

# On the improvement of the electroluminescent signal of organic light emitting diodes by the presence of an ultra-thin metal layer at the interface organic/ITO

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Received 4 September 2007, revised 1 October 2007, accepted 22 October 2007  
Published online 24 October 2007

PACS 73.40.Vz, 78.60.Fi, 81.15.Ef, 85.60.Bt, 85.60.Jb

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The electroluminescent (EL) signal of organic light emitting diodes (OLEDs) based on simple “hole transporting layer/electron transporting layer” (HTL/ETL) structures has been studied as a function of the anode/HTL interface, the anode being an indium tin oxide (ITO) film. It is shown that

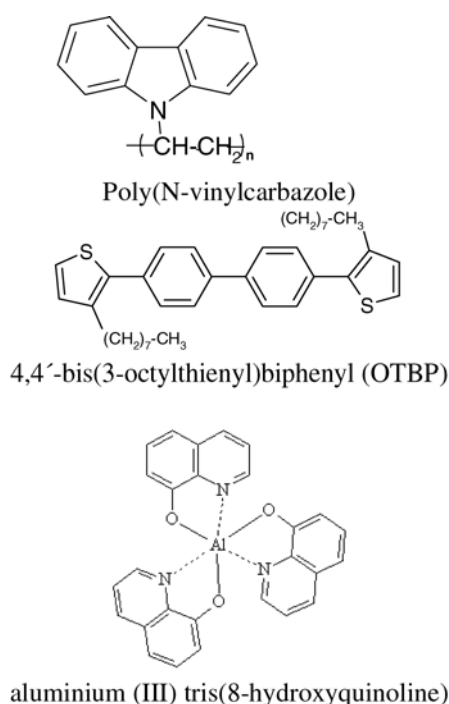
the electroluminescent (EL) signal increases when a metal ultra-thin layer is introduced between the anode and the HTL. Experimental results show that the work function value of the metal is only one of the factors which allow improving the EL signal via better hole injection efficiency.

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Organic light emitting diodes (OLEDs) have attracted considerable interest during the last twenty years and they are now available in the market [1]. However, for some applications such as TV sets, they still need better performances in efficiency and lifetime. Moreover, the device behaviour is not well understood and further research is necessary. It is known that in an OLED, holes and electrons are injected from an anode and a cathode, respectively, under application of an electric field. The carriers within the organic layers interact to produce excitons, which through recombination produce light emission [2]. In such devices, the process of charge injection is one of the main factors which control the electrical characteristics and the electroluminescence efficiency of the devices. Therefore electrode modification can allow achieving high performance OLEDs with low operating (turn-on) voltage and high electroluminescence efficiency. Indeed it appears that the anode/HTL interface is crucial to hole injection rather than the HTL bulk mobility limits charge injection. The injection depends in the barrier height at the interface, which, in a first approximation, is equal to the energy difference between the oxide work function  $\Phi_{\text{OTC}}$  and

the highest occupied molecular orbital of the HTL ( $\text{HOMO}_{\text{HTL}}$ ). Usually, in OLEDs the anode is a film of indium tin oxide (ITO). Therefore, for a heterojunction between ITO and a given organic material,  $\Phi_{\text{ITO}}$  will, in a first approximation, determine this energy barrier. Previous measurements of  $\Phi_{\text{ITO}}$  have shown that it varies from one layer to another one because it is strongly sensitive to the state of the surface [3], it varies from 4.1 eV to 5.5 eV depending on the surface treatment (chemical etching [4], plasma treatment [5] or grafting of molecules [6]). A great variety of engineering approaches have been applied to the ITO/HTL interface [3–6]. Also attempts have been made using different buffer layers at the interface ITO/HTL, phthalocyanines [7], oxides and metal [8] have been shown to improve, more or less, the OLED performances.

In this short note, we show that the presence of an ultra-thin metal layer at the ITO/HTL interface allows improving the OLED performance. However, the value of its work function  $\Phi_{\text{M}}$  is not the only factor which controls the device characteristics. We report on single junction ITO/M/HTL/ETL/LiF/Al/P cells. ITO is the transparent conductive indium tin oxide. M is an ultra-thin metal film:



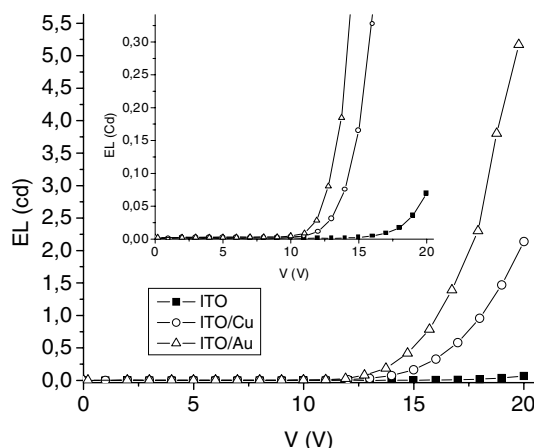
**Figure 1** Chemical structure of the organic materials used.

Au, Ni, Cu, the thickness of this layer is 0.5 nm or 0 nm for OLEDs used as reference. The organic hole transporting layer (HTL) is either poly(n-vinylcarbazole) or 4,4'-bis(3-octylthienyl)biphenyl (OTBP), the organic electron transporting layer (ETL) is aluminium (III) tris(8-hydroxyquinoline) ( $Alq_3$ ) (Fig. 1). The cathode upper electrode is the classical LiF/Al bilayer. P is a protective coating layer. The PVK and the  $Alq_3$  have been purchased from Aldrich, while the OTBP was synthesized following the cross coupling procedure of Kumada et al. [9], allowing to react two moles of the 3-alkylthiophene Grignard derivative with 4,4'-dibromobiphenyl.

After chemical cleaning [10], ITO coated glass substrates were introduced into the vacuum deposition apparatus. The ultra-thin metal layer and the layers of PVK or OTBP,  $Alq_3$ , LiF, aluminium were thermally deposited in a vacuum of  $10^{-4}$  Pa. The protective coating layer, an amorphous selenium layer, is also vacuum evaporated. The deposition rate and film thickness were measured in situ with a quartz monitor.

The electrode was deposited through a mask with  $2 \times 2 \text{ mm}^2$  active area. Electrical and optical characterizations were performed with automated electroluminescence-voltage (EL-V) testers. The electroluminescence (EL) characteristics were recorded through the transparent TCO electrode and glass. The light output was detected using a silicon photodiode and a Keithley 2000 multimeter.

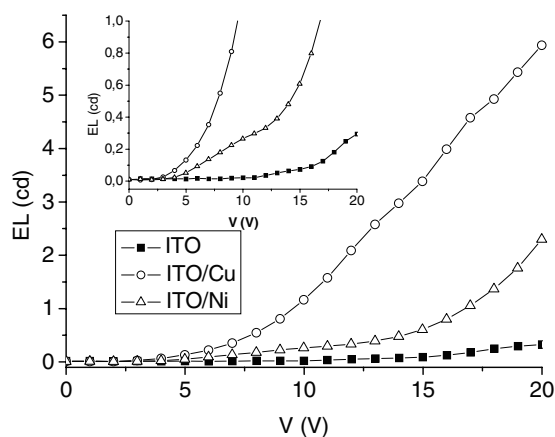
The nominal thickness of HTL (PVK or OTBP),  $Alq_3$ , LiF and Al layers were fixed at 40 nm, 70 nm, 1 nm and 100 nm, respectively. It should be noted that the study is devoted to the improvement of the ITO/HTL interface and the thickness of the organic films has not been optimised.



**Figure 2** (EL-V) characteristics of glass/ITO/M (M = 0.5 nm Au, Cu or 0 nm)/PVK/ $Alq_3$ /LiF/Al/P.

Two device families were investigated, the first one uses PVK as HTL and the second OTBP. Therefore the two cell families were ITO/M/PVK/ $Alq_3$ /LiF/Al/P and ITO/M/OTBP/ $Alq_3$ /LiF/Al/P with M = Cu, Au (thickness 0.5 nm or 0 nm).

EL-V characteristics of different OLEDs ITO/M/PVK/ $Alq_3$ /LiF/Al/P with M = Cu, Au (thickness 0.5 nm or 0 nm) are plotted in Fig. 2. It illustrates the typical behaviour of the performance of the ITO/Au, ITO/Cu diodes and the ITO reference diodes. It can be seen that the turn-on voltage decreases when an ultra-thin metal layer is present at the ITO/PVK interface. The turn-on voltages for light  $\approx 0.1 \text{ Cd}$  are  $11.50 \pm 1.00 \text{ V}$  and  $12 \pm 1 \text{ V}$  for an Au and Cu ultra-thin interlayer, respectively, while it is  $15.5 \pm 1.0 \text{ V}$  without metallic interlayer. With an Au ultra-thin interlayer, a reduction in threshold voltage of 2.5 eV to 4 eV is measured from one experiment to another. These threshold values, even if they are smaller in the presence of a metal interlayer, are quite large. These high values can be explained by the HOMO value of the PVK. Effectively, it is 5.7 eV, which should induce the presence of a quite large barrier height at the anode/PVK interface since the work



**Figure 3** (EL-V) characteristics of glass/ITO/M (M = 0.5 nm Ni, Cu or 0 nm)/OTBP/ $Alq_3$ /LiF/Al/P.

functions of the different anode are  $\Phi_{\text{Au}} = 5.1$  eV,  $\Phi_{\text{Cu}} = 4.8$  eV and  $\Phi_{\text{ITO}} \approx 4.7$  eV.

Therefore it could be interesting to probe another HTL with smaller HOMO value. It is well known that thiophene derivatives have HOMO in the range of 5–5.3 eV, for instance the HOMO of the poly(3-hexylthiophene), P3HT, often used in organic solar cells is 5.2 eV [11, 12].

The HOMO, LUMO values of the oligomer thiophene derivatives can be estimated by electrochemistry from the first oxidation and reduction potential, respectively, OTPB belongs to a family of thiophene derivatives whose HOMO is around (5.2 eV) [13].

In Fig. 3 the results obtained with this new HTL are shown, when the anode is ITO, ITO/Ni or ITO/Cu. There is a significant decrease of the turn-on voltage which is in good agreement with the smaller value of the HOMO of the HTL. Therefore, whatever the HTL is, the diodes with an ultra-thin metal layer at the ITO/HTL interface exhibits, systematically, better performance than a device without metal (Figs. 2, 3), the best result has been achieved with glass/ITO/Au(0.5 nm)/OTBP/Alq<sub>3</sub>/LiF/Al/P, thus, at 15 V the electroluminescent signal is 12 Cd.

However, if effectively the presence of an ultra-thin metal layer at the ITO/HTL interface decreases the value of the turn-on voltage, while it increases the electroluminescent signal, it appears clearly from Fig. 3 that the value of the anode work function is not the only factor controlling the hole injection efficiency. Indeed the work function of Ni is  $\Phi_{\text{Ni}} = 5.2$  eV, which means that the results achieved with Ni should be of the same order as those achieved with Au ( $\Phi_{\text{Au}} = 5.1$  eV) and better than those with Cu ( $\Phi_{\text{Cu}} = 4.8$  eV) (Fig. 4).

Therefore it can be concluded that, if an increase of the anode work function value allows improving the OLED performances, it is not the only important factor. Effectively considering the hole injection barrier, when Cu is used the device should not have a higher efficiency than a device with Ni. Some authors have already shown that the barrier height of the junction is not the only factor controlling the hole injection, the difference in surface morphology of the anode has also been evocated as important factor [14]. Moreover, the thickness of the ultra-thin metal film, 0.5 nm, induces that the film exists as metal nanodots, which makes difficult to predict the exact value of the energy barrier at the interface. The nanodots could introduce some surface morphology alteration which can imply higher electric field and hence lower voltage. However, the threshold voltage decrease measured in the case of PVK corresponds to a thickness variation of about 20 nm, which is hardly probable with metal films of thickness 0.5 nm. Therefore this effect can only partly explain the OLEDs performance improvement. The metal nanodots can modify the hydrophilic properties of the ITO, which can modify the interface properties. The presence of an interfacial di-

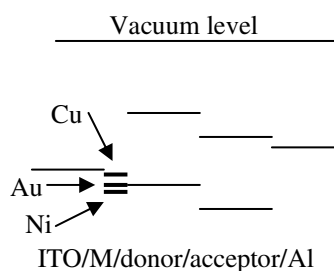


Figure 4 Energy band diagram.

pole between ITO and the HTL cannot be excluded, which value can be modified by the metal nanodots. It is conceivable that the improved injection from the metal modified ITO is partly due to a better mechanical contact between the electrode and the PVK/OTPB.

Clearly, additional studies are needed in order to separate the effects of energy level and morphology on injection.

**Acknowledgement** F.M. thanks Fondecyt, project No. 1040728 for funding.

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