Efficient Organic Light-Emitting Diodes with a use of Hole-injection Buffer Layer

Sang Keol Kim[a], Dong Hoe Chung[a], Taek Gyun Chung[b], and Tae Wan Kim[c]

[a]Department of Electrical Engineering, Kwangwoon University, Seoul 139-701, Korea

[b]Vistorm Co., Seongnam 463-816, Korea

[c]Deptartment of Physics, Hongik University, Seoul 121-791, Korea

Phone : +82-2-320-1626, E-mail : okaysk@hanmail.net

Abstract

We have seen the effects of hole-injection buffer layer in organic light-emitting diodes using copper phthalocyanine(CuPc), poly(vinylcarbazole)(PVK), and Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate)(PEDOT:PSS) in a device structure of ITO/ buffer/TPD/Alq_3/Al. Polymer PVK and PEDOT:PSS buffer layer was made using spin casting method and the CuPc layer was made using thermal evaporation. Current-voltage characteristics, luminance-voltage characteristics and efficiency of device were measured at room temperature with a thickness variation of buffer layer. We have obtained an improvement of the external quantum efficiency by a factor of two, four, and two and half when the CuPc, PVK, and PEDOT:PSS buffer layer are used, respectively. The enhancement of the efficiency is attributed to the improved balance of holes and elelctrons due to the use of hole-injection buffer layer. The CuPc and PEDOT:PSS layer functions as a hole-injection supporter and the PVK layer as a hole-blocking one.

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 making recombination zone away from electrode, we can make efficient organic light-emitting diodes with low turn-on voltage[1].

Essential improvement of the operational stability is desired for applications in information displays. Operational stability is insufficient with the fundamental bilayer structure[2]. A contact problem between hole transport layer and Indium-tin-oxide (ITO) anode can be considered as one of the causes of degradation. In order to enhance the organic light-emitting diodes performance, some organic materials are adopted for hole-injection buffer layer inserted between ITO anode and the emissive layer. The buffer layer is 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 provides 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 proved to be successful in spite of smaller conductivity than that of ITO[5]. The ITO/PEDOT:PSS combination has given the most promising results yielding an increase in device efficiency and lifetime and a reduction in the operating voltage[6]. Poly(vinylcarbazole) (PVK) is a non-conjugated polymer, but shows good conductive and photo-conductive properties due to the close packing of the conjugated chromophores pendant from the olefinic chain[7]. For this reason it was found a considerable application in electrophotography, while more recent work has focused on the use as a hole-injection layer in a variety 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.

2. Experimental

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

We have used N,N′-diphenyl-N,N′-bis(3-methylphe-nyl)-1,1′-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 it as received. And the Alq_3 was also purchased from the same company and used it after purification. Two device structures were made; one is ITO/TPD/Alq_3/Al as a reference and the other is ITO/buffer/TPD/Alq_3/Al to investigate the effects of buffer layer. Figure 1 shows the molecular structures of CuPc, PVK and PEDOT:PSS that are used as buffer layer.

A 0.1wt%(1mg/cc) PVK solution was made with a solvent of dichloroethane($ClCH_2CH_2Cl$). 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 photo-resist spinner of Headway Research Inc. And then the organic materials were successively evaporated under 10^{-6} torr with a rate of about 0.5~1Å/s.

The film thickness of CuPc was made to be 5, 15, 25, 35nm, and that of TPD and Alq_3 is 40nm and 60nm, 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 have reliable data, the reference device ITO/TPD/Alq_3/Al was made at the same time whenever 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.

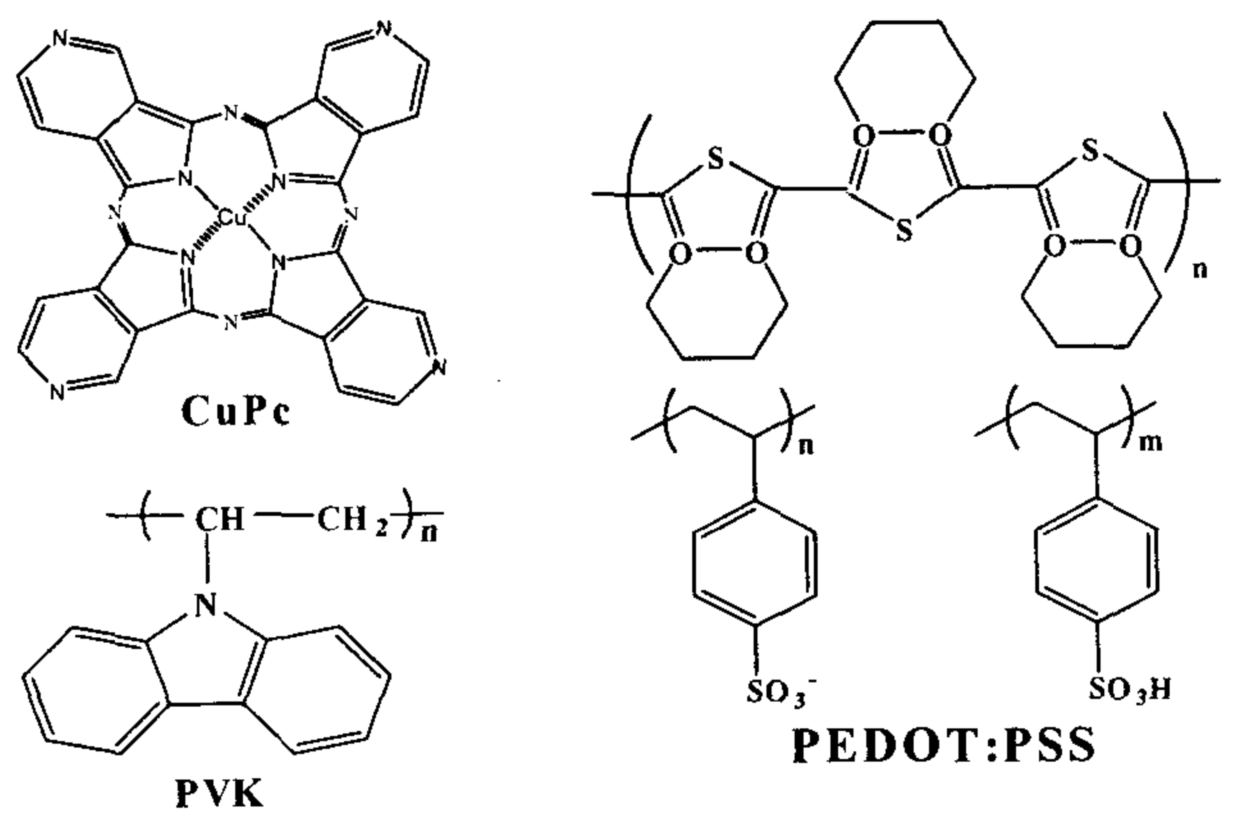

Figure 1 Molecular structure of organic material CuPc, PVK, PEDOT:PSS used as a buffer layer.

3. Results and discussion

Figure 2(a) and 2(b) show the current-voltage and luminance-voltage characteristics of ITO/CuPc/TPD/Alq_3/Al devices with a variation of CuPc layer thickness from 5 to 35nm. 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 luminance increase as the thickness of CuPc layer increases. To see how the electrical current affects on the luminance, the luminous efficiency of device was calculated using Figs. 2(a) and 2(b). Figure 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 5V and becomes a maximum near 10V. 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 0.5eV compared to ITO/TPD barrier height(0.7eV), the CuPc layer helps more holes to be injected into the emissive layer. As the CuPc layer thickness becomes thicker, the emitted light intensity becomes stronger. However, there is not much variation in efficiency in the film thickness range that we used.

Figure 3(a) shows typical nonlinear current-voltage characteristics of ITO/TPD/Alq_3/Al(reference) and ITO/PVK/TPD/Alq_3/Al devices with several different thickness of PVK layer such as 8.6, 9.2, and 12.5nm. Figure 3(b) is a corresponding luminance of device depending on the applied voltage. As the voltage

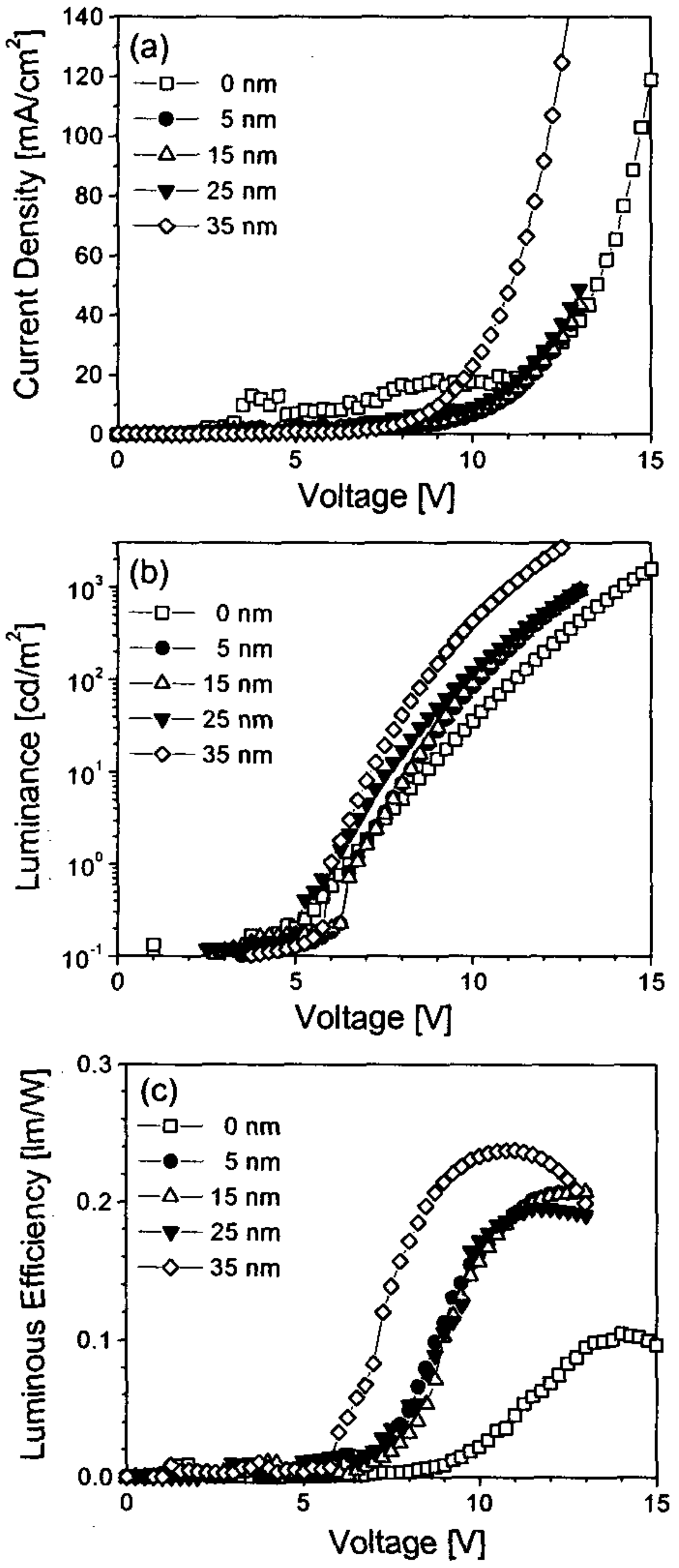

Figure 2 (a) Current density, (b) luminance, and (c) luminous efficiency, as a function of voltage in ITO/CuPc/TPD/Alq_3/Al devices.

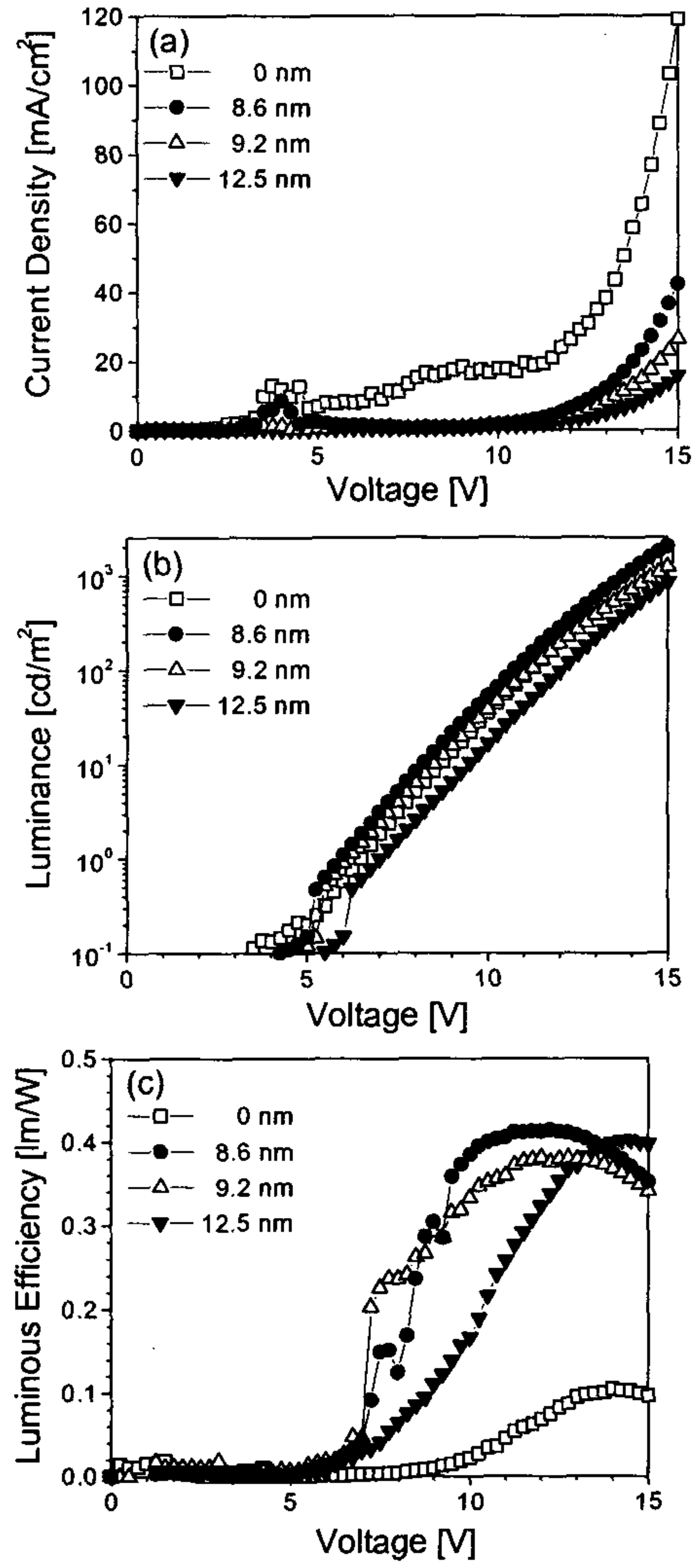

Figure 3 (a) Current density, (b) luminance, and (c) luminous efficiency as a function of voltage in ITO/PVK/TPD/Alq_3/Al devices.

increases above 5V, the current density and the luminance start to increase rapidly and there occurs 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.

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

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

Figure 5 shows the luminous efficiency in the device structure of anode/buffer/TPD/Alq_3/cathode depending on the anode energy barrier height between

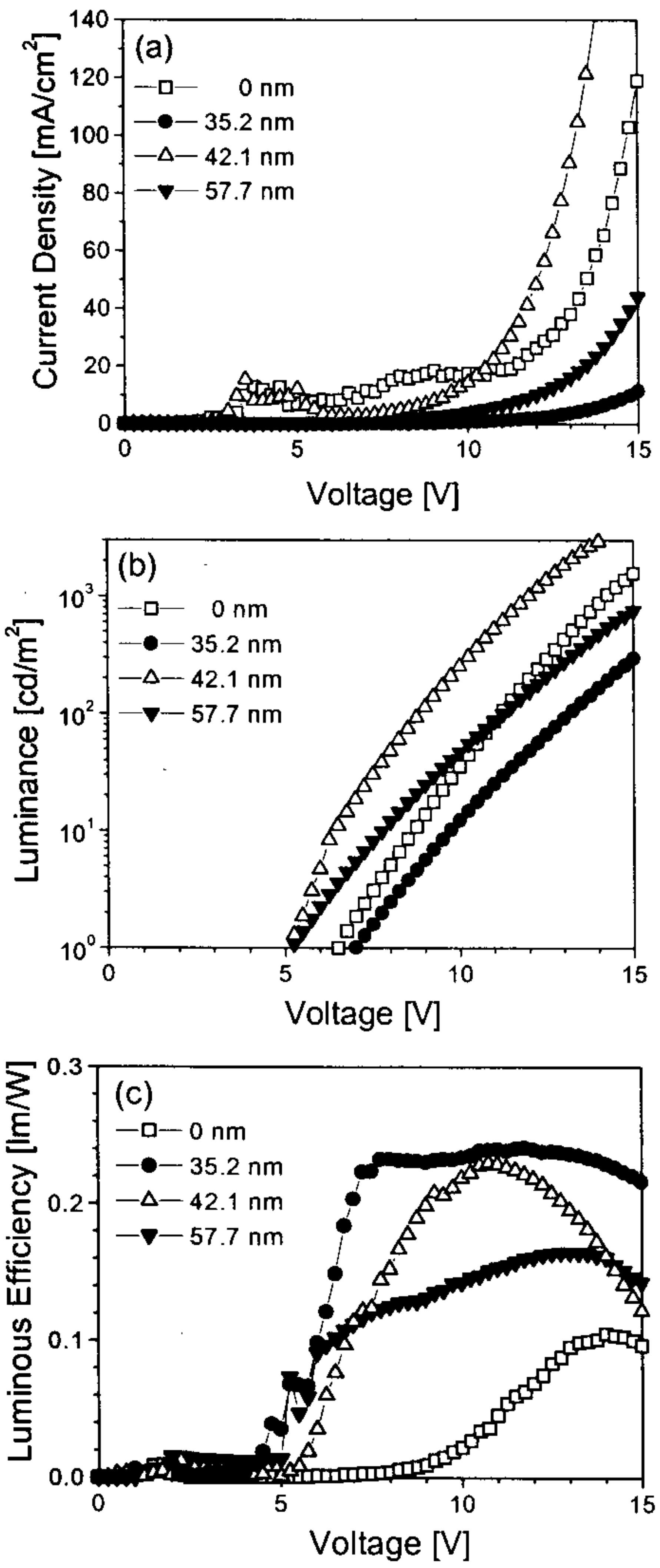

Figure 4 (a) Current density, (b) luminance, and (c) luminous efficiency as a function of voltage in ITO/PEDOT:PSS/TPD/Alq_3/Al devices.

the anode and buffer layer. As shown in the figure, the maximum luminous efficiency is about four times higher than the minimum one depending on the anode barrier height.

4. Conclusion

We have 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 has improved by a factor of four.

Also, we have obtained an improvement of the luminous efficiency by a factor of two when the CuPc buffer layer is used. This improvement of performance

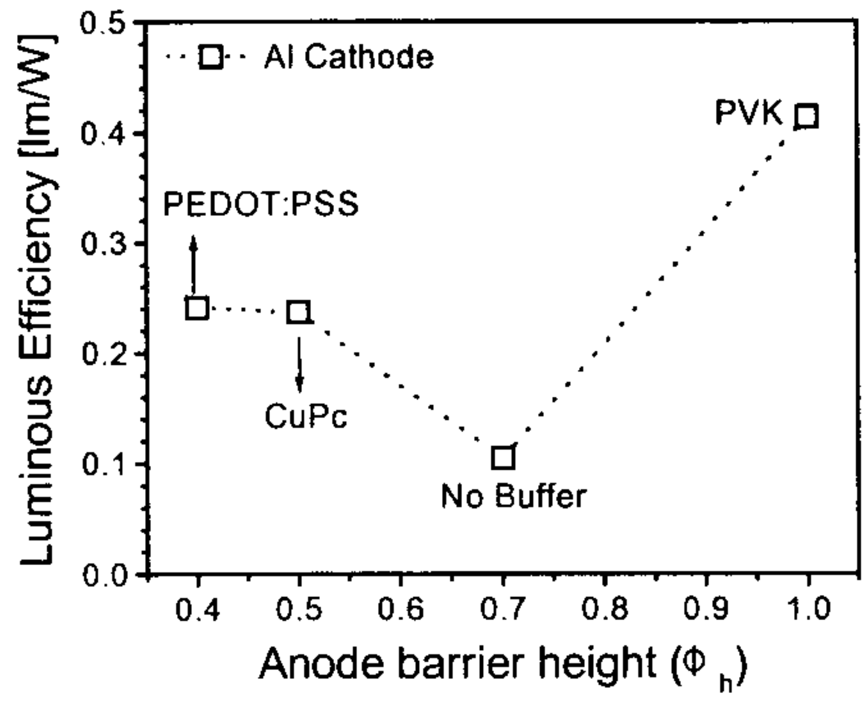

Figure 5 Luminous efficiency as a function of anode barrier height with Al cathode fixed.

could be achieved by using the buffer layer which works as either hole-blocking or hole-injection supportive layer. The PEDOT:PSS layer not only gives an improvement of efficiency by a factor two, but reduces an operating voltages as well. We were, in principle, able to understand the enhancement of device efficiency using the energy-level diagram. We are going to study further how the buffer layer affects on the stability of the device.

Acknowledgement

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