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Effect of copper phthalocyanine buffer layer on open circuit voltage in organic solar cells

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Abstract: The effect of copper phthalocyanine (CuPc) buffer layer on open circuit voltage in indium tin oxide/zinc phthalocyanine (ZnPc)/C60/CuPc/Al devices is investigated. A dependence of the open circuit voltage on the thickness of CuPc layer is observed. We analyze the current-voltage curves under illumination based on semiconductor device theory. A high ideality factor is found as the reason for the high open circuit voltage. We propose that both ZnPc/C60 junction and CuPc/Al contact contribute the high ideality factor. Our result shows that the open circuit voltage may be improved by introducing an extra rectifying buffer/cathode junction.

Key words: buffer layer, buffer/cathode junction, open circuit voltage, ideality factor

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酞菁铜缓冲层对有机太阳能电池开路电压的影响

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摘要:用 p 型有机半导体材料酞菁铜作为阴极缓冲层制作了器件结构为氧化铟锡/酞菁锌/碳六十/酞菁铜/铝的有机小分子太阳能电池,对器件进行电学测量发现酞菁铜缓冲层的厚度对器件的开路电压有明显影响.基于半导体器件物理分析了光照下测量得到的电流-电压曲线,由拟合结果得到的器件参数表明高理想因子导致了器件开路电压升高,其原因为器件的输运特性不只受酞菁锌与碳六十形成的 p-n 结影响,还与酞菁铜缓冲层与铝电极形成的肖特基接触有关.研究表明在有机太阳能电池器件中引入一个合适的缓冲层/阴极肖特基结可以提高器件的开路电压.

关 键 词:缓冲层;缓冲层/阴极结;开路电压;理想因子

中图分类号:TM914.4;TN36;TN304.5 **文献标识码:**A

Introduction

Organic solar cell is regarded as one kind of low-cost renewable energy source which may approach the commercial market in near future. The power conversion efficiency of organic solar cells keeps increasing during the last decade, and considerable progress in understanding their working mechanism is achieved in this process[1]. Interface engineering is one important work in organic photovoltaic devices[2]. By inserting a thin buffer layer between the acceptor layer and the cathode metal in planar heterojunction photovoltaic cells, higher power conversion efficiency is obtained due to an exciton-blocking effect[3]. Some small molecules, such as bathocuproine (BCP, insulator), tris-(8-hydroxyquinolinato) aluminium (Alq3, electron-transporting material) and copper phthalocyanine (CuPc, hole-transporting material), are used as the exciton-blocking materials, and similar behaviours are always measured[4-6]. Electron-transporting through thin buffer layer is thus supposed via the trap states.

Effect of cathode metal and buffer layer on the open circuit voltage (V_{oc}) in organic solar cells has been studied for a long time and reviewed in Ref. 2. There are two widely accepted models for evaluating V_{oc} in organic solar cells: metal-insulator-metal (MIM) model and effective energy gap model. In this work, we present another method to enhance V_{oc} by using a buffer layer which makes Schottky contact with the cathode metal. In an i-

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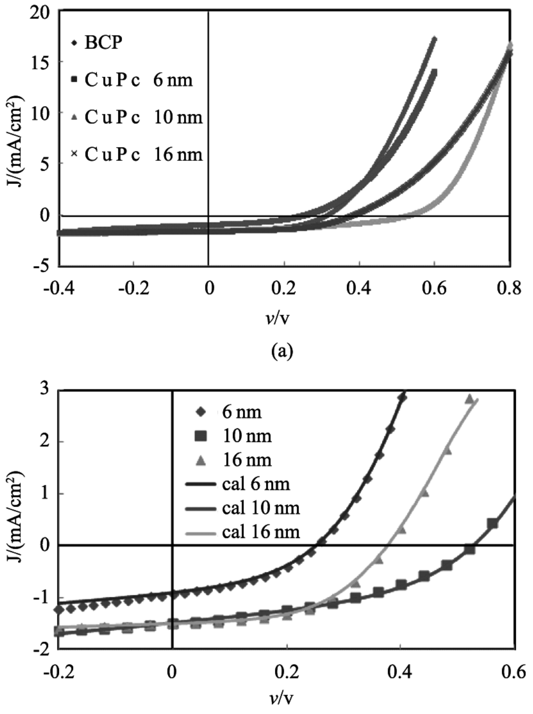
deal photovoltaic diode described by the traditional device physics[3], V_{oc} can be roughly calculated as $V_{oc} = n\frac{K_BT}{q}\ln(\frac{J_{sc}}{J_o})$, where n is the ideality factor, J_0 is the reverse saturation current density, J_{sc} is the short circuit current density, q is the electron charge, k_B is the Boltzmann constant, and T is the absolute temperature. This equation provides a clue to increase V_{oc} other than synthesis of new material: enhancing the value of n. We found that a large V_{oc} is obtained when a CuPc layer with the thickness of approximately 10 nm is inserted between C60 and Al. We propose that CuPc/Al Schottky contact increases the ideality factor of the photovoltaic device and the open circuit voltage show a significant improvement accordingly.

1 Experimental

Small molecule solar cells were prepared on cleaned indium tin oxide (ITO) glasses. Zinc phthalocyanine (ZnPc) (Yannuo Chem., purity 99%) and C60 (Acros Organics, purity 99%) were used as the donor and the acceptor materials, respectively. CuPc (Yannuo Chem., purity 99%) or BCP (J&K Scientific LTD, purity 99%) was used as the buffer materials. All above materials were used as received. The configuration for all devices is ITO/ZnPc (25 nm)/C60 (30 nm)/buffer layer/Al (150nm). The thickness of CuPc varies from 6 nm to 16 nm. Thinner and thicker CuPc layers deteriorate the photovoltaic effect severely. The devices were fabricated in a commercial vacuum deposition system (ULVAC-KIKO VWR-400M/ERH). Organic materials were deposited onto ITO substrates successively at a rate of ~0.05 nm/s under a pressure of 5×10^{-4} Pa. Then we broke the vacuum and changed the masks for electrode deposition. Aluminium was deposited at a rate of ~0.5 nm/s under a pressure of 5×10^{-3} Pa. The film thickness and deposition rate were monitored in situ using a quartz crystal oscillator. The area of a single device is 4 mm^2. Before IV measurement, the sample was annealed at 110°C for a half hour in a vacuum oven. A sunlight simulator (Newport Oriel 91160) was used to illuminate the sample with the power of 100 mW/cm^2. The current-voltage curves were measured with a digital source meter (Keithley 2602). All IV measurements were performed in air. Optical absorption was measured with a UV-Vis-NIR spectrophotometer (Cary 5000) in air.

2 Results and discussion

In our experiments, in order to obtain good rectifying *I-V* curves under both positive and negative bias voltage and to eliminate the influence of traps and disorder, thin active layer (25 nm ZnPc and 30 nm C60) was employed in all devices. This thickness was not optimized for a high efficiency. Figure 1(a) shows the current density-voltage (*J-V*) curves of the photovoltaic devices with CuPc buffer layers under illumination (AM 1.5, 100 mW/cm^2). The device with BCP buffer layer (thickness 7 nm) was also fabricated and measured as a reference (shown in Fig. 1(a)). The characteristics of all devices are summarized in Table 1.



(a)

(b)

Fig. 1 (a) Illuminated *J-V* characteristics of photovoltaic devices with different buffer layers, (b) Comparison of measured data (dots) versus simulated results (lines)
图 1 (a) 使用不同厚度缓冲层的光伏器件在光照下的 *J-V* 曲线,(b)测量数据与拟合值的比较

Typical rectifying curves were observed in all devices with CuPc buffer layers. The dependences of J_{sc} and V_{oc} on the thickness of CuPc layer are shown in Fig. 2(a). A slightly low J_{sc} is measured in the device with a thin CuPc layer (thickness 6 nm). This behavior is the same as the result in Ref. 7. We think the low J_{sc} mainly come from a reduction of the optical absorption in the device with a thin CuPc layer. We deposited ZnPc (25 nm)/C60(30 nm)/CuPc on quartz substrates and measured the absorption spectrum in air (shown in Fig. 2(b)). The absorbance of the sample with 6 nm CuPc layer is less than those of the samples with thicker CuPc

Table 1 Measured and extracted device parameters
表 1 测量和拟合得到的器件参数

Buffer layer	J_{sc}/(mA/cm^2)	V_{oc}/V	J_0/(mA/cm^2)	n	R_s/Ωcm^2	R_{sh}/Ωcm^2	J_{ph}/(mA/cm^2)
CuPc 6 nm	0.93	0.25	1.99×10^{-2}	2.71	13.4	1.06×10^3	0.92
CuPc 10 nm	1.48	0.53	5.37×10^{-3}	3.9	5.6	9.72×10^2	1.49
CuPc 16 nm	1.49	0.38	2.17×10^{-3}	2.24	29	3.12×10^3	1.50

layers within almost entire visible band. Another possible reason for the low J_{sc} may be the optical spacer effect, by which the optical/electrical field distribution is modified when the thickness of CuPc layer changes, as the calculating results in Ref. 8. This fact reveals that CuPc shows a much stronger influence on the optical absorbance inside the device than BCP due to its intermediate band gap. The values of J_{sc} in devices with 10 and 16 nm CuPc layers are almost the same with that in a device with 7 nm BCP layer. No reduction of J_{sc} occurs when the thickness of CuPc layer increases from 10 to 16 nm. This phenomenon may be explained by a half-filled energy level in thick α-phase CuPc layers, by which electrons transport from C60 to the cathode without surpassing any large barrier [7]. An interesting phenomenon in our experiments is that V_{oc} varies with the thickness of CuPc layers. The V_{oc}-thickness plot clearly demonstrates a peak at approximately 10 nm (shown in Fig. 2(a)). A value of 0.53 V (with 10 nm CuPc layer) is significantly larger than V_{oc} measured in devices with other thickness of CuPc layer. Above results show that 10 nm is the optimized thickness for CuPc buffer layer in our devices. A large variation of V_{oc} has not been reported and analyzed yet, although CuPc was used as a buffer material in literatures [6-7].

We use Shockley equation to analyze the current-voltage curves of planar heterojunction photovoltaic devices[9]. This equation is given as

$$J = J_0\left(\exp\left(\frac{V\text{-}R_sJ}{nk_BT/q}\right)\text{-}1\right)+\frac{V\text{-}R_sJ}{R_{sh}}\text{-}J_{ph} \qquad, \quad (1)$$

where J_{ph} is the photocurrent density, R_s is the series resistance, R_{sh} is the shunt resistance. The extracted values of the saturation current density (J_0), the photocurrent density (J_{ph}), the series resistance (R_s), the shunt resistance (R_{sh}) and the ideality factor (n) are listed in Table 1. Simulated data are calculated according to Eq. (1) and plotted in Fig. 1(b). Measured results are also plotted in Fig. 1(b) for comparison. Good agreement is seen in all devices, indicating the rationality of extracted parameters. The series resistance in the device with 10 nm CuPc buffer layer is smaller than that with 6 nm CuPc buffer layer. This phenomenon may be explained by high electron mobility through the intrinsic level than trap states in CuPc film[7]. A half filled b_{1g} energy state instead of trap states was proposed as the route for high efficiency electron-transporting through thick CuPc layer. This property makes it possible to improve the electron-transporting by an intrinsic energy level in buffer layers. The large series resistance in the device with 16 nm CuPc layer will be discussed in the following part. The most confusing parameter is the ideality factor, because the values of n in all devices with CuPc buffer layers are larger than 2. A particularly large value, 3.9, occurs in the device with 10 nm CuPc layer. We believe this high ideality factor induces the high open circuit voltage (0.53 V). We think that such an anomalously high ideality factor may come from the CuPc/Al contact, which makes an extra metal-semiconductor diode in our devices.

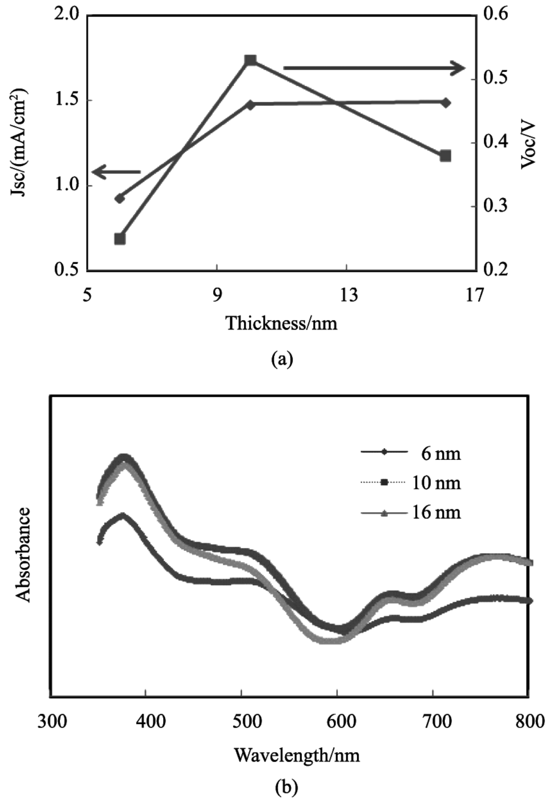


Fig. 2 (a) Effect of the thickness of CuPc layer on open circuit voltage (V_{oc}) and short circuit current density (J_{sc}). (b) Optical absorbance of ZnPc(25 nm)/C60(30 nm)/CuPc film deposited on quartz substrates
图 2 (a)CuPc 层厚度对 V_{oc}和 J_{sc}的影响.(b) CuPc 层厚度对 ZnPc(25 nm)/C60(30 nm)/CuPc 膜光吸收的影响

High ideality factor has been found in AlGaN/GaN diodes for a long time [11]. It is reported that in addition to the AlGaN/GaN p-n junction, a rectifying n-n junction and a metal-semiconductor contact create two other diodes in the real device. A formula of $n=\sum_i n_i$ was given in Ref. 11, in which n and n_i are the ideality factors of a real device and individual diodes, respectively. That is to say, an ideality factor much greater than 2 may be extracted from the measured IV curves if some extra rectifying contacts exist in a real diode device. In our experiments, a half-filling energy level in the thick α-phase CuPc layer makes CuPc/Al contact a Schottky diode. Schottky devices based on CuPc/Al contact have been studied by several groups [12-13]. It was demonstrated that a Schottky diode can be fabricated by depositing aluminium on thick CuPc film. The thickness of hole depletion layer in CuPc side is estimated to be 16 nm under zero bias voltage by CV measurements[13]. Our devices with thick CuPc buffer layers (thickness large than 10 nm) should also contain Schottky diode due to CuPc/Al contact. The schematic energy diagrams for organic photovoltaic devices with thin and thick CuPc buffer layers are drawn in Fig. 3(a) and (b), respectively. A band bending in thick CuPc layer (Fig. 3(b)) was proposed[12-13], whereas for thin CuPc layer (Fig. 3(a)), trap states are supposed as the transporting routes for e-

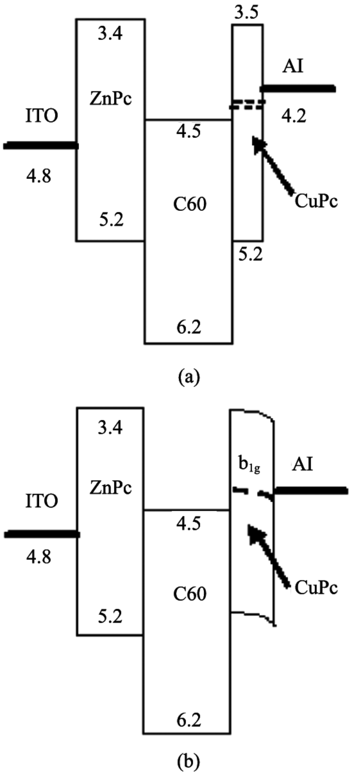


Fig. 3 Schematic energy level diagrams of ITO/ZnPc/C60/CuPc/Al devices. (a) Thin CuPc film (thickness 6 nm): trap states are routes for electron-transporting, constant vacuum level is supposed in CuPc layer. (b) Thick CuPc film (thickness > 10 nm): b_{1g} energy level is the route for electron-transporting and band bending exists in CuPc layer due to CuPc/Al contact, constant vacuum level is not valid in CuPc layer. The unit of all energy level values is eV. The values are adopted from Ref. 8 and 10.

图 3 ITO/ZnPc/C60/CuPc/Al 器件的能带示意图.（a）CuPc 膜厚为 6 nm 时,电子通过缺陷态输运,（b）CuPc 膜厚大于等于 10 nm 时,电子通过 b_1g 能级输运,CuPc 层内部出现能带弯曲

lectrons and constant vacuum level is assumed[6]. The band model for thick CuPc buffer layer shows some influences on the measured IV curves. A high ideality factor is therefore reasonable if there are two diodes (ZnPc/C60 and CuPc/Al) in series in our devices. In other words, 3.9 is the sum of two ideality factors.

The influence of the thickness of CuPc layer on the series resistance is evident. The series resistances of devices with 10 and 16 nm buffer layers are 5.6 and 29 $\Omega \cdot cm^2$, respectively. 5.6 $\Omega \cdot cm^2$ is close to the series resistances in other optimized small molecule solar cells[10], revealing that connecting two diodes (ZnPc/C60 and CuPc/Al) in series does not deteriorate the electron-transporting. This result reflects another benefit due to CuPc/Al contact, by which the band bending inside CuPc layer induces an extra built-in field for sweeping the electrons to the cathode. Negligible carrier loss occurs if the effective field (the sum of built-in field and bias field) helps the electron-transporting all the way through the CuPc layer, as in the case of 10 nm CuPc layer. In contrast, the resistance of 29 $\Omega \cdot cm^2$ in the device with 16 nm buffer layer means much more carrier loss due to thicker CuPc film. Based on the common knowledge of organic film, higher series resistance is expected when 16 nm CuPc layer is used instead of 10 nm layer. However, the resistance difference between 10 and 16 nm CuPc film itself may not cause such a big enhancement (from 5.6 to 29 $\Omega \cdot cm^2$). We think that for CuPc buffer layer, 16 nm is larger than the thickness of the depletion layer under a positive bias voltage, and the CuPc/Al contact behaves like a defective diode with a large series resistance. Then the current dependence on voltage in CuPc/Al contact will deviate from the standard exponential curve to an approximately linear plot. This change may lead two results in our devices: the enhancement of the series resistance and the reduction of the ideality factor.

3 Conclusions

In summary, a thickness dependent of open circuit voltage is observed when CuPc is used as the buffer material. The device with 10 nm CuPc film shows the highest open circuit voltage. An anomalously high ideality factor is proposed as the reason for this high open circuit voltage. Both ZnPc/C60 junction and CuPc/Al contact contribute the ideality factor of the device with thick CuPc buffer layer. Our result shows that an extra rectifying buffer/cathode junction may enhance the open circuit voltage of the organic photovoltaic devices.

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