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Modification of current-voltage characteristics of planar organic systems by nm-thick copper phthalocyanine or perylene dye interlayer

Research Article

Ryszard Signerski*, Grażyna Jarosz

Department of Applied Physics and Mathematics, Gdańsk University of Technology,
ul. Narutowicza 11/12, 80–233 Gdańsk, Poland

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Abstract: The effect of a nm-thick interlayer of copper phthalocyanine (CuPc) or perylene dye (MePTCDI) on current-voltage characteristics of planar organic systems is discussed in this work. The MePTCDI layer in the ITO/MePTCDI/CuPc/Au system strongly reduces reverse dark current by blocking injection of holes from ITO into CuPc leading to high values of rectification ratio. The CuPc interlayer in the ITO/CuPc/MePTCDI/Ag system causes a strong reduction in electron injection from ITO and reverses a forward polarity. Modification of current-voltage characteristics of illuminated systems with an interlayer of MePTCDI or CuPc is associated with a strong photovoltaic effect. This results from efficient excition dissociation at the CuPc/MePTCDI interface. Saturation current, determined by this process of charge carrier photogeneration, can be observed at particular voltage polarity.

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1. Introduction

Transport of charge carriers through metal-organic or ITO-organic interfaces quite often determine the properties of organic optoelectronic systems, in particular, organic photovoltaic cells and electroluminescent diodes. Research over the last few years indicates that buffer layers, either inorganic such as MoO_3, WO_3, V_2O_5, ZnO, LiF or organic, like PEDOT:PSS or BCP, with thicknesses usually less than 20 nm [1–7] can have beneficial effects on interface properties. A layer of transition-element oxide (with a thickness of a few nm) incorporated on an anode increases the flux of holes injected into (or extracted from) active organic layers [1–4, 6–8]. Additionally a layer of LiF (1 nm) or BCP (10 nm) incorporated on a cathode increases the injection of electrons [1, 7]. Buffer layers can improve morphology of active layers, performance and stability of system characteristics as well as enabling well-matched band structures at interfaces. The band structure determines the processes of injection and extraction of charge carriers occurring within electrode/organic layer interfaces. In general, however, the processes operating in systems provided with buffer layers are not well known.

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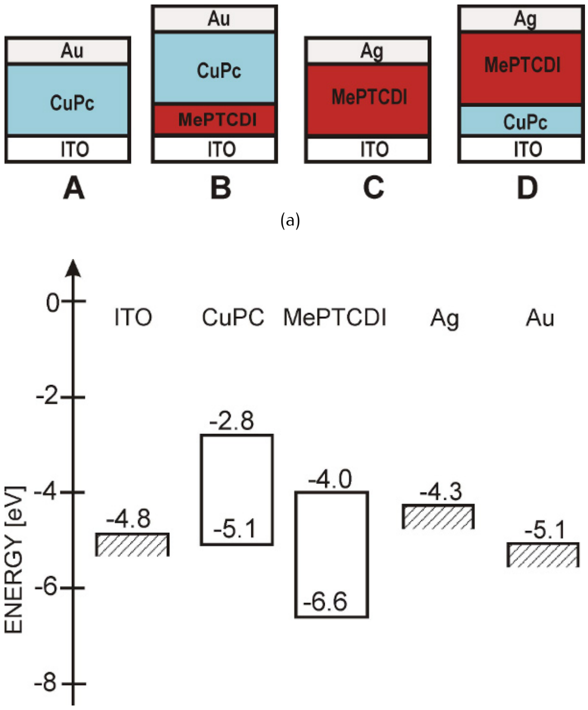
*E-mail: ryszard@mif.pg.gda.pl



(a)

(b)

Figure 1. Schematic representation of devices (a) and energy level diagram of materials used (b).

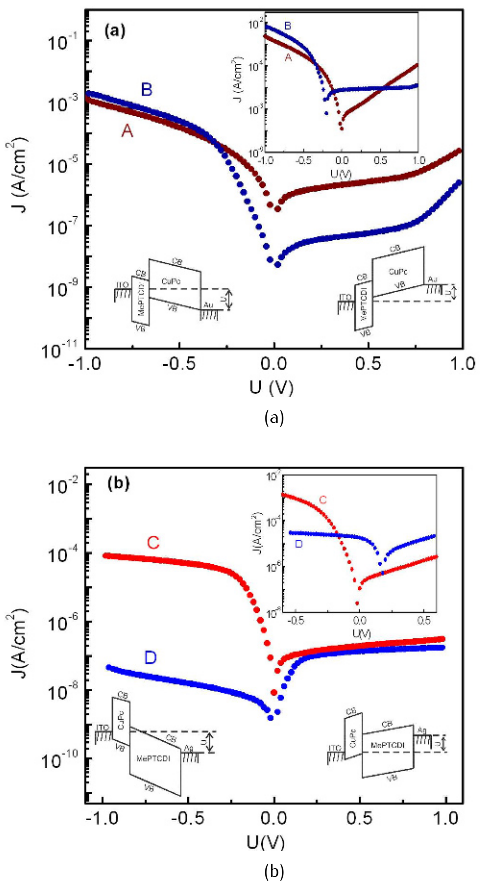
This work presents the results of our investigations on the current-voltage characteristics of planar systems formed by two organic materials, namely copper phthalocyanine (CuPc) and N-N′-dimethyloperylene-3,4,9,10-dicarboximide (MePTCDI). Both these materials are well known and widely used, particularly in organic photovoltaics [7, 9]. In photovoltaic cells based on small molecule materials, phthalocyanine (*e.g.* CuPc) transports holes, while perylene dye layers (*e.g.* MePTCDI or PTCBI) electrons. Charge carriers are generated as a result of exciton dissociation at the phthalocyanine/perylene dye interface. Layers of phthalocyanines can also be applied as buffer layers in organic electroluminescent diodes [10–12]. In another application, an organic layer of few nm in thickness can act as an effective quencher of excitons, which enables us to determine the exciton diffusion length [13].

The structures of our samples are shown in Fig. 1(a). They were obtained by vacuum evaporation of organic layers and Au or Ag electrodes onto glass substrates half covered with ITO layers. The aim of this work was the investigation of the modification of current-voltage characteristics caused by nm-thick layers of MePTCDI (sample B) or CuPc (sample D). Interlayers of thickness *ca* 10 nm are of appropriate thickness to get demanded properties of selective contact. Such layers simultaneously meet the requirement that voltage drop across the organic layer (usually of 100-200 nm thickness) is equal to applied voltage. Measurements of the current-voltage dependence of the systems without the nm-thick layers (samples A and C) were performed for comparison. Previous work [7] presents research performed on systems with CuPc and MePTCDI layers of equal thickness (80 nm) where the applied voltage was the sum of voltage drops across both organic layers.

A set of energy levels for the applied materials is shown in Fig. 1(b). The numbers present the position of the following energy levels expressed in eV with respect to a vacuum: Fermi levels for electrodes (ITO, Ag and Au), edges of valence bands (VB) (-5.1 eV for CuPc, -6.6 eV for MePTCDI) and conduction bands (CB) (-2.8 eV for CuPc, -4.0 eV for MePTCDI) for organic materials [7]. Such a diagram is useful for rough estimation of energy barriers limiting transport of charge carriers through a system. We must, however, bear in mind that uncertainty of energy values (in particular levels transporting electrons) is *ca* 0.5 eV. Additionally, in real structures dipole layers and band bending can considerably modify the alignments of energy levels at interfaces [14–17].

2. Experimental details

The samples (A, B, C and D) shown in Fig. 1(a) were obtained by vacuum evaporation (3×10^{-4} Pa, Auto 306 Turbo Edwards) of organic materials and electrodes Au or Ag onto an ITO/glass substrate (100 Ω/square, thickness 40 nm AWAT). CuPc was purchased from Aldrich, MePTCDI from Sensient Imaging Tech. Syn. Tec. Div. and Au and Ag from Kurt J. Lesker. Systems A and B were obtained in a single vacuum cycle as were C and D. The thickness of CuPc in systems A and B was 120 ± 10 nm and the thickness of MePTCDI in the B was 5 ± 1 nm. The thickness of MePTCDI in systems C and D was 145 ± 10 nm and the thickness of CuPc in D was 9 ± 2 nm. The thickness of the organic layers and their uncertainties were tested with a quartz oscillator (in vacuum), profilometer (Tencor Alpha Step 500 Profiler) and by optical absorption (spectrophotometer Shimadzu 1240). Roughness of the layers was estimated between 1 and 2 nm. The thickness of Ag and Au electrodes was the same in all the samples at 40 ± 5 nm. The active area of electrodes in each sample was 2×3 mm^2. The samples were illuminated through the ITO electrode with monochromatic light with constant intensity of 10^{15} photons/(cm^2 s). They showed weak absortion of interlayer and strong absorption of organic layer: $\lambda = 610$ nm for CuPc and $\lambda = 480$ nm for



(a)

(b)

Figure 2. Dark current versus voltage for A and B systems (a) and for C and D systems (b) with sketches of energy band diagram under adequate voltage polarity. Insets show photocurrents versus voltage.

MePTCDI (see absorption spectra in [7]). The measurements were performed under ambient air at room temperature using the equipment presented in our previous work [7].

3. Results and discussion

The current-voltage characteristics measured in these systems are presented in Fig. 2. The main body of the figures shows dark currents, while photocurrents are shown in the insets. Positive voltage ($V > 0$) refers to higher potential on ITO.

3.1. MePTCDI as interlayer in ITO/CuPc/Au system

From Fig. 1(b) and from sketches in Fig. 2(a) we can assume that in both the ITO/CuPc/Au system (A) and ITO/MePTCDI/CuPc/Au system (B) only hole current can flow through the CuPc layer. The barriers for electrons are too high. Both the systems exhibit the current-rectification effect with the rectification ratio of dark current (*i.e.* the ratio of forward current to reverse current at the same voltage) at 0.6 V equals 7.7×10^2 for system A and 5.7×10^4 for system B. For forward bias ($U < 0$), hole current flowing through the CuPc layers is formed by holes injected from Au electrode. If $U < -0.4$ V then the current values for both systems A and B are quite similar and we do not observe any effect of the MePTCDI layer. The presence of the MePTCDI layer is explicitly noticeable in reverse dark current (*i.e.* for $U > 0$). At this polarization, hole current injected by ITO electrode flows in system A, while in system B the presence of the MePTCDI layer strongly limits hole injection from ITO. Taking into consideration Fig. 1(b) we can assume that current flowing in this case is determined by thermal generation of charge carriers at the MePTCDI/CuPc interface (energy gap between hole band in CuPc and electron band in MePTCDI is 1.1 eV). The inset of Fig. 2(a) shows I-U curves for systems A and B illuminated with monochromatic light of wavelength $\lambda = 610$ nm (strong absorption of CuPc) and flux density of photons $I_o = 10^{15}$ 1/(cm^2 s). System A exhibits week photovoltaic effect: open-circuit voltage $U_{oc} = -6$ mV and short-circuit current $J_{sc} = 1.1 \times 10^{-7}$ A/cm^2 flowing through CuPc in the direction from ITO to Au. This current is formed by holes injected into CuPc as a result of exciton dissociation at the ITO electrode. For forward bias ($U < 0$) the layer of CuPc in both systems A and B carries hole current injected either thermally or optically (exciton dissociation) from the Au electrode. Density of this current is higher than density of dark current. For reverse bias ($U > 0$) the electric current in the A system is formed by holes injected thermally or as a result of exciton dissociation at ITO electrode.

System B exhibits explicit photovoltaic effect with the following parameters: $U_{oc} = -0.2$ V and $J_{sc} = 7.5 \times 10^{-6}$ A/cm^2. We observed linear dependence of J_{sc} on light intensity. The relation of $U_{oc}(I_0)$ was more complex and suggested the presence of interface states, in a similar maner to that discussed in [7]. This effect is a result of exciton dissociation at the MePTCDI/CuPc interface. An electron is transported through MePTCDI to ITO, while a hole through CuPc to Au. The process of photogeneration via exciton dissociation determines the saturation current, which had a magnitude of 10^{-5} A/cm^2 flowing through system B for reverse bias ($U > 0$).

3.2. CuPc as interlayer in ITO/MePTCDI/Ag system

In the ITO/MePTCDI/Ag system (C) and in the ITO/CuPc/MePTCDI/Ag system (D) an electron current can flow through the MePTCDI layer. This thesis can be derived from Fig. 1(b) and from sketches in Fig. 2(b), if the height of the potential barriers limiting injection of holes and electrons from electrodes are compared to each other. The dark current-voltage curve of system C (Fig. 2(b)) indicates that forward current flows for the -ITO/+Ag polarization. A rectification ratio at 0.6 V yields 2.5×10^2 which suggests that the injection barrier for electrons at ITO is lower than at Ag, which contradicts Fig. 1(b). This disagreement can result form interface dipole layers, however, we do not have any direct proof that the presence of such layers occurs in system C or in any similar system comprising MePTCDI [18]. Here, we can only refer to the work of Kahn *et al.*, who has observed dipole barriers at PTCBI/metal (Au, Ag, Mg) interface [14].

If a thin CuPc layer ($\sim$ 5 nm) is incorporated between ITO and MePTCDI, current density strongly decreases for $U < 0$ V (D curve in Fig. 2(b)). For instance, for $U = -0.6$ V the ratio of currents in C to D yields 2.75×10^3. For system D the forward polarization occurs for $U > 0$ and rectification ratio at 0.6 V yields 6.5. Due to the fact that for $U > 0$ the values of current in systems C and D are quite similar, we can conclude that the current is limited by thermal injection of electrons from Ag. In system D these electrons recombine at the CuPc/MePTCDI interface with holes injected into CuPc from ITO participating in this recombination. For $U < 0$ high barriers limiting injection of holes from Ag and electrons from ITO occur in system D. Let us assume that current flowing through the system is determined by thermal generation of charge carriers at CuPc/MePTCDI interface.

The photocurrent-voltage curves of systems C and D are shown in the inset in Fig. 2(b). In system C we observe week photovoltaic effect (a similar case was observed for system A). The short-circuit current is formed by electrons flowing through MePTCDI from Ag to ITO. These electrons are generated by exciton dissociation at the Ag electrode. For forward bias (-ITO/+Ag) electrons are either thermally or optically (by exciton dissociation) injected from ITO to MePTCDI. For reverse bias (+ITO/-Ag) thermal and optical injection of electrons from Ag occurs. As a result of optical injection the photocurrent for both directions of polarization is one order of magnitude higher than dark current.

System D, similarly system B, exhibits explicit photovoltaic effect: $U_{oc} = 0.18$ V, $J_{sc} = 1.8 \times 10^{-5}$ A/cm^2. Also $I_{sc}(I_0)$ and $U_{oc}(I_o)$ relations were generally similar to those for system B. Charge carriers are generated at the CuPc/MePTCDI interface. Following the exciton dissociation, electrons flow through MePTCDI to Ag, while holes through CuPc to ITO. For -ITO/+Ag polarization the photocurrent is determined by the same processes as the short-circuit current. For +ITO/-Ag polarization, when $U > U_{oc}$, the photocurrent is formed by electrons injected optically from Ag (exciton dissociation) and recombining at the CuPc/MePTCDI interface with holes injected by ITO.

4. Conclusions and summary

This work presents current-voltage curves of organic systems based on copper phthalocyanine CuPc and perylene dye MePTCDI. The measurements performed have proved that nm-thick interlayers of CuPc or MePTCDI affects significant changes in the dependence of dark current and photocurrent versus applied voltage. In the ITO/MePTCDI/CuPc/Au system the nm-thick MePTCDI layer strongly limits hole injection from ITO, while in the ITO/CuPc/MePTCDI/Ag system the nm-thick CuPc layer leads to a decrease in electron current injected from ITO by over 3 orders of magnitude. In both the systems with interlayers, explicit photovoltaic effect is observed. This effect is a result of dissociation of excitons at the CuPc/MePTCDI interface. From analysis of the surface profiles of the layers we noticed that the interlayers caused neither increase in roughness, or increase in interface area where charge separation took place. Therefore we conclude that the efficiency of exciton dissociation at CuPc/MePTCDI interface is greater than the efficiency of exciton dissociation at ITO/CuPc and ITO/MePTCDI interfaces.

We have researched organic interlayers deposited on ITO. Interlayers can be also deposited on other electrodes, for instance, on metal if high transmittance of light is not required. To select a proper material for an interlayer, which should lead to desired properties of organic system, we have to take into account work function of electrodes, electron affinity and ionization energy of organic materials. The fact that the interface dipole layers modify the height of barriers for electrons and holes can increase the complexity of the problem [14–17]. Gap states can participate in charge carrier transport through interlayer. In optoelectronic devices, interlayers and the investigated system should form an electron donor – electron acceptor couple (in our case it was CuPc-MePTCDI). This relation supports high efficiency of exciton dissociation and high value of photocurrent. Organic nm-thick interlayers enable us to get an energetic barrier for electrons or holes higher than in a system without an interlayer. As a result we can get monopolar current and high values of current rectification ratio, which is of particular importance in organic diodes. Illuminated systems with an interlayer can exhibit strong photovoltaic effect. Analysis of this effect and photocurrent measurements can be applied to the estimation of exciton diffusion length. Interlayers also enable a high value of photocurrent to dark current ratio, which is important for organic photodetectors.

Acknowledgements

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