CuPc/C_{60} heterojunction thin film optoelectronic devices

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Abstract: The optoelectronic properties of heterojunction thin film devices with ITO/CuPc/C_{60}/Al structure have been investigated by analyzing their current–voltage characteristics, optical absorption and photocurrent. In this organic photovoltaic device, CuPc acts as an optically active layer, C_{60} as an electron-transporting layer and ITO and Al as electrodes. It is observed that, under illumination, excitons are formed, which subsequently drift towards the interface with C_{60}, where an internal electric field is present. The excitons that reach the interface are subsequently dissociated into free charge carriers due to the electric field present at the interface. The experimental results show that in this device the total current density is a function of injected carriers at the electrode–organic semiconductor surface, the leakage current through the organic layer and collected photogenerated current that results from the effective dissociation of excitons.

Key words: organic semiconductor; optoelectronic device; thin film; heterojunction; CuPc; C_{60}
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1. Introduction

During the past decade, organic semiconductors have been investigated widely as conjugated polymers, oligomers and low molecular weight materials. Their lower material and fabrication costs are attracting extensive interest for their potential applications in organic devices[1−4]. Organic semiconductor phthalocyanines and in particular CuPc is one of the well-studied organic photosensitive semiconductors[5]. It has a high absorption coefficient in a wide spectrum and high photosensitivity at low intensities of radiation. Its deposition by vacuum sublimation is easy. Purification of CuPc is simple and economical as the sublimation occurs at relatively low temperatures (400–600 ℃).

Studies of dark conductivity by El-Nahass *et al.*[6] on copper phthalocyanine thin film with gold electrodes have shown that in the direction of the film's plane the conductivity increases with increasing thickness. These authors established that the conductivity–temperature relationship exhibits a change from extrinsic to intrinsic conduction at a temperature of ∼380 K. They also measured the Seebeck coefficient which showed that CuPc thin films behave as p-type semiconductors and the thermoelectric coefficient reaches a maximum at 400 K. At lower voltages, ohmic and, at higher voltages, space-charge limited current conductivities were observed[6].

C_{60} has a fully n-conjugated soccer-ball like structure unlike planar MPc[7] and forms heterojunctions with some p-type molecular semiconductors, such as poly (2-methoxy-5-(2′-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV)[8], poly (3-alkyl-thiophene)[9] and tetrathiafulvalene[10].

In this paper ITO/CuPc/C_{60}/Al cells were fabricated and their optoelectronic properties were investigated. The aim of this work was to show that a combination of C_{60} and CuPc will provide a photovoltaic cell with a p–n junction and to show experimentally the space charge limited current behaviour of the cell.

2. Experimental details

The CuPc and C_{60} were obtained in powder form from Sigma–Aldrich. The thin films of CuPc, C_{60} and Al, held in a molybdenum crucible at 400–450 ℃, were thermally sublimed in sequence on a conductive glass substrate (ITO) under a pressure of 2×10^{-4} Pa in an Edwards AUTO 306 vacuum coater with a diffusion pumping system. The deposition rate was 2 nm/min and the substrate's temperature in this process was held at about 40 ℃. The typical thicknesses of CuPc, C_{60} and Al films were 120, 150 and 50 nm respectively. The thicknesses of the thin films were measured by using an Edwards FTM5 film thickness monitor.

A Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer was used for measurements of absorption spectra. Figure 1 shows a cross-sectional view of the fabricated ITO/CuPc/C_{60}/Al cell. The effective surface area of the sample was equal to 0.00126 m^2. The cells were then carried through an annealing process at 150 °C for 2 h. To measure the illuminated I–V curve, the sample was kept under AM 1.5 solar illumination at 100 mW/cm^2 (1 sun) using a Sciencetech solar simulator, with the intensity calibrated using a silicon photodiode. The device was illuminated through an ITO electrode and the intensity of light was measured by using a luxmeter. The measurements of voltage and current were conducted at room temperature using digi-

Fig. 1. Cross-sectional view of ITO/CuPc/C_{60}/Al cell: 1-ITO, 2-CuPc, 3-C_{60}, 4-Al, 5 and 6-terminals.

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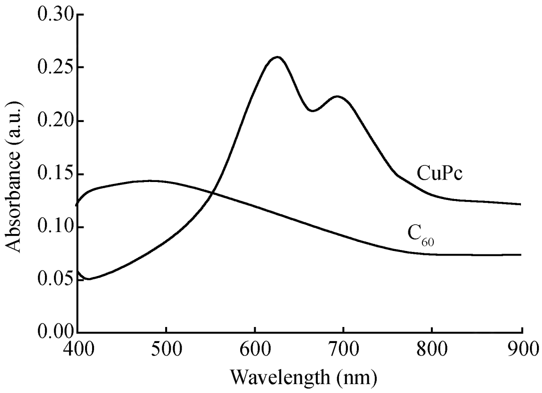

Fig. 2. Absorption spectra of the CuPc (thickness of 120 nm) and C_{60} (thickness of 150 nm) films deposited on conductive glass (ITO) substrate by vacuum evaporation.

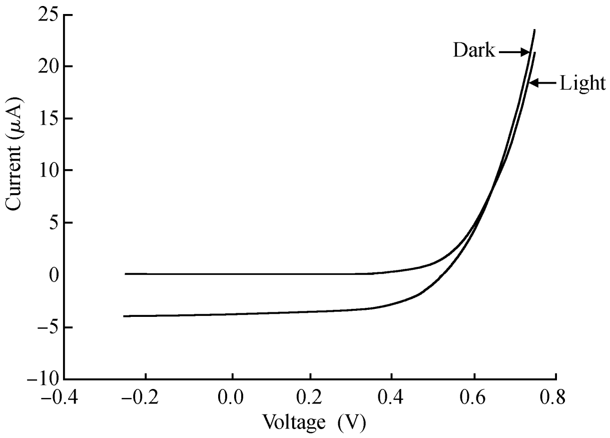

Fig. 3. Current–voltage characteristics in the dark and under illumination for the Al/C_{60}/CuPc/ITO device.

tal meters by applying positive and negative voltages across the Al and ITO electrodes respectively in the forward bias and vice-versa in the reverse bias.

3. Results and discussion

Figure 2 shows the absorption spectrum of the deposited CuPc and C_{60} films in the NIR-visible range. The spectrum of CuPc consists of strong transitions to the second excited state ($S_0 \rightarrow S_2$) at about 629 nm (the Soret or B band) and weak transitions to the first excited state ($S_0 \rightarrow S_1$) at about 698 nm (the Q band). From spectral broadening, as shown in Fig. 2, the energy bandwidths for CuPc films are estimated to be approximately 0.11–0.21 eV, while the bandwidths for C_{60} amorphous films are much wider and difficult to estimate in this way.

The current–voltage characteristics for the ITO/CuPc/C_{60}/Al device in the dark and under illumination are shown in Fig. 3. In the dark, a clear rectification behaviour is present, while under illumination photoconductivity is observed, i.e. a reduction in rectification. In the dark, the rectification ratio RR, defined as a ratio of forward to reverse current (with positive Al electrode) at the same voltages (here $\pm$ 0.25 V), was equal to 3.91. From the current–voltage characteristics and spectral response curves, it is clear that the device exhibits a photovoltaic effect. Photo-excited CuPc injects electrons into the conduction band of C_{60} which are transported to the Al electrode while holes traverse through the CuPc film to the ITO electrode.

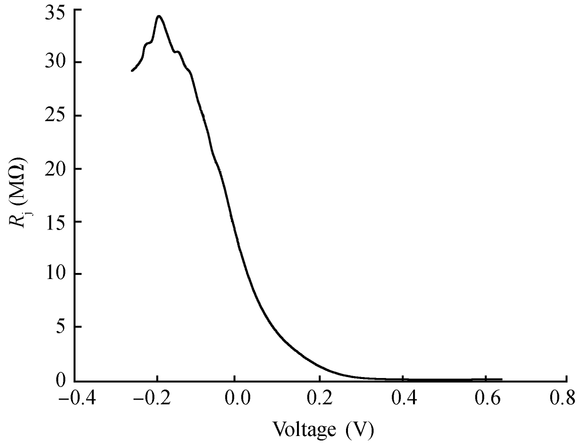

Fig. 4. Junction resistance versus applied voltage for the Al/C_{60}/CuPc/ITO device.

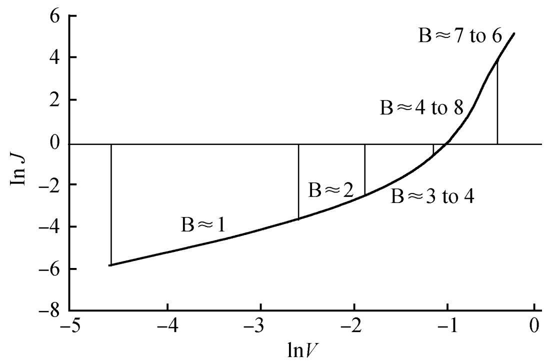

Fig. 5. Dark $\ln J$ versus $\ln V$ for the Al/C_{60}/CuPc/ITO device.

Figure 4 shows junction resistance ($R_j = dV/dI$) versus applied voltage for the sample. The maximum at reverse bias and minimum at forward bias may usually be considered as shunt (R_{sh}) and series (R_s) resistances[11] and are equal to 34.28 and 0.006 MΩ respectively in this case.

The forward bias current (I_f) is nonlinear and its dependence on the voltage, V, is given by[12]:

$$I_f = cV^B, \tag{1}$$

where c is the proportionality factor and B is the nonlinearity coefficient that may be determined from the following expression[12]:

$$B = \frac{\ln I_2 - \ln I_1}{\ln V_2 - \ln V_1}, \tag{2}$$

where I_1 and I_2 are currents measured at voltages V_1 and V_2 respectively. In Eq. (1), B = 1.5 for the case of negligible energy loss of the carriers known as the Child–Langmuir law, and B = 2.0 for the case of constant mobility known as the Mott–Gurney law. From the $\ln J$ versus $\ln V$ plot (Fig. 5), different linear regions are shown in our data. For low biases (V = 0–0.4 V), the value of B is between 1 and 1.5 which indicates that the transport behaviour is in a mixed regime governed by the ohmic law (B = 1) and the Child–Langmuir law (B = 1.5). However, as the electric field increases, a transition was observed from the ohmic law to the Mott–Gurney law, and during the transition a large value of B = 8 was obtained, which may be caused by the onset of carrier injection and trap filling[13].

To explain the electrical behaviour and the charge transport mechanism in organic semiconductor materials, the trapping model with a space-charge-limited current (SCLC) was used[15]. Traps at locations arise from disorders, dangling bonds, impurities, etc., and are called localized states that very often capture free charge carriers. Most frequently, an exponential distribution of traps in the energy band is assumed[14].

4. Conclusions

An Al/C_{60}/CuPc/ITO cell was fabricated using physical vapour deposition and its current–voltage characteristics in the dark and under illumination were investigated. It was found that the dark current–voltage characteristics show rectification behaviour and under illumination a photo-voltage was developed. The rectification ratio RR was equal to 3.91. It was found that a combination of C_{60} and CuPc will provide a photovoltaic cell with a p–n junction and the space charge limited current behaviour of the cell was observed.

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