

Use of Self Assembled Monolayer in the Cathode/Organic Interface of Organic Light Emitting Devices for Enhancement of Electron Injection

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Abstract

Self assembled monolayers (SAM) are generally used at the anode/organic interface to enhance the carrier injection in organic light emitting devices, which improves the electroluminescence performance of organic devices. This paper reports the use of SAM of 1-decanethiol ($H-S(CH_2)_9CH_3$) at the cathode/organic interface to enhance the electron injection process for organic light emitting devices. Aluminum (Al), tris-(8-hydroxyquinoline) aluminum (Alq3), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD) and indium-tin-oxide (ITO) were used as bottom cathode, an emitting layer (EML), a hole-transporting layer (HTL) and a top anode, respectively. The results of the capacitance-voltage (C-V), current density -voltage (J-V) and brightness-voltage (B-V), luminance and quantum efficiency measurements show a considerable improvement of the device performance. The dipole moment associated with the SAM layer decreases the electron schottky barrier between the Al and the organic interface, which enhances the electron injection into the organic layer from Al cathode and a considerable improvement of the device performance is observed. The turn-on voltage of the fabricated device with SAM layer was reduced by 6V, the brightness of the device was increased by 5 times and the external quantum efficiency is increased by 0.051%.

1. Introduction

There is a considerable interest in the use of organic as an emitter in multilayer structure of electroluminescence device [1]. In organic electroluminescence devices electrons from cathode and holes from anode are injected into the emitter where they form positively and negatively charged polarons. These polarons form polaron excitons with

an oppositely charged species after migrating under the influence of the applied electric field and subsequently undergo radiative recombination to emit light [2-4]. For best device performance, both the electron and the hole should be injected efficiently.

That is, a small injection barrier height at the cathode/organic interface is required. Monolayer of organic molecules, self assembled on the surface of a semiconductor or a metal electrode can modify the electrochemical potential of the injected carriers. SAMs are used to reduce the schottky barrier at the metal/organic interface and to increase the adhesion of the molecular semiconductor onto the electrode. It is convenient to provide a molecule with an electrical dipole typically from 5 to 15 debye in order to reduce the Schottky barrier and facilitate charge transfer. For increasing the adhesion between the organic and the electrode, the polarizability of both the layers should be matched [5]. Self assembled monolayer is generally used at the anode/organic interface to enhance the carrier injection and to increase the stability in an organic light emitting device. The reduction of pinhole formation at the anode/organic interface and increment of anode work function modify the hole injection barrier height and hence affect the electroluminescence characteristics of the devices [6]. The long term stability can also be improved by more than an order of magnitude in terms of half lifetime when a SAM is inserted. The SAM layer was tailored in such a way the absorbed water could be removed from the electrode surface, the energy barrier height could be lowered and the interfacial reaction could be blocked for the long term stability [7]. Insertion of an insulating layer between the cathode and the organic layer leads to a significant improvement in the current injection and electroluminescence output. The enhancement is due to increased charge carrier density near the TPD/Alq3 interface that results from enhanced electron

tunneling, and removal of exciton-quenching gap states that are intrinsic to the Alq3/Al interface [8-9]. We report the use of self assembled monolayer in the cathode/organic interface in enhancement of electron injection into the organic layer from Al cathode. There is considerable improvement of the turn-on voltage, electroluminescence intensity and external quantum efficiency in comparison to the device without SAM layer.

2. Experiment

Aluminum (Al), tris-(8-hydroxyquinoline) aluminum (Alq3), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD) and ITO were used as a bottom cathode, an emitting layer (EML), a hole-transporting layer (HTL), and an top anode, respectively in the structure of the of the top emission organic light emitting diode (TEOLED). The thickness of Al, Alq3, TPD, and ITO were 100, 48, 32 and 130 nm respectively. The ITO target, housed in a magnetron sputtering gun, was 10% SnO2 and 90% In2O3 by weight with 99% purity. The sputtering gas was 99.999 % pure argon (Ar). The base pressure of the sputtering chamber was 5×10-6 torr. The total pressure during the sputtering process was 6×10-3 torr, with the Ar flow regulated by a mass flow controller at 100 sccm. The r.f sputtering power was 20 W. The sheet resistance of a 100nm thick as-deposited ITO film was 200 Ω/□ which is sufficiently small for making the top electrode. For inserting the

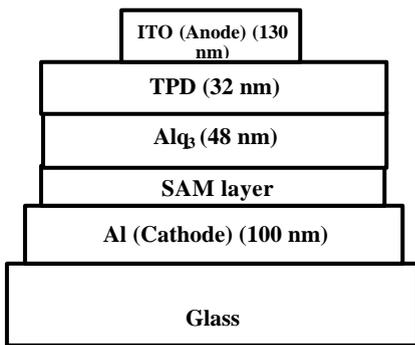


Fig. 1 The Structure of the OLED with SAM

SAM layer on Al substrate, decanethiol was absorbed for ~2 hour from a 0.1 mM solution prepared from ethanol, rinsed thoroughly with ethanol, and blown dried for 30 min in Vacuum. The OLEDs shown in figure 1 were operated in air for all the experiments.

The C-V measurement was done by using LF 4192A Impedance analyzer. A Keithley 2400 electrometer was used for measuring J-V characteristics as a voltage source and current measurement equipment. Brightness was investigated by measuring the photocurrent induced by the light emission for the TEOLEDs using Keithley 485 picoammeter.

3. Results and Discussion

The schottky energy barrier can be manipulated by inserting an oriented dipole layer between the metal and the organic material. Because of the ordering inherent in the SAM structure, the molecular dipoles are oriented relative to the metal surface [10]. We used SAM technique to attach a monolayer of polar molecules to the surface of the Al electrode.

The depletion layer capacitance per unit area is defined as $C = dQ_c/dV$, where Q_c is the incremental increase in charge per unit area upon an incremental change of the applied voltage dV . For one sided abrupt junctions, the capacitance per unit area is given

$$C = \frac{dQ}{dV} = \frac{d(qN_A W)}{d[(q(N_A/2\epsilon\epsilon_0)W^2)]} = \frac{\epsilon\epsilon_0}{W} \dots\dots\dots(1)$$

and the depletion width ,

$$W = \sqrt{\frac{2\epsilon\epsilon_0 V_{bi}}{qN_A}} \dots\dots\dots(2)$$

Where N_A is the ionized traps like acceptors and/or eventual impurities concentrations, V_{bi} is the built in potential, q is the electronic charge, ϵ_0 is the permittivity of free space and ϵ is the relative permittivity of the Alq3 layer. When a reverse bias voltage is applied at the junction the total electrostatic potential variation is given by $(V_{bi} - V)$. Here the depletion width for reverse bias becomes

$$W = \left(\frac{2\epsilon\epsilon_0 (V_{bi} - V)}{qN_A} \right)^{1/2} \dots\dots\dots(3)$$

The relationship between $1/C^2$ and V for an abrupt junction, where we assume that the traps are uniformly distributed in space, is given by

$$\frac{1}{C^2} = 2 \frac{(V_{bi} - V)}{(q\epsilon\epsilon_0 N_A)} \dots\dots\dots(4)$$

So according to equation (4), the Mott-Schottky plot ($1/C^2$ vs. V) for our devices, shows the linear behavior as shown in figure 2.

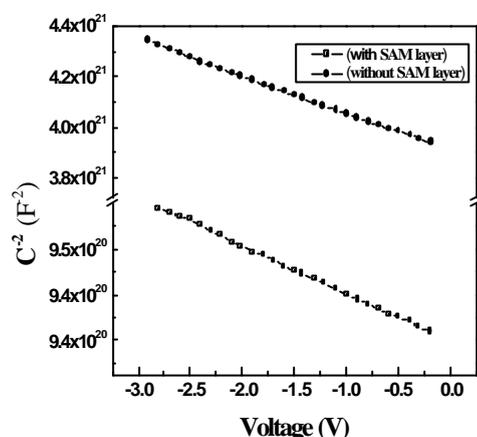


Fig. 2. The $1/C^2$ - V curves associated with the devices with and without SAM layer

Equation (1) shows that depletion layer width is an inversely varying function of capacitance. We see that for the device without SAM layer the capacitance varies from 0.533×10^{-11} F to 1.6×10^{-11} F, whereas for the device with SAM layer the capacitance varies from 13.227×10^{-11} F to 3.265×10^{-11} F for the same voltage level, so in the devices with SAM layer the depletion region width is decreased than that of devices without SAM layer. Again according to equation (2) the built-in potential or the barrier

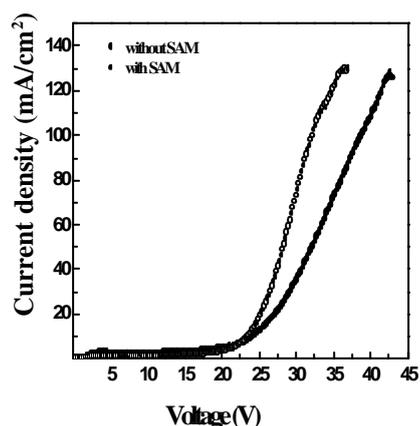


Fig. 3. The J-V characteristics for the devices with and without SAM layer

potential is a linearly varying function of the depletion width, so the barrier potential associated with the Al/organic interface is reduced with the introduction of SAM layer.

Figure 3 shows the J-V characteristics, determined by the transport mechanism in the organic layer, is found to be either injection dominated or bulk dominated, dependent on the nature of the barrier heights at the injection contacts for the devices with and without SAM layer. Tunneling, thermionic emission theories (injection dominated), and ohmic conduction, space charge limited conduction with traps have been proposed for small energetic barriers of injection. The J-V characteristic was measured to find the effect of SAM layer in the performance of the devices. We see that the turn-on voltage is around 22 V for the device without SAM layer, where it is around 16 V for the device with SAM layer. Figure 4 shows the brightness-voltage characteristics of the devices with and without SAM layer. Brightness or luminescence in organic semiconductor occurs via Langevin process of recombination of electron-hole pairs which decay radiatively in the bulk. Holes are injected from positive electrode (ITO) and electrons are injected from negative electrode (Al). Both carrier types move

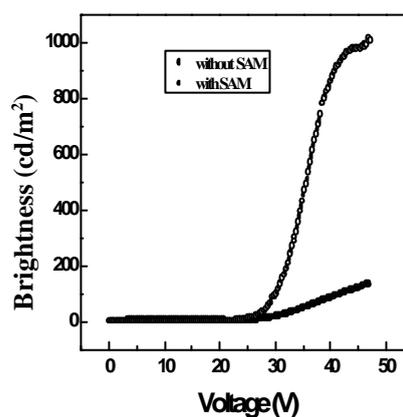


Fig. 4. The Brightness-Voltage characteristics of the devices with and without SAM layer

towards each other to the bulk under the external applied electric field. A brightness of 200 cd/m^2 for the device without SAM layer is noted. But with the insertion of the SAM layer, the brightness increases to 1000 cd/m^2 . The SAM layer shifts the turn-on voltage to a lower value and brightness to a higher value. This is due to reduced barrier height at the Al/organic interface with the insertion of the SAM layer. Figure 5 shows the luminance-voltage characteristics of the devices with and without SAM layer. We see that the maximum luminance efficiency for devices without SAM layer is around 0.026 lm/w , whereas the maximum luminance efficiency is around 0.043 lm/w

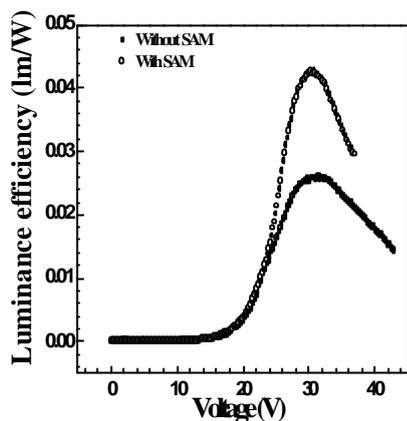


Fig. 5. Luminance efficiency of the devices with and without SAM layer.

for the devices with SAM layer. For the devices with SAM layer, the luminance efficiency is increased by 0.017 lm/w. Figure 6 shows the external quantum efficiency of the devices with and without SAM layer as a function of the applied voltages. The maximum external quantum efficiency for the devices without SAM layer is 0.091%, whereas the external quantum efficiency is increased by 0.051% and reaches to 0.142%, when a SAM layer is used at the cathode/organic interface.

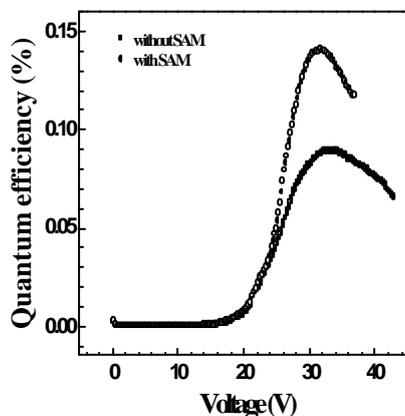


Fig. 6. External quantum efficiency of the devices with and without SAM layer

When the $\text{H-S(CH}_2)_9\text{CH}_3$ forms a monolayer film on the surface of Al, the hydrogen attached to the sulfur is removed and sulfur bonds to the Al. Then the dipole moment associated with the SAM layer decreases the electron schottky barrier between the Al and the organic interface. As a result, the devices with

SAM layer showed increased current, brightness, luminance and external quantum efficiency.

4. Conclusion

We see the enhancement of electron injection in organic electronic devices due to the improvement of the cathode/organic interface property by inserting the SAM layer in the cathode/organic interface. Due to the insertion of the SAM layer at the cathode/organic interface, the barrier height at the cathode/organic interface is reduced. The reduction of barrier height is mainly due to the dipole moment associated with the SAM layer. The results of the capacitance-voltage (C-V), current density -voltage (J-V) and brightness-voltage (B-V) measurements show a considerable improvement of the device performance. The turn-on voltage of the devices with SAM layer was reduced by 6 V, the brightness is increased by 5 times and the external quantum efficiency is increased by 0.051%..

7. References

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