

**Modification of Indium Tin Oxide for improved hole injection  
in organic light emitting diodes.**

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Organic light emitting diodes (OLEDs) represent a very promising technology for flat panel displays and are already appearing in consumer electronics products such as car stereos and cell phones. The ease of fabrication, robustness, high efficiency, and small weight and thickness are major advantages over competing technologies, such as liquid crystals. A large research effort in both academia and industry is focused on understanding the device physics and improving their efficiency and lifetime.

In its simplest case, an OLED consists of one or more organic semiconductor layers sandwiched between two metal electrodes, one with a high (anode) and one with a low (cathode) work function. Upon application of forward bias, electrons and holes are injected from the cathode and the anode respectively and recombine inside the organic layer(s) producing light emission<sup>[1]</sup>. The process of charge injection is of fundamental importance, as it can control the electrical characteristics and/or the efficiency of the device<sup>[2]</sup>. A great deal of contemporary research addresses various aspects of metal/organic interfaces, such as morphology<sup>[3,4]</sup>, energetics<sup>[5-11]</sup> and charge transport<sup>[12-15]</sup>. Modification of interfaces has also received considerable attention; especially on the cathode side of the device where the need to replace low work function metals such as Ca with more stable ones such as Al is pressing. The bulk of the work has been carried on ultrathin layers of LiF, CsF and low work function metals inserted between the organic and Al to produce OLEDs with higher efficiency than those with Al cathodes alone<sup>[16-19]</sup>.

On the anode-side of the device, Indium Tin Oxide (ITO) seems to be the electrode of choice. Although it comes with its own set of problems, such as large variation in properties depending on preparation<sup>[20-21]</sup>, release of indium and oxygen into the organic layer<sup>[22]</sup> and poor compatibility with some organic materials<sup>[4]</sup>, it offers a combination of transparency and

conductivity that is hard to replace. Modification of ITO with self-assembled monolayers and conducting polymers has been shown to increase OLED efficiency<sup>[18,23-27]</sup>.

The vast majority of interface modification work reported in literature has been carried out on an OLED configuration. Namely, devices with and without the modification layers were tested side by side and changes in the device performance (in terms of operating voltage and/or efficiency) were attributed to enhanced injection. The interpretation of such experimental data, however, is not always straightforward, since the introduction of an extra layer in an OLED simultaneously changes several parameters (such as charge extraction, shifts in the recombination profile and exciton quenching in the electrode neighborhood). Recently, Abkowitz et. al. proposed a technique to characterize the electrical behavior of metal/organic contacts<sup>[12]</sup>. The technique is based on the determination of the injection efficiency, the ratio between the injected current and the space charge limited current, where the latter is determined by an independent measurement of the charge carrier mobility. This technique was recently used to measure the influence of copper phthalocyanine layers in the performance of multi-layer OLEDs<sup>[28]</sup>.

In this Communication, we report on injection efficiency measurements that were carried out to characterize the contact between ITO and the organic semiconductor triphenyl diamine (TPD). We show that the hole current is injection limited. Coating ITO with an ultrathin layer of Pt dramatically enhanced its injection properties and the contact with TPD becomes nearly Ohmic. We apply these modified ITO electrodes to double layer organic light emitting diodes based on TPD and hydroxy quinoline aluminum ( $Alq_3$ ), with Ca cathodes. The results show that the operating voltage of these devices is limited by hole injection and can be improved with the modified ITO. We discuss the merits of ultrathin Pt films as interface modification layers.

ITO coated glass substrates were purchased from **Thin Film Devices**. They were cleaned just before the device fabrication with a series of detergent and DI water baths, drying under nitrogen and a 10 minutes exposure to UV/ozone (Jelight Co. Model 42). 5 Å thick Pt films were deposited by e-beam evaporation on clean ITO substrates at a rate of 1 Å/sec and cleaned again with UV/ozone. A suitable mask was used to cover only part of the ITO electrode with Pt. In this way, we could test devices with and without the Pt layer *on the same substrate*, therefore minimizing variations in the data that might arise due to different conditions during the deposition of the organic layers. An AFM from Thermomicro scopes was used for the investigation of the surface morphology of the ITO electrodes. A Kelvin probe tip (made of p<sup>+</sup> Si by Thermomicro scopes) was used to obtain the difference in the work function of the tip and the electrode.

TPD was provided by the Xerox Corporation. Alq<sub>3</sub> was purchased from Aldrich and was used without any further purification. The deposition of the organic layers and cathodes took place at 10<sup>-6</sup> mbar, in vacuum chambers fitted inside a nitrogen glove box with <1ppm oxygen and moisture. The rates of deposition were 1 and 5 Å/sec for the organic layers and the metals respectively. The cathodes were deposited through a shadow mask that defined six diodes per substrate (three over bare ITO and the other three over the Pt covered ITO) with a 3mm<sup>2</sup> active area each.

The injection efficiency measurements were described in a previous publication<sup>[29]</sup>. In short, the hole drift mobility in TPD was measured with the time-of-flight (TOF) technique in 20 μm thick TPD films sandwiched between ITO and Al electrodes. The measurements were carried under reverse bias (Al positive), where there was negligible current flow through the sample (Al is a bad hole injector and TPD does not support any measurable electron transport). Nondispersive & transients yielded mobilities in agreement with literature values. The space charge

limited current was subsequently determined from the measured values of the mobility, with the appropriate correction for the field dependence of mobility. The current injected from ITO (or ITO covered with a thin Pt layer) was subsequently measured under forward bias *on the same sample* and compared to the space charge limited current. The electrical characteristics of the OLEDs were measured with a Keithley 236 source-measure unit and the radiance with a calibrated UDT S370 optometer, coupled to an integrated sphere. The diodes were cycled a few times between typically -10 and 10V (or -7 and 7V for devices with modified ITO anodes) to test for reproducible characteristics and visually inspected for uniform emission. The measurements were carried out in the glove box or a vacuum cryostat.

The current that flows through a depleted semiconductor can either be limited by the semiconductor bulk or by the contact. In the first case, the contact makes available as much current as the semiconductor bulk demands and the current is limited by intrinsic transport properties of the semiconductor. This is the space charge limited current (SCLC) and for a trap-free material is given by the Mott-Gurney law<sup>[30]</sup>:

$$J_{\text{SCLC}} = (9/8) \epsilon \epsilon_0 \mu V^2 / L^3 \quad (1)$$

where  $\epsilon \epsilon_0$  is the dielectric constant of the organic layer,  $\mu$  the mobility,  $L$  its thickness and  $V$  is the applied bias. In other cases, however, the contact might not be able to supply the semiconductor with enough current to sustain a SCLC. The process of charge injection is then the rate limiting step that determines the current flow through the sample. A quantitative figure of merit for describing contact behavior is the injection efficiency,  $\eta$ , defined as the ratio between the current that is supplied by the contact (the current that flows under forward bias) to the SCLC<sup>[12]</sup>. By definition,  $\eta=1$  for an Ohmic contact and  $\eta<1$  for a current-limiting contact.

The behavior of ITO/TPD and ITO/Pt/TPD contacts is shown in Fig. 1. The injection efficiency was calculated by dividing the current at forward bias by the SCLC, determined from Eq. 1 (with the appropriate correction for a field dependent mobility<sup>[31]</sup>), using the measured values of the mobility. The open squares are data from a sample without the Pt layer. The injection efficiency varies from  $2 \times 10^{-3}$  at low fields to  $10^{-2}$  at high fields, indicating that the ITO/TPD contact acts as a bottleneck in the current flow through the sample. The injection efficiency was found to vary among different batches of ITO by as much as an order of magnitude, reflecting the sensitivity of the workfunction of ITO to its preparation conditions. ITO electrodes that were of the same batch and were cleaned using the protocol described above exhibited similar injection efficiencies. The current-limiting behavior can be attributed to the presence of a sizable energy barrier between the Fermi level of ITO and the highest occupied molecular orbital of TPD<sup>[29]</sup>. The electric field dependence of the injection efficiency was discussed in a previous publication<sup>[29]</sup>.

The open circles in Fig. 1 depict the injection efficiency for the sample with an ITO/Pt/TPD contact. Introduction of 5 Å of Pt at the interface between ITO and TPD causes a dramatic increase in the injected current and makes the contact nearly Ohmic. It should be noted that the SCLC was identical for both samples, as expected, and only the magnitude of the injected current changed between the two samples discussed in Fig. 1. A similar improvement in the injection efficiency was observed for Pt layers that were 2 and 15 Å thick.

The reason the character of the contact changes from current-limiting to Ohmic is not fully understood at present. Recent experiments indicate that the insertion of certain thin layers of low work function metals at the interface between Al and an organic semiconductor enhances electron injection<sup>[18-19]</sup>. This effect has been attributed to doping of the organic semiconductor by direct transfer of electrons from the low work function metal to the organic semiconductor. A

similar mechanism might be operational on Pt coated ITO substrates. Tadayyon et. al.<sup>[32]</sup> have recently shown that ultrathin Pt films increase the work function of ITO. Indeed, using a Kelvin probe attachment on the AFM we measured a 0.6 eV increase in the work function of the ITO electrode on the place where it was covered with Pt. In a previous study we found a barrier height of the order of 0.5 eV at the ITO/TPD interface<sup>[29]</sup>. Therefore, the Fermi level of the Pt modified ITO is lower than the highest occupied molecular orbital of TPD, and direct transfer of electrons from the organic semiconductor to the electrode is energetically favorable. This will create a reservoir of holes in TPD near the contact and will make the contact Ohmic. We have also observed a similar enhancement in the injection efficiency with ultrathin layers of other high work function metals such as Pd and Au. We wish to stress, though, that this is a very simplistic picture, as the presence of interfacial dipole layers (or, possibly, chemical reactions at the interface) makes it difficult to predict the exact value of the energy barrier at the contact<sup>[6]</sup>. We hope that this work will stimulate an investigation of the energetics of these modified interfaces to check the doping hypothesis.

In addition to energetics, the morphology of the interface can play a role in determining the injection efficiency. Recent device studies, for example, imply that the ability of the organic to wet the electrode might affect charge injection<sup>[33]</sup>. As shown in Fig. 2, deposition of Pt does not have a significant effect on the morphology of ITO. The rms roughness measured over an area of  $4\mu\text{m}^2$  was 5.0 and 4.6 Å for the bare and modified ITO respectively. The fact that the roughness of the electrode is of the order of the thickness of the Pt film suggests that Pt might not form a continuous film. Yet, scanning Kelvin probe measurements<sup>[34]</sup> showed that the work function of the Pt modified ITO was uniform over an area of  $4\mu\text{m}^2$  scanned with an estimated lateral resolution of 100 Å. The presence of Pt, however, seems to improve the ability of TPD to wet the ITO. The rms roughness of a 120 Å thick TPD film on bare and Pt modified ITO was found to be equal to 41 and 26 Å respectively. It is conceivable that the improved injection from the Pt modified ITO is partly due to a better mechanical contact between the electrode and TPD.

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

The injection efficiency measurements show that coating ITO with an ultrathin layer of Pt can dramatically enhance its hole injection properties. In order to investigate the potential of this ITO modification method in OLEDs, we fabricated devices with the modified ITO electrodes and compared their performance to devices with the bare ITO electrodes. The current-voltage and radiance-voltage characteristics are shown in Fig. 3. It is clear that the devices with the modified ITO show a lower operating voltage, *i.e.* they achieve a given current and radiance at a lower voltage than the ones with the bare ITO. A similar lowering in the operating voltage was observed by Beierlein et. al.<sup>[35]</sup> in TPD/Alq<sub>3</sub> OLEDs when ITO was replaced with solid (and therefore opaque) Pt electrodes. A more quantitative comparison however is not possible, since the devices in Ref. [35] had an extra copper phthalocyanine layer between the anode and TPD.

Modification of the ITO with Pt layers did not affect neither the quantum, nor the power efficiency. A similar result was recently obtained by Antoniadis et. al.<sup>[36]</sup>, who measured an identical efficiency in TPD/Alq<sub>3</sub> OLEDs that had different ITO anodes and therefore showed different operating voltages. The reason for this behavior lies in the fact that the efficiency in TPD/Alq<sub>3</sub> OLEDs is determined by the ratio of the densities of holes and electrons accumulated at the TPD and Alq<sub>3</sub> sides of the TPD/Alq<sub>3</sub> interface respectively<sup>[37-38]</sup>. Enhancement of hole injection from the anode leads to a higher hole density at the TPD side of the interface, which results on a higher electric field drop across the Alq<sub>3</sub> layer. This, in turn, results into enhanced electron injection and transport (mobility is field dependent) in Alq<sub>3</sub>, which tends to restore the ratio of charge densities at the interface. Therefore, modification of ITO with ultrathin layers of Pt results into a lowering of the operating voltage without affecting the device efficiency.

Ultrathin Pt films are a promising way to modify ITO electrodes for application in OLEDs. Since they are deposited by vacuum evaporation or sputtering, they are naturally compatible with the fabrication of small molecule OLEDs. Their optical transmission is better than 90% over the visible spectrum and better than 95% over the emission band of Alq<sub>3</sub>. Moreover, due to their very high lateral resistance they do not need to be patterned. They can easily be deposited over an array of ITO stripes without causing a short-circuit. This is an advantage compared to conducting polymer layers.

Although we have not carried out a systematic investigation of the influence of Pt layers in the lifetime of OLEDs, we have observed no difference in the degradation of devices with and without the Pt layers during routine testing and brief (three months) storage inside the glove box. We did, however, observe a lower breakdown threshold for the Pt modified samples used for the injection efficiency measurements compared to samples without the Pt layers (this limited the range of the injection efficiency curve shown in Fig. 1). We believe that this is due to the much higher current density achieved in the samples with the Pt modified contacts, which might have caused accelerated electromigration of electrode material into the TPD bulk<sup>[22]</sup>. We are currently analyzing the failure mechanism in these samples.

In conclusion, we have carried out injection efficiency measurements to characterize the contact between ITO and TPD. We found that the contact limits the supply of current to the TPD bulk but it can be improved by coating the ITO with an ultrathin layer of Pt. Application of the modified ITO anodes in TPD/Alq<sub>3</sub> organic light emitting diodes resulted into a lowering of the device operating voltage.

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## Figure Captions

Fig. 1. Electric field dependence of the injection efficiency of the ITO/TPD and the ITO/Pt/TPD contact. Lines are guides to the eye.

Fig. 2. Atomic force microscopy pictures of the bare (left) and the Pt modified ITO (right) electrodes.

Fig. 3. Current density and radiance versus voltage characteristics of ITO/TPD/A1q<sub>3</sub>/Ca/Al (open squares) and ITO/Pt/TPD/A1q<sub>3</sub>/Ca/Al (open circles) diodes. The thickness of the TPD and A1q<sub>3</sub> were 600 Å, while the thickness of Ca and Al layers were 200 Å. Lines are guides to the eye.

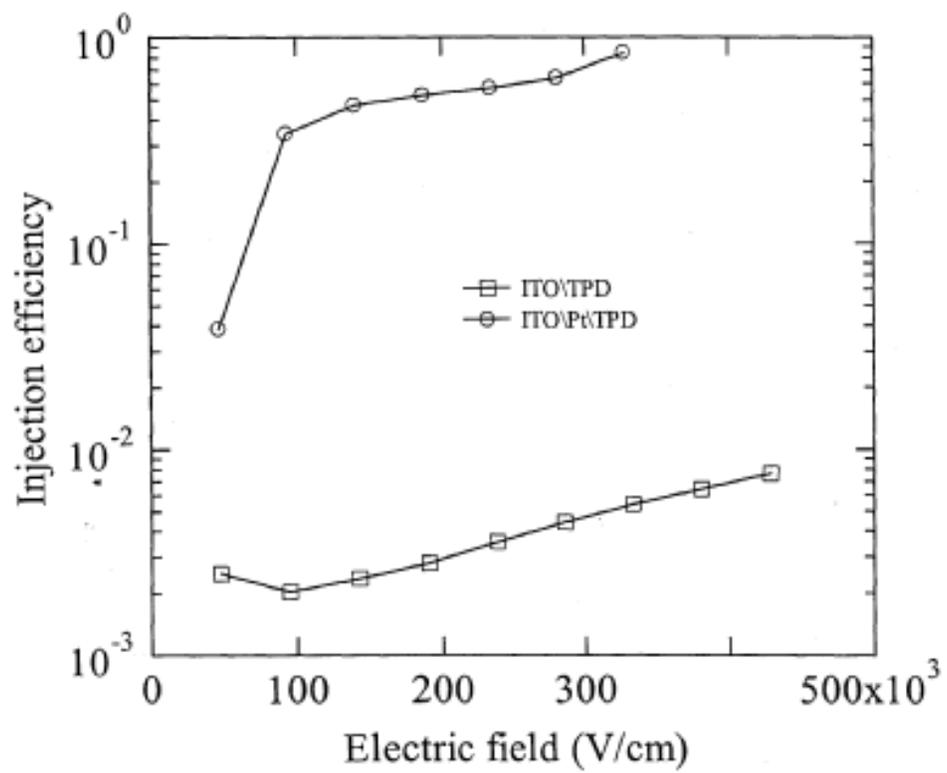


Fig. 1 Shen et. al.

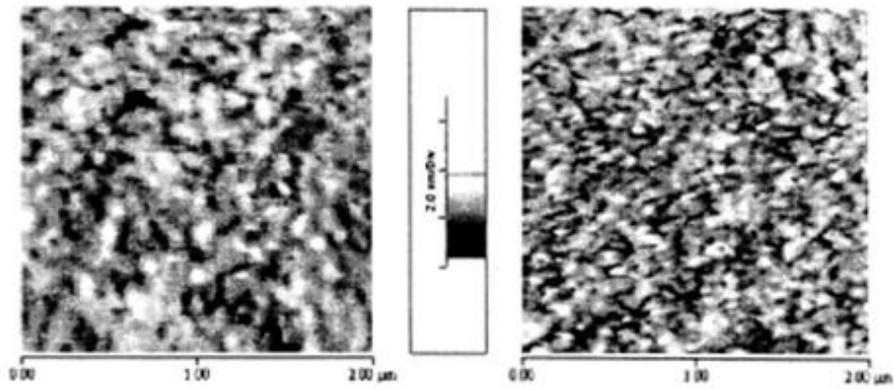


Fig. 2 Shen et. al.

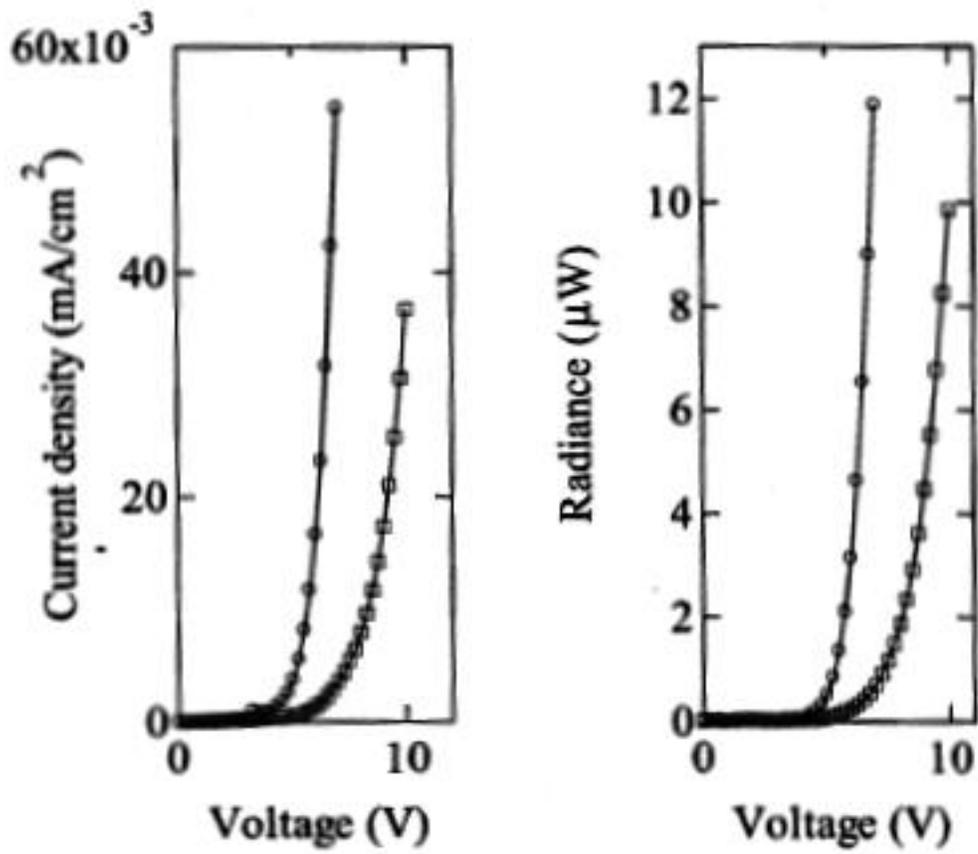


Fig. 3 Shen et. al.