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Effect of buffer layers on performance of organic photovoltaic devices based on copper phthalocyanine-perylene dye heterojunction

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The work presents the results of research on the systems formed from thin films of copper phthalocyanine (CuPc), N-N'-dimethylperylene-3,4,9,10-dicarboximide (MePTCDI), electrodes of ITO and Ag, and from buffer layers: MoO_3 at ITO and BCP at Ag. We have observed the effect of each buffer layer on voltage dependence of dark current and photocurrent, and on open circuit voltage-light intensity relationship. The system with both buffer layers exhibited the highest values of open circuit voltage and fill factor. The buffer layers improve transport of charge carriers within near-electrode regions, reduce dissociation of excitons on electrodes and reveal processes of charge carrier generation and recombination within the CuPc/MePTCDI junction.

Keywords: organic photovoltaics, phthalocyanine, perylene dye, buffer layers.

1. Introduction

Organic photovoltaic cells (OPVC) have already overcome 8%-energy conversion efficiency and their commercial application is of interest of many firms [1]. Nowadays, the best parameters are exhibited by multilayer small-molecule solar cells and polymer solar cells with bulk heterojunction. There are, however, many problems which should be overcome before OPVC is an attractive source of electric energy. Researchers are therefore focused on both new materials and designing of new photovoltaic structures. There are still many articles dealing with planar heterojunctions formed from small molecular weight semiconductors such as phthalocyanines, porphirins, perylene diimides, and fullerenes [2–4]. It is also worth noticing that devices with a single planar heterojunction are particularly appropriate for study of essential parameters of photovoltaic processes. Many researchers relate the beginning of modern organic photovoltaics to the Tang's work [5]. He has shown that heterojunction of CuPc/perylene dye allows to obtain energy conversion efficiency approaching 1%. The next works [6–11] confirmed significant role of phthalocyanines and perylene dyes as photovoltaic materials.

Important issue which has to be considered while designing OPVC is selection of proper electrodes. Unfortunately, transport of charge carriers through electrode/organic material interfaces is often limited by potential barriers which can make the parameters of solar cells poor. Moreover, metallic electrodes being in direct contact with active layer efficiently quench excitons, and this can lead to decrease in exciton concentration even within the region of heterojunction. These problems can be reduced by inclusion of a buffer layer. Additionally, the buffer layer can also prevent the active layer from damaging by hot metal atoms during electrode evaporation. In spite of publishing many works, dealing with the systems based on phthalocyanine/perylene dye heterojunction and provided with various interlayers at anode or cathode, understanding the effect of buffer layers on OPVC performance is still unsatisfactory.

Bathocuproine (BCP) is a material which was often used as 10–20-nm-thick buffer layer put between an active layer transporting electrons (e.g. perylene dye or C_{60}) and a cathode (e.g. Al, Ag). Authors of Refs. 9, 12–15 emphasize that BCP in their systems either plays the role of a layer blocking excitons (hence reducing quenching of excitons by metallic electrode [9,12,14]) or forms ohmic contact between active layer and electrode [12–14]. Gap states induced by atoms of metallic electrodes play an important role in the transport of electrons through the BCP layer [9,12–16]. The works mentioned above present beneficial influence of the BCP layer on such parameters as short-circuit current (j_{sc}) [9,12–15], open-circuit voltage (U_{oc}) [12,15] and power conversion efficiency [12,14,15].

A buffer layer can be also put between an anode (e.g. ITO) and a layer transporting holes (e.g. phthalocyanines like CuPc, ZnPc or polymers like MEH-PPV, P3HT). PEDOT:PSS or metal oxides (MoO_3, WO_3, V_2O_5, NiO) seem to be most often used as such a layer. In this work, a particular attention will be paid to the effect of MoO_3 interlayer on performance of small molecular OPVC [17–20]. MoO_3 is a wide energy gap semiconductor with high work function [Fig. 1(b)]. Taking this into account, the

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authors of Refs. 17, 18, and 19 explained the results of their researches assuming that a thin MoO_3 layer (of several nm thick) blocks the transfer of electrons into anode and therefore reduces electron leakage current, which leads to the increase of U_{oc}, j_{sc}, and power conversion efficiency. On the other hand, the authors of Ref. 20 believe that the layer of MoO_3 improves transport of holes from CuPc to ITO. The holes can cross MoO_3 by multiple tunnelling steps between the gap states introduced by oxygen vacancies. The most beneficial effect of the presence of the MoO_3 layer is the increase in fill factor (FF).

As it is seen, there are different opinions on the effect of MoO_3 on photovoltaic properties of organic devices in literature. Moreover, some works published recently indicate that conduction and valance band energies of MoO_3 are higher by over 4 eV than it is usually assumed [see Fig. 1(b), dashed lines for MoO_3] and that big energy jumps resulting from dipole layers occur at ITO/MoO_3 and MoO_3/organic interfaces [21,22]. Analysis of these interfaces was based on ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). The authors of Ref. 21 came to the conclusion that injection of holes from ITO electrode to the system with MoO_3 interlayer proceeded via electron extraction from HOMO of organic material (α-NPD) through the conduction band of MoO_3. Reference 22 describes the electron structure of ITO/MoO_3/chloro-aluminium phthalocyanine (AlClPc). The presence of the MoO_3 layer results in reduction of barrier height for hole transfer and creates an electric field, which directs holes towards the MoO_3 layer. Transport of holes through MoO_3 is possible due to the presence of gap states originating from oxygen deficiency. Consequently, the layer of MoO_3 may significantly reduce series resistance of the system.

As we can see in spite of many works on the role of buffer layers in OPVC published so far there exist significant differences in interpretation of obtained results. This situation constitutes motivation for further researches. Our work presents the results of research on the systems formed from thin films of copper phthalocyanine (CuPc), N-N'-dimethylperylene-3,4,9,10-dicarboximide (MePTCDI), electrodes of ITO and Ag, and from buffer layers: MoO_3 at ITO and BCP at Ag [Fig. 1(a)]. We produced and investigated three types of systems [Fig. 1(a)]: ITO/CuPc/MePTCDI/Ag (named as A), ITO/MePTCDI/BCP/Ag (named as B) and ITO/MoO_3/CuPc/MePTCDI/BCP/Ag (named as C). The systems were produced at the same conditions and the thicknesses of active organic layers (CuPc, MePTCDI) were equal to (80 ±5) nm. We did not expect particularly effective photovoltaic performance, since the exciton diffusion lengths measured in CuPc and MePTCDI lay mostly within the range of 5–30 nm [2,4,9,10,23], which is several times smaller than the thickness of our active layers. Figure 1(b) shows a set of energy levels of the applied materials. Values of the energies were taken from [4,19,21,24–26] and their uncertainties were equal to about 0.5 eV.

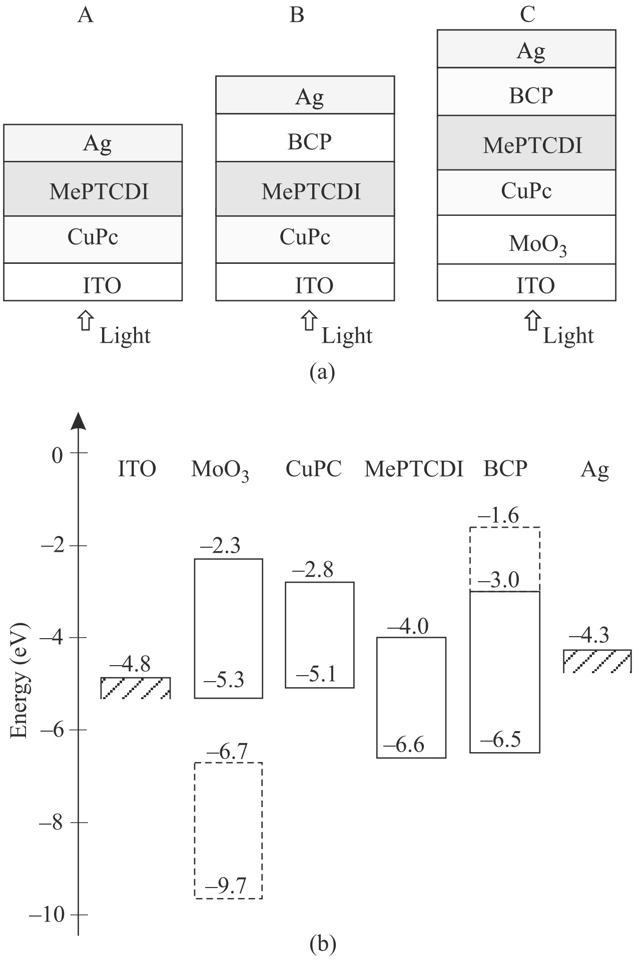

Fig. 1. Schematic representation of devices (a) and energy level diagram of materials used (b).

2. Experimental details

The A, B, and C devices [Fig. 1(a)] were obtained by vacuum evaporation (3×10^{-4} Pa, Auto 306 Turbo Edwards) of the materials on an ITO/glass substrate (100 Ω/square, AWAT). The thicknesses of layers were as follows: MoO_3 – 5 nm, CuPc – 80 nm, MePTCDI – 80 nm, BCP – 15 nm, Ag – 40nm. MoO_3, CuPc, BCP and Ag were purchased from Sigma-Aldrich, while MePTCDI from Sensient Imaging Tech. Syn. Tec. Div. Organic materials were additionally purified by sublimation. The active area of electrodes in each sample was equal to 6 mm^2. The apparatus used in measurements was described in our previous work [27]. All measurements were performed under ambient air at room temperature.

3. Results and discussion

Figure 2 shows spectral dependence of short-circuit current [$j_{sc}(\lambda)$] for A system and absorption spectra of CuPc and MePTCDI layers. It is seen that $j_{sc}(\lambda)$ is symbatic with respect to the absorption spectrum of MePTCDI and rather antibatic with respect to the absorption spectrum of CuPc.

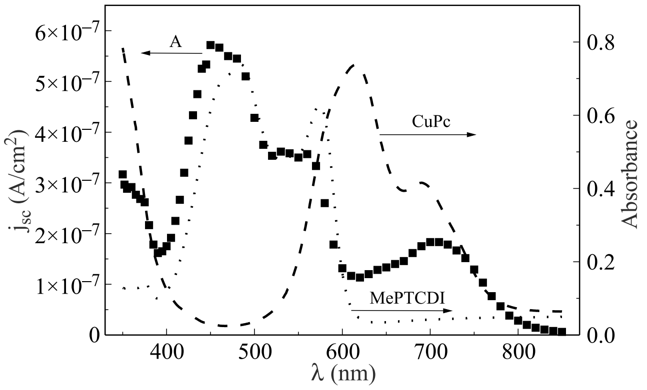

Fig. 2. Spectrum of short-circuit current at light intensity $I_o = 10^{14}$ ph/(cm^{2}s) and absorption spectra of CuPc and MePTCDI layers.

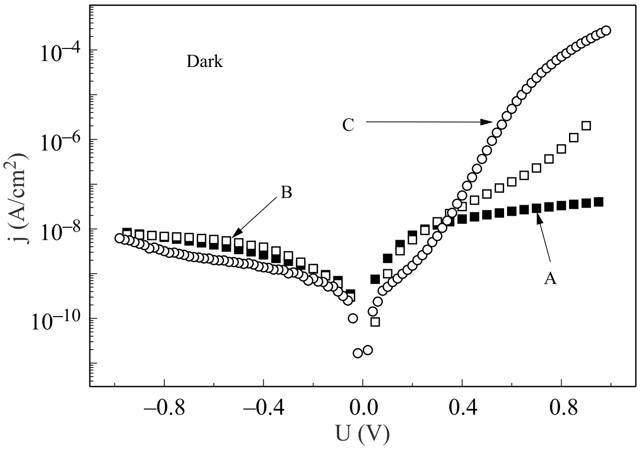

Fig. 3. Dark current-voltage curves of the A, B, and C systems.

Such shape of $j_{sc}(\lambda)$ at illumination through ITO indicates that charge carrier photogeneration takes place at the nearest vicinity of phthalocyaninne/perylene dye interface [2–10]. Charge carriers are generated via dissociation of excitons reaching the interface. At final stage of photogeneration process a hole appears in CuPc, while an electron appears in MePTCDI. Charge carriers generated in this way diffuse and drift towards electrodes. Dissociation of excitons generated in CuPc or MePTCDI is possible due to adequate system of energy levels at the CuPc/MePTCDI interface [see Fig. 1(b)]. The mechanism of charge carrier photogeneration described here operates in all our systems. Differences between the A, B, and C systems presented in further passage result from the effect of buffer layers on transport of charge carriers through the near-electrode regions.

Figure 3 shows dark current-voltage relationships of A, B, and C systems. We assumed that positive voltage ($U > 0$) referred to higher potential on ITO. It is seen that at reverse bias ($U < 0$) the current density for all the systems approaches common value of about 10^{-8} A/cm^2. We suppose that it is saturation current of CuPc/MePTCDI heterojunction.

For forward bias ($U > 0$) it can be noticed that MoO$_3$ layer affects a certain limit for charge carrier transport within the range of low voltage (C curve, $U < 0.34$ V). However, for $U > 0.34$ V we observe strong increase in current resulting from inclusion of BCP (B curve) and MoO$_3$ (C curve) layers.

The C system exhibits strong current rectification. Its ratio at $|U| = 0.8$ V yields 2.2×10^4. For forward bias two linear regions are noticeable on C curve. It means that the relation

$$j \propto \exp\left(\frac{eU}{nkT}\right), \tag{1}$$

is fulfilled within these regions. We observed $n = 3.65$ within the range from 0.06 V up to 0.30 V and $n = 1.83$ within the range of 0.32–0.54 V. Simple theoretical model predicts that the quality factor n should take a value from the range $\langle 1,2 \rangle$ [28]. Value of n close to 2 suggests the occurrence of strong recombination of charge carriers within heterojunction. So, we may assume that within the range from 0.32 V up to 0.54 V curve C is a characteristic of CuPc/MePTCDI heterojunction and current flowing through the junction is determined by recombination of charge carriers (i.e. holes coming from the CuPc side and electrons coming from the MePTCDI side). For higher values of voltage ($U > 0.8$ V) we observe probably space-charge-limited current within the bulk of organic layers, however, we do not know if the limitation dominates within CuPc or MePTCDI.

Current-voltage curves of the systems illuminated with monochromatic light of $\lambda = 470$ nm and $I_o = 10^{14}$ photons/(cm^{2}s) through ITO are shown in Fig. 4. Light of this wavelength is well transmitted by CuPc and strongly absorbed by MePTCDI. So, the photocurrent is mainly determined by dissociation of excitons produced in the vicinity of CuPc/MePTCDI interface. It is seen that at reverse bias only the MoO$_3$ layer affects values of photocurrent. The decrease in reverse photocurrent observed for C system can be treated as the result of reduction of the rate of hole transfer from CuPc into ITO by the MoO$_3$ layer. It is not, however, clear why the effect is stronger for photocurrent than for dark current.

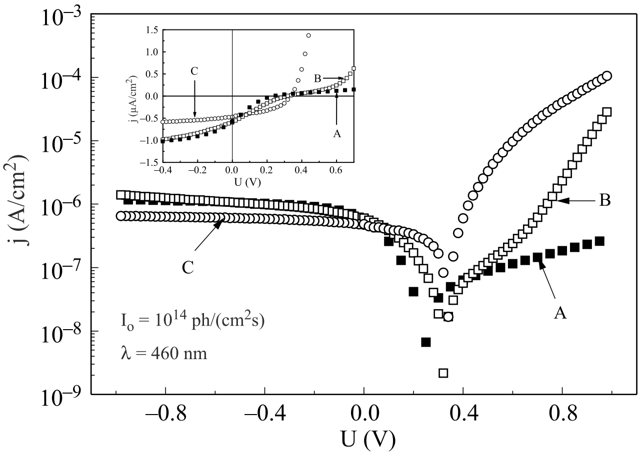

Fig. 4. Photocurrent-voltage curves of A, B, and C systems illuminated with light of 460 nm and intensity $I_o = 10^{14}$ ph/(cm^{2}s). Inset: the same relations in photovoltaic region in lin-lin plot.

Both layers, namely BCP and MoO_3, explicitly have an influence on photovoltaic properties of our devices and on characteristics at forward bias. For $U > U_{oc}$, current flowing through A, B, and C systems is formed by charge carriers thermally injected from electrodes and by charge carriers resulting from exciton dissociation. The ITO electrode injects holes into CuPc, which while reaching CuPc/MePTCDI interface recombine either with electrons generated by exciton dissociation or with electrons injected into MePTCDI by Ag. Holes resulting from exciton dissociation are transported by MePTCDI to Ag. At both electrodes there exist potential barriers limiting thermal injection of charge carriers. Inclusion of BCP layer reduces the barrier limiting electron injection from Ag into MePTCDI and this leads to transition from A curve to B curve. If we additionally put the MoO_3, the barrier at ITO also undergoes reduction and much higher current will flow through the system (C curve). The effects of putting buffer layers observed here are in quantity agreement with models proposed in Refs. 16 and 22, in which the authors take into account both the presence of dipole layers at interfaces and gap states.

The effect of buffer layers on photovoltaic performance is presented in Figs. 4 (inset), 5, and 6. It is seen that the presence of these layers leads to a small drop of short-circuit current (j_{sc}). This effect can be related to the increase in series resistance of the system. The relation of short-circuit current versus light intensity for all the systems are almost linear (Fig. 5)

$$j_{sc} \sim I_o^m, \qquad (2)$$

where $m = 0.95$–0.97. In the light of Ref. 29, it means that the monomolecular recombination related to huge density of states trapping charge carriers dominates within CuPc/MePTCDI heterojunction.

On the other hand, Fig. 6 shows strong effect of buffer layers on the relation of open circuit voltage (U_{oc}) *vs.* the light intensity (I_o). The A curve (the system without buffer layers) for higher values of light intensity approaches saturation value with $U_{ocsat} \approx 350$ mV. The effect of this saturation can be related to quenching of excitons by Ag electrode, since the efficiency of this process can increase with the increase in light intensity. As a result of vacuum evaporation, the surface of this electrode is quite well developed and the Ag particles deeply penetrate MePTCDI layer (up to about 15 nm). If the system is provided with BCP layer, the quenching of excitons by the Ag electrode is impossible and the effect of saturation of U_{oc} is not observed. The effect of inclusion of MoO_3 is different, in this case we observe the increase of U_{oc} within the whole range of I_o (curve C). Formally, the relation of $U_{oc}(I_o)$ obtained for C system can be approximated by the following relation [28]

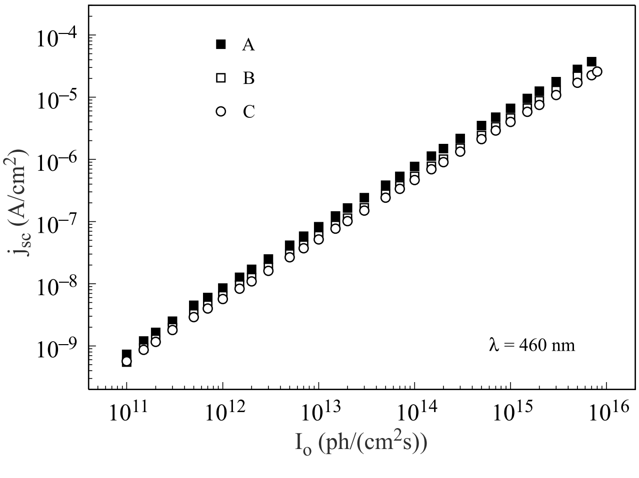

Fig. 5. Relations of short-circuit current against light intensity at $\lambda = 460$ nm for A, B, and C systems.

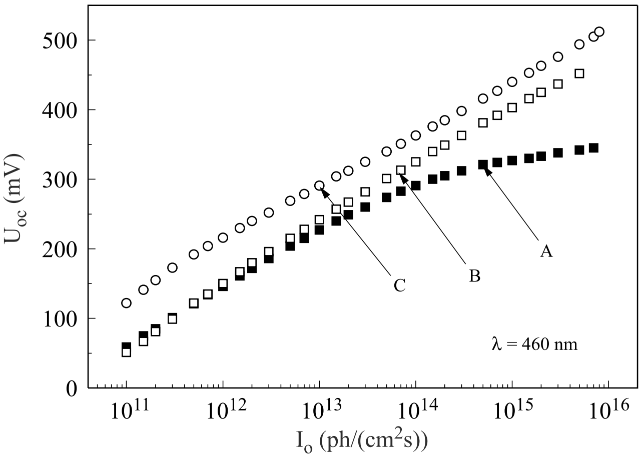

Fig. 6. Relations of open-circuit voltage against light intensity at $\lambda = 460$ nm for A, B, and C systems.

$$U_{oc} = n' U_T \ln(\alpha I_o), \qquad (3)$$

where $U_T = kT/e = 25$ mV is the thermal potential, the constant α equals 4.3×10^{-10} cm^{2}s, and ideality factor n' equals 1.33. The case when $n' > 1$ we can treat as a result of charge carrier recombination via interface states of heterojunction [27,30]. It can be noticed, however, that the factor n in Eq. (1) and the factor n' in Eq. (3) are not the same and therefore the Schockley equation does not describe our heterojunction [28]. As the inclusion of MoO_3 layer leads to the increase of U_{oc}, we come to the conclusion that ITO/CuPc contact is not ohmic one and its electric properties can be characterized by the finite value of majority carrier recombination rate. Reference 31 shows that too small majority carrier recombination rate at an electrode can result in S-shaped current-voltage curve and small value of U_{oc}. Taking this into account we can suggest that the MoO_3 layer increases the rate of hole recombination at an anode. However, we can also quite differently interpret the role of MoO_3 layer. Namely, the photovoltage for the illuminated B system has got two parts of different polarity: the first, higher, generated at the interface of CuPc/MePTCDI and the second, smaller, generated at the ITO/CuPc contact. In C system, the second part does not exist and therefore the value of U_{oc} is higher in comparison with B system.

Other important photovoltaic parameter is fill factor. It is defined as the ratio of maximum power produced by a system to the product of I_{sc} multiplied by U_{oc}. FF for an organic system depends, among others, on architecture of system, on generation-recombination processes in heterojunction, on processes of charge carrier transport and on properties of electrodes. Theoretical model describing this fundamental photovoltaic parameter has not been formed, yet. Inset in Fig. 4 shows the influence of buffer layers on the shape of current-voltage characteristics and obviously also on FF. The value of FF for A system equals 0.19, for B system it is 0.22 and for C system it is 0.41. So, only C system exhibits acceptable value of FF. The efficiency of photovoltaic power conversion for this system is, however, quite low and it equals 0.16%. Further improvement in photovoltaic performance of our systems can be done by optimizing thickness of all layers which form the structure.

4. Conclusions

In the work we have presented the results of researches on the effect of near-electrode buffer layers of BCP and MoO_3 on dark current-voltage, photocurrent-voltage and on light intensity dependences of open-circuit voltage and short-circuit current in the system with CuPc/MePTCDI heterojunction. The buffer layers reduce the effect of non-Ohmic electrodes on these characteristics and reveal properties of the organic heterojunction. The C system, i.e., the system provided with both buffer layers, exhibits strong effect of dark-current rectification and photocurrent-voltage characteristic is not of S-shape. The photovotage and the fill factor for this system are much higher than for the case without buffer layers. The buffer layers improve transport properties of the near-electrode regions and reduce exciton dissociation at the electrodes.

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