

Characteristic Effects of Buffer Layers on Organic Light Emitting Devices

Jae-Hoon Park, Yong-Soo Lee, Yun-Hee Kwak and Jong-Sun Choi

Abstract - The stability and efficiency of organic light emitting devices are the most critical problems to be solved. The devices based on tris-8-(hydroxyquinoline) aluminum (Alq_3) and N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-biphenyl-4,4-diamine (TPD) were used to study the effects of buffer layers on their characteristics. We have investigated the characteristic effects of CuPc (copper phthalocyanine) and pentacene buffer layers on the device performances with varying the buffer layer thickness. In order to study the effects of the buffer layers on the device characteristics, the (5~20 nm thick) CuPc layers and the (10~20 nm thick) pentacene layers were deposited. Efficiency was slightly improved and the turn-on voltages of the devices with the buffer layers were observed to have lower values than those of the devices without the buffer layers. It is believed that this result is attributed to the improvement of hole injection capability through the buffer layers into hole transport layer (HTL). We have also studied the atomic force microscopic images of the TPD layers deposited on the buffer layer and the bare ITO.

Keywords - organic light emitting diode, buffer layer, CuPc, Pentacene, AFM

1. Introduction

Since the first report of highly efficient electroluminescence (EL) from an organic hetero-junction light-emitting diode (LED) by C. W. Tang and S. A. VanSlyke, organic light emitting devices (OLEDs) have shown remarkable progress in efficiency and stability to meet the commercial demands for flat panel displays [1,2]. Devices based on tris-8-(hydroxyquinoline) aluminum (Alq_3) and N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-biphenyl-4,4-diamine (TPD) were fabricated. Device characteristics can be enhanced by interposing a buffer layer on the indium-tin-oxide (ITO) anode [3]. It has been suggested by other workers that the CuPc buffer layer lowers the turn-on voltages of OLEDs by reducing the effective barrier between ITO and (N, N'-Di (naphthalen-1-yl)-N, N'-diphenyl-benzidine (NPB) hole-transporting layers [4,5]. Using ultraviolet photoemission spectroscopy, the ionization potential for the thin CuPc layer was determined to have a value of 5.3 eV [6,7], and 4.99 eV for the thin pentacene layer measured by cyclic voltametry. From these results, the highest occupied molecular orbital (HOMO) of CuPc and pentacene might be expected to align energetically between the Fermi level of ITO and the estimated HOMO level of TPD, thereby enhancing hole injection from the

effective anode. Conversely, other researchers have shown that relatively thick CuPc layers would in fact reduce the rate of hole injection from the ITO anode leading to the better balance with the electrons arriving from the cathode to the recombination zone [8,9]. From the point of device performances, it is one of the critical problems to maintain the proper population balance between holes and electrons, because excess holes in the Alq_3 layer would create an unstable cation population leading to a rapid degradation in the device performance.

In addition to changing the energetic alignment of the layers for OLEDs, the inserted buffer layers can affect the growth modes for the subsequent organic layers [3]. As a result, the TPD film can be deposited in a highly ordered structure. (c.f. TPD molecules grow in island-like structures during the initial film formation on a relatively rough ITO substrate [10].)

In this article, we present the characteristic effects of buffer layers on OLED's operational properties. Different buffer materials (CuPc and pentacene) were used here in order to investigate the effects of the buffer materials on the device performances. We also varied the thickness of the buffer layers for the investigation of the effects according to their thickness. In order to observe structural characteristics, we employed the conventional atomic force microscopy (AFM) measurement.

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2. Experimental

The device structure is schematically shown in Fig.

1(a). Glass substrates pre-coated with a 100 nm thick layer of ITO ($20 \Omega/\square$) were ultrasonicated. Organic layers were deposited in the following sequence: CuPc or pentacene buffer layers were deposited (5, 10, 15 and 20 nm thickness for CuPc buffer layers, and 10 and 20 nm thickness for pentacene buffer layers, respectively) and then, 50 nm thick TPD and 50 nm thick Alq₃ were deposited as the hole-transporting and electron-transporting layers under the base pressure of 1.6×10^{-6} Torr. A 150 nm thick Al layer was deposited as the cathode under the same pressure. The molecular structures used here are shown in Fig. 1(b).

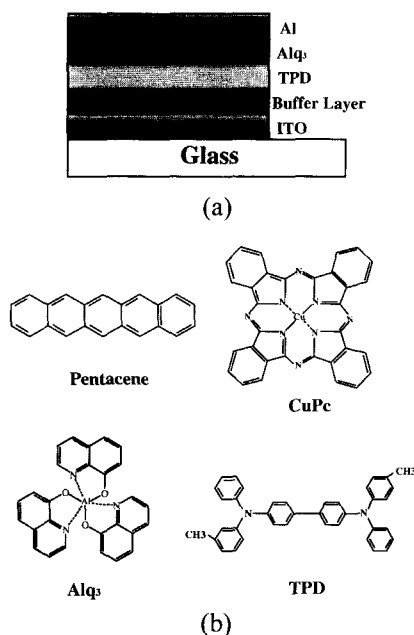


Fig. 1 (a) OLE Device configuration. (b) Molecular structures of the materials.

ITO has a work function of around 4.8 eV, while TPD has a value of 5.4 eV (HOMO level). The HOMO level of the buffer materials should be positioned between the Fermi level of the anode and the HOMO level of the subsequent organic material to enhance hole injection from the anode. CuPc and pentacene are used as the buffer materials, since CuPc has a work function of 5.3 eV (HOMO level) [6,7] and pentacene 4.99 eV (HOMO level), which were measured by the cyclic voltametry measurement. Fig. 2

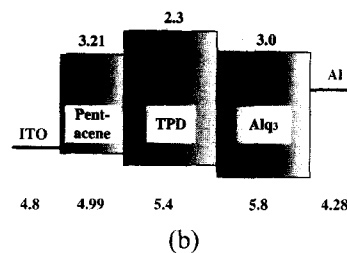
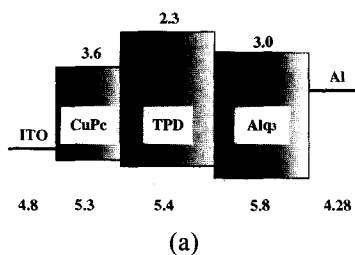


Fig. 2 Schematic energy-level diagrams of the devices with (a) CuPc and (b) pentacene buffer layers.

shows the energy-level diagrams of the fabricated devices.

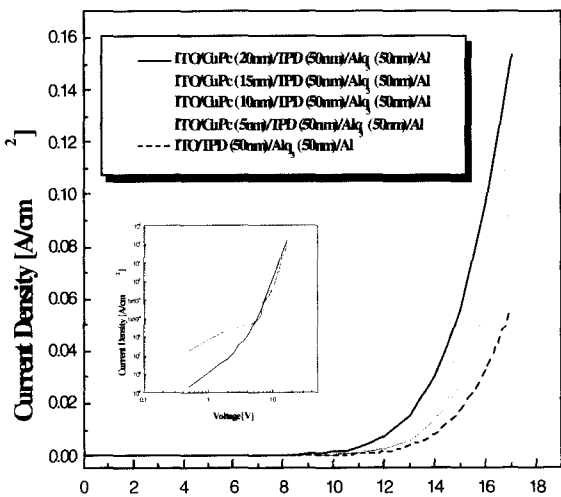
J-V characteristics were measured using a Keithley 238 Electrometer in order to investigate the effects of the buffer layers on the device characteristics according to the buffer materials and their thickness. We calculated the luminance efficiency of each device [lm/W] using a Keithley 238 Electrometer and a Minolta Chromameter. We observed electro-luminescence (EL) at different applied voltages using an LS50B (Perkin Elmer). Using atomic force microscopy (AFM), we also observed the influence of the buffer layers on the surface properties of the TPD layers.

3. Results and Discussion

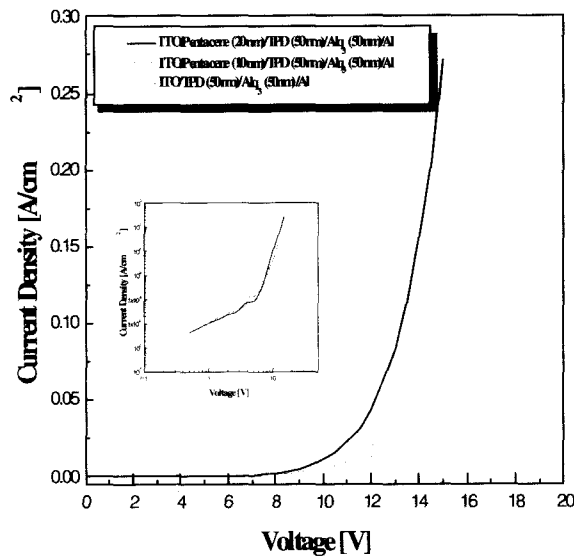
Fig. 3 shows the J-V characteristics of the devices with the buffer layers in comparison with the device without the buffer layer. The inclusion of buffer layers has only a modest effect on the efficiency of the device as long as these layers are sufficiently thin (below 20 nm) [3]. In order to investigate the dependence of the OLED performances on the buffer layer thickness, the buffer materials were thermally deposited in 5, 10, 15 and 20 nm thickness for CuPc layers, and 10 and 20 nm thickness for pentacene layers. In the device with the 20 nm thick CuPc buffer layer, the turn-on voltage was measured as 4.00 V. Comparing with the values of 4.80, 4.85 and 5.80 V for the devices with the 15, 10 and 5 nm thick CuPc buffer layers, respectively and 6.00 V for the device without the buffer layer, it is considered that the optimum thickness of the CuPc buffer layer is 20 nm for the improvement of the device characteristics (see the inset of Fig. 3(a)). Similarly, in the device with the 20 nm thick pentacene buffer layer, the turn-on voltage was measured as 4.30 V. This is the lowest value, compared with the values of 5.4 V for the device with the 10 nm thick pentacene buffer layer and 6.3 V for the device without the buffer layer. Therefore, it is also considered that the optimum thickness of the pentacene buffer layer is 20 nm for the improvement of the device characteristics (see the

inset of Fig. 3(b)).

Due to the mismatch between the work function of ITO (4.8 eV) and the ionization potential of TPD (5.4 eV) [3], an injection barrier is formed at the ITO/TPD interface. The observed advantage of the buffer layer over the bare ITO is that the effective hole injection barrier can be reduced by the formation of energy barrier, between ITO and TPD (see Fig. 2), which results in enhanced hole injection efficiency. Thus, it is expected that the reduced turn-on voltage of the device with the buffer layer would be originated from the enhanced hole injection capability.



(a)



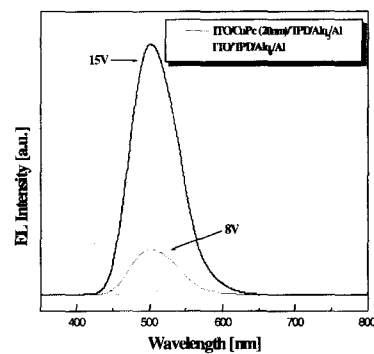
(b)

Fig. 3 J-V characteristics of (a) CuPc and (b) pentacene buffer layer devices.

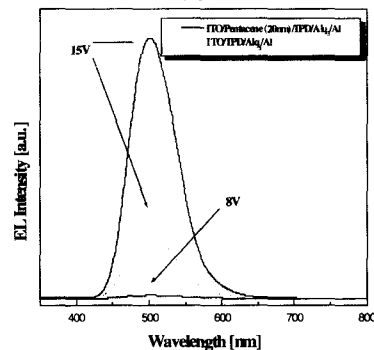
Fig. 4(a) shows the relative EL intensities of the device with the 20 nm thick CuPc buffer layer and the device without the buffer layer. There was no shift

in EL peaks and any other shoulder was not observed, which means that the deposited CuPc layer did not influence the luminance. The EL intensity of the devices with the 20 nm thick CuPc buffer layer was measured higher than that of the device without the buffer layer. This means that the hole injection efficiency from the ITO anode was improved through the lowered interfacial energy barrier (ITO/CuPc/TPD, see Fig. 2). This improvement of the hole injection gave rise to the increased hole density near the emission region and allowed the electron-hole pairs to be much more generated in the emission layer, which led to the increased EL intensity. Similar results were also observed in the devices with the 5, 10, and 15 nm thick CuPc buffer layer. Fig. 4(b) shows the relative EL intensities of the device with the 20 nm thick pentacene buffer layer and the device without the buffer layer. There was no shift in EL peaks and any other shoulder was not observed in the device with the pentacene buffer layer, which indicates that the deposited pentacene layer does not influence the luminance. Similar result was also observed in the devices with the 10 nm thick pentacene buffer layer.

Therefore, we could confirm that the insertion of the buffer layer (CuPc and pentacene) results in the increased electroluminescence (EL) intensity, while the used buffer materials do not emit light itself.



(a)



(b)

Fig. 4 EL spectra of the devices with the 20 nm thick (a) CuPc and (b) pentacene buffer layer compared with the devices without buffer layer.

In addition, the buffer layer over-coated on ITO anodes plays a significant role in controlling the growth modes of the subsequent TPD organic layers [9]. Organic molecules of CuPc and pentacene grow in highly ordered structures independent of substrate lattice matching [10]. Fig. 5(a) illustrates the AFM image for the surface state of the as-received ITO. The average area roughness, R_a is 6.7 Å and the rms area roughness, R_{rms} is 9.7 Å. The surface state of the ITO substrate looks like islands. Fig. 5(b) illustrates the AFM image of the surface state of the TPD layer deposited on the bare as-received ITO electrode. The surface state of the TPD layer were directly influenced by the surface state of the ITO substrate ($R_a = 108\text{Å}$, $R_{rms} = 157\text{Å}$). Therefore, the deposited TPD film grows in the island shape on the bare ITO electrode and forms spike which leads to dark spots. Fig. 5(c) and Fig. 5(d) illustrate the AFM images of the surface states of the TPD layers deposited onto ITO/CuPc (20 nm) ($R_a = 35\text{Å}$, $R_{rms} = 45\text{Å}$) and ITO/pentacene (20 nm) ($R_a = 135\text{Å}$, $R_{rms} = 108\text{Å}$). The subsequent TPD film is now deposited on the buffer layers and shows improved roughness, compared with the island-like growth observed for the TPD molecules deposited onto the bare ITO substrate. It is expected that the device life-time would be enhanced because of the reduced spike in the TPD film, which cause dark spots during the device operation.

From the time-of-flight measurement, it has been reported that modifying the initial growth modes for

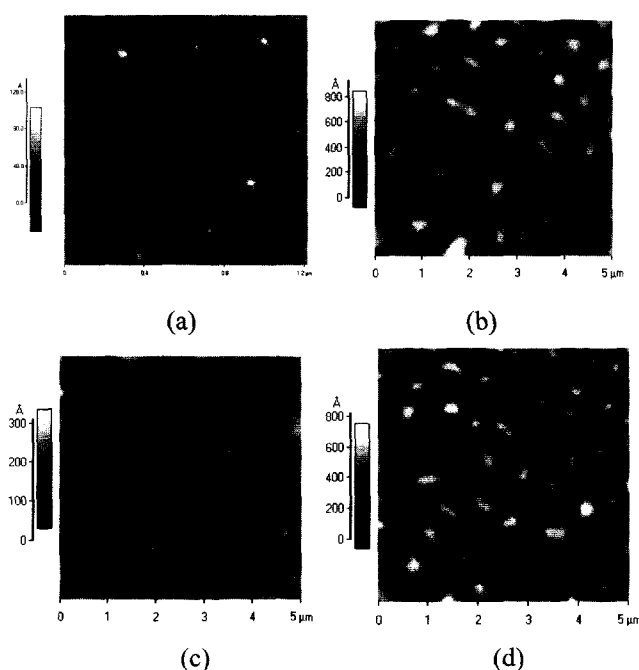


Fig. 5 Contact mode AFM images for (a) as-received ITO, (b) the surface of ITO/TPD, (c) the surface of ITO/CuPc/TPD, and (d) the surface of ITO/pentacene/TPD.

NPB molecules does not influence the bulk mobility of the NPB films, using the CuPc film on ITO as a substrate [9]. Therefore, it is assumed that modifying initial growth modes for TPD molecules also does not influence the bulk mobility of the TPD films because TPD molecule compound is very similar to NPB's. Thus, the insertion of the buffer layers modifies the growth of the TPD layer, compared with depositing the TPD films directly onto the ITO substrate, without altering the electrical characteristics of TPD.

We calculated the luminance efficiency [lm/W] of the fabricated device using equation (1), where η_L is luminance efficiency, L is brightness [cd/m^2], J is current density and V is the applied voltage:

$$\eta_L = \frac{\pi L}{JV} \quad [\text{lm/W}] \quad (1)$$

Fig. 6(a) shows the luminance efficiency-current density spectrum of the device with the 20 nm thick CuPc buffer layer and the device without the buffer layer. Under 150 mA/cm^2 , the efficiency of the devices with the 20 nm thick CuPc buffer layer was measured to have lower values than that of the device

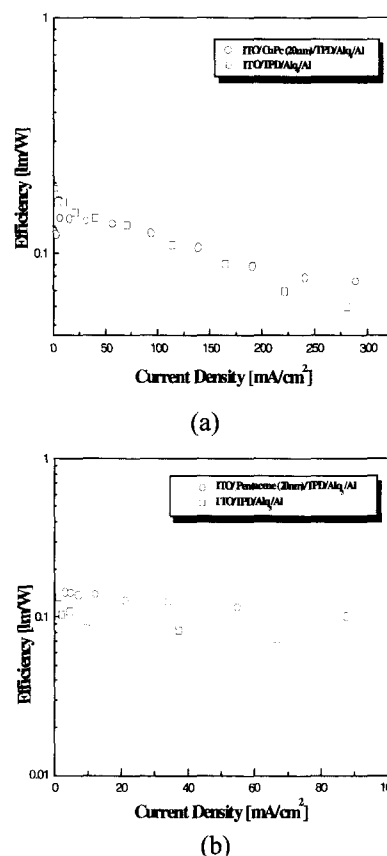


Fig. 6 Luminance efficiency-current density spectra of the devices with the 20 nm thick (a) CuPc/ (b) pentacene buffer layer and without the buffer layer.

without the buffer layer. This result is thought to be due to the rapid conduction of the initially injected holes without recombination. The number of electrons in the recombination zone is much less than that of holes, because the electron mobility is low and the barrier height for electrons from Al to Alq₃ (see Fig. 2) is very high. But the devices with the 20 nm thick CuPc buffer layer showed improvement in the device efficiency and long term operating efficiency above 150 mA/cm². In this condition, the injected holes into the recombination zone can efficiently recombine the injected electrons into emission layer (EML) due to the increased number of electrons in the recombination zone. Fig. 6(b) shows the luminance efficiency-current density spectrum of the device with the 20 nm thick pentacene buffer layer and the device without the buffer layer. The device with the 20 nm thick pentacene buffer layer showed stable operating efficiency in all current densities. It is thought that there must be good balance in the injection of holes and electrons, even under 150 mA/cm².

Thus, we suggest that the balance between electrons and holes in the emission region, by interposing the buffer layer between the ITO anode and the TPD layer, would result in the improvements of the luminance efficiency and the operational stability.

4. Conclusion

We have investigated the characteristic effects of the buffer layers on the OLED performances. The thin films of CuPc and pentacene were used as the buffer layers. We have observed the device characteristics according to the buffer layer thickness. The devices with the 20 nm thick CuPc and pentacene buffer layers showed the lowest turn-on voltage in each case, while the buffer layers did not emit light. The optimum thickness of CuPc and pentacene buffer layers was 20 nm for the device characteristics. The CuPc and pentacene buffer layers enhanced the surface state of the subsequent TPD layer compared with the TPD film directly deposited on the bare ITO substrate.

Upon the investigation, we have determined that the improved hole injection efficiency by the addition of the 20 nm thick CuPc and pentacene buffer layers, results from the lowered interfacial barrier between the ITO anode and the TPD layer. Furthermore, the roughness of the subsequent TPD layer can be reduced. As a result, the operational stability and the improved luminance efficiency can be improved. But other workers reported that the buffer layer limits hole injection efficiency and showed improvement in device efficiency by reducing hole injection efficiency. Further investigations are needed to analyze the roles of the buffer layer.

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