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Effects of the buffer layer inserted between the transparent conductive oxide anode and the organic electron donor

A. Godoy^a, L. Cattin^b, L. Toumi^c, F.R. Díaz^d, M.A. del Valle^d, G.M. Soto^b, B. Kouskoussa^a, M. Morsli^e, K. Benchouk^a, A. Khelil^a, J.C. Bernède^{e,*}

^a *Facultad Ciencias de la Salud, Universidad Diego Portales, Ejército 141, Santiago de Chile, Chile*

^b *Université de Nantes, Nantes Atlantique Universités, Institut des Matériaux Jean Rouxel (IMN)-CNRS, Faculté des Sciences et Techniques, 2 rue de la Houssinière, BP 92208, Nantes F-44000, France*

^c *LPCM2E, Université d'Oran Es-Senia, LPCM2E, Algérie*

^d *Laboratorio de Polímeros, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile*

^e *Université de Nantes, Nantes Atlantique Universités, LAMP, Faculté des Sciences et Techniques, 2 rue de la Houssinière, BP 92208, Nantes F-44000, France*

In optoelectronic devices, the work function of the transparent conductive oxide, which is used as anode, does not match well the highest occupied molecular orbital of the organic material, which induces the formation of a barrier opposed to hole exchange at this interface. Therefore a thin buffer layer is often used to achieve good matching of the band structure at the interface. From experimental results it can be deduced that the main effects of the buffer layer consist in a better matching of the band structure at the interface anode/organic material and in a more homogeneous organic layer growth. We show that, whatever the nature of the buffer layer-metal, oxide, organic material—the classical Schottky–Mott model allows to anticipate, at least roughly, the behaviour of the contact, even if some dipole effect are often present. A good correlation between the “metal/buffer layer” work function and the barrier Φ_b for hole exchange at anode/organic electron donor interfaces is obtained, as expected by the model.

1. Introduction

Although impressive progresses have been done during last years [1], the organic solar cells (OSC) efficiency is still in need of improvement. A general problem in organic electrical devices is the transport of charge carriers at the interfaces electrode/organic material. Interfacial phenomena represent a challenge and important area in organic devices science and technology. A variety of interfacial treatments have been applied to both the cathode/organic and the anode/organic interfaces, different more or less thin buffer layers have been placed at these interfaces, resulting in varying degrees of devices improvement in term of charge exchange.

For instance, several attempts to improve the interface anode/electron donor have been done. The experience has shown that the surface chemistry of the transparent conductive oxides (TCOs) is difficult to control [2]. Effectively, it has been shown that the reproducibility of the results obtained, when ITO is used as anode, is in need of improvement. Usually, a thin layer of poly(ethylene dioxythiophene doped with polystyrene sulfonic acid) (PED-

OT:PSS), which is a conductive polymer, is deposited by spin coating onto the ITO film before organic deposition. This buffer layer is very efficient since it allows achieving good adjustment of the work function, passivation of surface defects and it smoothes the ITO surface. However, PEDOT:PSS is problematic since it degrades under UV illumination, it introduces water into the active layer and it is slightly acidic [3]. Therefore different organic monolayers have been used for ITO electrode passivation in organic solar cells [2–7]. Moreover high work function anode are desirable to decrease the series resistance. High and reproducible work functions are also difficult to obtain for ITO [8]. In order to achieve good TCO surface properties, different treatments have been proposed such as air plasma or phosphonic acid with alkyl chains modification [9]. Oxidation of ITO surface by O₂ plasma or UV ozone treatment can increase its work function to nearly 5 eV [10].

In the case of multilayer heterojunctions solar cells, the structures are usually based on metal phthalocyanine (MPc)/fullerene (C₆₀) bilayer [11]. Using such cells, we have shown that an ultra-thin metal film deposited onto the conductive substrate, whatever the transparent conductive oxide (TCO), can also be used to improve the interface TCO/donor and therefore the devices performances [12,13]. In the case of OLEDs [14–20], organic thin film transistors [21,22], and organic solar cells

* Corresponding author. Tel.: +33 2 5112 5530; fax: +33 2 5112 5530.
E-mail address: jean-christian.beruede@univ-nantes.fr (J.C. Bernède).

[23,24] different attempts have been done, with some success, using different oxide thin films as buffer layer between the TCO and the organic material. The use of such buffer layers is based on the idea that the potential barrier at the interface ITO/organic donor can be reduced by elevation of TCO surface work function, giving high hole transport at this interface.

Moreover, it should be underlined that ITO, which is usually used as anode, is not ideal due to the scarcity of its main component: indium. Indeed, today, ITO is widely used as electrode in optoelectronic devices and demand for indium is expected to outstrip supply these years, making devices based on ITO expensive.

Different materials have been probed as alternatives to ITO. For example, many groups have used carbon nanotubes [25], however the sheet resistance of nanotubes thin films is higher than that of ITO. An increase of their thickness to reduce their sheet resistance results in a decrease of their transparency.

Therefore it can be said that the improvement of carrier exchange for organic material/electrode is still a large open field.

We propose in the present manuscript a state of the art of the interfaces through our last investigations. On one side, we show that, whatever the transparent conductive oxide used as anode (TCO: ITO, ZnO, SnO₂), the introduction of a thin metal, oxide or even organic layer at the interface anode/electron donor allows to improve significantly the energy conversion efficiency of the organic solar cells [12,13,26,27]. The efficiency improvement is even more remarkable as regards to TCO initial quality. The performances of organic solar cells, using this thin metal or oxide layer, are nearly similar, whatever the TCO used. This suggests that organic devices, indium free and with high-efficiency, can be achieved and can contribute to the sustainable development.

2. Experimental, organic solar cells realization and characterization

Three different TCOs have been used as anode: indium tin oxide (ITO), aluminium doped zinc oxide (AZO) and fluorine doped tin oxide (FTO). The optical and electrical properties of these TCO are nearly the same (transparency in the visible light > 90%, conductivity $2 \times 10^3 (\Omega \text{ cm})^{-1}$). It should be noted that the studies are devoted to investigate the effect of different buffer layers inserted at the interface anode/electron donor on the device performance. We would like to stress here that we do not intend achieving the best overall cell performance. We rather show that a simple improvement of interface carrier exchanges can be obtained through the deposition of different buffer layers. Therefore, more information is given by the relative variation of the value of the energy conversion efficiency from one anode configuration to another one, than by the absolute value of the efficiency. So, we have used a known multilayer heterojunction structure based on copper phthalocyanine (CuPc)/fullerene (C₆₀) junction with an exciton blocking layer between the fullerene and the aluminium cathode. In such structures, bathocuproine (BCP) is often used as exciton blocking buffer layer [28]; however, in the present work, the aluminium tris(8-hydroxyquinoline) (Alq₃) has been chosen because it has been shown that it allows to grow solar cells with higher lifetime [29], moreover it has been proven to be a very efficient buffer layer in other papers [12,27,30].

The buffer layer, CuPc, C₆₀ and Alq₃ have been deposited in a vacuum of 10^{-4} Pa. The thin film deposition rates and thickness were estimated in situ with a quartz monitor. The deposition rate and final thickness were 0.05 nm/s, 35 nm; 0.05 nm/s, 40 nm and 0.1 nm/s, 9 nm for CuPc, C₆₀ and Alq₃, respectively. After organic thin film deposition, without breaking the vacuum, the aluminium upper electrodes, through a mask with $2 \times 5 \text{ mm}^2$ active

area, and then an encapsulating layer of amorphous selenium (Se-a), thick of about 100 nm, were thermally evaporated. The selenium coating layer (P) has been proved to be efficient to protect the under layers from oxygen and water vapour contamination [31], at least during the first hours of room air exposure [27]. Therefore, the structures used were glass/TCO/BF/CuPc/C₆₀/Alq₃/Al/Se-a, with TCO=ITO, AZO and FTO.

Electrical characterizations were performed with an automated *I-V* tester, in the dark and under 1 sun global AM1.5 simulated solar illumination. Performances of photovoltaic cells were measured using a calibrated solar simulator (Oriel 300 W) at 100 mW/cm² light intensity adjusted with a PV reference cell (0.5 cm² CIGS solar cell, calibrated at NREL, USA). Measurements were performed at an ambient atmosphere. All devices were illuminated through TCO electrodes.

3. Experimental results

If PEDOT:PSS is the most often used buffer layer as said above, it is not ideal. Therefore different other buffer layers have been probed, three of them have been probed in the laboratory: a metal, an oxide and recently an organic layer.

In the case of ultra-thin metal buffer layer [12,13], among the different metals probed (Au, Cu, Ag, Ni, Ni:Cr, Pd, Pt, Au:Pt) Au has given the best results. It should be noted that the improvement of the cell efficiency is present whatever the TCO used (FTO, AZO, ITO). The thickness of the ultra-thin buffer layer is $0.5 \pm 0.2 \text{ nm}$. Thinner films are not efficient, while thicker films decrease sensibly the light transmission and therefore the power conversion efficiency. Globally, whatever the TCO, the efficiencies achieved when it is covered with gold is around 2%, while they are far smaller without this buffer layer (# 1% for ITO and # 0.2% for AZO and FTO). Poor results (0.14%) are obtained when the buffer layer is an Ag ultra-thin film.

In order to understand the ultra-thin gold layer effect, TCO covered with such gold layers have been characterized by scanning electron microscopy (SEM), atomic force microscope (AFP), X-ray photo-electron spectroscopy, optical transmission measurement, etc. [12,13]. We have shown that the ultra-thin film is discontinuous, while the roughness of the TCO/Au electrode is no different from that of bare TCO. Moreover, the mean roughness of a CuPc film deposited onto ITO is 1.77 nm, while it is only 1.06 nm when it is deposited onto an Au covered ITO anode. Also, in previous XPS study we have observed that the CuPc grow more homogeneously when it is deposited onto gold covered TCO, which is corroborated by SEM study (Fig. 1). As

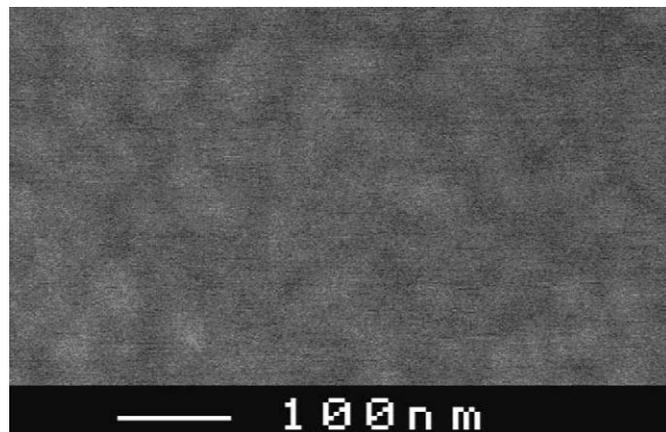


Fig. 1. Microphotographs of ITO/Au (0.5 nm)/CuPc (12 nm) superposed thin films.

shown in Fig. 2 the shape of the J - V characteristics depends on the anode configuration. In the case of bare TCO a “kink” effect is clearly visible, while classical diode characteristics are obtained when the ultra-thin gold layer is present.

After metals, different oxides (MoO_3 , WO_3 , ZnO) have been probed as buffer layers. In the case of ZnO , the heterojunction used was $\text{CuPc}/\text{PTCDI-C7}$ (Table 1, Fig. 2). The optimum efficiencies are achieved when oxide thickness is around 3.5 ± 1 nm. The oxide film does not completely cover the anode surface, since it has been shown that 5 nm are necessary to obtain continuous thin MoO_3 film, using thermal evaporation [32]. For thicker oxide films, if the fill factor (FF) stays far higher than the value obtained with bare ITO, the short circuit current (J_{sc}) is slightly smaller. It decreases progressively with oxide thickness increase. With thinner oxide films, the inflection point in the J - V characteristics, typical of the bare ITO anode (Fig. 2), is still present. It should be highlighted that the main improvement induced by the oxide concerns the fill factor. Here also the improvement induced by the oxide does not depend of the TCO used (Table 1).

At least an organic molecule, a perylene derivative, has been used as buffer layer. Perylene derivatives are promising compounds, for application in electronic devices, as molecular semiconductors. While most organic conducting materials can be described as p-type semiconductors (electron donors) perylene derivatives are usually described as n-type semiconductors (electron acceptors) [33]. N,N' -diheptyl-3,4,9,10-perylene-tetracarboxylic diimide (PTCDI-C7) is one of them. It is a liquid crystal and

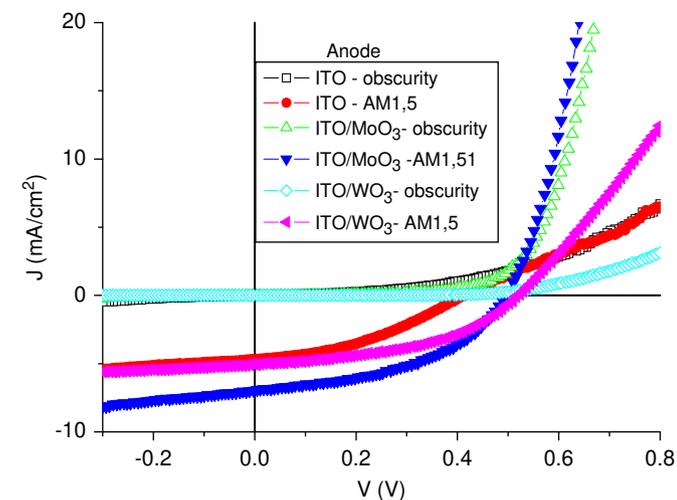


Fig. 2. J - V characteristics in the dark (open symbols) and under AM1.5 illumination (full symbols) of solar cells with different anode configuration.

Table 1

Photovoltaic performance under AM1.5 conditions of devices using ITO or FTO, anode treated or not by different oxides (3.5 nm thick).

Anode	J_{sc} (mA/cm ²)	V (V)	FF	η
Anode/CuPc/C ₆₀ /Alq ₃ /Al				
ITO	6.80	0.40	0.25	0.67
ITO/MoO ₃	6.9	0.527	0.44	1.60
ITO/ WO ₃	5.0	0.52	0.43	1.19
SnO ₂ :F	3.0	0.4	0.225	0.27
SnO ₂ :F/MoO ₃	6.32	0.500	0.54	1.70
Anode/CuPc/PTCDI-C7/Alq ₃ /Al				
ITO	1.55	0.49	40	0.30
ITO/ZnO	1.70	0.52	54	0.48

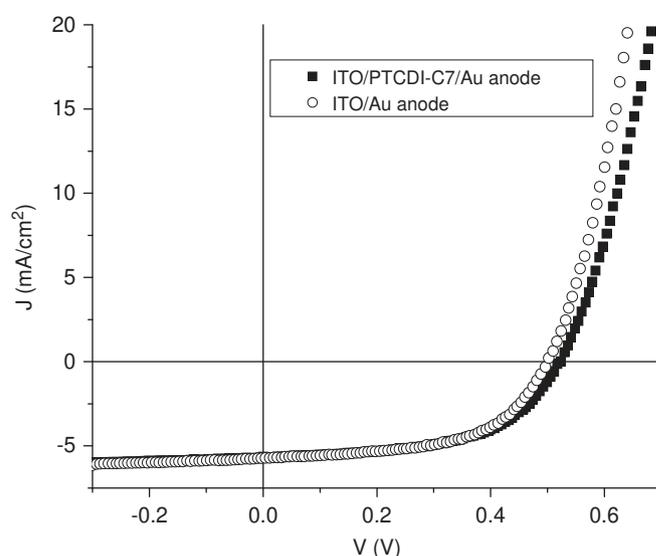


Fig. 3. J - V characteristics of solar cells under AM1.5 illumination with ITO/Au (o) and ITO/PTCDI-C7/Au (■) as anode.

Table 2

Photovoltaic characteristics, under light AM1.5 (100 mWcm⁻²), for different cells using PTCDI-C7 as buffer layer in devices based on the heterojunction $\text{CuPc}/\text{C}_{60}$.

Au thickness (nm)	0.5	0.5	0.5	0.5	0.5	0	0
PTCDI-C7 thickness (nm)	0	1	2	3	4	2	0
V_{oc} (V)	0.48	0.50	0.52	0.48	0.47	0.1	0.44
J_{sc} (mA/cm ²)	5.63	5.62	5.64	3.75	2.88	0.35	3.21
FF %	57	56	56	34	26	22	0.24
% η	1.52	1.58	1.63	0.61	0.35	0.008	0.33

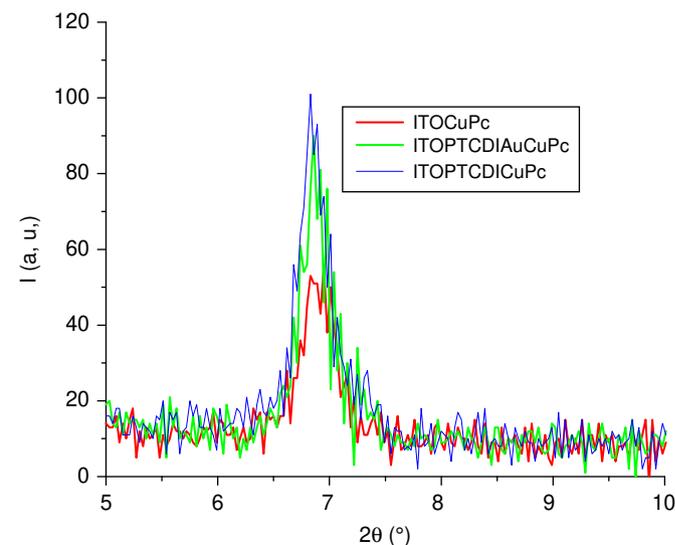


Fig. 4. XRD diagram of CuPc thin films deposited onto bare ITO, ITO covered with PTCDI and PTCDI/Au.

possesses the ability to self-organize spontaneously into ordered structures [34,35]. A thin PTCDI-C7 ultra-thin layer has been introduced at the interface anode/CuPc. The results are summarized in Fig. 3 and Table 2. It can be seen that, if, as expected, the presence of Au improves significantly the devices performances [12,13], it is not the case when PTCDI-C7 is substituted to Au.

However, when a PTCDI-C7 ultra-thin film (0.2 nm) is deposited onto ITO and then covered with Au (0.5 nm) there is a significant increase of V_{oc} , this effect is reproducible. A systematic study of the thickness of this buffer layer, has shown that 2 nm is the optimum value. For thicker PTCDI-C7 film there is a fast decrease of J_{sc} , FF and therefore the efficiency of the cells (Table 2). Sullivan et al. [36] have shown that, in the case of PTCDA buffer layer, there is some structural templating of CuPc, which results in a higher carrier mobility and therefore J_{sc} increase. However, in our study, the more significant effect of the PTCDI-C7 buffer layer is an increase of the open circuit voltage (V_{oc}). An X-ray diffraction study shows some structural modification of the CuPc film (Fig. 4). Indeed the presence of PTCDI allows obtaining diffraction peak of CuPc with higher intensity, which testifies of a better order of these films when the PTCDI-C7 is present as bottom layer.

All these examples described above will be discussed in the light of different updated contributions in the following section.

4. Discussion

The most common buffer layer inserted at this interface is the PEDOT:PSS, its contribution to the improvement of the solar cells

performances has been attributed to:

- The smoothing effect of the quite rough TCO surface; therefore, any possible short circuiting due to the spiky roughness of the TCO surface is prevented.
- The physical separation, which avoids direct contact between the oxygen of the TCO and the organic material.
- Its work function ($\varphi_{M(PEDOT:PSS)}=5.1$ eV), which allows to decrease the barrier height at the interface, since the work function of the TCO is smaller than 5 eV (4.5–4.7 eV for ITO), while the HOMO of CuPc is 5.2 eV.
- The improvement of the contact between the polymer and the TCO. It is admitted that this buffer layer enhances the homogeneity of the organic layer.

It can be seen immediately that the two first contributions can be excluded when an ultra-thin gold film is substituted to PEDOT:PSS, since the gold film is discontinuous and does not modify the TCO anode roughness. The two last contributions seem more probable. The work function of gold is 5.1 eV and therefore the gold layer can improve the matching between the work function of the anode and the highest occupied molecular orbital (HOMO) of the organic electron donor (Fig. 5a–c). Such contribution will be discussed more carefully below. The fourth contribution is in good

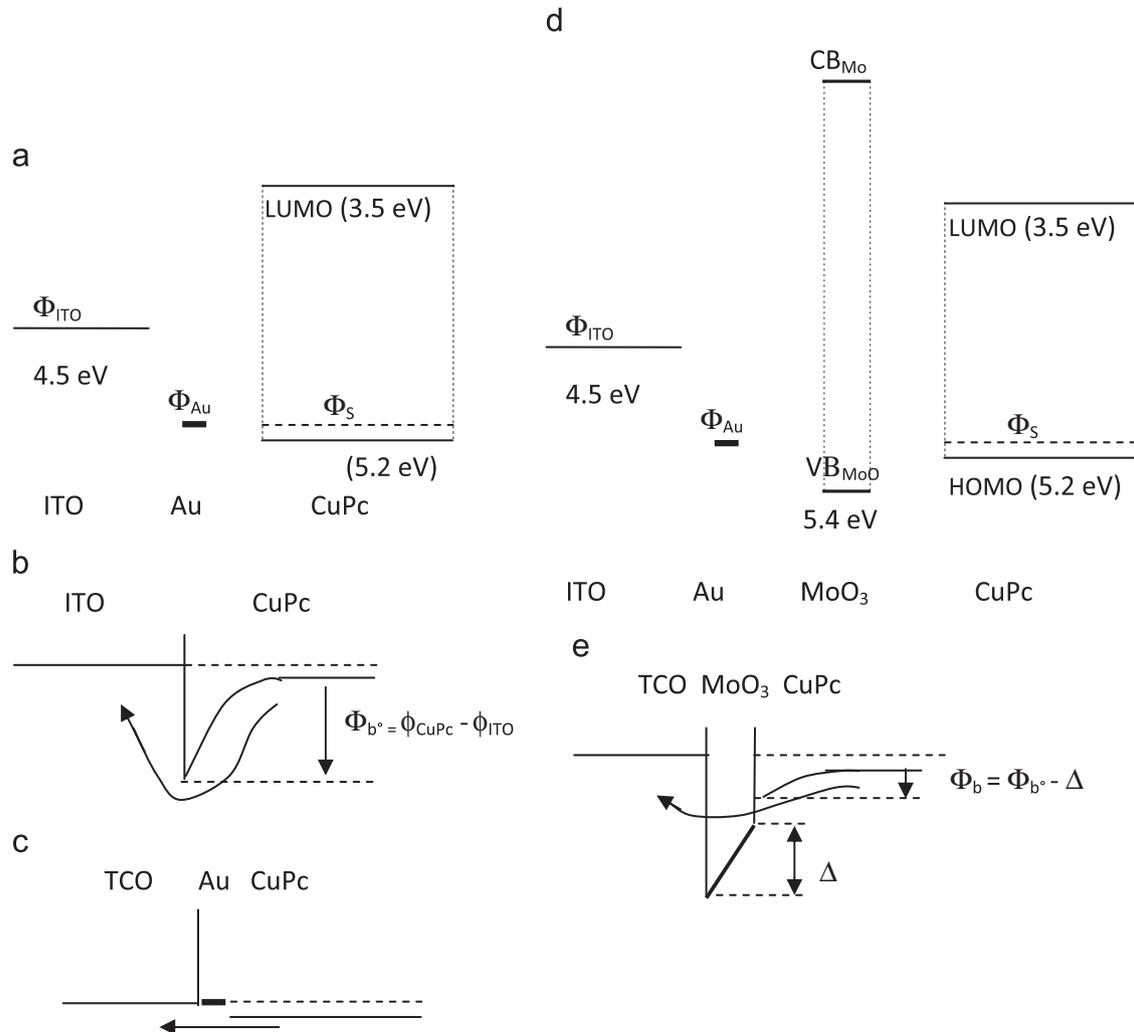


Fig. 5. Band scheme before contact and after contact: hole transfer from the organic electron donor to the anode for different anode configurations after contact.

agreement with the XPS study, which shows that the CuPc films are more homogeneous when deposited onto gold modified TCO [12].

In the case of oxide buffer layer, the results are quite similar to those achieved with gold and therefore the same causes of enhancement should be invoked, mainly a better matching of the band scheme. It will be also discussed below.

At last, the PTCDI-C7 films have small conductivity, and, as shown by the XRD study, CuPc deposited onto PTCDI-C7 buffer layer, are more homogeneous. This avoids any current leakage path and justifies the increase of the shunt resistance. We have already shown that such diode improvement allows increasing the V_{oc} value [37]. When the film thickness is only 2 nm, the carriers can cross the film by tunnel effect and the photocurrent is not decreased, for thicker buffer layer, the tunnel effect efficiency decreases, which induces a decrease of the photocurrent.

Therefore from the three examples presented above it can be concluded that the two main contributions to the interface improvement by inserting a buffer layer between the TCO anode and the CuPc are a better matching of the band structure and a higher homogeneity of the organic film.

The study of the equivalent circuit model of a solar cell help us to discuss the matching between the work function of the anode and the HOMO of the organic electron donor is decisive. An equivalent circuit model could be helpful in understanding of organic solar cells by providing a quantitative estimation for losses in the cells. The equivalent circuit commonly used to interpret the $I-V$ characteristics of solar cells consists of a photogenerator connected in parallel with a diode, which represents the $I-V$ characteristics in the dark. This corresponds to an ideal model in absence of parasitic resistances. However, in real organic solar cells, it is necessary to introduce a series resistance, R_s , and a shunt resistance, R_{sh} (Fig. 6a). For such solar cells the mathematical description of this circuit is given by the following equation:

$$I = I_0 \left[\exp\left(\frac{V - I \times R_s}{nkT}\right) - 1 \right] + \frac{V - I \times R_s}{R_{sh}} - I_{ph} \quad (1)$$

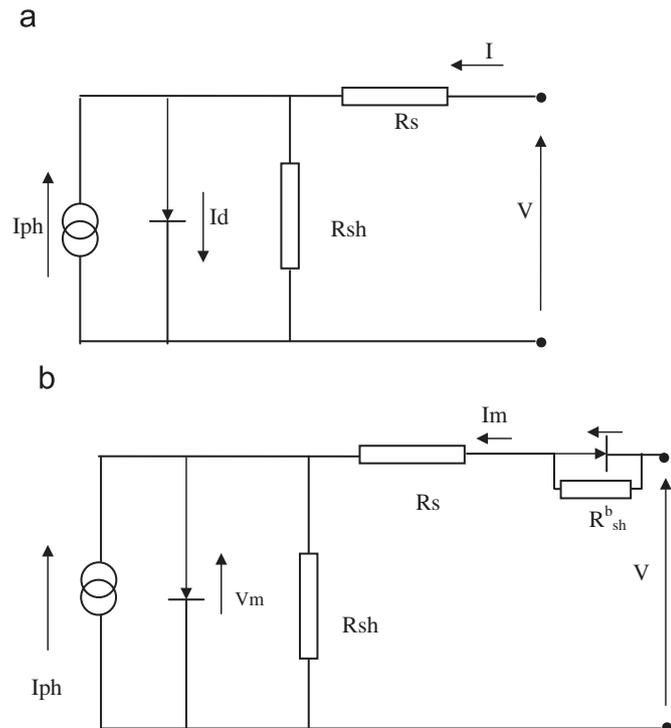


Fig. 6. Equivalent circuit of: (a) solar cell with ohmic contacts. (b) solar cell with rectifying back-contact.

In a recent contribution [38], we have shown that the Lambert W -function method can be used to determinate R_s , the series resistance, R_{sh} the shunt resistance, n the ideality factor of the diode and I_{ph} the photo-generated current. The problem to be solved is the evaluation of a set of five parameters R_s , R_{sh} , n , I_{ph} and I_s in order to fit a given experimental $I-V$ characteristics using a simple diode circuit.

A good agreement between the experimental and theoretical fitted curves is achieved with ITO/Au anode (Fig. 7a) but not for bare ITO.

Table 3 shows that the ideality factor, n , decreases, while R_{sh} increases, when the ITO anode is covered by an ultra-thin Au layer, which corresponds to a significant improvement of cell performances. When Ag is used the improvement is not significant. As said above no agreement could be achieved in the case of a bare ITO or Ag covered anode, whatever the series and shunt resistance proposed. Such impossibility show that the simple equivalent scheme used in this theoretical study cannot explain the experimental results obtained with a bare ITO anode.

In the case of bare and Ag covered ITO anode, it is necessary to assume the presence a back-contact barrier at the interface ITO/CuPc (Fig. 6b), to achieve a good fit between experimental and theoretical results. Assuming a thermoionic current at this interface, the hole current is

$$I_b = -I_{b0}(\exp(-qV_b/kT) - 1) \quad (2)$$

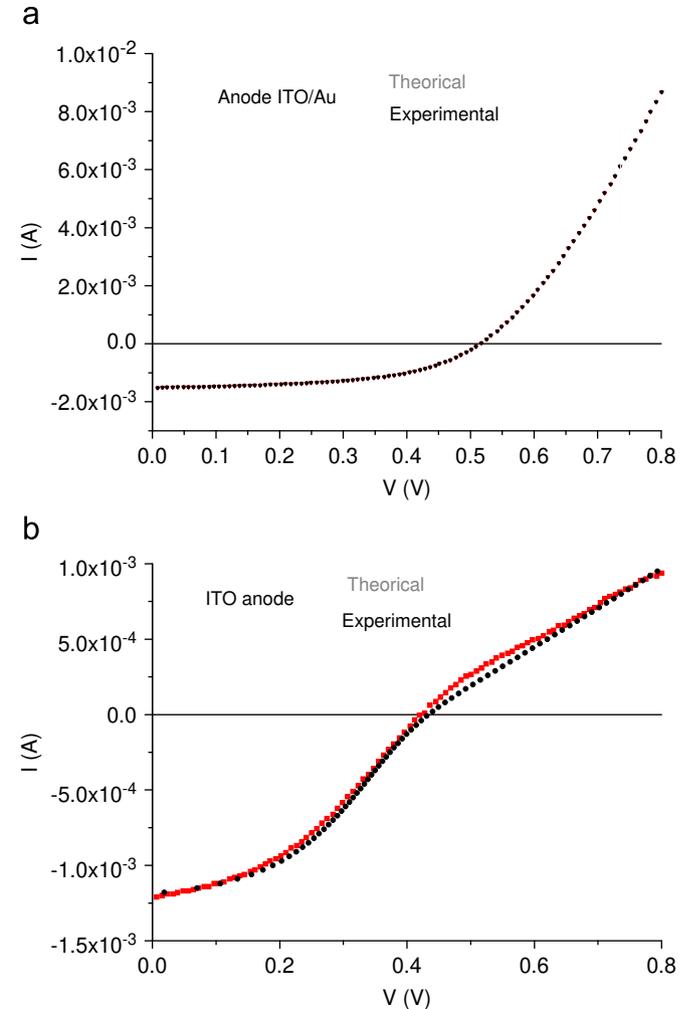


Fig. 7. $I-V$ characteristics under AM1.5 illumination of a solar cell using a ITO/Au anode (a) and a ITO anode (b), (●) experimental and (□) theoretical curves.

Table 3

Parameters calculated using a main diode and (or not) a back contact diode.

Anode	Main junction CuPc/C ₆₀				Back-contact junction	
	<i>n</i>	<i>R_{sh}</i>	<i>R_s</i>	<i>I_{m0}</i> (A)	<i>R_{sh}^b</i> (Ω)	<i>I_{b0}</i> (A)
ITO	2.55	330	20	2 × 10 ⁻⁶	15000	2.58 × 10 ⁻⁶
ITO/Ag	2.6	400	40	1 × 10 ⁻⁶	13200	2.24 × 10 ⁻⁶
ITO/Au	1.5	6900	25	2.23 × 10 ⁻⁹	-	-

where I_{b0} is the saturation current, V_b the voltage across the back contact, k the Boltzmann constant and T the temperature.

Therefore the current-limiting effect, “rollover”, is due to the back-contact barrier height. It occurs because the total current saturates at a value J_{b0} [39]. The value of J_{b0} is the current value where the J - V curve starts to show rollover.

Demtsu and Sites [39] have treated the main junction and the back-contact junction (Fig. 6b) as independent circuit element. Here, when a forward bias V is applied to the circuit, the voltage is divided between V_m across the main CuPc/C₆₀ junction, V_b across the back-junction TCO/CuPc and IRs across the series resistance:

$$V = V_m + V_b + IR_s$$

Under illumination the current across the main junction is

$$I_m = I_{m0}(\exp(qV_m/nkT) - 1) - I_{ph} + V_m/R_{sh} \quad (3)$$

And through the back contact it is

$$I_b = -I_{b0}(\exp(-qV_b/kT) - 1) + V_b/R_{sh}^b \quad (4)$$

Equating Eqs. (3) and (4):

$$I_{m0}(\exp(qV_m/nkT) - 1) - I_{ph} + V_m/R_{sh} + I_{b0}(\exp(-qV_b/kT) - 1) - V_b/R_{sh}^b = 0 \quad (5)$$

The parameters R_s and I_{m0} , n , R_{sh} of the main diode are calculated in the region far from the saturation current I_b . As said above, I_{b0} is the current value where the J - V curve starts to show rollover. Then Eq. (5) can be solved.

A good agreement can be achieved between experimental and theoretical curves (Fig. 7b), which validates the hypothesis of the presence of a rectifying effect at the contact ITO/CuPc. The parameters extracted are reported in Table 3. It should be noted that when ITO is covered with Ag, two diodes are necessary to obtain a good fit between the experimental and theoretical curves. Since the work function of Ag is only 4.3 eV, this result is in good agreement with the present discussion. One can see in Table 3 that, when the two diodes model is used, the estimated R_s values are of the same order of magnitude as those of ITO/Au anode. Therefore the introduction of a back junction diode is a good interpretation of the interface ITO/CuPc. It justifies the small fill factor and short circuit current values when bare ITO is used as anode in the heterojunction solar cells.

A similar approach can also be used in the case of oxide buffer layer. If the buffer layer material exhibits a high work function value (Fig. 5d), that is to say a work function in good agreement with the HOMO of the organic layer, it is suggested that there is a simple alignment of the energetic levels of the anode and the organic material, without any discussion of the electrical properties of the buffer layer. However the electrical behaviour of conductive, semiconducting and insulating materials is very different and therefore the nature of their interfaces will depend on the properties of the materials.

If we introduce an insulating film (I), between the metal (M) (or degenerated semiconductor) and the semiconductor (S), the contact behaves like a MIS structure. This means that there is no band alignment between the TCO, the insulating layer and the

organic semiconductor but, qualitatively, the band diagram of Fig. 5e. This results from the fact that the Fermi level must be constant throughout the metal/insulating layer/semiconductor and therefore [40]:

$$\Phi_b = \Phi_b + \Delta \quad (6)$$

The distribution between Φ_b and Δ depends on the insulating properties of the oxide and the semiconductor properties. The space charge, which forms in the depletion layer of the semiconductor, can be expressed as an equivalent surface state density Q_{sc} . In the ideal case, the absence of any space charge effects in the interfacial insulating layer implies that an exactly equal and opposite charge Q_m develops on the metal surface. The potential Δ across the interfacial layer can be obtained, following the application of Gauss' law to the surface charge on the metal and semiconductor:

$$\Delta = \delta(Q_m/\epsilon_i) \quad (7)$$

ϵ_i being the dielectric constant of the insulating layer and δ its thickness [41]. Therefore, even if there is not a simple alignment of the work function of the insulating film with those of the conductive anode and of the semiconductor, the presence of this layer can significantly modify the barrier value at the interface through the potential Δ [42].

Many studies have experimentally demonstrated a strong correlation between the metal work function and the barrier Φ_b for hole exchange at anode/organic electron donor interfaces [43,44], which justifies the discussion above, based on the Schottky-Mott model and ideal insulating oxide.

However, the real energy level alignment should consider the vacuum level discontinuity associated with an interface dipole, Δ' , resulting from charge rearrangement upon interface formation [45]. Therefore, analogous to the case of inorganic metal/semiconductor contacts two limit models have been proposed. The Schottky-Mott model where the vacuum level of the organic and metal aligned, forming a region of net space charge at the interface (Fig. 5a) and the Bardeen model, where a large density of surface states induces a pinning effect of the Fermi level and the presence at the interface of a barrier independent of the metal work function. The Cowley-Sze model is an intermediate model, where interface states would be induced in the original band gap of the semiconductor upon contact with a metal giving the interfacial dipole Δ' . The effective barrier height for hole exchange $\Phi_{b,eff}$ is therefore given by

$$\Phi_{b,eff} = \Phi_b - \Delta'$$

Δ' is proportional to the amount of charge transferred due to energy difference between the metal Fermi level and the organic charge neutrality level (CNL). If we assume a uniform distribution of metal-induced interface state, it can be shown that $\Phi_{b,eff}$ vary linearly with the metal work function with a slope, S , smaller than one. In the absence of metal-induced interface state, the injection barrier follows the Schottky-Mott limit with $S=1$. The other limit corresponds to $S=0$, the interface dipole reach a saturated value with the organic CNL aligned to the metal's Fermi level. There is Fermi level pinning and the variation of the metal work function is fully compensated by the metal-induced interface state dipole.

The fact that many studies have experimentally demonstrated a strong correlation between the metal work function and the barrier Φ_b for hole exchange at anode/organic electron donor interfaces means that, usually, the behaviour of a contact metal (or semimetal such as the TCOs)/organic is intermediary between the two extreme cases. The experimental results presented here are a good illustration of such intermediary behaviour. The study of the influence of the metal buffer layer lets appear that the metal work function is a key parameter to adjust the work

function of the anode to the HOMO of the organic material. In the case of oxide buffer layer we have presumed that its structure is ideal. On the other hand, if interface states are present, the Δ value of Eq. (6) includes the value Δ' issue from these interface states and the band scheme is roughly similar.

5. Conclusion

It is well known that the anode can greatly influence the organic solar cells efficiency. In the present work we show that the work function of the anode is one of the main factor influencing the hole exchange at the interface anode/organic electron donor. The introduction of a buffer layer can allow achieving a good matching between the work function of the anode and the HOMO of the organic material. It is shown that even if dipole effect is often present at the interface due to interface states, a first approach can be done using the Schottky–Mott model. This study has allowed highlighting, for different nature of buffer layer, a good correlation between the “metal/buffer layer” work function and the barrier Φ_b for hole exchange at anode/organic electron donor interfaces. The other important factor to achieve efficient anode configuration is the influence of the buffer layer on the homogeneity of the organic layer growth.

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