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Study of the insertion of a metal layer in an organic solar cell

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Abstract
This work consists in studying solar cells whose active layer is made up small molecules: CuPc and C_{60} with the insertion of a nano metal layer enter the anode and the donor of electron. The aluminum doped zinc oxide ZnO:Al instead of indium tin oxide ITO is used as the anode. An ultrathin gold film is introduced among ZnO:Al, transparent conductor oxide, and the CuPc donor layer.
Various analyses were carried out on this solar cell and its materials to try to understand the various processes intervening on a molecular scale during its manufacture and of its operation in order to improve its performances. Voltage measurements were taken to obtain the characteristics of the cell (current of short-circuit, tension of open circuit, factor of filling, output). XPS studies were used to determinate of the Cu 3d and Zn 3d peak binding energies.

Key Words: *solar cell, materials organics, thin layer,*

1. Introduction
Organic photovoltaic cells have received increasing attention in the last fifteen years because of their potential application for low-cost energy conversion. This new interest is due to the need for alternative energy sources. Organic photovoltaic cells are based on, at least, two organic materials. One of them – either an organic dye or a semi conducting polymer – donates the electrons. The other component serves as the electron acceptor. Plastic organic solar cells consist either of two organic layers (multilayer heterojunctions) or an homogeneous mixture of two organic materials (bulk heterojunctions). Bulk heterojunctions [1] have reached power conversion efficiency of 6% [2], while planar mixed molecular multi-heterojunctions have reached 5.7% [3]. In the case of bilayer structuresbased on copper pthtalocyanine (CuPc)/fullerene (C_{60}) bilayer structures, the introduction of a thin layer, called exciton blocking layer (EBL), at the interface electron acceptor/cathode improves strongly the device performance [3–4]. The experience has shown that the surface chemistry of TCO is difficult to control [5]. Indeed, it has been shown that the reproducibility of the results obtained, when ITO is used as anode, is in need of improvement.

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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 and 40 nm in the case of CuPc, 0.05 nm/s and 40 nm in the case of C_{60} and 0.1 and 9 nm for Alq_3. These thicknesses have been chosen after optimisation. After organic thin film deposition, the aluminium top electrodes were thermally evaporated, without breaking the vacuum, through a mask with 2 mm× 8 mm active areas. Then, without breaking the vacuum, an approximately 100 nm encapsulating layer of amorphous selenium (Se-a), is evaporated thermally. This Al film behaves as the cathode, hile the ITO is the anode. Some ITO anodes have been covered with an ultra thin metal film deposited by vacuum evaporation. Finally, the structures used were: glass/ ITO(100 nm)/M (0 –*x*- 1.2 nm)/CuPc(40 nm)/C60(40 nm)/Alq_3(9 nm)/ Al (80 nm)/P.

In the present manuscript we propose a very simple and reproducible process allowing simultaneously passivating the ITO surface and increasing its work function. Indeed, we show that the depositing of an ultra-thin metal film onto ITO allows achieving reproducible good level performance devices**.**

2. Materials and methods

1. ITO substrates

The ITO coated glass substrates used in this study were commercially obtained. Different batches (a, b, c. . .) have been used. ITO films have been characterized in the laboratory.

The standard substrate dimensions were 30 mm by 30 mm. Since ITO covered the whole glass substrates, some ITO must be removed to obtain the under electrode. After masking a broad band of 30 mm by 20 mm, the ITO was etched by using Zn+HCl as etchant [2]. After scrubbing with soap, these substrates were rinsed in running deionised water. Then the substrates were cleaned by using the H_2O_2 treatment following a process described by Osada and colleagues [6], which corresponds to the first solution (SC1) of the RCA process first described by Kern and Puotinen [4]. The substrates were treated with a 80 ◦C H_2O–H_2O_2 (30%) –NH_4OH (25%) solution (5:1:1 vol. parts) for 20 min, followed by rinsing with boiling distilled H_2O for 5 min. The use of boiling water was proven to be helpful to obtain impurity free surfaces. The substrates were dried with an argon flow and then loaded into a vacuum chamber (10^{-4} Pa). Some ITO substrates have been cleaned only with deionised water and soap.

2. Photovoltaic cells realisation

The electron donor used was copper phthalocyanine (CuPc), the electron acceptor was fullerene (C_{60}) and the electron blocking layer was the tris(8-hydroxyquinoline) (Alq_3) [5,7]. They have been provided by Aldrich. They were used without any purification. Indeed, it has been shown that, using the same charge in the evaporation crucible, there is an "auto purification" of the product after approximately five thin film depositions [8]. Experiments have shown that, in the experimental conditions used in the laboratory, ten CuPc thin films depositions (which correspond to a film thickness of about 400 nm) are necessary to be sure to achieve performing devices. Therefore, the results presented here correspond to cells deposited after, at least, ten evaporation cycles of the CuPc. CuPc, C_{60} and Alq_3 have been deposited in a vacuum of 10^{-4} Pa. Finally, the structures used were: glass/ITO(100 nm)/M (0 -*x* -1.2 nm)/CuPc(40 nm)/C60(40 nm)/Alq3(9 nm)/Al(80 nm)/P.

3. Results and discussion

The *J-V* characteristics of typical devices under illumination of AM1.5 solar simulation -100 mW/cm^2_ are shown in (Figure.1.) It can be seen that the photovoltaic performances of the devices using Au coated ZnO:Al are significantly improved relative to the performances of those with ZnO:Al alone (Figure 2). The conversion power efficiency was enhanced by one order of magnitude, and their performances are of the same order of magnitude of those using ITO/Au as anode. The depth profile was studied by recording successive XPS spectra obtained after argon ion etching. Etching was accomplished at pressure of less than 5 x 10^{-4} Pa, a 10 mA emission current and a 3 kV beam energy using an ion gun. The Ar+ ion could etch the entire sample surface. It shown a significant shift of Cu 3d and Zn 3d peaks. This exhibits a binding energy about 5 and 10 eV with high intensity from ZnO:Al/Au/CuPc and ZnO:Al/CuPc repectivily.

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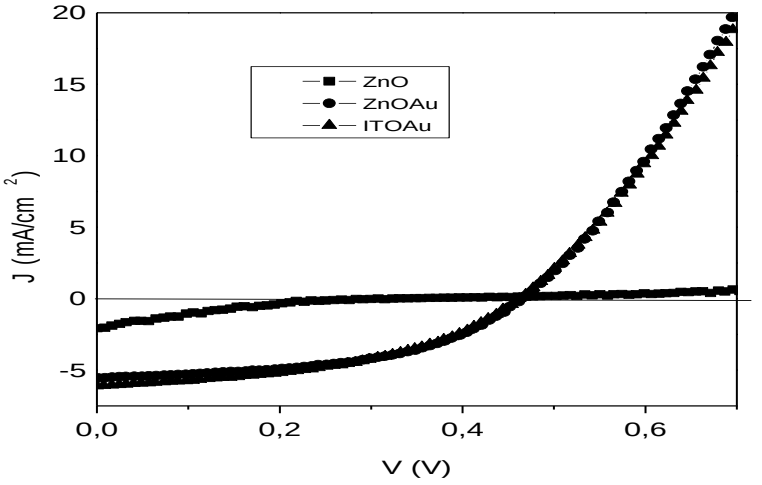

Figure 1. *J-V* characteristics under illumination of AM1.5 solar simulation 100 mW/cm^2 for cells grown in the same run:
ZnO:Al/CuPc/C_{60} /Alq_3 /Al , ZnO:Al/Au/CuPc/C_{60} /Alq_3 /Al and ITO/Au/CuPc/C_{60} /Alq_3 /Al

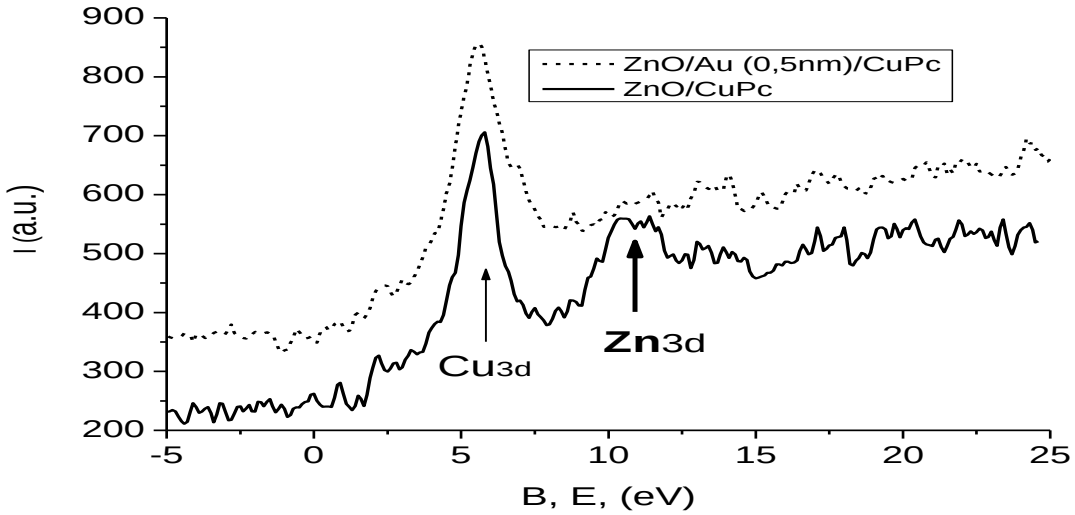

Figure 2. XPS signal in the window of Zn 2*p* in ZnO:Al/CuPc and ZnO:Al/Au/CuPc.

Conclusion

We have shown that the insertion of a 0.5 nm thick gold layer between a ZnO:Al anode and the organic electron donor results in a power conversion efficiency which is ten times larger as than the values achieved for similar solar cells without gold interlayer(no reported here). This means that these cells achieved performances of the same order of magnitude as those using ITO as the anode. It suggests that this ultrathin metallic film allows the growth of high efficiency organic devices, which are indium-free and PEDOT: PSS free. In order to separate the effects of energetics and morphology on injection, additional studies are needed.

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