Photocurrent analysis of organic photovoltaic cells based on CuPc/C_{60} with Alq_3 as a buffer layer*

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The performance of an organic photovoltaic (OPV) cell based on copper phthalocyanine CuPc/C_{60} with a tris-(8-hydroxyquinolinato) aluminum (Alq_3) buffer layer has been investigated. It was found that the power conversion efficiency of the device was 1.51% under illumination with an intensity of 100 mW/cm^2, which was limited by a square-root dependence of the photocurrent on voltage. The photocurrent–optical power density characteristics showed that the OPV cell had a significant space-charge limited photocurrent with a varied saturation voltage and a three quarters power dependence on optical power density. Also, the absorption spectrum was measured by a spectrophotometer, and the results showed that the additional Alq_3 layer has a minor effect on photocurrent generation.

Keywords: organic photovoltaic (OPV) cells, buffer layer, Alq_3, space-charge limited current
PACC: 8630J, 7240, 7360T

1. Introduction

Since the first double layer organic photovoltaic (OPV) cell with heterojunction structure was introduced by Tang in 1986,[1] a great deal of research on OPV cells has accomplished significant progress. So far, the power conversion efficiency (η_p) has reached up to 4.2% for small-molecule cells based on copper phthalocyanine (CuPc) and fullerene (C_{60}).[2] In particular, the η_p of polymer OPV cells based on a solution processible blend of semiconducting polymers and fullerene derivatives has reached more than 6% with a tandem architecture.[3] Recently, by simulation, the relation of optical absorption and power conversion efficiency versus the film thickness was obtained[4] and it was found that the optical interference effect and the carrier lifetime played a very important role on the performance of devices.[5] However, to achieve a device efficiency high enough for practical application, it is still necessary to scrutinize the optoelectrical properties such as the photocurrent of OPV cells.

In OPV cells, the photocurrent generation is not only solely dependent on the creation, diffusion and dissociation of excitons, but also on charge carrier transport and collection.[6−9] Based on Onsager's theory, Mihailetchi *et al.* have shown that the dissociation efficiency of bound electron–hole pairs at the donor-acceptor interface dominates the photocurrent of polymer-fullerene blend devices.[10] Subsequently, they demonstrated the existence of space-charge limited (SCL) photocurrent due to the imbalance between electron and hole transport in semiconductors.[11] Narayan *et al.* have observed that it is the cathode-polymer interface morphology, not the fingerprint of the bulk material property, that determines the charge carrier collection efficiency.[12,13] Bolm *et al.* reported that the photocurrent was recombination limited by a short lifetime of bound electron–hole pairs.[14] The study on the photocurrent limiting factor has received considerable attention. Also, we have observed that an OPV cell based on CuPc and C_{60} has significant square-root dependence of photocurrent on voltage and this leads to lower efficiency.[15]

Using a buffer layer between C_{60} and the cathode has been an important and popular approach to improve the performance of organic photovoltaic cells since Peumans *et al.* introduced bathocuproine (BCP) as an exciton blocking layer (EBL).[16] Subsequently, Lee *et al.* found that bathophenanthroline (Bphen) was better than BCP as EBL in OPV cells due to its good electron transporting ability.[17] Also, Song *et al.* have shown that a thin Alq_3 buffer layer be-

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tween C_{60} and the cathode can effectively improve device stability.[18] By comparing Alq_3 with other buffer materials such as BCP, CuPc and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)1,3,4-oxidiazole (PBD) experimently, it was found that the device with Alq_3 as buffer layer also had a competitive power conversion efficiency.[19] In this work, we present an electrical and optical study of OPV cells based on a CuPc/C_{60} heterojunction with Alq_3 as a buffer layer. The photocurrent–voltage and photocurrent–optical power density characteristics of the devices were investigated to gain more insights into the photon-to-electron mechanism in the device with an Alq_3 buffer layer.

2. Experimental

The devices were fabricated onto indium-tin oxide (ITO) coated glass substrates with a sheet resistance of 10 Ω/□ by an OLED-V (Shenyang Vaccum Co.) organic multifunctional vacuum deposition equipment. The glass substrates were cleaned consecutively in ultrasonic baths containing detergent, acetone, ethanol and deionized water for 10 min each, and finally dried by a high purity nitrogen blow. Then the substrates were treated by O_2 plasma for 5 min prior to the deposition of organic layers. After the substrates were cooled to room temperature, organic materials and Ag cathode were deposited onto the ITO substrates successively at pressures of 3×10^{-4} Pa and 3×10^{-3} Pa, respectively. The deposition rate was 1–2 Å/s (1 Å=0.1 nm) for organic materials and ∼10 Å/s for Ag cathode, which was in situ monitored using a quartz crystal oscillator mounted to the substrate holder.

The active area of OPV cells is 4 mm×3 mm. The current–voltage curves in the dark and under illumination from a xenon lamp (CHF-XM35) were measured with a Keithley 4200 programmable voltage–current source. The absorption spectrum was measured with a SHIMATZU UV1700 system. All the measurements were performed in air at room temperature.

3. Results and discussion

Figure 1 shows the configuration of the OPV device and the energy level diagram in this work. The current density–voltage (J–V) characteristics measured in the dark and under illumination are shown in Figure 2 for ITO/CuPc(20 nm)/C_{60}(40 nm)/Alq_3(7.5 nm)/Ag (100 nm). The short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (η_p) of the device are 8.85 mA/cm^2, 0.41 V, 0.42, and 1.51% under illumination with an intensity of 100 mW/cm^2. The device efficiency was higher than 0.87% of the ITO/CuPc/C_{60}/Ag device, but was still lower than that of Bphen as a buffer layer.[15] Especially, FF was approximately 14% lower than 0.49 of the Bphen buffer layer. In general, as a buffer layer, Alq_3 still can protect C_{60} film from deterioration during Ag deposition. Also, it can improve the electron collection capability and enhance device performance accordingly.[20] However, when Alq_3 is 7.5 nm with optimum efficiency, the device performance is still lower than that of other material as a buffer layer in our study.

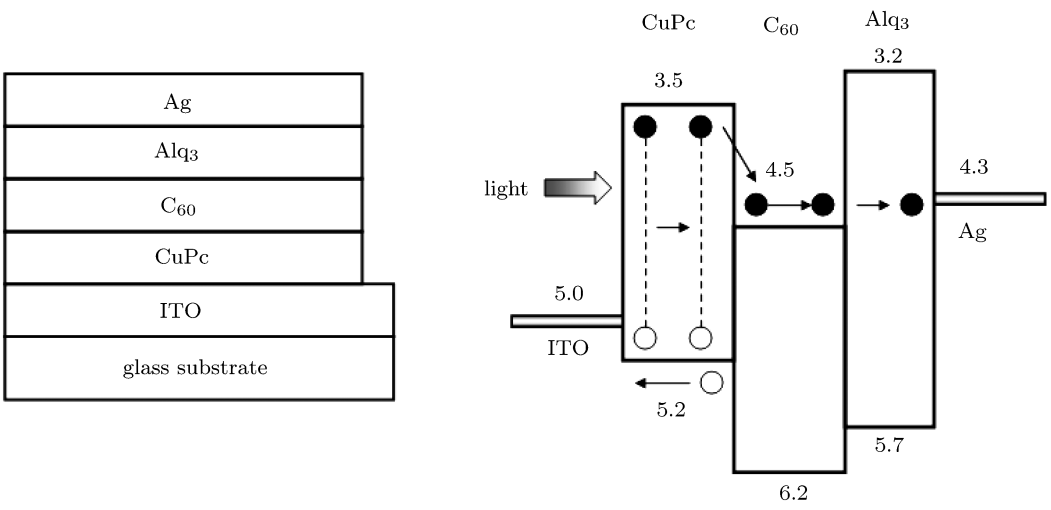


Fig. 1. Device configuration and energy level diagram.

In order to find the main limiting factor for device performance, $J_{\rm ph}$ against the effective applied bias voltage (V_0-V) is depicted in the inset of Fig. 2. The photocurrent is given by $J_{\rm ph}=J_{\rm L}-J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are the current densities under illumination and in the dark, respectively. The compensation voltage (V_0) is determined by the voltage at which $J_{\rm ph}=0$. It can be seen that the photocurrent at lower effective applied bias voltage decreases rapidly, which results in a rather low fill factor. At higher reverse voltage, $J_{\rm ph}$ tends to saturate, which shows no charge carrier recombination. Particularly, a square-root dependence of $J_{\rm ph}$ on voltage is observed at intermediate voltage. Compared to Ref. [15], Alq_3weakened the square-root dependence of ITO/CuPc/C_{60}/Ag, but it was different from the case of Bphen as a buffer layer, where no significant square-root dependence was observed. It has also been demonstrated that due to the SCL case with square-root dependence on effective applied bias voltage, a maximum FF is limited to only 0.42.[11] The square-root dependence of photocurrent on voltage should play some role in limiting the performance of ITO/CuPc(20 nm)/C_{60}(40 nm)/Alq_3(7.5 nm)/Ag (100 nm) in our work.

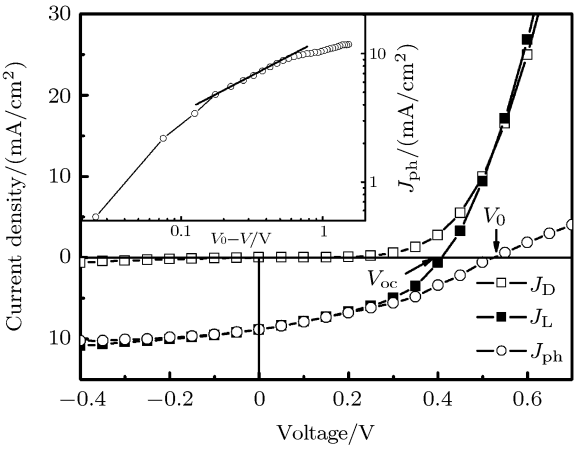


Fig. 2. $J-V$ characteristics of ITO/CuPc(20 nm)/C_{60}(40 nm)/Alq_3(7.5 nm)/Ag(100 nm) in the dark and under illumination with an intensity of 100 mW/cm^2. Inset: photocurrent ($J_{\rm ph}$) as a function of effective applied bias voltage (V_0-V); the solid line indicates a square-root dependence.

Goodman and Rose[21] and Mihailetchi *et al.*[11] have pointed out that the square-root dependence of photocurrent originates from two conditions. When the mean electron and (or) hole drift lengths $\mu_{\rm e(h)}\tau_{\rm e(h)}$ are less than the photoactive layer thickness and their transport is unbalanced, square-root dependence comes from the recombination of free charge carriers.

$$J_{\rm ph}=qG\left(\mu_{\rm h(e)}\tau_{\rm h(e)}\right)^{1/2}, \qquad (1)$$

where q is electronic charge, G is the generation rate of electron–hole pairs. Due to the buildup of space charge, when the photocurrent is equal to the space-charge limited current, a maximum photocurrent can be described as

$$J_{\rm ph}\leq(qG)^{3/4}\left(\frac{9\varepsilon_0\varepsilon_{\rm r}\mu_{\rm h(e)}}{8}\right)^{1/2}V^{1/2}. \qquad (2)$$

As Blom *et al.* previously discussed in polymer/fullerene solar cells,[14] the question is whether the photocurrent of the device is limited by recombination or the buildup of space charge in our device. The way to distinguish these two cases is to vary the incident optical power density. The saturation voltage ($V_{\rm sat}$), at which the square-root regime transits into the saturation regime, is independent of incident optical power density in the recombination limit and varies with the incident optical power density in the space charge limit.[11] Moreover, G is proportional to optical power density. As given by Eqs. (1) and (2), $J_{\rm ph}$ have a linear and a three quarters power dependence on incident optical power density for these two cases respectively.

Figure 3 shows $J_{\rm ph}-(V_0-V)$ as a function of incident optical power density. The optical power density varied from 25 to 150 mW/cm^2. It can be seen that for different illumination levels, $J_{\rm ph}$ shows a clear transition between the square-root and saturation regimes. Also, as indicated by the arrow in Fig. 3, the saturation voltage varied with increasing illumination power. This indicates that the $J_{\rm ph}$ for ITO/CuPc

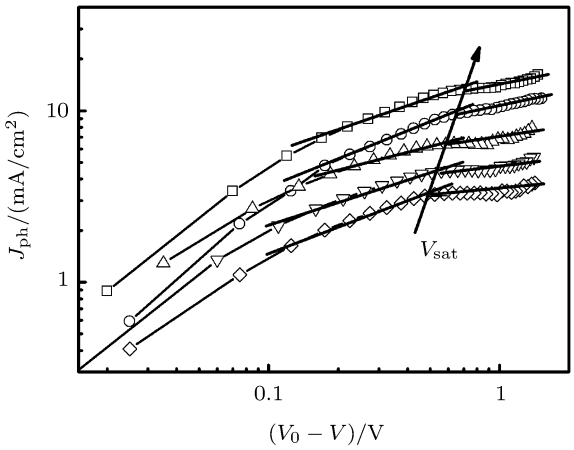


Fig. 3. Photocurrent of ITO/CuPc(20 nm)/C_{60} (40 nm)/Alq_3(7.5 nm)/Ag(100 nm) as a function of applied voltage for incident power densities from 25 mW/cm^2 to 150 mW/cm^2.

(20 nm)/C_{60}(40 nm)/Alq_3(7.5 nm)/Ag(100 nm) in this work is space-charge limited. Moreover, Fig. 4 shows the $J_{\rm ph}$ deducted from Fig. 3 as a function

of optical power density at $V_0 - V = 0.4$ V in the square-root regime and $V_0 - V = 1$ V in the saturation regime. It can be seen that from linear fitting, the slopes (S) are 0.73 and 0.83, respectively. This indicates a three quarters power dependence of $J_{\rm ph}$ on optical power density in the square-root regime, which is in good agreement with the change of $V_{\rm sat}$. The space-charge limited photocurrent of ITO/CuPc(20 nm)/C_{60}(40 nm)/Alq_3 (7.5 nm)/Ag(100 nm) can be comfirmed.

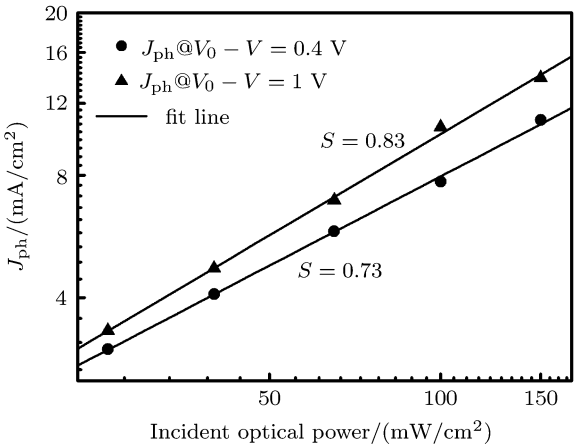


Fig. 4. Photocurrent of ITO/CuPc(20 nm)/C_{60} (40 nm)/Alq_3 (7.5 nm)/Ag (100 nm) as a function of optical power density at $V_0 - V = 0.4$ V in the square-root regime and $V_0 - V = 1$ V in the saturation regime.

To study the effect of the Alq_3 buffer layer on light absorption distribution, Fig. 5 shows the absorption spectra of CuPc, C_{60}, Alq_3 and Bphen films. It can be seen that due to the small energy gap (E_g), Alq_3 has an absorption peak at 391 nm in the visible region, which is different from Bphen with a high optical transparency there. As a result, Alq_3 can absorb the light reflected from the Ag cathode and change the light distribution in the device.[22,23] The absorption spectra of devices without and with Alq_3 or Bphen as a buffer layer are shown in Fig. 5. It can be seen that all of the spectra have a significant contribution from both CuPc and C_{60}. Due to the light absorption of Alq_3, the absorption spectra of the device with Alq_3 as a buffer layer have a minor shift, and the light absorption intensity is enhanced between 390 and 550 nm. In general, Alq_3 does not have other significant effects on the absorption of the device compared with Bphen. This is consistent with the photocurrent, which is almost identical in the saturate region of different devices.

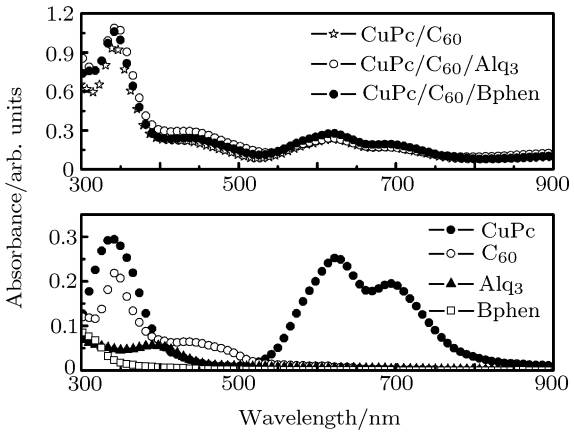


Fig. 5. Absorption spectra of CuPc, C_{60}, Alq_3, Bphen films, CuPc/C_{60} devices without and with Alq_3 or Bphen buffer layers.

4. Conclusions

In summary, by introducing Alq_3 as a buffer layer, the power conversion efficiency of ITO/CuPc/C_{60}/Ag was enhanced. The device's photocurrent was investigated to gain insight into the photon-to-electron mechanism of the ITO/CuPc/C_{60}/Alq_3/Ag device. By varying the incident optical power density, it was found that the saturation voltage is not constant and the photocurrent has a three quarters power dependence on optical power density. We revealed that the limiting factor of device performance was the space-charge limited photocurrent due to unbalanced charge carrier transport. Furthermore, the absorption spectrum showed that the Alq_3 layer does affect the light absorption of ITO/CuPc/C_{60}/Ag device, but this effect is secondary for device performance.

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