Efficient Organic Light-emitting Diodes using Hole-injection Buffer Layer

Dong Hoe Chung[a], Sang Keol Kim[a], Joon Yng Lee[a], Jin Woong Hong[a], Hyun Nam Cho[b], Young Sik Kim[b], and Tae Wan Kim[b]

Abstract

We have investigated the effects of hole-injection buffer layer in organic light-emitting diodes using copper phthalocyanine (CuPc), poly(vinylcarbazole)(PVK), and Poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) in a device structure of ITO/buffer/TPD/Alq_3/Al. Polymer PVK and PEDOT:PSS buffer layer were produced using the spin casting method where as the CuPc layer was produced using thermal evaporation. Current-voltage characteristics, luminance-voltage characteristics and efficiency of device were measured at room temperature at various a thickness of the buffer layer. We observed an improvement in the external quantum efficiency by a factor of two, four, and two and half when the CuPc, PVK, and PEDOT:PSS buffer layer were used, respectively. The enhancement of the efficiency is assumed to be attributed to the improved balance of holes and elelctrons resulting from the use of hole-injection buffer layer. The CuPc and PEDOT:PSS layer function as a hole-injection supporter and the PVK layer as a hole-blocking one.

Keywords : organic light-emitting diodes, buffer layer, efficiency.

1. Introduction

For vapor-deposited organic light-emitting diodes, the best performing devices are usually bilayer structures, in which a hole-transport layer is used to transport holes and an electron-transport layer to transport electrons. By optimizing electron and hole mobility and placing recombination zone away from electrode, we can produce efficient organic light-emitting diodes at low turn-on voltage[1].

It is desirable to improve the operational stability. The current for applications in information displays. Operational stability is insufficient with the fundamental bilayer structure[2]. A contact problem between the hole transport layer and indium-tin-oxide (ITO) anode can be considered as one of the causes for degradation. In order to enhance the performance of the organic light-emitting diodes, some organic materials have been adopted for hole-injection buffer layer inserted between ITO anode and the emissive layer. The buffer layer was used to improve the performance of organic light-emitting diodes in several aspects, such as a good mechanical contact, energy-band adjustment, suppressing noisy leakage current, reducing the operating voltage, and enhancing the thermal stability and quantum efficiency. However, a unique buffer layer that can efficiently provide all the above mentioned functions is yet to be found.

There is a report that the CuPc buffer layer in organic light-emitting diodes improves the electrical stability and life time of the organic light-emitting diodes based on Alq_3 thin films[3]. The CuPc layer prevents the organic light-emitting diodes from deteriorating the organics as well as the electrode layers[4]. Polymeric anodes, such as polyaniline and PEDOT:PSS have been proven to be successful in spite of the smaller conductivity than that of ITO[5]. The ITO/PEDOT:PSS combination has given the most promising results,

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Corresponding Author : Sang Keol Kim
a. Department of ElectricalEngineering, Kwangwoon University 447-1, Wolgye-dong, Nowon-gu, Seoul 139-701, Korea
b. Electronic Materials and Devices Research Center, KIST, P.O.Box 131, Chenongyang, Seoul, Korea
E-mail : okaysk@hanmail.net **Tel** : +2 320-1626 **Fax** : +2 3142-0335

yielding an increase in device efficiency and lifespan and reduction in the operating voltage[6]. Poly (vinylcarbazole) (PVK) is a non-conjugated polymer, but shows good conductive and photo-conductive properties due to a close packing of the conjugated chromophores pendant from the olefinic chain[7]. For this reason, a considerable application in electrophotography has focused on the use as a hole-injection layer at various of organic light-emitting diodes[8,9].

In this paper, we report the effects of CuPc, PVK and PEDOT:PSS hole-injection buffer layer in organic light-emitting diodes based on TPD/Alq_3 thin film by investigating current-voltage characteristics, luminance-voltage characteristics and the efficiency of the device.

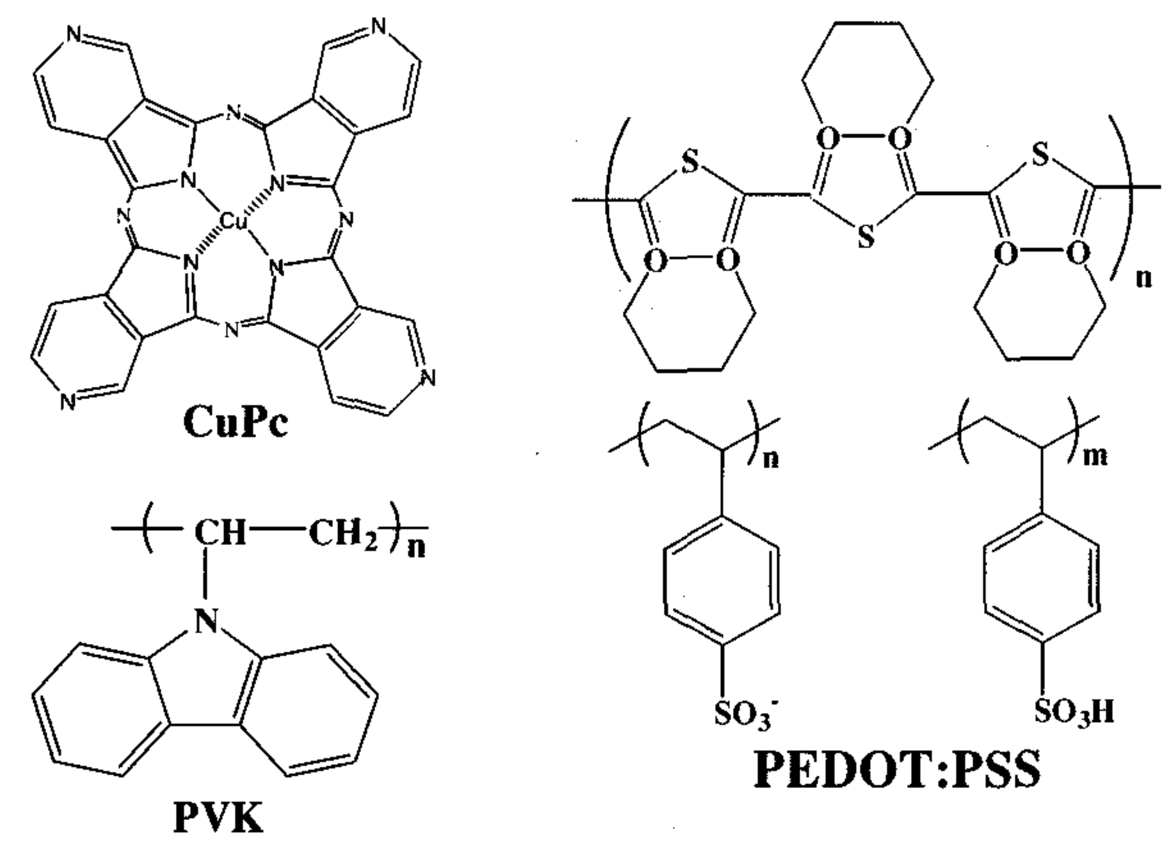

Fig. 1. Molecular structures of organic material CuPc, PVK, PEDOT:PSS used as a buffer layer.

2. Experiments

The ITO glass, having a sheet resistance of 15 Ω/□ and 170nm thick, was received from Samsung Corning Co. A 5mm wide ITO strip line was made by selective etching in vapor of solution by mixing with hydrochloric acid(HCl) and nitric acid(HNO_3) at a volume ratio of 3:1 for 10~20 minutes at room temperature. The distance between the ITO and etchant was about 2 cm. Then, the patterned ITO glass was cleaned by sonicating it in chloroform for 20 minutes at 50 °C, after which the ITO glass was heated at 80 °C for 1 hour in solution made with second distilled deionized water, ammonia water and hydrogen peroxide at a volume ratio of 5:1:1. We sonicated the substrate again in chloroform solution for 20 minutes at 50 °C and in deionized water for 20 minutes at 50 °C. After sonication, the substrate was dried with N_2 gas stream and was stored under vacuum.

We used N,N′-diphenyl-N,N′-bis(3-methylphenyl)-,1′-biphenyl-4,4′-diamine (TPD) as a hole-transport and 8-hydroxyquinoline aluminum (Alq_3) as an electron transport and emissive material. The TPD was purchased from TCI and used as received. The Alq_3 was also purchased from the same company and used after purification.

Two device structures were made; one is ITO/TPD/Alq_3/Al as a reference, while the other is ITO/buffer/TPD/Alq_3/Al to be used to investigate the effects of buffer layer. Fig. 1 shows the molecular structures of CuPc, PVK and PEDOT:PSS that are used as a buffer layer.

A 0.1 wt%(1mg/cc) PVK solution was produced with a solvent of dichloro ethane($ClCH_2CH_2Cl$). Polymer PVK and PEDOT:PSS buffer layer was fabricated onto pre-cleaned ITO by static spin-casting method in the range of 2000 ~ 6000 rpm using photoresist spinner of Headway Research Inc. And then, the organic materials were successively evaporated under 10^{-6} torr at a rate of about 0.5~1 Å/s.

The film thickness of CuPc was made to be 5, 15, 25, 35 nm, and that of TPD and Alq_3 were 40 nm and 60 nm, respectively. Al cathode(150nm) was deposited at 1.0×10^{-5} torr. Light-emitting area was defined using a shadow mask to be 0.3×0.5 cm^2. To obtain reliable data, the reference device ITO/TPD/Alq_3/Al was fabricated simultaneously when the new device with buffer layer was made.

Current-voltage characteristics and luminance-voltage characteristics of OLEDs were measured using Keithley 236 source-measure unit, 617 electrometer and Si-photodiode. All these units are computer-controlled using Test point software. The efficiency was calculated based on the luminance, EL spectrum and current densities.

3. Results and Discussion

Figs. 2(a) and 2(b) show the current-voltage and luminance-voltage characteristics of ITO/CuPc/TPD/Alq_3/Al devices with a thickness variation of CuPc layer from 5 to 35 nm. As the voltage increases, the current density and the luminance also increase as well. As seen in the figure, the current density and the corresponding

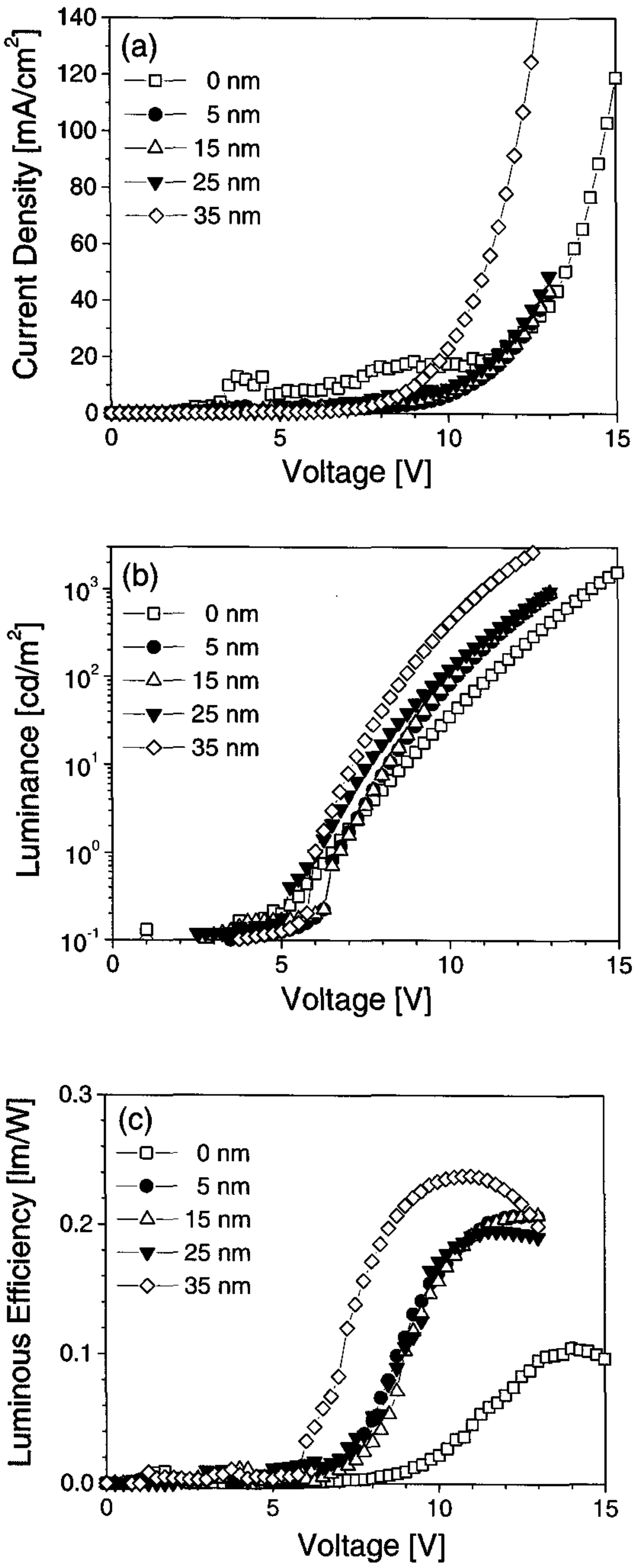

Fig. 2. (a) Current density, (b) luminance, and (c) luminous efficiency, as a function of voltage in ITO/CuPc/TPD/Alq_3/Al devices.

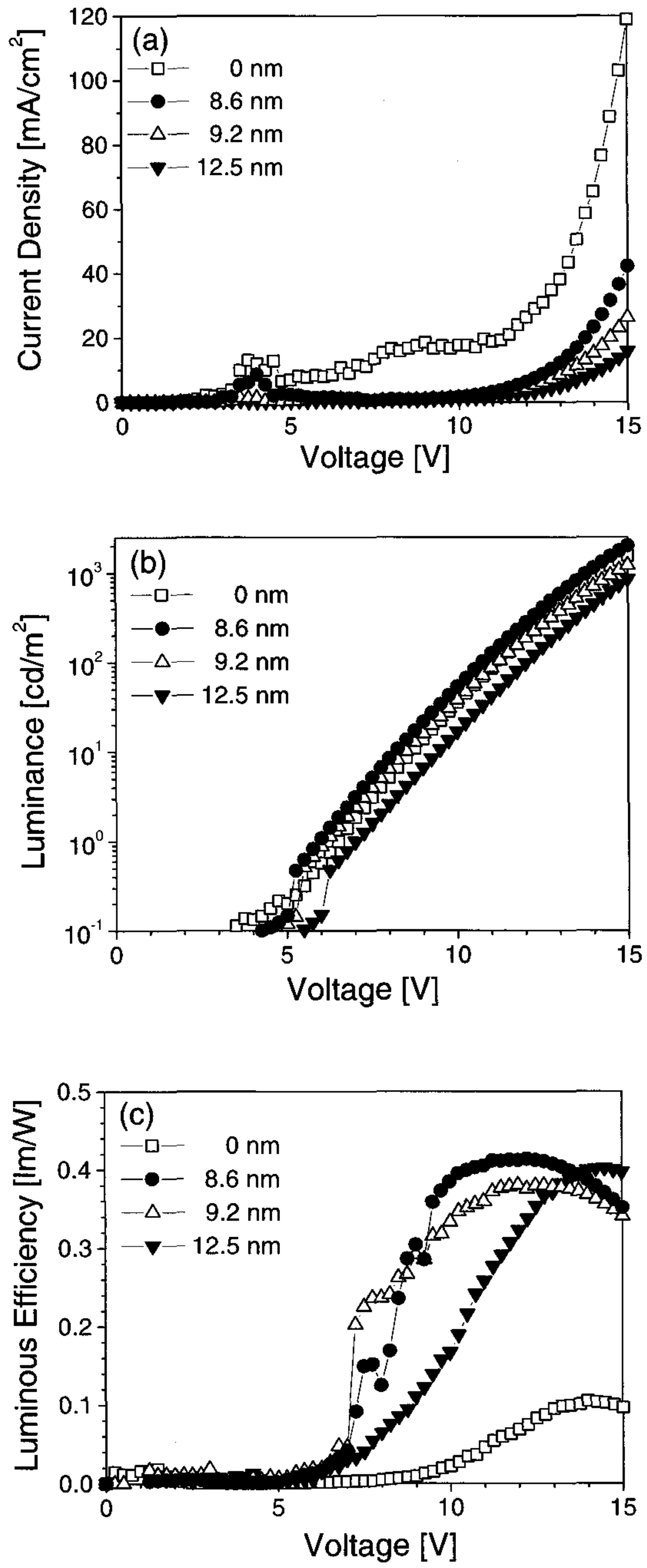

Fig. 3. (a) Current density, (b) luminance, and (c) luminous efficiency, as a function of voltage in ITO/PVK/TPD/Alq_3/Al devices.

luminance increase as the thickness of CuPc layer increases. To investingtate the effects of the electrical current on luminance, the luminous efficiency of device was calculated using Figs. 2(a) and 2(b). Fig. 2(c) shows the luminous efficiency as a function of voltage when the CuPc buffer layer is used. The luminous efficiency starts to increase from 5 V and reaches a maximum at almost 10 V.

Compared to that of reference device, there is a reduction of operating voltage and an improvement of efficiency by a factor of two. Since the barrier-height in anode between ITO and CuPc is reduced to 0.5 eV compared to ITO/TPD barrier height(0.7 eV), the CuPc layer allows more holes to be injected into the emissive layer. As the CuPc layer thickness becomes thicker, the emitted light intensity becomes stronger. However, it was found that there was not much variation in efficiency in the film thickness range that was used.

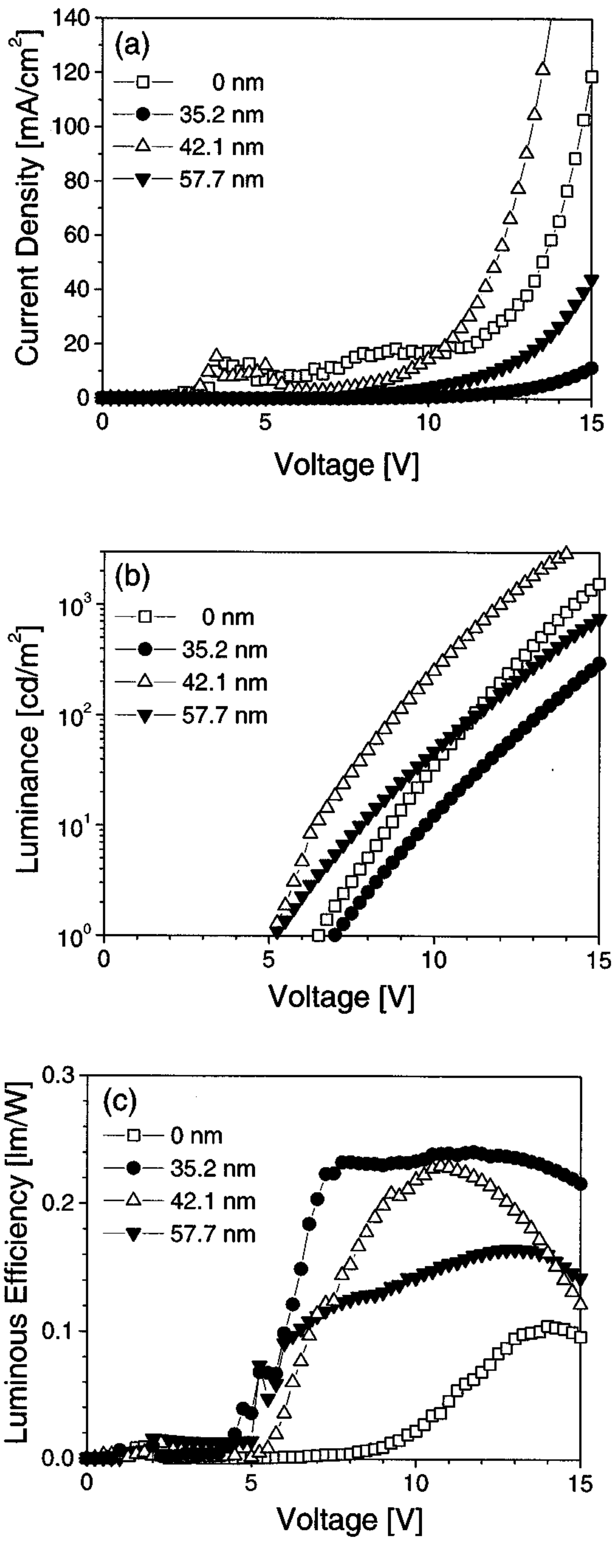

Fig. 4. (a) Current density, (b) luminance, (c) luminous efficiency, and (d) external quantum efficiency as a function of voltage in ITO/PEDOT:PSS/TPD/Alq_3/Al devices.

Fig. 3(a) shows typical nonlinear current-voltage characteristics of ITO/TPD/Alq_3/Al(reference) and ITO/PVK/TPD/Alq_3/Al devices for several different thickness of PVK layer, such as 8.6, 9.2, and 12.5 nm. Fig. 3(b) is a corresponding luminance of device depending on the applied voltage. As the voltage increases to over 5 V, the current density and the luminance started to increase rapidly, resulting in a light emission. In general, as the thickness of PVK layer increases, the current density and the corresponding luminance decrease. These results suggest that the PVK layer functions as a hole-blocking.

Fig. 3(c) shows the luminous efficiency as a function of applied voltage. The maximum luminous efficiency of reference device is 0.1 lm/W. However, the devices with PVK buffer layer show a maximum luminous efficiency of 0.42 lm/W. This is an improvement of efficiency by a factor of four. In reference device, the luminous efficiency increased gradually and reached a maximum near 14 V. However, when the thickness of PVK layer was 8.6 and 9.2 nm, the luminous efficiency increased rapidly near 6 and 7 V and be came saturated over a relatively wide voltage range.

Fig. 4(a) and 4(b) are current-voltage and luminance-voltage characteristics in ITO/PEDOT: PSS/TPD/Alq_3/Al devices, which were measured in the same way as in Fig. 2. Fig. 4(c) shows that the device with PEDOT:PSS layer not only improves of efficiency but also reduces the operating voltage as well. The efficiency data shows that there is a turn-on voltage near 5 V. The way efficiency suddenly increase at around 5 V is similar to that of PVK device, as shown in Fig. 3.

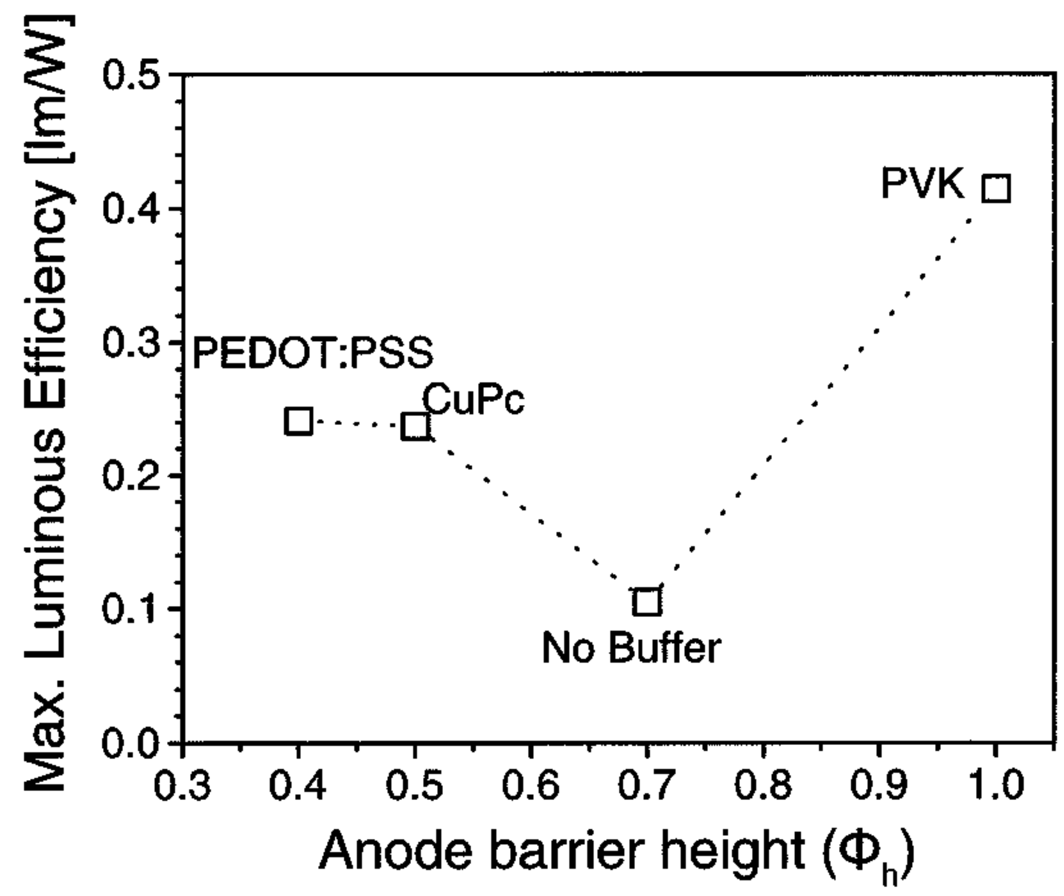

Fig. 5. Maximum luminous efficiency as a function of anode barrier height with Al cathode fixed.

Fig. 5 shows the maximum luminous efficiency in the device structure of anode/buffer/TPD/ Alq3/ cathode depending on the anode energy barrier height between the anode and buffer layer. As shown in the figure, depending on the anode barrier rib height, the maximum luminous efficiency is about four times higher than the minimum one.

4. Conclusions

We fabricated the efficient OLEDs using the CuPc, PVK, and PEDOT:PSS buffer layer in a device structure of ITO/buffer/TPD/Alq_3/Al. By using the PVK buffer layer, the luminous efficiency of device was improved by a factor of four. Also, we were able to successfully improve the luminous efficiency by a factor of two when the CuPc buffer layer was used. Such improvement in performance could be achieved by using the buffer layer that functions as either a hole-blocking or hole-injection supportive layer. The PEDOT:PSS layer not only improves efficiency by a factor two, but reduces an operating voltages as well. We were able to understand, in theory, the enhancement of device efficiency using the energy-level diagram. Based on own finding in this study, we plan to study further on how the buffer layer affects on the stability of the device.

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