IUG Journal of Natural and Engineering Studies
Peer-reviewed Journal of Islamic University-Gaza

ISSN 2409-4587

IUGNES
Vol 24, No 1, 2016, pp 54-59

The Influence of Thin Layer Copper Phthalocyanine on the Performance of PVK/ Rhodamine B Device

Taher M. El-Agez[1], Mohammed S. Al-Qrinawi[1], Monzir S. Abdel-Latif[2], Sofyan A. Taya[1,*]

[1]Department of Physics, Faculty of Science, Islamic University of Gaza, Gaza Strip, Palestine

1Department of Chemistry, Faculty of Science, Islamic University of Gaza, Gaza Strip, Palestine Palestine

Received on (05-08-2015) Accepted on (14-12-2015)

Abstract

In this paper, the influence of copper-phthalocyanine (CuPc) hole-injection layer on the current voltage characteristic and the electroluminescence performance of ITO/CuPc/PVK/ Rhodamine B/Pb devices was investigated. The characteristics were measured at room temperature and without glove box with a thickness variation of CuPc layer. The results showed that the turn-on voltage of the devices can be dramatically lowered by inserting the CuPc layer.

Keywords OLED, Copper-Phthalocyanine, J-V Curves, Electroluminescence.

تأثير طبقة Copper-Phthalocyanine على ثنائي عضوي باعث للضوء ذو التركيب PVK/Rhodamine B

ملخص

تم دراسة تأثير طبقة copper-phthalocyanine (CuPc) التي تعتبر كطبقة مزودة للشحنات الموجبة على ثنائي عضوي باعث للضوء ذو التركيب التالي ITO/CuPc/PVK/Rhodamine B/Pb من خلال دراسة منحنيات التيار مع الجهد. أخذت القياسات في درجة حرارة الغرفة، كما وقد تركزت الدراسة على تغير سمك طبقة CuPc وكانت النتيجة أن جهد العتبة للعينات تقل تدريجياً مع زيادة سمك طبقة CuPc.

كلمات مفتاحية: ثنائي عضوي باعث للضوء، فثالوسيانين النحاس، منحنيات التيار–الجهد، الإضاءة الكهربية.

---

* Corresponding author e-mail address: staya@iugaza.edu.ps

1. Introduction:

Organic light-emitting diodes (OLEDs) are currently considered as promising candidates for large-area, full-color, flat-panel displays due to their prominent advantages such as ease in fabrication and convenience of use in applications. An extensive research has been made to improve device structures and understand their operating mechanisms. In OLEDs, three major physical processes exist: (i) charge injection and transport, (ii) charge recombination and excitons energy transfer, and (iii) light emission. Each of these processes plays an important role in such factors as the turn-on voltage, external quantum efficiency and luminance of OLEDs.

In 1963, Prop et.al studied electroluminescence in anthracene using very thick fabricated devices (up to 5mm) and very high voltages (400 – 2000V) and their devices were not commercialized. Tang and Van Slyke (1987) created the first multilayer organic cell using small Alq_3 molecule as a green emitter and diamine as a hole transport layer (HTL) [1]. In this device, they used a transparent indium tin oxide (ITO) as an anode and Mg:Ag as a cathode. This device was the first accepted one in OLED industry due to its low threshold-voltage, quantum efficiency of 1% photon/electron and luminance of about 1000 cd/m^2.

Recently, large development in OLED industry has been conducted. These developments not only involve the improvement of processing technology, but also understanding of the device physics and synthesis of new organic material. The basic current structure of OLED has a high work function conducting transparent anode, one or more organic layer and low work function cathode. Most OLEDs use ITO as an anode due to its relatively high work function and high transparency (90%) to visible light. The band gap of ITO is in the range (E_g = 3.5 – 4.3 eV) and it consists of indium oxide (In_2O_3) and small amount of tin oxide (SnO_2).

Another important parameter is it's work function (Φ_0) or Fermi energy level (E_F) relative to the organic materials, because the highest occupied molecular orbital (HOMO) energies of organic material that inject holes to organic layer are typically $E_{HOMO} = 5 – 6$ eV. A high Φ_0 is needed for anode to have more efficient OLEDs. The injection efficiency is a critical parameter that depends largely, on the work function of the electrode and the alignment of energy levels of the organic layer. The potential barrier between indium tin oxide (ITO) and the organic layer severely limits the efficiency of hole injection. On other hand, a low work function of the cathode is required to allow a lot of electrons to inject into the organic layer for more efficient OLEDs.

Transient electroluminescence from single- and multilayer OLEDs was investigated by driving the devices with short, rectangular voltage pulses [2]. The performance of OLED devices was shown to be improved by introducing a thin layer of copper phthalocyanine (CuPc) between the anode and the hole-transport layer [3]. The effect of thickness variation of hole injection and hole blocking layers on the performance of fluorescent green organic light emitting diodes (OLEDs) was investigated [4]. Emission properties of OLEDs were investigated with the use of a hole-injection layer of copper(II)-phthalocyanine (CuPc) [5].

In 2006, Po-Ching Kao et at. studied the influence of the metal-phthalocyanine (MPcs) hole-injection layer on the electroluminescence performance of ITO/ MPc/ Alq3/ Al devices [6]. They found that the turn-on voltage (Vt) is lowered by inserting MPc layers and remains virtually the same as the MPc layer thickness is adjusted in the range of 5-15nm. In addition, the turn-on voltage decreases significantly with the increase of the HOMO levels of the MPc films.

Poly(9-vinylcarbazole) (PVK) is a well-known polymer with interesting properties. Its excellent electrical properties combined with its chemical and thermal resistance make it useful in the electronics industry.

In this work, we report the effect of CuPc hole-injection layer with different thicknesses on the electrical characteristics, such as the turn-on voltage, maximum current, and luminescence of ITO/ PVK/ Rhodamine B /Pb OLEDs.

2. Experiment:

ITO-coated glass substrates (Delta Technologies, USA) were cut into pieces of dimension 2.5cm × 2.5cm and used as anode electrodes. The substrates were chemically cleaned using acetone, isopropanol and distilled water in an ultrasonic cleaner. After the chemical cleaning, the ITO glasses were dried by heating at 60 °C for 24 hours.

In this work, two types of OLED devices were fabricated. The first is a double layer with the structure ITO/ PVK/ Rhodamine B/ Pb as shown in Fig. 1. 15mg of PVK powder with an average molecular weight of 11×10^5 were weighed using a sensitive electrical balance (ESJ182-4) with a resolution of 10^{-4} gm. The PVK was dissolved in mixed solvents consisting of 5ml tetrahydrofuran (THF) and 1ml toluene. A homogenous solution was then deposited on the ITO substrate to form a thin film with thickness of about 45 nm. The thickness was measured using FILMETRICS F20-UVX thin-film analyzer. Filmetrics analyzer works on the principle of light reflection from a surface. When a thin film is deposited on the top of substrate, both the top and the bottom of the film reflect light. The total amount of reflected light is the sum of these two individual reflections. Constructive interference occurs when the light path is equal to one integral multiple of the wavelength of light $2nd=m\lambda$, where d is the thickness of the film, m is an integer, n is refractive index, and λ is the wavelength of the reflected light. On the other hand, destructive interference takes place when $2nd=(m+1/2)\lambda$. The cumulative overall uncertainties in the reported thicknesses were about 6% for all devices.

The thin film of PVK was obtained by placing a small amount of desired solution on the substrate. The substrate was inclined at an angle of 45° for several minutes. The solution spreads on the surface of the substrate due to gravity forming a thin film on the surface. This process is sensitive to the variation in temperature due to different evaporation rate of solvents [7]. A 30nm Rhodamine B layer was then deposited on the PVK layer by thermal vacuum deposition at 1.0×10^{-5} torr using MiniLab 080 system made by Moorfield Associates, UK. Finally, 35nm Pb was deposited as a cathode electrode on Rhodamine B layer. The negative terminal of the applied voltage was connected to the Pb electrode through a drop of Hg.

The second device is a multilayer having the structure ITO/ CuPc/ PVK/ Rhodamine B/ Pb as shown in Fig.2. After cleaning the ITO surface, CuPc layers were deposited by thermal vacuum evaporation at 1.0×10^{-5} torr. PVK and Rhodamine B layers were deposited on the CuPc layer as described above in the first device. Evaporation rates and film thicknesses of CuPc, Rhodamine B, and Pb materials were determined by a quartz crystal monitor through thermal vacuum evaporation process.

The aim of this work is to reduce the hole injection barrier (ΔE_h) of the device by adding a CuPc layer as a hole injection layer (HIL) with different thicknesses (5nm, 10nm, 30nm, and 50nm).

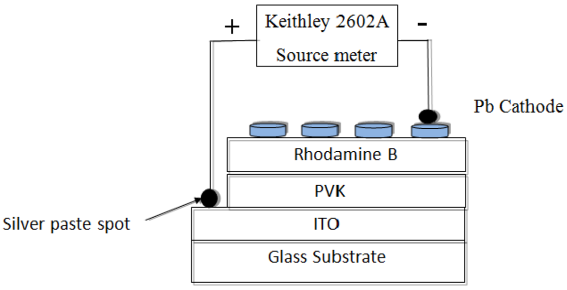

Figure 1 *Schematic drawing of a double-layer ITO/PVK/Rhodamine B/Pb OLED*

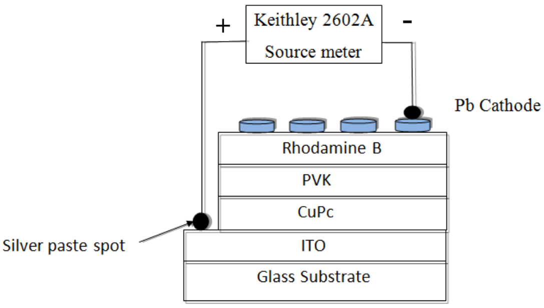

Figure 2 *Schematic drawing of a multilayer ITO/ CuPc/PVK/Rhodamine B/Pb OLED*

The voltage-current signals were applied and recorded through a Keithley 2602A source meter Electrical measurements were carried out at room temperature and normal ambient conditions. The relative light intensity emitted from the samples was measured using a photodiode. The output of the photodiode was amplified then collected by the Keithley 2602A source meter.

3. Results and Discussion:

Figures 3 and 4 show the current density-voltage (J-V) and electroluminescence -voltage curves of the double layer OLED device with the structure ITO/ 45nm PVK/ 30nm Rhodamine B/ 35nm Pb. The currents flowing through the samples are attributed to the injection of charges from the metallic electrode. The turn-on voltage (V_t) of this device is about 7.84±0.190 volt from the J-V curve. As can be seen from Fig. 4, the voltage at which the light is detected is about 14±0.190 volt.

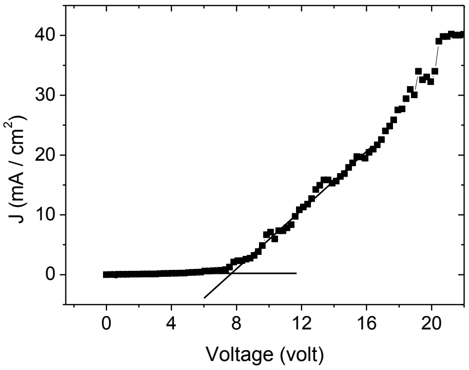

Figure 3 *Current density- voltage characteristic curve of the device consisting of ITO/45nm PVK/ 30nm Rhodamine B/ 35nm Pb*

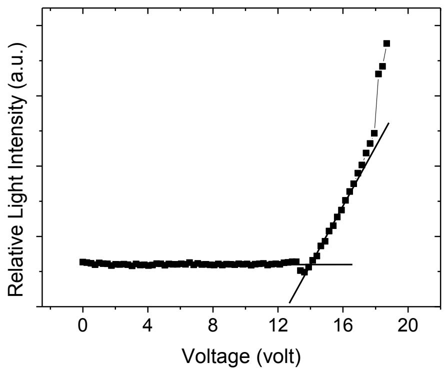

Figure 4 *Relative light intensity-voltage characteristic curve of the device consisting of ITO/45nm PVK/ 30nm Rhodamine B/ 35nm Pb*

The energy level diagram of the double-layer device is shown in Fig. 5. The barrier to hole injection at the anode is obtained by the equation $\Delta E_h = IP - \Phi_A$ where Φ_A is work function of anode and IP is the ionization potential or HOMO level relative to the anode. We find that $\Delta E_h = -1$eV. As shown in Fig. 6, the hole injection barrier (ΔE_h) of the device in the presence of the CuPc layer is about ($\Delta E_h \sim$ -0.4 eV).

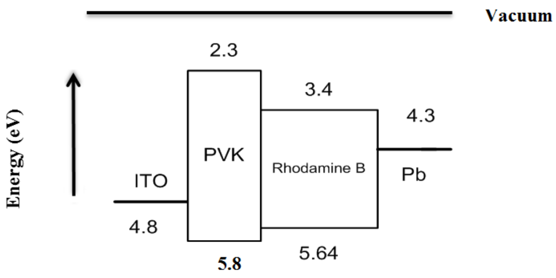

Figure 5 *Energy level diagram for the device consisting of ITO/PVK/ Rhodamine B/ Pb. (all listed energies are negative values (eV), with respect to vacuum)*

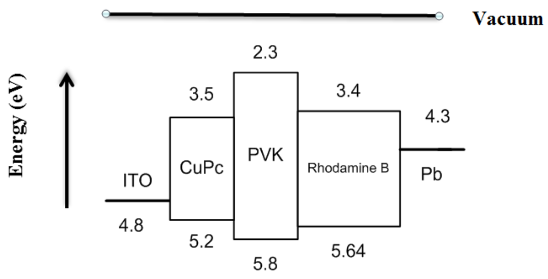

Figure 6 *Energy level diagram for the device consisting of ITO/ CuPc/ PVK/ Rhodamine B/Pb. . (all listed energies are negative values (eV), with respect to vacuum).*

Figures 7, 8, 9 and 10 illustrate the J-V characteristic curves for OLED devices with different CuPc layer thicknesses under forward bias. All figures show almost the same behavior of J as a function of V. The forward J-V curves have two regions, a low-current region with weak voltage dependence and a high-current region with a steeper current rise as a function of the voltage. Compared to the double layer device in which the turn-on voltage was 7.84±0.190V, it is obvious that the insertion of the CuPc layer reduces significantly the turn-on voltage. Figure 7 shows that the turn-on voltage is 7.48±0.75V for a thickness of 50 nm of the CuPc layer. Figures 8 and 9 show that the turn-on voltages are 5.56±0.69V and 1.43±0.52V for a CuPc layer thickness of 30 nm and 10 nm where it is about 1.00±.011 volt for the 5 nm CuPc layer thickness, as shown in Fig. 10.

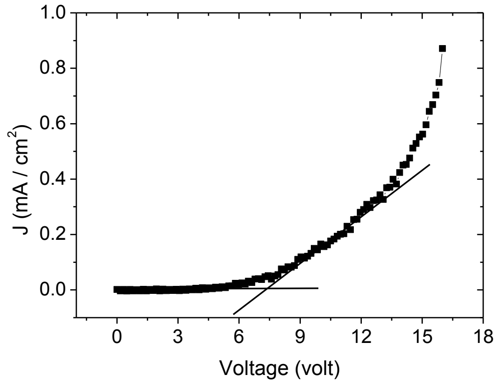

Figure 7 *Current density- voltage characteristic curve of the device consisting of ITO/ 50nm CuPc/ 45nm PVK/ 30nm Rhodamine B/ 35nm Pb.*

As can be clearly seen, the turn-on voltage decreases as the CuPc film thickness decreases. The reduction in turn-on voltage can be attributed to a decrease in the hole-injection barriers between CuPc and PVK. This is because the HOMO level of CuPc is between that of PVK and the Fermi level of the ITO anode. When the CuPc film is sandwiched between the PVK layer and ITO anode, a ladder effect makes it easier for holes to inject into the organic material which in turn leads to enhanced hole injection. It was reported that the decrease in the overall barrier height to hole injection depends weakly on the CuPc film thickness [6]. On the other hand, it seems that the injected holes are the dominant charge carriers because the hole injection barrier is smaller than the electron injection barrier. Injection of electrons from the cathode into the organic layer is smaller compared to injection of holes from the anode into the organic layer (figure 6). Therefore, this makes the device increasingly single carrier "hole-only". The current in the device is controlled, almost exclusively, by the holes [8].

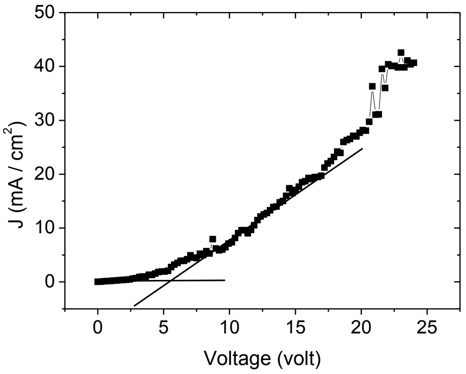

Figure 8 *Current density- voltage characteristic curve of the device consisting of ITO/ 30nm CuPc/ 45nm PVK/ 30nm Rhodamine B/ 35nm Pb*

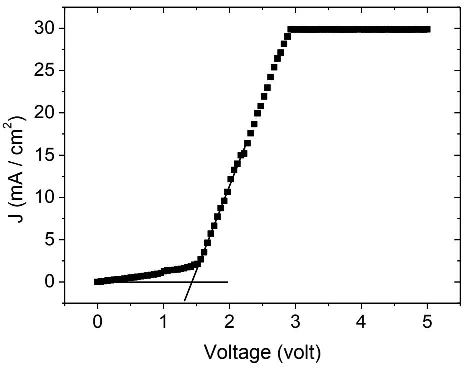

Figure 9 *Current density- voltage characteristic curve of the device consisting of ITO / 10nm CuPc/ 45nm PVK/ 30nm Rhodamine B/ 35nm Pb*

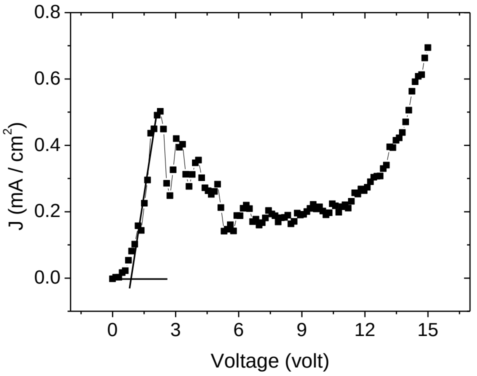

Figure 10 *Current density- voltage characteristic curve of the device consisting of ITO/ 5nm CuPc/ 45nm PVK/ 30nm Rhodamine B/ 35nm Pb*

When the thickness of CuPc film was 5nm, negative differential resistance (NDR) characteristics were observed at a low voltage region. Present understanding of NDR in molecular system is not definitely clear. Several models have been found in the literature [9]. In all figures, V_t was determined when the current density starts increasing. In Fig. 10, negative resistance region appeares so V_t was determined at the first increase of current density.

The turn-on voltage and maximum current density for different CuPc film thickness devices are listed in Table 1. The maximum current was recorded just before the device damage occurred. It is worth mentioning that the current density has an optimum CuPc film thickness at which the current density is maximum. For thickness beyond the optimum one, another conduction mechanism appears. Similar results for optimum CuPc film thickness were also reported [3,4]. Increasing the thickness leads to morphological changes in CuPc film, and other parameters like ionization potential, electron affinity, and transport parameter will also change. Moreover, possible oxygen diffusion from ITO surface into CuPc layer may have a leader effect on the charge mobility.

It should be mentioned that no luminescence was detected in the devices containing CuPc as HIL layer. This may suggest that there is an easier route for electron injection other than that for the LUMO level of Rhodamine B dye. It is expected that using a polymer, with a low-lying LUMO, instead of the organic material could cause light emission because the turn-on voltage of such a polymer light emitting diode should be smaller than that of OLED device.

Table 1 *V_t and maximum current density for OLED devices with different CuPc layer thickness.*

Thicknes of CuPc (nm)	**0 nm**	**5 nm**	**10 nm**	**30 nm**	**50 nm**
V_t (Volt)	7.84± 0.190	1.00± 0.011	1.43± 0.052	5.56± 0.69	7.48± 0.75
J_{max} (mA/cm^2)	39.92± 0.382	0.69± 0.023	29.87± 0.02	40.39± 0.64	0.87± 0.01

Conclusion:

In this work, two types of OLED devices were fabricated. The first was a double layer with the structure ITO/ PVK/ Rhodamine B/Pb and the second device was a multilayer with the structure ITO/ CuPc/ PVK/ Rhodamine B/Pb. The J-V characteristics and electroluminescence-voltage curves of the double layer OLED were investigated and the turn-on voltage of this device was determined to be 7.8 volt. The effect of CuPc hole-injection layer on the J-V characteristics and the electroluminescence performance of ITO/ CuPc/ PVK/ Rhodamine B/Pb devices was investigated. The results showed that the turn-on voltage of the devices can be dramatically lowered by inserting the CuPc layer. On the other hand, no luminescence was detected in these devices.

Acknowledgement:

The authors would like to express gratitude to the ministry of higher education (scientific research council) for the financial support of this work.

References:

[1] Tang, C., and VanSlyke, S. Organic Electroluminescent Diodes. *Appl. Phys. Lett.*, ***51(12)***, (1987) 913-915.

[2] Barth, S., ller, P., Riel, H., Seidler, P., and Rieß, W. Electron Mobility in Tris(8-hydroxy-quinoline) Aluminum Thin Films Determined via Transient Electroluminescence from Single- And Multilayer Organic Light-Emitting Diodes. *J. Appl. Phys.*, ***89(7)***, (2001) 3711- 3719.

[3] Tadayyon, S., Grandin, H., Griffiths, K., Norton, P., Aziz, H., and Popovic, Z. CuPc Buffer Layer Role in OLED Performance: A Study of the Interfacial Band Energies. *Organic Electronics*, ***5(4)***, (2004) 157–166.

[4] Narayan, K., Varadharajaperumal, S., Mohan Rao, G., Manoj Varma, M., and Srinivas, T. Effect of Thickness Variation of Hole Injection And Hole Blocking Layers on the Performance of Fluorescent Green Organic Light Emitting Diodes. *Current Appl. Phys.* ***13(1)***, (2013) 18-25.

[5] Lee, J., Lee, W., and Kim, T. Electroluminescent Properties of Organic Light-Emitting Diodes with Hole-Injection Layer of CuPc. *Transections on electrical and electronic materials*, ***15(1)***, (2014) 41-44.

[6] Kao, P., Chu, S., Liu, S., You, Z., and Chuang, C. Improved Performance of Organic Light-Emitting Diode Using a Metal-Phthalocyanine Hole-Injection Layer. *Journal of The Electrochemical Society*, ***153(6)***, (2006) H122-H126.

[7] El-Agez, T., Taya, S., El Tayyan, A., Abdel-Latif, M., and Afghjani, A. Electroluminescence from Single PVK Layer Organic Light Emitting Diode Using Different Dyes at Different Concentrations. *Physical Review & Research International*, ***3(4)***, (2013) 306-320.

[8] Shrotriya, V., and Yang, Y. Capacitance-Voltage Characterization of Polymer Light-Emitting Diodes. *J. Appl. Phys.*, ***97(5)***, (2005) 054504.

[9] Kratochvilova, I., Kocirik, M., Zambova, A., Mbindyo, J., Mallouk, T., and Mayer T. Room Temperature Negative Differential Resistance in Molecular Nanowires. *J. materials chemistry,* ***12(10)***, (2002) 2927-2930.