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Electro-optical characterization and analysis of CuPc-based solar cells with high photovoltage

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Abstract. Organic solar cells using the CuPc and PTCBI semiconductor layers were studied. A high open circuit voltage of 1.15 V was obtained in a device with ITO/PEDOT:PSS/CuPc (15 nm)/PTCBI (7 nm)/Al structure. Results were interpreted in terms of a modified CuPc–Al Schottky diode for the thin PTCBI case and a CuPc–PTCBI heterojunction for the thick PTCBI case. Also, the formation of a thin aluminum oxide layer under the aluminum electrode was postulated. This layer has a beneficial aspect wherein shunting losses are reduced and a high photovoltage is enabled. However, it adds greatly to the series resistance to a point where the short circuit current density is reduced. CuPc Schottky diodes with an ITO/PEDOT:PSS/CuPc/Al structure yielded a high V_{oc} of 900 mV for a CuPc layer of thickness 140 nm. The V_{oc} increased with increase in CuPc layer thickness.

Keywords. Organic semiconductors; photovoltaics; heterojunctions; Schottky diodes.

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1. Introduction

Photovoltaic cells made of organic semiconductors hold great promise for low cost, portable, lightweight, flexible and wearable solar cell applications [1,2]. In particular, copper phthalocyanine (CuPc) has been used extensively as an absorber in organic solar cells [2–5]. Tang [3] achieved an open circuit voltage (V_{oc}) of 450 mV and a short circuit current density (J_{sc}) of 2.3 mA/cm^2 in CuPc-based devices. Later, Peumans *et al* [4] reported a V_{oc} of 480 mV and J_{sc} of 4.2 mA/cm^2 in this system. Performance of these cells at present is limited by a very small exciton diffusion length (∼10 nm) of the absorber layer [1], thus limiting the practical thickness and hence light absorption and short circuit currents in planar device structures.

Short circuit current density of organic solar cells remains much lower than in thin film solar cells based on inorganic semiconductors [5–9], and the mechanisms of carrier generation and transport are not well understood [7–9].

Here we report on the characteristics of a CuPc/PTCBI/Al device that exhibited high photovoltage as well as other devices based on CuPc.

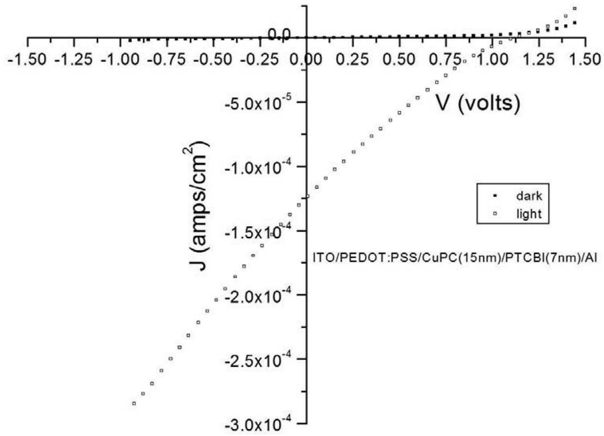

Figure 1. Current density–voltage characteristics of an ITO/PEDOT:PSS/CuPc/PTCBI/Al device in the dark and under 'one Sun' illumination.

2. Experimental procedures

For fabricating the CuPc/PTCBI/Al device, ITO-coated glass substrate was cleaned and a thin buffer layer of PEDOT:PSS was spin-coated on ITO and subsequently annealed in vacuum at 100°C for 15 min. Layers of CuPc and PTCBI, as well as the metallic electrode were thermally evaporated. Aluminum, silver, copper and gold electrodes were thermally evaporated through a mask with 1/8-inch diameter holes, resulting in multiple devices, each with an area of 0.079 cm^2. Electrical characterization was performed with an automated I–V tester, solar simulator and an HP 4192A LF impedance analyzer.

3. CuPc–PTCBI heterojunction devices

J–V characteristics of the CuPc/PTCBI/Al cell in dark and under 'one Sun' illumination are plotted in figure 1. A V_{oc} of 1.15 V, fill factor (FF) of 25% and a J_{sc} of 0.125 mA/cm^2 were observed [10,11]; both FF and J_{sc} are series-resistance limited. For this cell, thicknesses of CuPc and PTCBI layers were 15 nm and 7 nm respectively.

Effects of the CuPc layer thickness on cell performance were studied. The PTCBI layer thickness was fixed at 7 nm and devices with CuPc thicknesses of 3, 7, 15, 30 and 60 nm were made. Their V_{oc} and J_{sc} variations are shown in figure 2. We observe that the optimal CuPc thickness is close to 15 nm while the optimal PTCBI thickness is between 7 nm and 15 nm.

Electron microscopy was used to study the effect of varying PTCBI layer thickness. For a PTCBI layer thickness of 3 nm, the surface of CuPc seemed to form a blend with PTCBI. For a PTCBI layer thickness of 7 nm, needle-like structures were formed on the surface of CuPc, as shown in figure 3a. For thicker (30 nm and

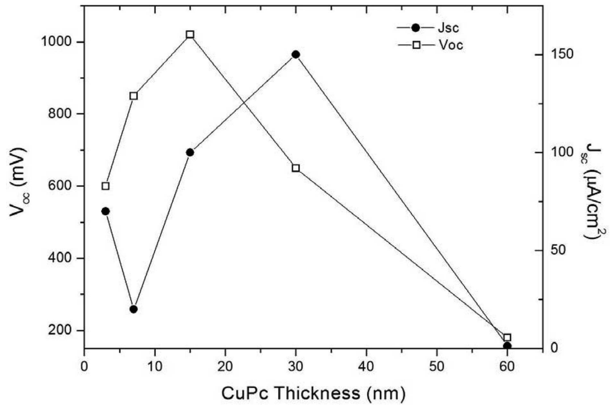

Figure 2. Effect of CuPc thickness on the open-circuit voltage and short-circuit current. The device configuration was that of figure 1 and the thickness of PTCBI was fixed at 7 nm.

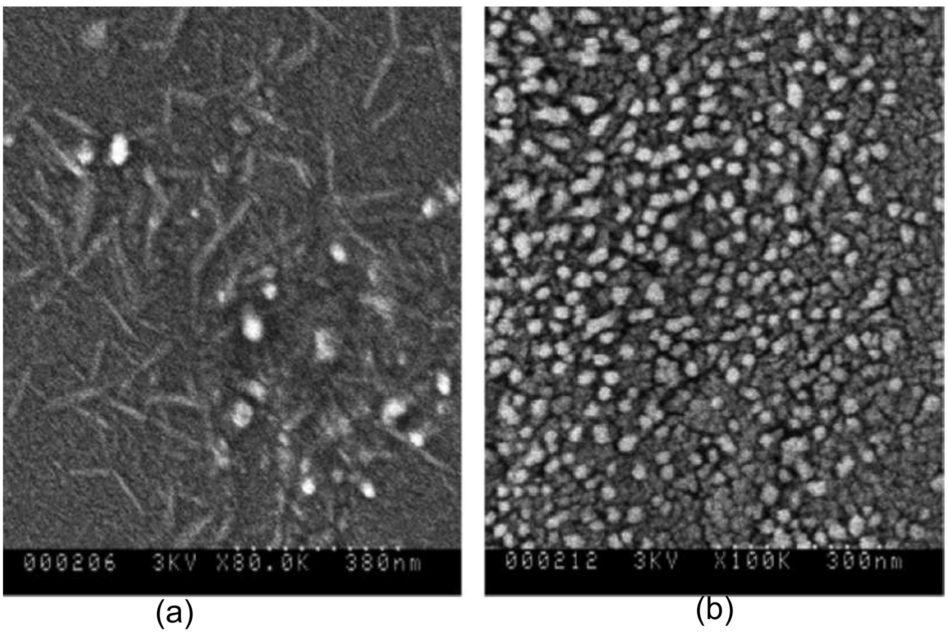

Figure 3. Scanning electron micrographs of (**a**) 7 nm layer of PTCBI deposited on 15 nm of CuPc showing needle-like structures; (**b**) 30 nm layer of PTCBI deposited on 15 nm of CuPc showing phase segregation.

60 nm) PTCBI layers, phase segregation is observed. PTCBI formed aggregates of approximately spherical shape on the surface of CuPc, as shown in figure 3b.

Silver has been used as a contact to PTCBI in CuPc/PTCBI solar cells in the past [2–4]. In our experiments, high V_{oc} values were obtained when aluminum was used as the top electrode next to PTCBI, instead of silver.

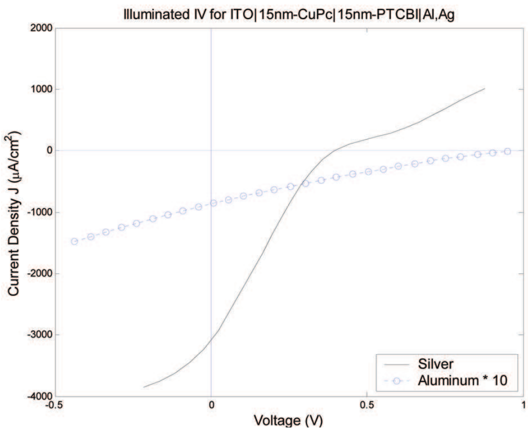

Figure 4. Comparison of J–V characteristics with aluminum and silver electrodes under 'one Sun'. The thicknesses of the CuPc and PTCBI layers were 15 nm each. Current for the Al case is multiplied by a factor of 10.

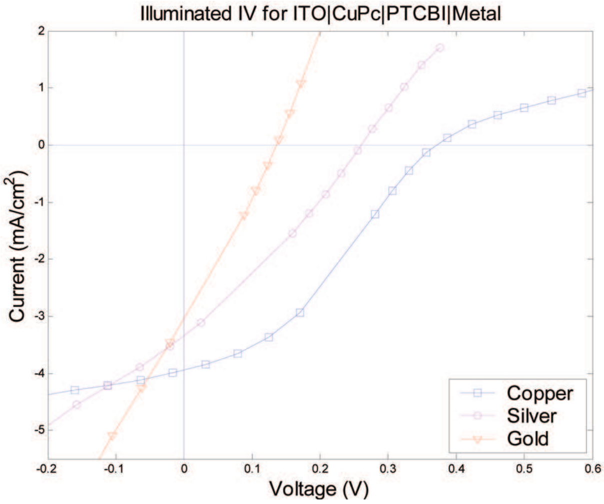

Figure 5. Current–voltage characteristics under 'one Sun' illumination for ITO/PEDOT:PSS/CuPc/PTCBI/metal cells. The metal electrode was (**a**) copper, (**b**) silver, (**c**) gold.

This is illustrated in figure 4 where the I–V characteristics of the otherwise identical devices having aluminum and silver electrodes, and under illumination, are plotted. CuPc and PTCBI thicknesses were 15 nm each. With aluminum, V_{oc} was 950 mV, while with silver it was 450 mV; corresponding J_{sc} values were 0.1 mA/cm^2 and 3 mA/cm^2 respectively.

To further probe the effect of electrode material on the device behavior, gold, silver and copper were compared as electrodes on the same substrate. I–V characteristics under illumination are shown in figure 5.

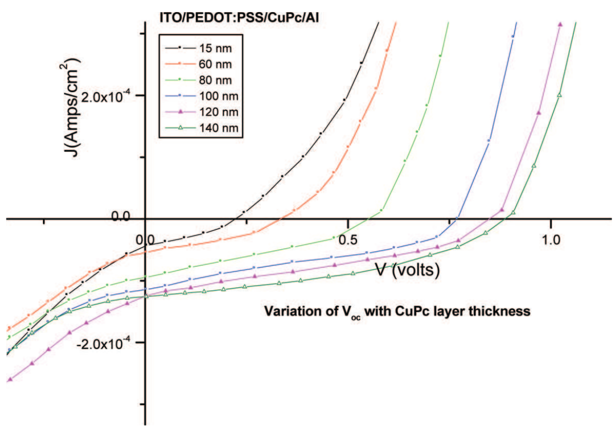

Figure 6. *J–V* characteristics of ITO/PEDOT:PSS/CuPc/Al Schottky diode solar cells as a function of CuPc thickness.

For this experiment, thicknesses of CuPc and PTCBI were 15 nm and 7 nm respectively. All three yielded comparable J_{sc} values. V_{oc} values however, varied substantially. The V_{oc} values were 0.4 V, 0.28 V and 0.15 V for Cu, Ag, and Au respectively.

Results described in this section can be understood in terms of a model where the CuPc– PTCBI–Al device with thin (7 nm or less) PTCBI layer is conceived as a Schottky diode between the CuPc layer (modified by thin PTCBI) and aluminum [10,11]. Thus, the thin PTCBI layer is thought to be entirely incorporated into the CuPc, now described as the 'modified CuPc'.

4. CuPc–Al Schottky diodes

CuPc Schottky diodes in the ITO/PEDOT:PSS/CuPc/Al configuration were investigated. CuPc thickness was varied from 15 nm to 200 nm and the results obtained are summarized in the curve shown in figure 6.

An increase in the CuPc layer thickness results in reduced shunting losses, yielding higher V_{oc}. The highest open circuit voltage (900 mV) was observed for a device with CuPc layer of thickness 140 nm. The short circuit current density (J_{sc}) increases with increase in CuPc layer thickness and shows a saturation after 100 nm. The current through the device is limited by the series resistance, through the formation of an Al_2O_3 layer during deposition of the Al electrode.

5. Conclusions

Photovoltaic cells involving CuPc and PTCBI were studied. A high open circuit voltage of 1.15 V was obtained in an ITO/PEDOT:PSS/CuPc/PTCBI/Al device with a thin PTCBI layer of 7 nm thickness. Results were interpreted in terms of a modified CuPc–Al Schottky diode for the thin PTCBI case and a CuPc–PTCBI heterojunction for the thick PTCBI case. Also, the formation of a thin aluminum oxide layer under the aluminum electrode was postulated. This layer has a beneficial aspect wherein shunting losses are reduced and a high photovoltage is enabled. However, it adds greatly to the series resistance to a point where the short-circuit current density is reduced.

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Acknowledgements

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