

## Nanostructured solar cells based on MoO<sub>3</sub> film deposition

Y. Boutaleb<sup>1\*</sup>, R. Rehamnia<sup>1</sup>, Y. Berredjem<sup>2</sup> and J.C. Bernède<sup>3</sup>

<sup>1</sup> Laboratoire d'Electrochimie, Université Badji Mokhtar  
B.P. 12, 23000 Annaba, Algeria

<sup>2</sup> Laboratoire d'Etude et de Recherche des Etats Condensés, LEREC  
Département de Physique, Université Badji Mokhtar, B.P. 12, 23000 Annaba, Algeria

<sup>3</sup> LAMP, EA 3825, Faculté des Sciences et des Techniques, Université de Nantes  
Nantes Atlantique Universités, 2 Rue de la Houssinière, B.P. 92208, Nantes, F-44000 France

(reçu le 14 Août 2014 – accepté le 20 Mai 2015)

**Abstract** - *Electrodeposited molybdenum oxide thin films are used as a buffer layer between the indium tin oxide (ITO) anode and the organic electron acceptor film in organic solar cells. The MoO<sub>3</sub> films are deposited at room temperature using a solution of molybdic, acid and citric acid as complexing agents. Such electrodeposited MoO<sub>3</sub> ultra thin films (10-20 nm) has been used as buffer layer (BF) in ITO/BF/copper phthalocyanine (CuPc)/fullerene (C<sub>60</sub>)/ aluminium tri (8-hydroxyquinoline) (Alq<sub>3</sub>)/aluminium photovoltaic cells. It is shown that this electrodeposited MoO<sub>3</sub> buffer layer enhances the charge transfer from CuPc to ITO through a decrease of the effective barrier, present at the interface CuPc/ITO. This improving effect is directly highlighted by the shape of the J-V curves. The kink effect, due to the barrier present at the interface ITO/organic, disappears when the electrodeposited molybdenum oxide buffer layer, is introduced at this interface, which testifies of the decrease of the barrier.*

**Résumé** - *Les couches minces d'oxyde de molybdène obtenu par électrodéposition à température ambiante à partir d'une solution d'acide molybdique, et d'acide citrique qui est utilisé comme complexant, sont utilisés comme une couche tampon entre l'oxyde d'indium et d'étain (ITO), l'anode et le film organique accepteur d'électrons dans les cellules solaires organiques. L'obtention de MoO<sub>3</sub> par électrolyse de films ultra-minces (10-20 nm) a été utilisé comme couche tampon (BF) en ITO/BF/phtalocyanine de cuivre (CuPc)/fullerène (C<sub>60</sub>) / aluminium tri (8-quinoléine) (Alq<sub>3</sub>)/aluminium photovoltaïque cellules. Il est montré que cette couche tampon de MoO<sub>3</sub> par électrolyse améliore le transfert de charge de CuPc à ITO par une diminution de barrière efficace, présente à l'interface CuPc / ITO. Cet effet d'amélioration est directement mis en évidence par la forme des courbes J-V. L'effet de vrillage, en raison de la barrière présenté à l'interface ITO/organique, disparaît lorsque la couche électro déposée de mémoire tampon de l'oxyde de molybdène, est introduit au niveau de cette interface, ce qui témoigne de la diminution de la barrière.*

**Keywords:** Electrochemical deposition – Organic solar cells – Molybdenum oxide buffer layer.

### 1. INTRODUCTION

Organic solar cells have attracted considerable interest during the last fifteen years because they are a possible way to achieve low cost energy. Organic solar cells are usually fabricated in two configurations, bilayer heterojunction, and bulk heterojunction. In bulk heterojunction, an electron acceptor (organic or inorganic) is

---

\* boutaleb\_yassira@yahoo.fr

blended into the polymer, which induces a high interface area between the electron donor and the electron acceptor [1-3].

Bulk heterojunction with conversion efficiency higher than 5 % have been reported [1]. The other configuration is based on a bilayer heterojunction. The smaller donor/acceptor interface area is offset by the introduction of thin films at the interfaces of the structure [4].

Both device families are based on, at least, two organic materials. One of them - either an organic dye or a semiconducting polymer - donates the electrons. The other component serves as the electron acceptor. In these devices, indium tin oxide (ITO) coated substrates are used as transparent anode, while a low work function metal, such as aluminium, is usually used as cathode.

A systematic difficulty in organic optoelectronic devices is the charge carrier transport between the organic materials and the electrodes. A common solution is to introduce thin interlayers, called buffer layers, which adjust the electronic behavior of the adjacent materials.

We have shown recently that thermally evaporated  $\text{MoO}_3$  thin films ( $3.5 \pm 1$  nm thick) can be used as a buffer layer at the interface anode/organic material [5]. Such the  $\text{MoO}_3$  buffer layer allows 50 % improvement the efficiency of the solar cells. In order to limit the cells cost, limitation of the number of films deposited under vacuum is desirable.

In the present letter we show that efficient solar cells can be grown using a  $\text{MoO}_3$  buffer deposited by electrochemistry.

## 2. EXPERIMENTAL

Molybdenum oxide, which is a wide band gap n-type semiconductor, has been deposited in thin film form by several methods, among them low temperature electro deposition is an attractive low cost technique. Electrochemical synthesis using different precursor solutions has been use with success [6-8].

The process proposed by Pathan *et al.* [8] allows obtaining directly  $\text{MoO}_3$  thin films, without any annealing, and it has been used in the present work. Following this technique,  $\text{MoO}_3$  films have been electrodeposited from an aqueous solution of molybdic acid with citric acid as a complexing agent.

The solutions were prepared by dissolving calculated amount of molybdic acid in distilled water, then acid citric salt was added. In order to achieve very thin homogeneous  $\text{MoO}_3$  thin films, highly dissolved solutions were probed. After a first cycle of rough investigations, a finest study has been done using initial molybdic acid concentrations of 0.1 mM/l. The working substrates were ITO coated glass, in order to use them as anode in organic solar cells.

After scrubbing with soap, these substrates were rinsed in running deionised water.

A standard three electrodes glass cell was used for electrochemical deposition. A platinum wire was used as a counter electrode and an  $\text{Ag}/\text{AgCl}$  was used as a reference electrode. The spacing between the working electrode and the counter electrode was 1 cm. All experiments were performed at room temperature.

The cyclic voltametry (CV) was used to study the oxide deposition process. The CV curves were carried out between -1.2 and 0.8 V at a scan rate of  $500 \text{ mVs}^{-1}$ . After

deposition the films were rinsed with distilled water and then heated for an hour at 100°C.

In order to check the bulk properties of the electrodeposited MoO<sub>3</sub> films, thick films have been deposited, from the same solution, by increasing the number of cycles to 6, while only 2 or 3 deposition cycles have been used for MoO<sub>3</sub> films.

After deposition the films are amorphous because no diffraction peaks are visible in the X-ray diffraction diagram. Mo has been detected by microprobe analysis. However the films are too thin for quantitative analysis despite the fact that constituents of the substrate, In, Sn and O (ITO) are detected and are dominant.

### 3. RESULTS AND DISCUSSION

In order to compare the energy conversion efficiency of cells using MoO<sub>3</sub> buffer layer deposited onto In<sub>2</sub>O<sub>3</sub> either by vacuum evaporation or by electrochemical synthesis, we have used an already known multilayers hetero-junction structure based on copper phthalocyanine (CuPc)/fullerene (C<sub>60</sub>) junction with an electron blocking layer, the aluminium tris(8-hydroxyquinoline) between the fullerene and the aluminium cathode. The organic materials were commercially obtained. The organic donor is copper phthalocyanine (CuPc), while organic acceptor is fullerene (C<sub>60</sub>).

CuPc, C<sub>60</sub> and Alq<sub>3</sub> have been deposited in a vacuum of 10<sup>-4</sup> Pa. The thin film deposition rate 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 respectively and of C<sub>60</sub> and 0.1 nm/s and 10 nm for Alq<sub>3</sub>, respectively.

For comparison, organic solar cells using different anodes have been deposited in the same run. The different anodes were ITO, ITO covered by MoO<sub>3</sub> deposited by evaporation and by electrochemistry. A simple improvement of TCO surface can be introduced by the deposition of a thin oxide buffer layer (onto the TCO), which allows to enhance the devices efficiency.

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. After organic thin film deposition, without breaking the vacuum, the aluminium upper electrodes, through a mask with 2 mm × 5 mm active area.

Therefore the structures used were glass/TCO/BF/CuPc/C<sub>60</sub>/Alq<sub>3</sub>/Al with BF = MoO<sub>3</sub> deposited by vacuum evaporation or by electrochemistry. Furthermore some cells were grown without any buffer layer.

Electrical characterizations were performed with an automated I-V tester, in the dark and under 1 sun global AM 1.5 simulated solar illumination. Performances of photovoltaic cells were measured using a calibrated solar simulator (Oriel 300W) at 100 mW/cm<sup>2</sup> light intensity adjusted with a PV reference cell (0.5 cm<sup>2</sup> CIGS solar cell, calibrated at NREL, USA). Measurements were performed at an ambient atmosphere. All devices were illuminated through TCO electrodes.

In figure 1 typical J-V characteristics of solar cells using different anode configuration are reported. When ITO without buffer layer was used as anode, a kink effect is clearly visible on the J-V characteristics. We have already shown that such a

behaviour can be interpreted by introducing a second diode in the equivalent electrical scheme of the solar cell [9].

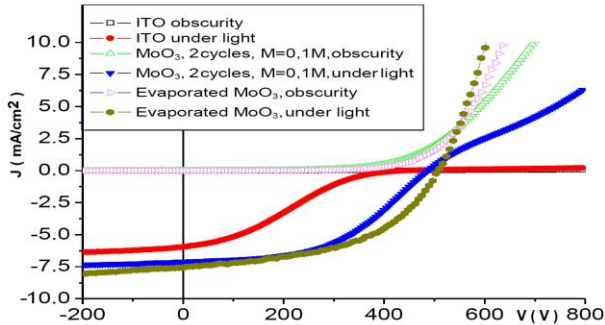


Fig. 1:  $J-V$  characteristics in the dark (open symbols) and under AM 1.5 illumination (full symbols) of solar cells with different anode configuration

In figure 1 typical  $J-V$  characteristics of solar cells using different anode configuration are reported. When ITO without buffer layer was used as anode, a kink effect is clearly visible on the  $J-V$  characteristics. We have already shown that such a behaviour can be interpreted by introducing a second diode in the equivalent electrical scheme of the solar cell [9].

This second diode is issued from the non-ohmicity of the contact ITO/CuPc and it has a parasitic effect on the cell performance. It induces a decrease of the cell performance. When an  $\text{MoO}_3$  thin film is deposited by evaporation onto the ITO before cell realisation (Fig. 1), the kink effect has disappeared and the cell exhibits better performance. Such device performance enhancement can be attributed to the decrease of the barrier height at the interface ITO/CuPc, which induces the extinction of the parasitic diode and of When the  $\text{MoO}_3$  buffer layer is deposited by electrochemistry, the kink effect has nearly disappeared and that the cell efficiency is significantly improved. (as show on figure 1).

**Table1:** Photovoltaic performance data under AM1.5 conditions of devices using ITO, ITO/ $\text{MoO}_3$  (3 nm) and ITO/ $\text{MoO}_3$  (6 nm) anodes

Anode	Deposition technique	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	FF	$\eta$ (%)
ITO		0.49	5.9	0.37	0.99
ITO/ $\text{MoO}_3$	Voltametry	0.49	7.1	0.46	1.59
ITO/ $\text{MoO}_3$	Evaporation	0.51	7.1	0.53	1.91

The overall cell performances are presented in **Table 1**. the  $\text{MoO}_3$  buffer layer induces a significant enhancement of the solar cells performances, whatever the origin of  $\text{MoO}_3$  is.

The results presented have been obtained with a  $\text{MoO}_3$  film thickness of around 2 nm. However for thicker  $\text{MoO}_3$  electrodeposited films the device performance decreases and the current through the structure becomes very small. Such effect should be attributed to the  $\text{MoO}_3$  buffer layer. Indeed, for thickness of around 2 nm, the tunnel

effect allows the carriers to cross the insulating layer with a tunnel effect coefficient near 100 %.

This value, the tunnel effect coefficient decreases quickly as well as the current. For film thickness greater than the results are not reproducible. J–V characteristics typical of cells needing an electrical equivalent scheme with two diodes are sometime obtained, which shows that the thickness of the MoO<sub>3</sub> films is not sufficient to decrease reproductibility the barrier at the interface ITO/MoO<sub>3</sub>.

Moreover it is well known that the work function of ITO can be electrochemically modified [10]. It means that during the deposition of the first layers, this modification can compete with the effect of deposited MoO<sub>3</sub>.

We have already discussed the effect of the MoO<sub>3</sub> buffer layer. The contact ITO/MoO<sub>3</sub>/CuPc behaves like a MIS structure, which allows a reduction of the energy barrier due to the difference between the work function of ITO and the highest occupied molecular orbital of CuPc.

The optimum MoO<sub>3</sub> thickness corresponds to a compromise between an optimum ITO cover age and a sufficient transparency of the trapezoidal barrier for tunnelling of the charge carriers [5]. Therefore the present study shows that electrodeposited films allow similar good adaptation of the band scheme between the ITO anode and the electron donor CuPc.

#### 4. CONCLUSION

Stable reproducible and low reduced molybdenum oxide films were obtained over ITO electrode employing potentiostatic techniques. These films were successfully tested as anodes in a bilayer heterojunction organic solar cell arrangement improving the surface properties of the device.

Further characterization of the deposit shows that amorphous molybdenum oxide films of appropriate thickness were prepared. Films deposited by potentiostatic technique are more homogeneous than those deposited by cyclic voltammetry.

Optimization of the electrochemical techniques here employed is still an attractive scope of investigation, because there has not yet been a rigorous study concerning different electrolytic media, substrate, electrochemical perturbation and/or convective regime effect as a function of the solar cell performance. Hence a new research line may be envisaged.

#### REFERENCES

- [1] J.Y. Kim, K. Lee, N.E. Coates, D. Moses, T.Q. Nguyen, M. Dante and A.J. Heeger, 'Efficient Tandem Polymer Solar Cells Fabricated by All-Solution Processing', Science, Vol. 317, N°5835, pp. 222 – 225, 2007.
- [2] P. Neumanns, S. Uchida and S.R. Forrest, 'Efficient Bulk Heterojunction Photovoltaic Cells Using Small-Molecular-Weight Organic Thin Films', Nature, Vol. 425, pp. 158 – 162, 2003.
- [3] B. Kippelen and J.L. Brédas, 'Organic Photovoltaics', Energy & Environmental Science Vol. 2, pp. 251 – 261, 2009.
- [4] B. Johnev, M. Vogel, K. Fostiropoulos, B. Mertesacker, M. Rusu, M.C. Lux-Steiner and A. Weidinger, 'Monolayer Passivation of the Transparent Electrode in Organic Solar Cells', Thin Solid Films, Vol.488, N°1-2, pp. 270 , 2005.

- [5] L. Cattin, F. Dahou, Y. Lare, M. Morsli, R. Tricot, S. Houari, A. Mokrani, K. Jondo, A. Khelil, K. Napo, J.C. Bernède, '*MoO<sub>3</sub> Surface Passivation of the Transparent Anode in Organic Solar Cells Using Ultrathin Films*', British Journal of Applied Physics Vol. 105, N°3, pp. 034507, 2009.
- [6] T.M. McEvoy, K.J. Stevenson, J.T. Hupp and X. Dang, '*Electrochemical Preparation of Molybdene Trioxide Thin Films: Effect of Sintering on Electrochromic and Electroinsur Properties*', Langmuir, Vol. 19, N°10, pp. 4316 – 4326, 2003.
- [7] C.S. Hsu, C.C. Chan, H.T. Huang, C.H. Peng and W.C. Hsu, '*Electrochromic Properties of Nanocrystalline MoO<sub>3</sub> Thin Film*'; Thin Solid Films, Vol. 516, N°16, pp. 4839 – 4844, 2008.
- [8] H.M. Pathan, S.K. Min, K.D. Jung and O.S. Joo, '*Electrosynthesis of Molybdenum Oxide thin Films onto Stainless Substrates*', Electrochemistry Communications, Vol. 8, pp. 273 – 278, 2006.
- [9] B. Kouskoussa, M. Morsli, K. Benchouk, G. Louarn, L. Cattin, A. Khelil and J.C. Bernède, '*On the Improvement of the Anode/Organic Solar Celles by the Presence of an Ultra-thin Gold Layer*', Physica Status Solidi (a), Vol. 206, N°2, pp. 311 – 315, 2009.
- [10] Y. Shi, S.C. Luo, W. Fang, K. Zhang, E.M. Ali, F.Y.C. Boey, J.Y. Yin, J. Wang, H.H. Yu and L.J. Li, '*Work Function Engineering of Electrodes via Electropolymerization of Ethylene dioxythiophenes and its derivatives*', Organic Electronics, Vol. 9, N°5, pp. 859 – 863, 2008.