verified the roles of electron-trapping and distinguished the degradations near the Al contact and within the C60 layer by analyzing the results of the device with a tris (8-hydroxyquinolinato) aluminum (Alq_3) buffer.

2. Experiment

CuPc and C60 were used as the donor and the acceptor, respectively, in this study. Indium tin oxide (ITO)-coated glass substrates were cleaned by the ultrasonic cleaning in acetone and isopropanol successively, followed by oxygen plasma treatment. A bilayer structure device of ITO/CuPc (20 nm)/C60 (40 nm)/Al was fabricated by thermal evaporation without any further encapsulation. The effective area of the device was $2.5 \times 2\ mm^2$ to ensure it can be fully covered by the light hitting spot. After the aluminum cathode was deposited, the fabricated devices were then exposed to ambient conditions for degradation. Except carrying out the measurements under the illumination, the devices were kept in the dark.

For the steady state characteristics, the external quantum efficiency (EQE) spectra and the current–voltage (*J–V*) characteristics under a solar simulator were examined. EQE spectra were measured by lock-in technique under the 100 W xenon light illumination through a monochromator. And the *J–V* curves of device were recorded by a Keithely 2400 SourceMeter under constant simulated sunlight illumination from Newport AM 1.5G. The light intensity was varied by using neutral density filters calibrated by an optical power meter (THORLABS, PM100).

For the transient photovoltage (and photocurrent) measurements, a high brightness InGaN light-emitting diode (Beijing Yuji-Xinguang, XG03-6-CBOQMOLBO-CA, 455 nm peak emission, 3W) was driven by a pulse generator (Agilent 8114A) to generate the square-pulse optical excitation. The frequency of 1 kHz and pulse width from 10 μs to 500 μs were chosen. The rise/fall time of light was measured to be less than 50 ns by a photo-multiplier (Hamamatsu, H5783-01) with resolution of 0.78 ns. Signals of photovoltage were recorded by a digital oscilloscope (Tektronix TDS 3054C) series to the device with input resistance of 1 MΩ. And the transient photocurrent was obtained by measuring the voltage of a 50 Ω resistance series to the device. Light intensity was varied by adjusting the bias applied on the light-emitting diode, which was calibrated by a laser power meter (Field Mate). The constant background light was imposed on the device by setting the offset voltage above turn-on voltage of the InGaN light-emitting diode.

It should be mentioned that if the light spot was moved outside the effective area, no signals of transient photovoltage (or photocurrent) could be observed. So, we ensure that only light hitting the effective area contributed to the results.

3. Results and discussion

3.1. Steady state characteristics

Fig. 1 presents the steady-state characteristics of the device before and after degradation. From *J–V* curves in Fig. 1a, the freshly fabricated device shows the best performance, in particular, with J_{sc} of 2.1 mA/cm^2, V_{oc} of 0.52 V, and *FF* of 52%. After degradation of 48 h, the device performance becomes poor, only with J_{sc} of 0.46 mA/cm^2, V_{oc} of 0.42 V, and *FF* of 51%. Moreover, the dark current of the aged devices (8 h and 48 h) shifts to a smaller scale as compared to that of fresh device, indicating charge trapping as a result of the buildup of traps. The energy loss can be also reflected by EQE spectra as shown in Fig. 1b where the decrease of power conversion efficiency can be seen. The overall decline of EQE spectra correlates with the changes of current density loss in the *J–V* curves with degradation time, which could be attribute to the electron trapping in the C60 layer (discuss in Section 3.2). It should be noted that there are complicated pathways for charge trapping to cause the loss of EQE and photocurrent density, such as quenching of excitons by the traps [11], reduced charge separation efficiency by decreased net internal electric field [13–15], trap-assisted recombination [16,17], or even poorer contact of C60/Al due to the ingress of water and oxygen [9,10]. However, the light intensity dependence of V_{oc} could reveal the impacts of trap-assisted recombination and enhanced bimolecular recombination [16,17,28,29]. For the organic heterojunctions in absence of traps where the bimolecular recombination is the only loss mechanism, the V_{oc} was given by Koster et al. [30]:

$$V_{oc} = \frac{E_{gap}}{q} - \frac{kT}{q} \ln\left[\frac{(1-P)\gamma N_c^2}{PG}\right] \quad (1)$$

where E_{gap} is the energy difference between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor, q is the elementary charge, k is the Boltzmann constant, T is temperature, P is polaron-pairs dissociation probability into free carriers, γ is the