Influence of a Stacked-CuPc Layer on the Performance of Organic Light-Emitting Diodes

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Abstract: Vacuum deposited copper phthalocyanine (CuPc) was placed as a thin interlayer between indium tin oxide (ITO) electrode and a hole transporting layer (HTL) in a multi-layered, organic, light-emitting diode (OLEDs). The well-stacked CuPc layer increased the stability and efficiency of the devices. Thermal annealing after CuPc deposition and magnetic field treatment during CuPc deposition were performed to obtain a stacked-CuPc layer; the former increased the stacking density of the CuPc molecules and the alignment of the CuPc film. Thermal annealing at about 100 °C increased the current flow through the CuPc layer by over 25%. Surface roughness decreased from 4.12 to 3.65 nm and spikes were lowered at the film surface as well. However, magnetic field treatment during deposition was less effective than thermal treatment. Eventually, a higher luminescence at a given voltage was obtained when a thermally-annealed CuPc layer was placed in the present, multi-layered, ITO/CuPc/NPD/Alq$_3$/LiF/Al devices. Thermal annealing at about 100 °C for 3 h produced the most efficient, multi-layered EL devices in the present study.

Keywords: copper phthalocyanine, molecular stacking, magnetic field, semiconductor material, OLED.

Introduction

Macrocyclic organic materials like metallophthalocyanines (MPc) have recently attracted considerable interests due to their applications such as nanoscale devices, sensors, non-linear optics, magnetic storage media, organic film transistors, and anisotropic conductors and they possess their unique properties in electronic, optical, and magnetic aspects. Typically, the electrical properties of evaporated thin films of copper phthalocyanine (CuPc) have been widely studied to improve the performance of organic light emitting devices (OLEDs).[1-8] In OLEDs, light is emitted after opposite charges are injected from the electrodes into the organic layers, where they then recombine and form excitons. The injection efficiency is a critical parameter in such devices.[9-16] It has been found that the use of a thin interlayer of CuPc between indium tin oxide (ITO) electrode and a hole transporting layer (HTL) in OLED leads to stable and high efficiency devices by reducing the carrier injection barrier at the interface between the ITO anode and hole transport layers such as naphthyl-phenyl-diamine (NPD).[17-21] Furthermore, LiF has been also used for the cathode-buffer layers of OLEDs.[22,23] It is considered that enhancement of the electron injection is caused by the low work function induced by mixing of Al (as a cathode) and LiF or a tunneling effect.[22,23]

Among volatile organometallic compounds, copper phthalocyanine derivatives were found that the molecules could stack in solution and/or on the liquid phase as Langmuir-Blodgett films giving rise to a number of interesting properties such as semiconductivity or conductivity.[24-29] However, most of CuPc thin films are formed by vacuum deposition. It is known that highly ordered MPc thin films are of great importance for device purposes because charge injection/mobility is improved. Controlling the orientation of molecular stacking of metallophthalocyanines can be achieved by thermal treatment as well as a magnetic field. It is known that many metallophthalocyanines possess magnetic behavior.[3,6] However, there were no reports on the influence of the magnetic field on the topology of the CuPc films and device efficiency.

In the present study, in a typical vacuum-deposited multi-player OLED, copper phthalocyanine is inserted between the HTL and the transparent anode (ITO) to play the role of a hole-injecting buffer layer and improve the performance of the device. CuPc was deposited onto quarts substrates via vacuum process and post-deposition thermal annealing as thermal treatment was carried out in air with increasing temperature in order to investigate the effect of post-deposition thermal annealing on the structural alignment of CuPc thin films and on the current-voltage (I-V) and the luminescence-voltage (L-V) characteristics of the multi-layered EL device. CuPc thin films are vacuum-deposited under a magnetic

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field as well and then the effect of magnetic field on the topology of the CuPc films and device efficiency will be mainly discussed in the present study. It will be discussed that enhanced hole injection, induced by the molecular stacking of CuPc, into the HTL can lower the operating voltage and turn-on voltage and thus improve the photoluminescence efficiency of the device.

Experimental

Materials. Copper phthalocyanine (CuPc) was sublimed to obtain thin films via vacuum process and the chemical structure of CuPc (formula: $C_{32}H_{16}CuN_8$, molecular weight: 576.078, melting point: >360 °C, T_g: 240 °C, Tokyo Kasei Kogyo Co. Ltd.) is shown in Figure 1. Other materials used are 4,4′bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPD) (formula: $C_{44}H_{32}N_2$, molecular weight: 576.078, melting point:
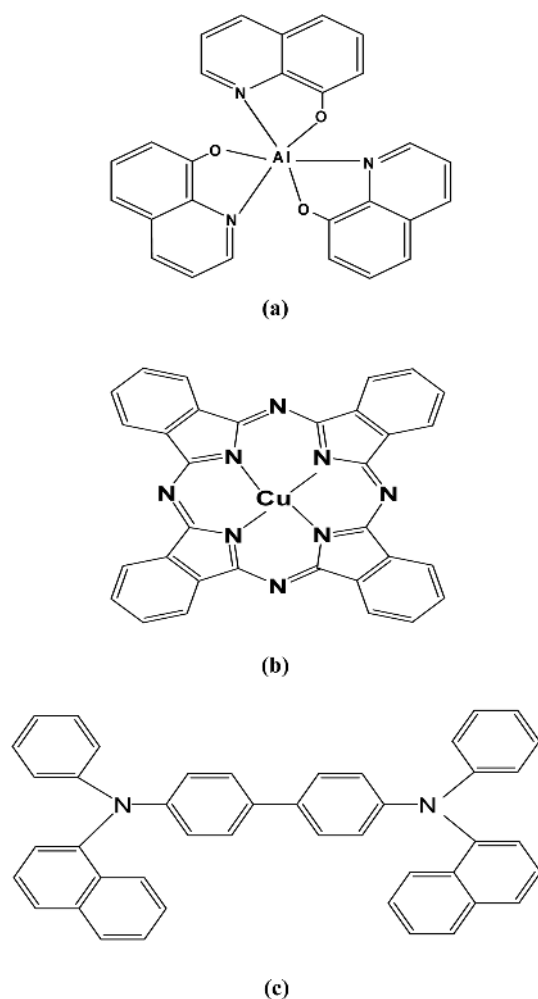
>277 °C, T_g: 96 °C, T H.W. Sands Corp.), Alq₃ (tris(8-hydroxyquinoline)aluminum, formula: $C_{27}H_{18}AlN_3O_3$, molecular weight: 459.437, melting point: >410 °C, T_g: 174 °C, Aldrich), and lithium fluoride (LiF) (molecular weight: 25.9374, melting point: 870 °C, Tokyo Kasei Kogyo Co. Ltd) and the chemical structures of Alq₃ and NPD are shown in Figure 1.

Film Formation. Vacuum deposition technique by thermal evaporation was used to obtain a homogeneous layer with well-controlled thickness. Before deposition, the ITO-coated glass was treated by acid solution followed by rinsing with de-ionized water and acetone and dried under nitrogen gas for cleaning the ITO-coated glass. CuPc was deposited onto the pre-patterned ITO glass and the deposition rate was controlled to 0.42 nm/min to obtain 50 nm thickness of the CuPc films. At this deposition rate the surface of the deposited films were found preferentially uniform throughout the deposition experiments in the present study. The deposition of all the organic materials was carried at a base pressure of 10^{-6} Torr and the substrate was not intentionally heated during the device fabrication process. The cathode in all devices was composed of 100 nm of aluminum. The active area of the all devices was subject to the pre-patterned ITO glass as shown in Figure 2.

Film Treatment. CuPc thin films were deposited under a magnetic field (~6 mT) and without a magnetic field to investigate the effect of a magnetic field on the orientation of CuPc molecules during deposition process. After deposition, thermal treatment of the deposited CuPc thin films was performed in a cylindrical furnace in which the magnetic field (~6 mT) was selectively applied as well. During thermal treatment or thermal annealing, the temperature was 50, 100, and 150 °C and the duration was 3 h. The film annealed in a magnetic field was compared to both the as-deposited sample and the sample annealed at the same temperature but without the magnetic field.

Film Analysis. Film thickness was measured with a profilometer model Alpha-step 100 (KLA-Tencor Co. Ltd.) and SEM (HITACHI S-4200). The conductivity of organic films was estimated using four-point probe measurement technique using a source multi-meter (KEITHLEY 2400). The luminescence-voltage (L-V) characteristics and luminescence
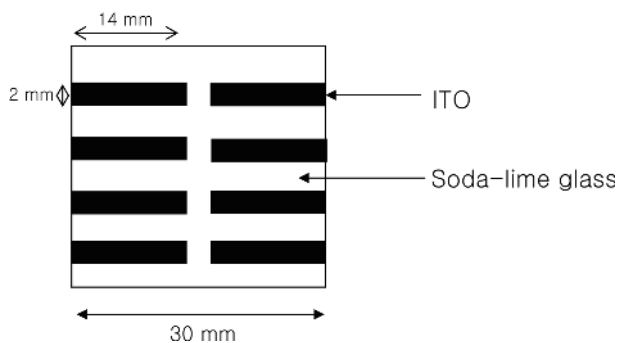

Figure 1. Chemical structures of (a) tris(8-hydroxyquinoline)aluminum (Alq₃), (b) copper phthalocyanine (CuPc), and (c) 4,4′bis [N-(1-napthyl)-N-phenyl-amino]biphenyl (NPD).

Figure 2. Dimension of pre-patterned ITO glass.

efficiency of the fabricated OLEDs were measured using a source multi-meter (KEITHLEY 236) and a HP semiconductor parameter analyzer (HP-4155). XRD (Rigaku Model D/Max 2400) and AFM (Nanoscope III-a, Digital Instruments Co. Ltd.) analysis were employed to characterize the molecular orientation and surface morphology of the CuPc thin films, respectively.

Fabrication of OLEDs. The multi-layered ITO/CuPc/NPD/Alq$_3$/LiF/Al devices were fabricated as shown in Figure 3(a) and the luminescence-voltage (L-V) and luminescence efficiency characteristics were measured to investigate the effect of the alignment of CuPc molecules on the enhancement of hole injection from ITO (Indium Tin Oxide) into HTL (Hole Transporting Layer) through a well-aligned CuPc layer. In Figure 3(b), the encapsulation process is shown and the device thickness excluding the substrate is about 1 mm. Water absorbing material is placed inside the metal can to improve the stability of the device.

Results and Discussion

Formation of Stacked-CuPc Films. The thickness of the
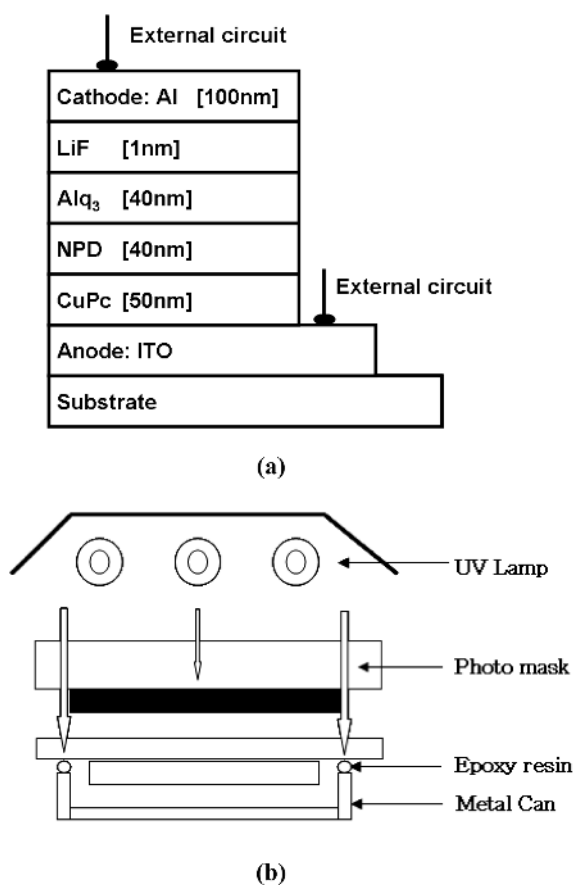

(a)

(b)

Figure 3. Schematic drawing of (a) ITO/CuPc/NPD/Alq$_3$/LiF/Al device and (b) encapsulation process.

vacuum-deposited CuPc thin films was about 50 nm. High purity and homogeneous films were obtained. As-deposited films were weakly oriented according to the XRD results as shown in Figure 4(a), in which a weak intensity of the peak around 7.6° is still seen. The peakwidth of 7.6° is typically observed for the well-stacked CuPc films. The conductivity values of the as-deposited CuPc thin films were $8.0 \times 10^{-8} \sim 3.5 \times 10^{-7}$ $\Omega^{-1}cm^{-1}$, which is within the value range of typical metallophthlocyanines (i.e., the conductivity is $1.4 \sim 6.0 \times 10^{-7}$ $\Omega^{-1}cm^{-1}$). Relatively lower values of the conductivity were observed since the CuPc molecules were not oriented in the films resulting in poor electron transporting.

For the CuPc films grown under a magnetic field, even though most of metal-substituted macrocyclic materials possess polar and/or magnetic behavior, a weak peak intensity at the typical peakwidth of 7.6° was found but a higher peak compared to the as-deposited CuPc films grown without magnetic field was observed as shown in Figure 4(b). Thermal annealing after deposition had the CuPc film well-aligned as shown in Figure 4(c), in which a higher peak intensity around 7.6° was observed. Thus, CuPc films were oriented in the (200) direction according to the XRD results. Thermal annealing participates to increase the interaction of the CuPc molecules. The interaction between the CuPc molecule and the surface of the substrate may lead to closer stacking of CuPc molecules as well. Thermal annealing under a magnetic field is also recognized to improve the molecular stacking of the CuPc films as shown in Figure 4(d). It can be said that thermal annealing mainly participates to increase the molecular orientation rather than a magnetic field in the formation of stacked-CuPc films.

ITO/CuPc/Al Layers. A schematic diagram of the generic device structure of a single layer is shown in Figure 5(a). The organic layer was evaporated to an overall thickness of 50 nm, while the top electrode was 100 nm. The typical current–voltage (I-V) characteristics of the ITO/CuPc/Al device are shown in Figure 5(b). The CuPc thin film after thermal annealing at 100°C for 3 h showed much better orientation and the I-V characteristics showed much better current flow at a given voltage compared to an as-deposited CuPc film. This behavior was due to closer stacking of CuPc molecules in a CuPc layer. An increase in current flow through the CuPc layer by over 25% is observed. These results indicate that the enhancement of the capability of hole injection from ITO into the HTL lowers the turn-on voltage and thus improves the device power efficiency in the fabricated OLEDs.

Surface images of CuPc thin films before and after thermal annealing were shown in Figures 6 and 7. Before thermal annealing, there were a couple of sharp spikes on the surface in an AFM image. A sharp spike can lead to a severe current shortage due to a concentrated current flow through a spike. In this reason the control of the surface morphology is very important. After thermal annealing, it was found that surfaces
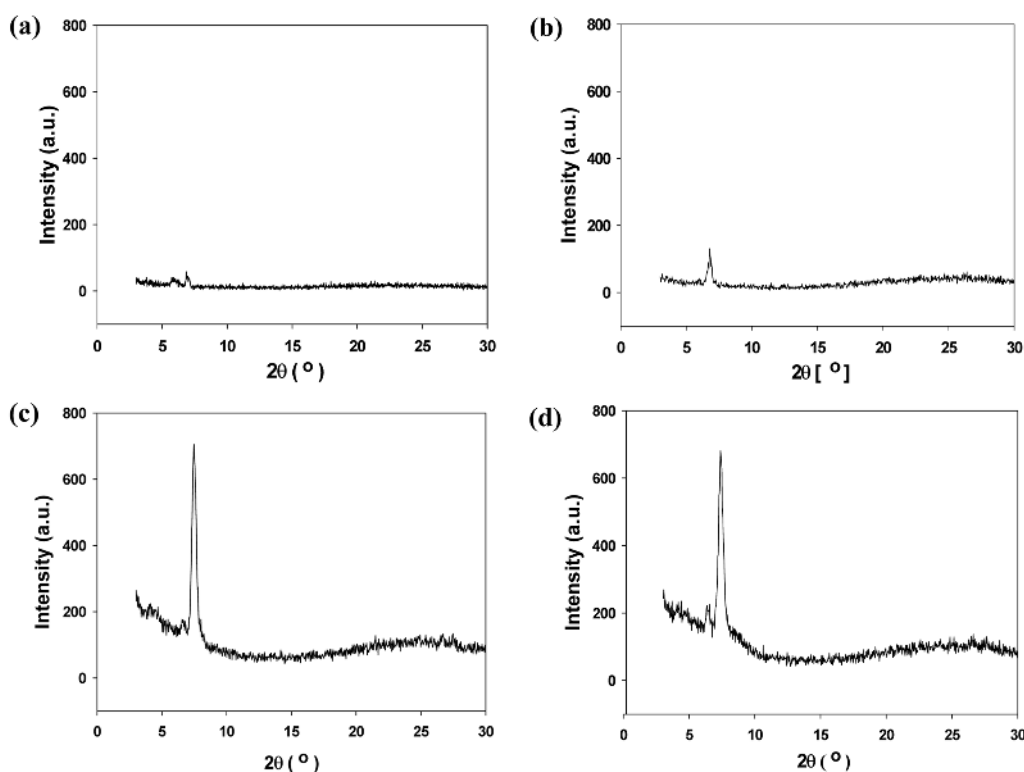
Figure 4. X-ray diffraction patterns of CuPc films: (a) as-deposited film, (b) film deposited under magnetic field (~6 mT), (c) after thermal annealing at 100 °C for 3 h, and (d) after thermal annealing at 100 °C for 3 h under magnetic field.

roughness decreased and lowered spikes at the surface were observed, which resulted in preventing current shortage at the elevated voltages during the current-voltage tests. In Figure 6, though the sharp spikes still remained on the surface, it was clear that the value of the averaged surface roughness decreased from 4.12 to 3.65 nm and the spikes were lowered. While thermal annealing at 100 °C for 3 h, the CuPc molecules were reorganized to form self-organized nanowire-like structures on the surface as shown in Figure 7(c) and 7(d). These structures may enhance hole injection in some ways through the stacked molecules and thus lower the operating voltage of the device. However, magnetic field mainly participates to improve the topology of the CuPc films. Therefore, it is concluded that magnetic field should influence only on the topology of the CuPc films and thermal annealing should influence both on the topology and molecular orientation of the CuPc films.

ITO/CuPc/NPD/Alq$_3$/LiF/Al Layers. The luminescence-voltage (L-V) characteristics and luminescence efficiency of the present ITO/CuPc/NPD/Alq$_3$/LiF/Al devices were measured to investigate the effect of the alignment of CuPc molecules on the enhancement of hole injection from ITO into HTL through a well-aligned CuPc layer. The L-V characteristics of the multi-layered EL device were shown in Figure 8. The higher luminescence at a given voltage was observed when a thermally-annealed CuPc layer was placed
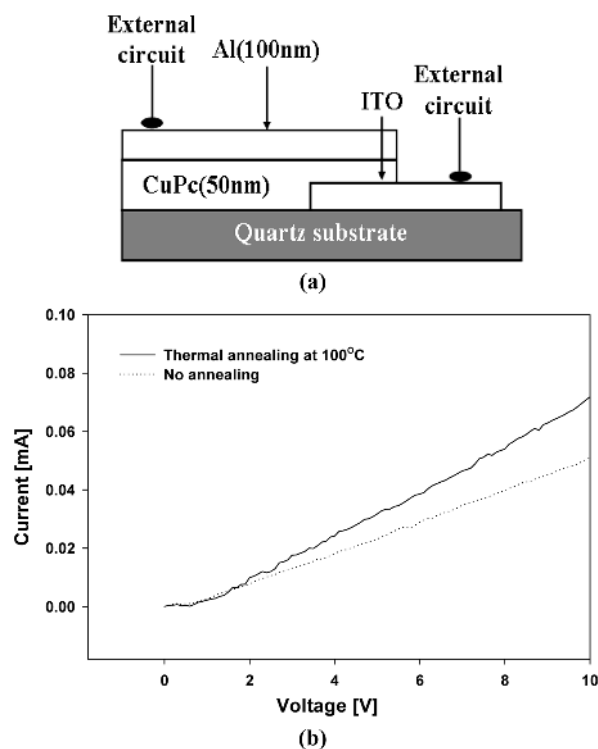

Figure 5. Schematic diagram of (a) the generic device structure of the single layer and (b) I-V characteristics of the ITO/CuPc/Al device.
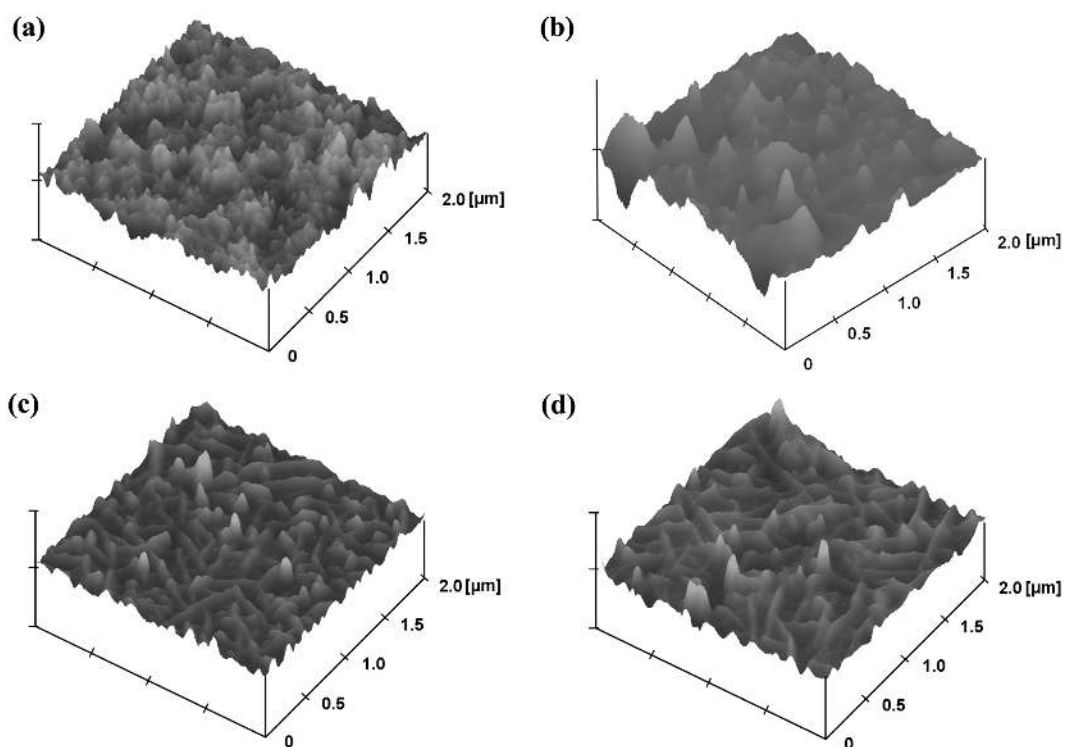
Figure 6. AFM images (3D) of CuPc film surfaces: (a) as-deposited film, (b) film deposited under magnetic field (~6 mT), (c) after thermal annealing at 100 °C for 3 h, and (d) after thermal annealing at 100 °C for 3 h under magnetic field.
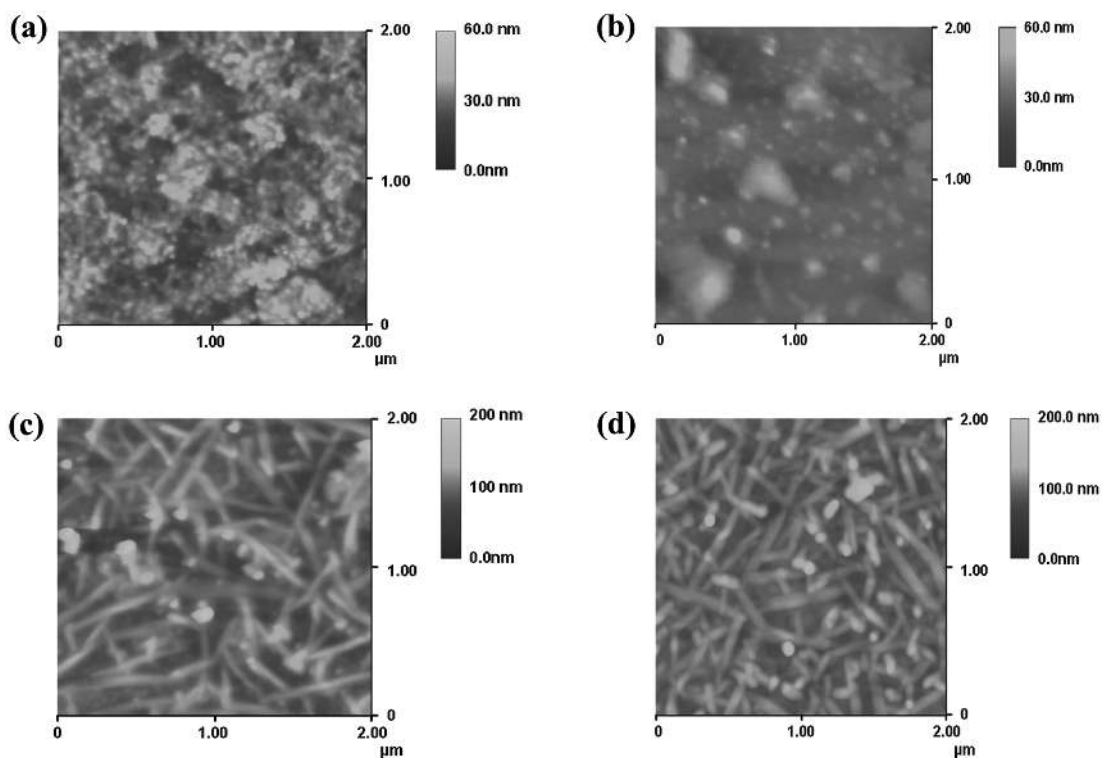

Figure 7. AFM images (2D) of CuPc film surfaces: (a) as-deposited film, (b) film deposited under magnetic field (~6 mT), (c) after thermal annealing at 100 °C for 3 h, and (d) after thermal annealing at 100 °C for 3 h under magnetic field.
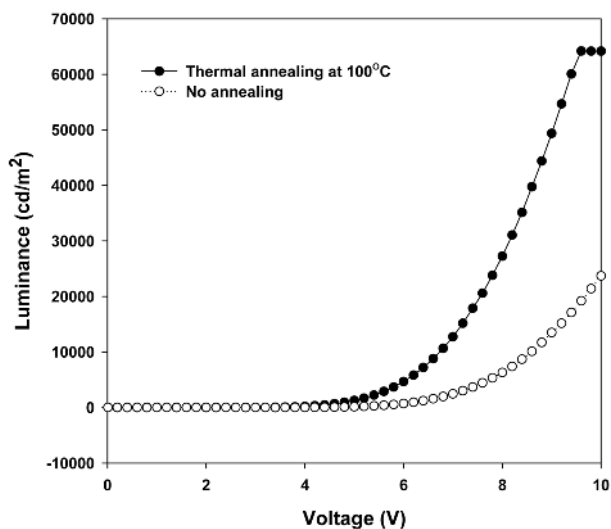
Figure 8. L-V characteristics of the present ITO/CuPc/NPD/Alq$_3$/LiF/Al device.

Figure 9. Luminescence efficiency characteristics of the present ITO/CuPc/NPD/Alq$_3$/LiF/Al device with a CuPc layer treated at various temperature.

in the present multi-layered EL devices. The higher luminescence at a given voltage are highly influenced by the optimized ITO/HTL interface, at which the enhancement of hole injection from ITO into HTL occurs. The luminescence at a given voltage depends on the number of holes which are injected into and are present in the Alq$_3$ layer. The luminescence of the devices corresponds to a higher concentration of holes at lower voltages. Therefore, a proper thermal annealing of an organic layer in the organic EL devices leads to a higher luminescence efficiency as well as a higher power efficiency. The luminescence efficiencies of the multi-layered EL devices, in which the CuPc thin film annealed at different temperatures was placed, were shown in Figure 9. Annealing temperature was 50, 100, and 150 °C, respectively. At over 150 °C, the luminescence efficiency began to decrease because the CuPc thin films were deformed and not uniform anymore at the higher temperature as shown in Figure 10. In the present study, thermal annealing at about 100 °C for 3 h was preferred to obtain the most efficient multi-layered EL devices.

Conclusions

A preferentially-oriented CuPc thin layer has played an important role in achieving a higher luminescence efficiency as well as a higher power efficiency of the multi-layered organic EL devices in the present work. It was found that thermal annealing made CuPc film well-aligned and thermal annealing at about 100 °C for 3 h was preferred to obtain the most efficient multi-layered EL devices. However, the luminescence efficiency began to decrease at higher annealing temperature over 150 °C because the surface of the CuPc films were deformed and not uniform anymore at
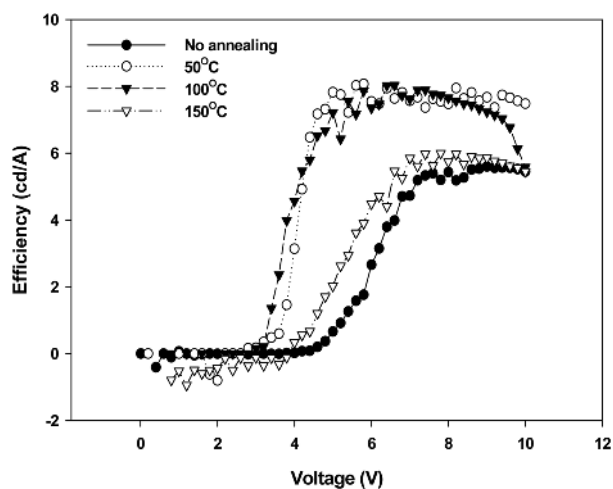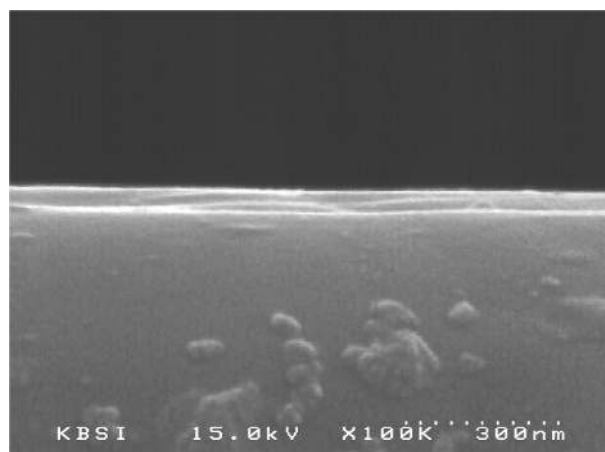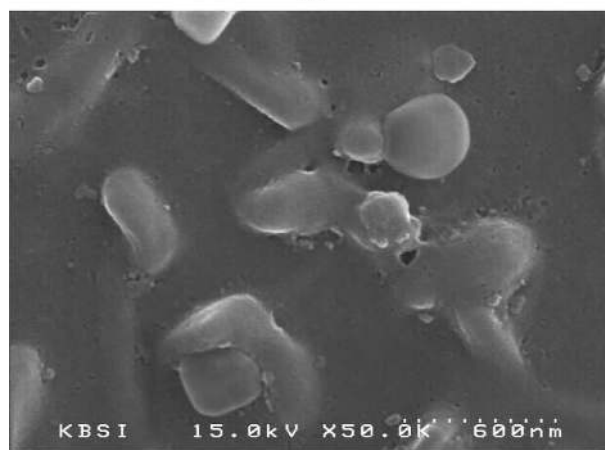

Figure 10. SEM images of CuPc films (a) before thermal annealing (side view) and (b) after thermal annealing at 150 °C for 3 h (top view).

higher temperature. By thermal annealing, an increase in current flow through the CuPc layer by over 25% is observed. This behavior was due to closer stacking of CuPc molecules in a CuPc layer. However, a magnetic field was less effective in obtaining the stacked-CuPc molecules.

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