

## Novel OLED structure allowing for the in-situ ohmic contact and reduction of charge accumulation in the device

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### Abstract

*We have demonstrated the enhancement of the power efficiency and device lifetime of organic light-emitting diodes (OLEDs) by introducing the ETL 1 / ETL2 (composite ETL) structure between EML and cathode and the HIL1 (composite HIL) / HIL2 between anode and HTL. Compared to reference devices retaining conventional architecture, novel OLED structure shows an outstanding EL efficiency that is 1.6 times higher (~4.5 lm/w versus ~ 2.71 lm/w for the reference device) and lower driving voltage ( $\Delta V > 1V$ ), but also a longer lifetime and smaller operating voltage drift over time. It is suggested in this work that the device performance can be improved by in-situ ohmic contact through novel electron controlled structure and reduction of charge accumulation in the interface through composite HIL*

### 1. Introduction

In recent years OLED technology has reached the status, when it is considered to be rivaling LCD in flat panel market. Unfortunately, despite a number of inherent advantages, OLED still lags behind in some areas, such as lifetime and certain electrical properties. In order to successfully challenge LCD technology, the breakthrough in those areas is needed.

A lot of effort has been put forth to develop organic electro-luminescent devices, using both organic and inorganic materials, having similar electrical characteristics to those of inorganic semiconductors [1-2]. Essential to the efficient and stable operation of these electronic devices is the process of charge injection from metal electrodes. The physics of charge injection in organics is currently receiving a great deal of attention, and has been reviewed recently [3-5]. The

fact that transport in these materials takes place in a manifold of localized states rather than in a band of extended states makes the quantitative understanding of the process challenging. Recently the results of other groups indicate that the presence of high charge density in an organic semiconductor near the interface improves charge injection [6]. The majority of evidence comes from studies of organic light emitting diodes where introduction of a doped organic layer between the metal and (undoped) organic material improves device performance. A number of different approaches have been attempted to explain the effect of the doped layer. But with exception of the PIN structure, its mechanism has remained ambiguous.

Although the presence of the doped layer can contribute to the device performance via decrease of the injection barrier, it cannot solve all the problems associated with organic semiconductors. One of the most important is the lack of charge balance due to characteristic prevalence of hole mobility over electron mobility in OLEDs.

These inherent demerits in organic electronics can contribute to such problems as voltage increase and light efficiency reduction during the operation, as well as shorter lifetime comparing to inorganic LEDs. Generally, lifetime decrease can be attributed to the degradation of EML materials, but an unbalance of carrier density can cause a steep initial drop of the lifetime.

The electroluminescence phenomenon in organic solids can be divided into several steps including the injection, transport, capture and radiative recombination of positive and negative charge carriers inside an organic layer with suitable band gap. In order to achieve significant improvement of OLED

performance it's essential to address different issues separately.

In this paper we will consider two of the aforementioned steps – injection and transport, we will introduce and explain a new approach that will allow us to achieve injection barrier reduction and improve carrier balance in organic electro-luminescent devices. We will also show how those improvements can affect operating voltage and lifetime by charge unbalance at the initial stage.

## 2. Experimental

Devices with active area of  $4\text{mm}^2$  were fabricated. In case of the multilayer device, the bottom electrode is a patterned layer of indium tin oxide (ITO) / Metal (reflective layer) / ITO deposited on glass to make the top emitting device. Prior to coating with organic materials, anode substrates were subjected to UV- $\text{O}_3$  treatment for 5min, followed by annealing on a hot plate for 5min at  $250^\circ\text{C}$ . It is known from earlier studies that this treatment increases the ITO work function and eliminates any water residue on a substrate.

OLED fabricated as reference device had the following structure: Anode / HIL / HTL / Blue-EML / ETL / EIL / Cathode / CPL. Where the abbreviations stand for hole injection layer, hole transport layer, emissive layer, electron transport layer, electron injection layer and cathode protection layer respectively. In order to improve the lifetime and the carrier injection, composite HIL and composite ETL (ETL2) were introduced into the conventional structure. Composite HIL containing two different materials is deposited by using the co-evaporation technique. Materials used for co-deposition are Metal Oxide (such as  $\text{MoO}_x$ , WO or  $\text{V}_2\text{O}_5$ ) and conventional HIL. Conventional HIL material was deposited on top of composite HIL. In case of the composite ETL, the conventional ETL such as  $\text{Alq}_3$  and conventional EIL such as CsF (Cesium Fluoride) were co-deposited on top of ETL 1 that possesses higher electron mobility than ordinary employed ETL materials (e.g.  $\text{Alq}_3$ ). The structure of the resulting device is as follows:

Anode / Composite HIL / HIL / HTL / Blue-EML / ETL 1 / composite ETL (ETL2) / Transparent cathode

For some of the devices that will be referred to as the in-situ electron-only devices, the ITO on glass substrates were used as anodes. To block the hole injection in such devices, the hole blocking layer was introduced between the anode and ETL. The aluminum electrode is used as the common cathode.

The devices were mounted on the cold finger of cryostat under vacuum. The I-V characteristics were measured in the temperature range between 14 and 400K with a Keithley 2400 source meter. The intensity of the EL emission from the devices was simultaneously measured with a Keithley 200 multimeter equipped with a calibrated Si Photodiode or an ARC P2 PMT through an ARC 275 monochromator.

## 3. Results and discussion

A lot of new OLED structures have been reported to reduce the driving voltage and increase the light efficiency. For instance, introduction of the PIN structure allows for OLED driving at low-electric fields and higher quantum efficiency. But the drawback of such technique is the low doping ratio, which makes it difficult to maintain good reproducibility on a commercial scale production. If such a problem can be avoided in a new structure it would make it much more appealing for the OLED industry.

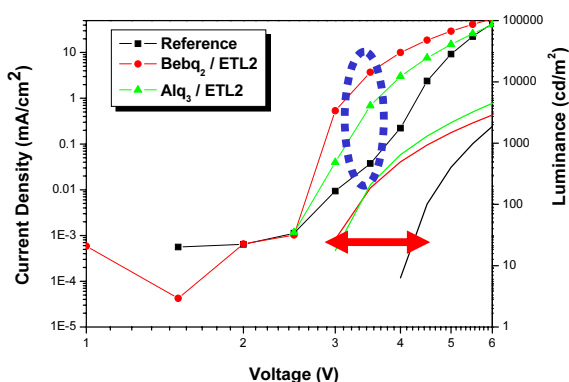
In this work the proposed structure utilizes composite HIL and ETL materials. The difference between those materials and conventional doped transport layers are not only compounds used, but also a doping ratio, which is much higher in our case.

### 3. 1. Injection and Transport

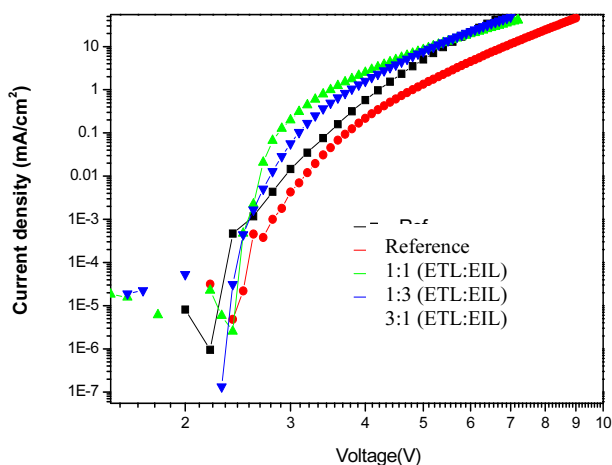
The blue emitting devices fabricated with the proposed structure show power efficiency improved up to 1.8 times compared to reference devices and the current behavior similar to ohmic contact conditions. Conventionally, in OLED fabrication for electron injection and transport a bi-layer, consisting of the single injection and single transport layers respectively is employed. In this case, the electron injection barrier is depended on the EIL and cathode materials (interface dipole). In this work, to realize the efficient and controlled electron transporting structure, the EIL was co-deposited with electron transporting material.

In Figure 1 the current density – voltage – luminance (J-V-L) characteristics of three devices with different ETL structures are compared: the reference device, the devices with the EIL doped ETL on top of Beq2 (a) and on top of  $\text{Alq}_3$  (b). Compared to the reference device, both devices with (a) and (b) exhibit much lower EL onset voltage ( $\Delta V > 1\text{V}$ ), higher current density and luminance at any forward bias voltage. Since the total thickness of the organic layers

is the same and the only difference is the electron transporting structure, the enhanced current density implies that the ETL1/ETL2 structure effectively increase the electron-injection efficiency. Generally, the charge carrier injection is the current limiting factor for OLEDs at low electric fields. Thus, in order to reduce driving voltage and increase efficiency at these conditions, the charge carrier injection must be in-situ ohmic contact and current must become space-charge limited. It can be seen from J-V-L plot that the ETL1 / ETL2 structure indeed makes it possible to achieve the ohmic contact between the metal of the cathode and organics, and SCLC similar to those of inorganic semiconductor characteristics, as well as high luminance at low electric field.



**Fig.1** The current density-voltage-luminance (J-V-L) characteristics for the reference device, the device with the EIL doped ETL on BeBq<sub>2</sub> and Alq<sub>3</sub>.



**Fig.2** The current-voltage characteristic of reference device, the device with the EIL doped ETL

To survey the fundamental effect of EIL doping into ETL, we have used different doping ratio of EIL materials, such as CsF. Figure 2 shows the J-V-L characteristics dependence on ETL structure with EIL doped transport layers. The built-in voltage ( $V_{bi}$ ) for carrier injection is similar for all the devices as shown in Fig.1, but the conductance responsible for the current flow is different and depends on the EIL material doping ratio. This result implies that the composite ETL (ETL2) structure can lead to a better electron injection and thereby the device operating voltage reduction compared to the reference (ETL/EIL) structure. Uniquely, the devices with composite ETL having different doping ratio of EIL show dissimilar I-V behavior as shown in Fig.2

### 3. 2. In-situ electron only device

To analyze the relation between ETL and EIL, we have fabricated the in-situ electron only devices. As shown on Fig.1 and Fig.2, the composite ETL attains the Space charge limited current (SCLC) characteristics. The SCLC model predicts a power-law dependence of the current on the voltage and the thickness  $d$ , with the exponent  $m$  varying with the temperature  $T$ :

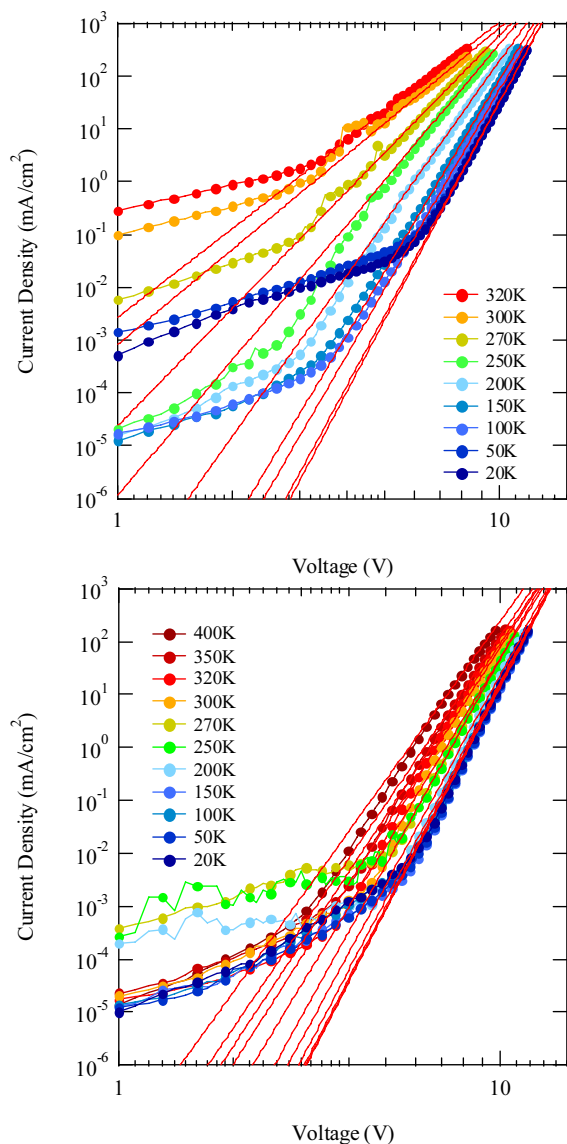
$$I \propto \frac{V^{m+1}}{d^{2m+1}} \quad \text{---- (1)}$$

$$m = \frac{E_t}{k_b T} \quad \text{---- (2)}$$

where  $k_B$  is Boltzmann's constant and  $E_t$  is the characteristic trap energy of the exponential trap in the band gap [7].

It is evident from Figure 3 that composite ETL shows different I-V characteristics from conventional one with temperature changing from 20K to 400K. Such behavior suggests that doping with EIL can significantly affect bulk properties of the ETL material. Generally, the organic semiconductors are characterized by high level of disorder, which causes a large amount of various traps. The trap energy level can be derived from Fig.3. It's higher in composite ETL ( $\sim 0.253\text{eV}$ ) compared to reference device ( $\sim 0.147\text{eV}$ ). Normally, deeper traps result in low carrier mobility, which is typically between  $10^{-3}$  and  $10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$  at room temperature. But, in our case, traps distributed throughout composite ETL in such a manner (gradient profile) that seem to contribute to

easier injection. It still remains to be seen what is the exact mechanism of this phenomenon, but judging from our results not published here, it can be suggested that the dopant makes the electron tunneling much easier.



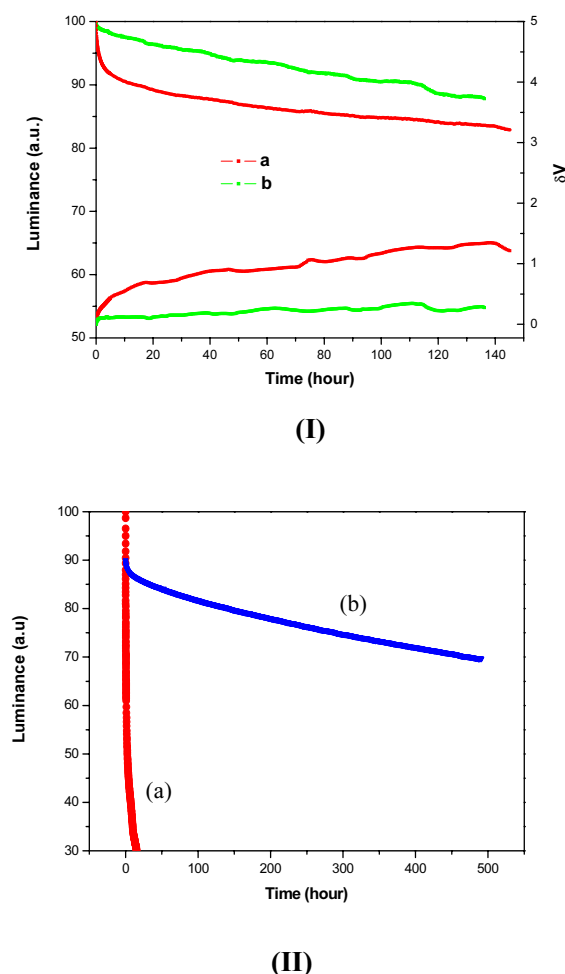
**Fig.3 The I-V characteristics versus Temperature for reference device and composite ETL device**

### 3. 3. Interface and Lifetime

Along with the improving electron control to achieve better carrier balance, in this paper we address the issue of the anode / HIL interface. With the deposition of most of organic materials onto a substrate, a significant amount of structural defects is

being formed on the interface between an electrode and organic layer. These defects could cause the increase of leakage current and charge traps formation, as a result, the luminance could decrease rapidly and the resistance could gradually increase.

Devices containing composite HIL have been fabricated and compared to references with conventional structure. For the constant current (C.C.) driving mode the increasing resistance of a device during its degradation is being compensated by raising driving voltage to keep the current constant. While for the constant voltage (C.V.) driving mode no such compensation is possible. As a result we can collect different data from these two different driving modes. Due to compensation for any damages causing the resistance increase in the C.C. mode, most of the luminance decrease is due to the degradation of the bulk of organic material, whereas in the C.V. mode the damage to the interface is the major contributor.



**Fig.4 The lifetime of devices with reference (a) and composite HIL (b) at room temperature. The**

**devices were driven at C.C (I) at 50 mA/cm<sup>2</sup> and C.V (II) corresponding to initial current of 50mA/cm<sup>2</sup>.**

Figure 4 shows the lifetime measurements in both modes, as well as changes of driving voltage for the C.C. mode. From the C.C. lifetime it is easily can be seen, that except for the initial drop the luminance intensity decrease is very similar for both device types. It is generally believed that initial drop is connected to filling up the trap sites close to the interfacial area. The smaller magnitude of the initial drop in device 2 is consistent with the suggestion of the reduced number of charge traps caused by Metal oxide introduction into the HIL.

Assuming that luminance and current density are directly proportional in our devices, from the C.V. lifetime plot it is noticeable that the resistance increase for the device (b) is much slower then for the device (a), which translates in less rapid luminance decay. This type of behavior is consistent with reduced rate of charge accumulation on the electrode-organic interface that may correspond to lower initial trap density in the device using composite HIL.

#### 4. Summary

The new concept of OLED architecture has been proposed, involving composite HIL and ETL layers. This new structure resulted into great device lifetime improvement (up to 3 times), especially in case of image sticking. It also allowed for the significant increase of the emission efficiency and decrease in operating voltage that adds up to ~30% reduction of the device power consumption. Such improvement of OLED performance came as a result of in-situ ohmic contact formation on cathode / organic interface that led to a better charge balance, and reduction of the initial trap density on the anode / organic interface that resulted in higher device stability.

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