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XPS Study of the Band Alignment at the Interface ITO/CuI

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Abstract: The band alignment at the interface of an ITO/CuI heterojunction is studied by X-ray photoelectron spectroscopy (XPS). The measurements have been performed on samples obtained under the same experimental conditions as those used to achieve organic photovoltaic cells. The CuI upper layer was 3 nm thick. The semidirect XPS technique used to measure the band offsets allows us to estimate the band discontinuities at the interface ITO/CuI: $\Delta E_v = 2.10$ eV and $\Delta E_c = 1.56$ eV. This band alignment induces an increase of the work function of the anode when the structure ITO/CuI is used as electrode in organic solar cells for instance. As a matter of fact, the measurement, by means of a Kelvin probe, of the work function of the structures ITO/CuI, shows that it is significantly higher than that of ITO alone: 5.2 eV and 4.8 eV.

Keywords: *Organic solar cells, Anode buffer layer, templating effect, CuI.*

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1 Introduction

Organic photovoltaic cells (OPV cells) have received considerable attention as an attractive alternative to inorganic based photovoltaic devices. However, their power conversion efficiency needs improvement for commercialisation. The limiting factors are well known, small carriers mobility μ , exciton diffusion length L_D and optical absorption. For example, usual exciton diffusion length in organic conjugated material is on the order of 10-20 nm, while organic film thickness necessary to achieve good optical absorption is one order of magnitude greater. Different cells configurations have been employed to improve photon absorption, charge separation and transport in organic solar cells [1]. Usually, plastic

organic solar cells consist either of two multilayers layers or an homogeneous mixture of two organic materials [2]. The homogeneous mixture of two organic materials are based on bulk heterojunction (BHJ) architecture, where an electron acceptor molecule is dispersed in an electron donor, usually a conjugated polymer [3]. The BHJ allows improving power efficiency by increasing the area of interface between the electron donor and the electron acceptor, through spontaneous phase segregation of both phases. However, such spontaneous phase separation results in a disordered morphology, with cul-de-sac regions that impede transport of charge to the electrodes [4]

Recent improvement of the performance of small molecules OPV cells induces a new growing interest for this type of OPV cells [5]. Small molecules OPV cell are based on an organic bilayer, sandwiched between two electrodes. One of these electrodes must be highly reflexive and the other must be transparent. The bilayer is an heterojunction, between an electron donor (ED) and an electron acceptor (EA). Moreover, at least one of the organic materials must absorb the light, usually it is the electron donor. About the electrodes, while aluminium is often used as reflexive cathode, it is well known that the transparent conductive anode which gives the best optoelectronic devices is the indium tin oxide (ITO). However, often, the hole exchange at the interface ED/anode is a limiting factor of the device performance. The yield of hole collection by the anode must be high, while it must be electron selective. Ideally, the donor's HOMO (Highest Occupied Molecular Orbital) should match the work function of the anode [6]. To achieve this good band matching an anode buffer layer (ABL) is usually introduced between the ED and the ITO in order to improve the work function of the ITO. About this ABL, we have shown that an ultra thin gold film [7] and/or a thin MoO₃ thin film [8] are highly efficient. More recently, it was shown that ABLs can also be used to template the ED layer [9]. For instance we have shown that a thin film of CuI introduced between the ITO anode and the CuPc electron donor film allows to growth films with CuPc molecules perpendicular to the plan of the anode and not parallel as usual. Such modification induces an improvement of the absorption CuPc films and of the power conversion efficiency of the organic cells which use such CuPc films [10]. If this templating effect was largely discussed [9-11], no study was dedicated to the effect of CuI on the band structure of the anode.

In the present manuscript we proceed to an XPS study of the properties of the interface ITO/CuI and we show that the positive effect of CuI on the OPV cells efficiency is not only due to its templating effect but also to the fact that it improves the work function of the ITO anode.

2 Experimental

The thin films were obtained by sublimation under vacuum (10^{-4} Pa). The thin films thicknesses and the deposition rates were estimated *in situ* using a quartz monitor. The substrates were ITO coated glasses. Before introduction in the vacuum chamber, the substrates were scrubbed with soap, rinsed with distilled water and dried. For the characterization of the structures ITO/CuI the thickness of the CuI was 3 nm for the study of interface properties and 30 nm for the study of bulk properties.

The main focus of this work was the study of the influence of the CuI ABL on the band matching at the interface anode/ED and on OPV cells performances through an increase of the ITO work function.

The film absorbance was measured at wavelengths of 1 to 0.30 μm .

X-ray photoelectron spectroscopy (XPS) measurements (Leybold LHS12, University of Nantes-CNRS) were performed to investigate the CuPc thin films and the band alignment at ITO/CuI interface. XPS analyses were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA. During the measurements the vacuum was 10^{-7} Pa, the pass energy for high resolution spectra was 50 eV. The samples were grounded with silver paste to prevent charge effect. At the surface of the samples air exposed there is systematically a carbon-carbon bond corresponding to surface

contamination. In the apparatus used the C1s peak of the C-C bond had a well defined position at 284.6 eV and this carbon value was used as a reference to estimate the electrical charge effect. The quantitative study of CuI films was based on the determination of the I3d_{5/2} and Cu 2p_{3/2} peak areas with 6.4 and 5.3, respectively, as sensitivity factors.

The work function of the anodes was measured using a Kelvin Probe instrument (KPTechnology Model SKP5050). All measurements were made at ambient conditions at around 23°C. The vibrating probe consists of a stainless steel tip of 10 mm diameter having a work function of 4.947 eV. The tip was calibrated against a gold surface before and after each measurement. The calibration value varied by approximately 20–30 meV before and after each measurement, thus keeping the measurement error within ±30 meV. The sampling surface is illuminated by a Hg–Zn–Cd discharge lamp giving a peak wavelength at about 253 nm (4.947 eV), which is short enough to be absorbed in the ITO. Non scanning mode is used to measure the work function with about 500 repetitions for a single point. Work function of the sample is given by adding the measured work function (W_F) with the correction factor (4.947eV). The work function of the sample is given by adding the measured work function (WF) to the correction factor (4.947 eV). The Kelvin method measures the contact potential difference (CPD) between the tip and the surface of the sample that are brought into contact, as a result of Fermi energy equalization. The resolution of the measures is 3 meV.

3 Results and discussion

3.1 Characterization of the CuI film thick of 30 nm

The absorption coefficient, α , in the high absorption domain deduced from the optical measurements has been used to

estimate the optical band gap E_g . CuI is a direct band gap semiconductor, therefore E_g can be obtained from the relation: $(\alpha h\nu)^2 = A(h\nu - E_g)$ in which $h\nu$ is the photon energy. The figure 1 shows that the optical band gap E_g deduced from the high absorption domain is 3.16 eV. This value is in good agreement with reported values [12, 13].

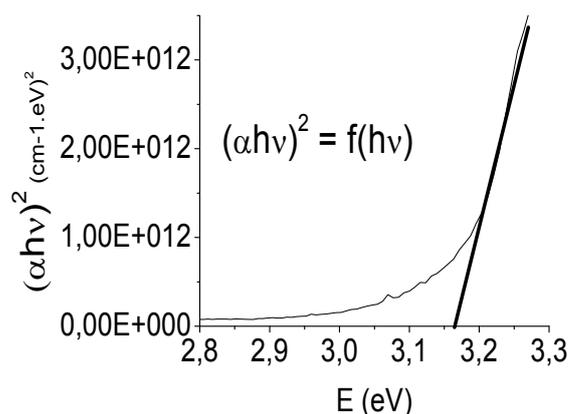


Fig 1 $(\alpha h\nu)^2$ versus $h\nu$ for a CuI thin film.

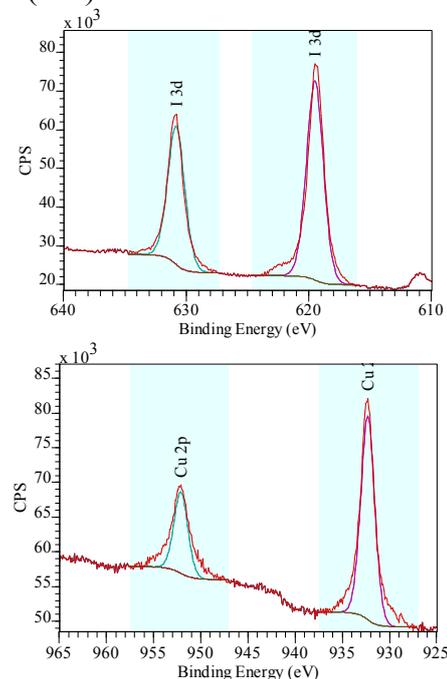


Fig 2 XPS spectra of a CuI thin film thick of 50 nm: I3d doublet and Cu2p doublet.

We proceeded to XPS measurements of thin (3nm) and thick (30 nm) CuI films deposited onto ITO. In the case of thick

films, the substrate is not detected by XPS and we can consider that the CuI film behaves as bulk material. The C1s peak of the surface contaminant carbon, is situated at 284.6 eV. The I3d and Cu2p photoelectron peaks are shown in figure 2. The binding energy of the I3d_{5/2} peak is 619.5 eV, which is close to the values given in the literature [13]. For Cu2p_{3/2}, the peak appears at 932.3 eV. This corresponds to the expected value for Cu⁺ of CuI [14]. In Figure 2, each peak could be fitted with a single peak indicating that only one type of iodine and copper are present in the CuI film. For copper, the shape of the oxidized copper peak is typical [15] and very different from that in figure 3b. Moreover the O1s peak energy is 531.5 eV, which corresponds to oxygen surface contamination and not to copper oxide, which is situated at 530-530.5 eV [15]. It can be concluded that Cu is bonded to I only, even in the surface region. This shows the high chemical stability of the CuI deposited by Joule heating under vacuum. The relative atomic concentration of the surface of the CuI films is around 52% of I and 48% of Cu.

The electrical conductivity of these films was estimated to be around 10^{-3} Scm^{-1} .

3.2. XPS study of the band alignment at ITO/CuI interface.

The transport properties of OPVCs strongly depend on interface characteristics: potential barrier height, interfaces states, and band discontinuities. The change in the forbidden gap across the interface ($E_{g\text{CuI}} = 3.16 \text{ eV}$, $E_{g\text{ITO}} = 3.7 \text{ eV}$) is distributed between a valence-band discontinuity, ΔE_v , and a conduction-band discontinuity, ΔE_c .

In order to understand the interface properties, we study the properties of the contact ITO/CuI. Usually, interface studies are performed by UPS (uv photoelectron spectroscopy) on structures realized in

experimental conditions which are very different than those used for real OPVCs. For UPS studies, the layers of the heterojunction, exception made of the TCO film, are deposited in ultra-high vacuum, which is very different from the experimental conditions used by the classical OPVCs technology. Such differences may induce large spreads in the band discontinuities values measured. Therefore, here, we study by XPS the contact ITO/CuI that we use in our OPVCs.

The band discontinuity, ΔE_v (ΔE_c) is positive (negative) when the valence (conduction) band edge of the wide gap n-type semiconductor is lower than that of the smaller gap p-type semiconductor [16]. For measuring ΔE_v (ΔE_c) two methods based on XPS measurements can be used [17]. In the first one, the valence-band XPS spectra for the bare under layer surface and for increasing upper layer coverage of this surface are measured. At intermediate coverage (1.5 to 3 nm) both valence band leading edges are visible and a direct measurement of ΔE_v is possible by linear extrapolation of the two edges. This method is direct but cannot be applied to real interfaces obtained with the deposition processes used to obtain OPVCs. The second method, known as the semi-direct XPS technique, is less direct but can be applied to all interfaces [16]. This second technique is used here and allows us to estimate ΔE_c and ΔE_v at the interface of the heterojunction ITO/CuI. Measurements have been repeated on different samples to check their validity.

In order to accurately determine the band offsets, we measured the In4d and the Cu3p core levels as well as the valence band maxima (VBM) E_v . The accuracy of this method was about $\pm 0.05 \text{ eV}$ for each measure. The valence band discontinuity ΔE_v at the heterojunction interface is given by

$$\Delta E_V = (E_{Cu3p} - E_{VCuI}) - (E_{In4d} - E_{VITO}) - \Delta E_{CL} \quad (1)$$

and the conduction band discontinuity is given by

$$\Delta E_C = \Delta E_V + E_{gCuI} - E_{gITO} \quad (2)$$

where E_{Cu3p} (E_{In4d}) is the binding energy in the bulk of CuI (ITO), E_{VCuI} (E_{VITO}) is the valence band maximum in the bulk of CuI (ITO), and ΔE_{CL} is the energy difference between the Cu3p and In4d levels at the interface ITO/CuI. One can determine Cu3p (E_{In4d}) and E_{VCuI} (E_{VITO}) from CuI (ITO) film. ΔE_{CL} is obtained from an XPS spectrum of an ITO/CuI sample with a very thin CuI layer. The accuracy of this indirect analytical method has been checked by Chichibu et al. [17] and Hashimoto et al. [16] for inorganic materials.

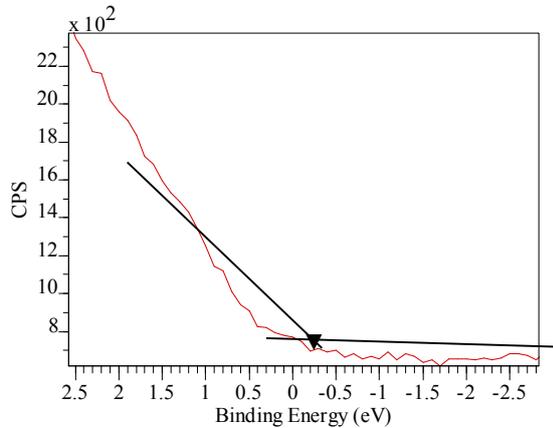


Fig 3 Valence band edge (Ev) of CuI.

Figures 3 and 4 show typical XPS spectra. From figure 3, the majority carrier type of CuI can be checked. As said above, the absolute value of the energy had been corrected using the Cls signal ($Cl_s = 284.6$ eV), the CuI films are p type. We can determine the energy difference ΔE_{CL} from Figure 4. The ITO film is a n^+ -type transparent conductive oxide and therefore the n^+ -ITO/p-CuI contact is an abrupt heterojunction. In that case, it has been shown that the bands are very flat near the

surface and that no significant shift is observed in the band feature when it is covered with a thin layer [18, 19]. This indicates that the flat band condition remains in the ITO with CuI coverage and the structure becomes dominated by the CuI bands.

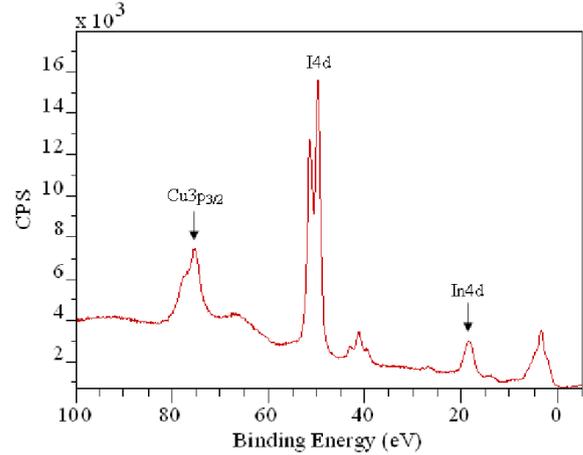


Fig 4 XPS spectrum of thin ITO/CuI heterostructures (CuI thickness = 3 nm).

Table 1 XPS binding energies and bandgap of ITO and CuI.

	In4d	18.50
ITO (eV)	BV	3.10
	In4d-BV	15.40
	Eg	3.7
CuI (eV)	Cu3d	74.77
	BV	0.27
	Cu3d -BV	74.50
	Eg	3.16

The band gap of the CuI is 3.16 eV while that of the ITO used in this work is 3.70 eV. All the measured values are reported in table 1, 2 and in Figure 5. Firstly, the fact that the bandgap of our ITO thin films is 3.7 eV, while $E_{VITO} = 3.10$ eV, means that,

at the surface of the ITO film, the Fermi level, E_F , is below the CB minimum.

Table 2 XPS binding energies band offsets at the interfaces ITO/CuI
(The values are given in eV).

ITO/CuI (eV)	In4d	18.40
	Cu3d	74.77
	ΔE_{CL}	57
	ΔE_V	2.10
	ΔE_C	1.56

Actually, the energetic position of E_F with respect to the band edge can be directly determined from the binding energy of the V_B maximum, E_V , as the zero binding energy corresponds to the position of E_F .

This result is unexpected since, as shown by the slow increase of its resistance with the temperature, the ITO is degenerated. Indeed, it is known that the surface chemistry of TCO is difficult to control [20]. As said above, the ITO used in the present work is only scrubbed with soap and then rinsed in distilled water, and therefore it is not completely degenerated at the surface of the films, while it is in the bulk of the films. The surface of ITO is hydrophilic and it has been shown that IT surfaces are terminated in hydrolyzed oxides, including, $In(OH)_3$, $InOOH$, which form immediately upon exposure of the as-deposited ITO surface to atmosphere [20]. This surface contamination can explain the fact that at the surface the ITO films are not degenerated, while they are below this first contaminated atomic layer. Such an apparent difference in surface and bulk Fermi level positions has already been shown. This has been attributed to carrier depletion near the surface [21]. Since the ITO surface is not degenerated the ITO flatband hypothesis could be questioned.

As discussed by Gassenbauer et al. [22, 23], as the ITO surface is not degenerated, a thin depleted zone is present at the ITO surface. The width of the depleted zone depends on the density of carriers present at the surface. In the present work, as ITO film is degenerated, the carrier density in their bulk is very high ($>10^{21} \text{ cm}^{-3}$). Therefore, even if at the surface the ITO films are not degenerate the carrier density stays order of magnitude higher than that of the semiconducting CuI films of the present study and therefore approximation of an abrupt heterojunction n+ITO/p-CuI remains valid.

Therefore, Figure 5 depicts the energy band diagram of the ITO/CuI heterostructure based on the band parameters. This band diagram allows us to estimate ΔE_V to 2.10 eV and ΔE_C to 1.56 eV. The accuracy of the XPS measurements in the present work is ± 0.05 eV.

The accuracy of the present work is less than that obtained with in situ grown heterojunction [16, 17]. However, the samples were grown under the same experimental conditions as those used to achieve OPV cells [24]. Therefore, the values obtained here give more practical information for real solar cell performance.

Besides, the work function of ITO, measured in room air using a Kelvin probe is $WF_{ITO} = 4.8$ eV and that of ITO/CuI is 5.2 eV.

The band scheme configuration of the interface ITO/CuI is shown in figure 5, here the CB of CuI is far above the CB of ITO, while its V_B is below the CB of ITO, but closer to it than to the V_B of ITO. Therefore, it can be said that it allows an improvement of the band matching between the ITO anode ($WF_{ITO} = 4.8$ eV) and the HOMO of the organic electron donor, which are usually situated between

5 eV and 5.5 eV. Actually, the VB of CuI is more or less situated at the level of the HOMO of the electron donor, as verified by the Kelvin Probe measurement. Therefore, the semi-direct XPS technique used in the present work allows, for the first time, to estimate the ΔE_v and ΔE_c values of ITO/CuI structures grown under the inexpensive deposition conditions needed for photovoltaic applications.

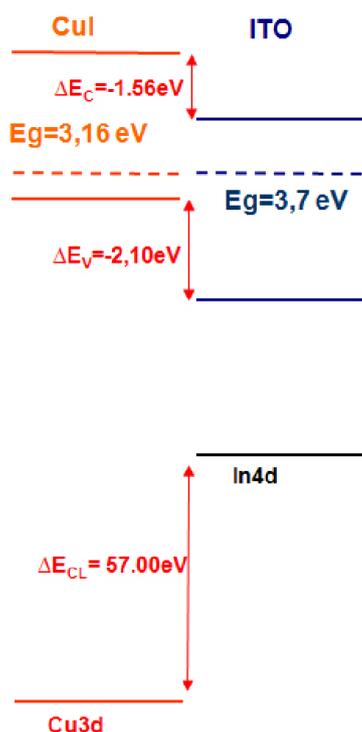


Fig 5 Determined energy-band diagram at the ITO/CuI interface.

Usually the performances of the OPV cells are improved through the introduction of an ABL between the anode and the ED. The improvement of OPV cells efficiency using these anodes so modified can be due to an improvement of the band matching at the interface anode/ED, which is often verified, and the improvement of the properties of the organic layer due to the influence of the ABL on the growth of the organic layer. The former effect is related to the surface work function of the

modified anode and the latter to its surface properties, such as surface energy and chemical reactivity.

5. Conclusion

The nature of the ABL can influence strongly the structural properties of the organic layer deposited onto this ABL, which can modify significantly the performance of OPV cells grown from these structures. For instance, CuI modifies the CuPc molecule orientation onto the anode. While the templating effect of the CuI ABL on the ED layer in organic solar cells was already shown [9-11], in the present work, we show through the XPS study and Kelvin probe measurements that there is an increase of the work function of the CuI modified anode, which allows improving the band matching at the interface anode/ED. It should be noted that the value of the band structure discontinuities measured in the case of ITO/ CuI, $\Delta E_v = 2.10 \text{ eV}$ and $\Delta E_c = 1.56 \text{ eV}$, are near those measured in the case of the interface ITO/NiO, $\Delta E_v = 2.10 \text{ eV}$ and $\Delta E_c = 1.90 \text{ eV}$ [25]. Since it is known, that NiO is also efficient in improving the band matching anode/ED in organic solar cells [25-30], the similarity of the band interface alignment of these two structures comforts our proposition that the CuI ABL not only modifies the texturation of the organic film but also improve the band matching between the anode and this organic material. All this results in a significant improvement of the efficiency of the CuPc based OPV cells using CuI as ABL [9-11].

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