Effects of Polymeric Hole Transporting Layer on the Stability of Organic Light Emitting Device

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A polymeric hole transporting layer (HTL) in organic light emitting devices (OLED) helps oppositely charged carriers to meet away from the cathode, so that the emitting efficiency is increased, and can also help the constituent layers to become thermally and mechanically more stable. Two experimental results concerning the operation of polymeric HTL layer, made of poly [N-(p-diphenylamine) phenylmethacrylamide] (denoted as PDPMA), are presented and analyzed. Firstly, OLED devices composed of ITO/PDPMA/Alq$_3$/Al were prepared and heat-treated systematically to study the influence of the resulting structural changes in the polymeric layer on the device performance. It was observed that the power efficiency of the device could be improved, especially at higher voltage, by annealing at a temperature above the glass transition temperature of PDPMA. The results are thought to come from the rearrangement of the polymer chains in the film, that reduces the vacant volume present within the amorphous chains and helps chains to be packed close to each other, which is expected to be advantageous for charge transport and also for ensuring better thermal stability. Secondly, a fluorescent dopant (Nile red) was added in the light emitting Alq$_3$ layer (ITO/PDPMA/dye doped Alq$_3$/Al) and on the other hand in the PDPMA layer (ITO/dye doped PDPMA/Alq$_3$/Al), so that the energy could be transferred to the dopant molecules. The lifetimes of the devices were compared, and it was shown that the device with the dye doped PDPMA had superior stability to the one with dye doped Alq$_3$ layer.

I. INTRODUCTION

Intensive attention has been given to novel organic light-emitting or electroluminescent devices (OLED or OELD) through various approaches during the last few years [1–4]. Stability of the device has been shown to be influenced by the quality of the thin films, the interfacial state between organic materials and the metal electrodes, and various environmental conditions which have to be controlled during the device manufacturing process as well as device operation [5–7]. OLEDs which consist of low molecular weight molecules especially lack durability against degradation by heat and oxidation process, and local deterioration in the emitting sites would inevitably develop [5]. Moisture also induces recrystallization of the organic molecules, which causes a reduction in emission due to the concentration quenching problem. Such devices would therefore have crucial drawbacks in terms of efficiency as well as lifetime [8]. Overcoming these problems is one of the main topics in recent OLED research.

During the device fabrication process, the organic films are generally annealed at a temperature near the boiling temperature of the solvent for the constituent molecules, so that the residual solvent can be removed, or often heat treatment is not carefully conducted. After spin coating, residual solvent remains in the film and the polymer molecules exist in nonequilibrium conformation extended toward the surface and radial direction of spinning, and surplus free volume should also be left over, due to abrupt evaporation of solvent. Polymer molecules are not mobile enough below the glass transition temperature (T_g) to relax back to equilibrium conformation or to move around to fill up that free volume. They act as a barrier or pinhole for the charge carriers for charge injection or transportation, which correspondingly affects the emission efficiency [10]. Therefore, annealing the film above T_g of the constituent polymer would allow this nonequilibrium tension to be removed, so that the chain conformation could revert to the most disordered Gaussian one and the density of the film could come back to the equilibrium value. In this report, spin coated thin films of poly [N-(p-diphenylamine) phenylmethacrylamide] (PDPMA, Figure 1) which were used as a hole transporting layer (HTL) [11] were heat-treated systematically to study the physical changes in the film and the
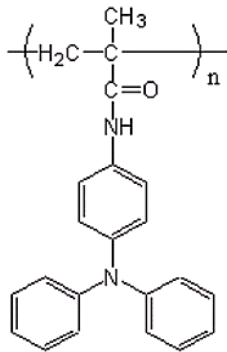
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Fig. 1. Molecular structure of PDPMA which was used as a HTL material.

influence of these on electrical and optical properties. Tris (8-quinolinolato) aluminum, Alq$_3$, was used as an emitting layer, Al as cathode, and ITO as a transparent anode.

Recently, it has also been reported that the EL device of host-guest type using a dye doped layer has improved characteristics such as emission efficiency [12] and good physical and chemical stability [13]. However, the EL device of this type still has some significant problems such as short lifetime in operation, because the fluorescent dye molecule is very sensitive to heat, humidity and oxygen. By using fluorescent dyes (Nile red) as guest emitting materials with color tunable function [14,15], organic EL devices using PDPMA and Alq$_3$ as a host material were fabricated: organic EL devices with a dye-doped polymeric hole transporting layer, *i.e.* a device consisting of ITO/Nile red+PDPMA/Alq$_3$/Al, and the ones with a dye-doped light emitting Alq$_3$ layer, *i.e.* a device consisting of ITO/PDPMA/Nile red + Alq$_3$/Al, were fabricated and the operational lifetimes of these were compared.

II. EXPERIMENTAL DETAILS

PDPMA, which was used as a polymeric hole transporting layer has a methacrylate main chain with triphenylamine side group, which was synthesized by radical polymerization [11]. The molecular weight of PDPMA was about 18,000. PDPMA was dissolved in monochlorobenzene at concentrations of 0.5 wt.%, 1.0 wt.%, and 1.5 wt.%, and spin-coated at 2000 rpm on Si wafer. The thickness and the refractive index of the film were measured by ellipsometry. The T$_g$ of PDPMA measured by DSC was 227 °C and the boiling point of cholrobenzene (solvent for PDPMA) was 130 °C. Nile red was purchased from TCI and purified by sublimation at 350 °C under 10^{-3} Torr before deposition.

PDPMA (or mixtures of PDPMA and 0.8 wt.% Nile red [14,15]) was dissolved in monochlorobenzene at 1.0 wt.%; this was spin-coated at 2000 rpm onto ITO coated glass. The thickness of the PDPMA layer was 60 nm. To

study the effect of heat treatment, we imposed the following three conditions under vacuum of 0.1" Hg: the device was manufactured (1) right after the polymeric film was spin coated, (2) after the polymeric film was heat-treated at a temperature (150 °C) above the boiling point of the solvent for 60 minutes, (3) after the polymeric film was heat-treated at a temperature (240 °C) above its T$_g$ for 30 minutes. The reason for limiting the annealing time to 30 minutes in the case of (3) was to allow chain molecules to relax to the equilibrium state and to avoid degradation of the materials during excessively long annealing. It was checked that giving more annealing time did not change the thickness of the film any further. After the heat treatment, the films were transferred to be cooled in a vacuum desiccator. Alq$_3$ (or coevaporated with Nile red) was deposited on this layer under a pressure of 1 × 10^{-5} Torr by ULVAC VPC-200F evaporator. The thickness of Alq$_3$ layer was about 40 nm. An Al cathode was finally deposited above it.

Current-voltage characteristics were measured by using a programmable Keithley 236 electrometer. Luminance was measured with a Minolta LS 100 portable luminance meter. It was observed that the wavelength at the maximum of the photoluminescence and electroluminescence spectra was about 520 nm in all cases, which means that the emissions in all cases were caused by the same mechanism from the Alq$_3$ layer.

In addition, to study the stability of the devices made of dye-doped PDPMA and Nile red-doped Alq$_3$, two devices composed of ITO/PDPMA/Alq$_3$-Nile red/Al and ITO/blend (PDPMA-Nile red)/Alq$_3$/Al were fabricated, respectively.

III. RESULTS AND DISCUSSION

Firstly, the changes of the thickness and refractive index of the PDPMA layers on Si wafer made from the solutions with the above three concentrations were measured by ellipsometer (Figure 2(a)). Small molecules were removed after annealing at 150 °C and 240 °C, but the thickness was further reduced at 240 °C, which comes from the rearrangement of the chains at a temperature above T$_g$. This densification of the film was verified by the increase in the refractive indices (Figure 2(b)).

I-V characteristics for cases (1), (2), and (3) are shown in Figure 3. The device for case (2) manifested the lowest turn on voltage of about 9 V and the other two cases showed similar values of 11 V. The current density at 20 V was about 480 A/m^2 for case (2), 270 A/m^2 for case (1), and 300 A/m^2 for case (3), respectively. The low turn on voltage in case (2) may be attributed to the penetration of Alq$_3$ into the sparse polymer film during its deposition.

A luminance-voltage experiment was performed, to further investigate the relation between EL and current density. Data obtained under three different annealing
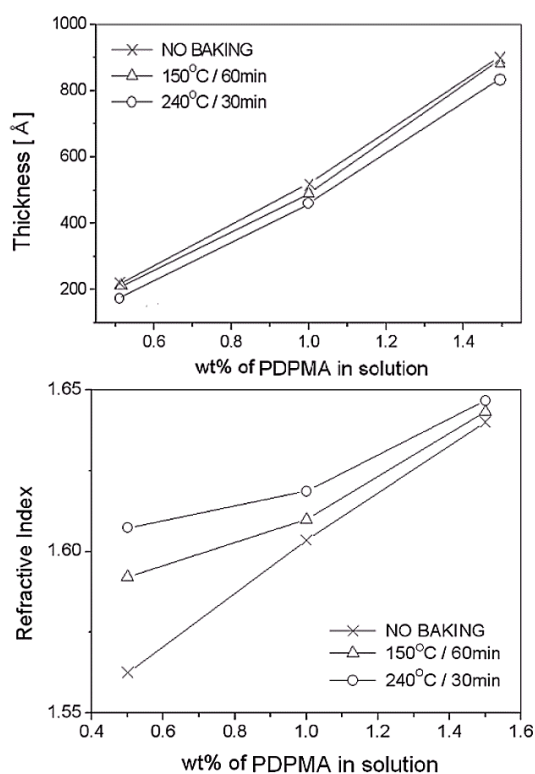
Fig. 2. (a) Thicknesses of the PDPMA films prepared from solutions with different concentrations in chlorobenzene after various heat treatments; (b) Refractive indices of the PDPMA films prepared from solutions with different concentrations in chlorobenzene after various heat treatments.
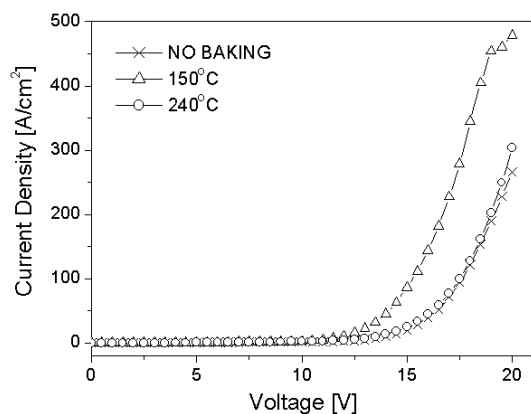

Fig. 3. I-V curves of the ITO/PDPMA/Alq$_3$/Al device after various heat-treatments.

Fig. 4. Luminescence versus voltage curves of the ITO/PDPMA/Alq$_3$/Al device after various heat treatments.

Fig. 5. Power efficiency versus voltage curves of the ITO/PDPMA/Alq$_3$/Al device after various heat treatments.

conditions are shown in Figure 4. The luminance was the lowest for the unannealed specimen. Furthermore, a dark spot appeared on the surface most frequently in this case, especially as the voltage was increased, which may be due to the small molecules remaining inside the film that induces inhomogeneous passage of the current. Also, the interaction at the interface between Alq$_3$ and unannealed film containing the small molecules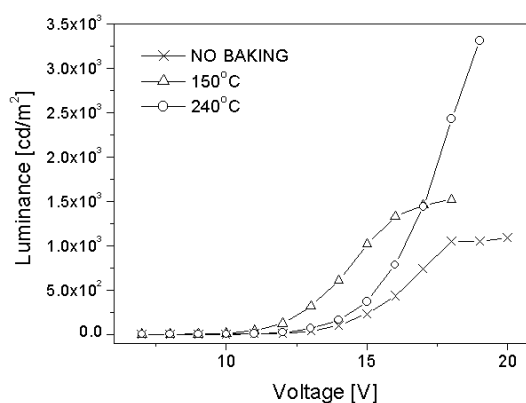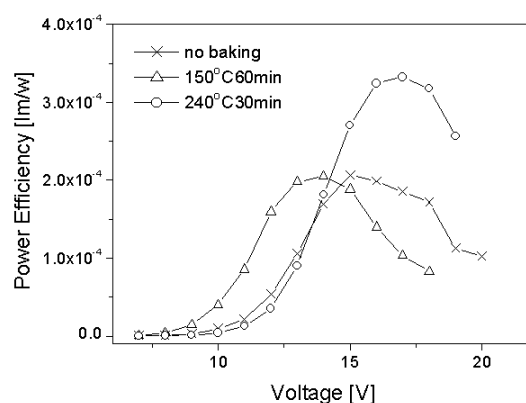 may influence the emission efficiency. At voltage below 17 V the luminance for case (2) was the highest, but above 17 V the luminance was the largest for case (3). The luminance for case (3) continued to increase up to 19 V, while the data in case (2) soon stopped increasing. Also, the maximum luminance for case (3) was 3300 cd/m^2 at 19 V, which is 2 ∼ 3 times larger than those for case (1) (1000 cd/m^2 at 19 V) and for case (2) (1500 cd/m^2 at 18 V).

Luminance power efficiency (lm/W) was calculated by using the relation πL/JV, where L is the brightness (sr cd/m^2) and J is the current density (A/m^2). The results are shown in Figure 5. The efficiency was, on the whole, the lowest for the unannealed case, and it was rather larger for case (2) at low voltage. However, the efficiency for case (2) decreased rapidly after 13 V and became the smallest after 14 V, while the best efficiency was achieved for case (3) after 14 V. A similar pattern was also shown previously in Figure 4, there the luminance was the largest for case (3) after 17 V. This implies that annealing the polymer at a temperature above T$_g$ drives the device to function more efficiently and stably. A similar trend was observed reproducibly, which leads us to suggest that annealing the polymer layer at a temperature above T$_g$ would be necessary for fabricating
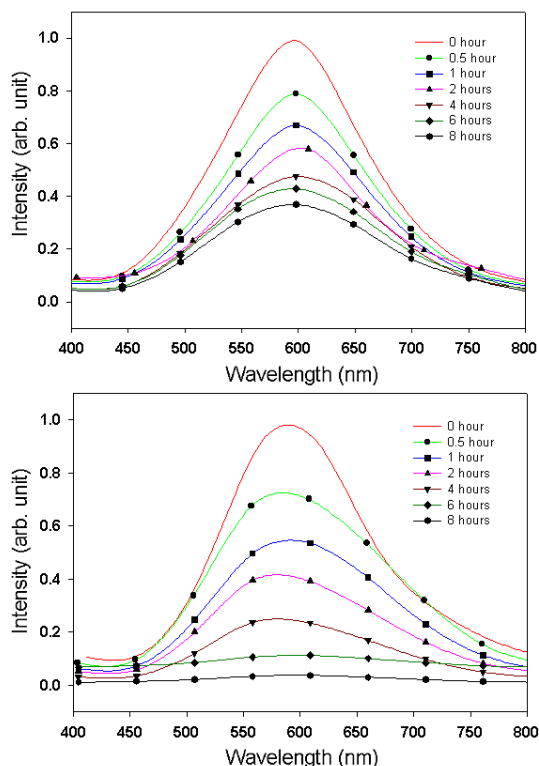
Fig. 6. (a) Luminance intensity versus wavelength for ITO/blend (PDPMA-Nile red)/Alq$_3$/Al device after various operational times; (b) Luminance intensity versus wavelength for ITO/PDPMA/Alq$_3$-Nile red/Al device after various operational times.

LEDs containing polymer.

On the other hand to study the stability of LEDs which have a blend of PDPMA and Nile red fluorescent dopant, a device composed of ITO/PDPMA/Alq$_3$-Nile red/Al and one composed of ITO/blend (PDPMA-Nile red)/Alq$_3$/Al were fabricated. The wavelengths at maximum emission for Alq$_3$ and Nile red individually were 550 nm and 605 nm, respectively, and these have been shown to have a sufficient spectral overlap region so that energy could be transferred to Nile-red, and further, the emission could be dominated by Nile red in both device structures. It was, in fact, observed that the device composed of ITO/blend (PDPMA-Nile red)/Alq$_3$/Al started to emit light centered at 605 nm when the voltage was larger than 14 V [15]. The emission characteristics in air as a function of operational time were measured by using a luminance meter. The results are shown in Figures 6(a) and (b).

The change of the emission characteristics monitored for the device composed of ITO/blend (PDPMA-Nile red)/Alq$_3$/Al shows that the initial intensity at 605 nm was reduced to about 50 % after 4 hours, and about 40 % of the initial intensity was maintained after 8 hours. For the case of the device composed of ITO/PDPMA/Alq$_3$-Nile red/Al, the initial intensity at 605 nm was also re-

duced to about 50 % after 4 hours, but the emission nearly disappeared after 8 hours. This result shows that the device with polymer-dopant blended HTL operates more stably in air than the one made with Alq$_3$-dopant coevaporated layer. It is thought that the organic fluorescent molecule which is sensitive to moisture and oxygen in the air could be easily affected inside the Alq$_3$ layer, while the dopant molecules inside the PDPMA polymer matrix could be confined more or less safely, which could extend the lifetime of the device.

IV. CONCLUSIONS

Electroluminescent (EL) devices composed of ITO/PDPMA/Alq$_3$/Al were prepared, to study the influence of different thermal annealing of the PDPMA polymer layer on the electrical and optical characteristics of the devices. It was observed that the efficiency could be improved for the sample which was annealed at a temperature above the T$_g$ of the polymer, compared to the one unannealed or thermal-treated near the boiling temperature of the solvent. This effect is considered to come not only from the complete removal of residual volatile molecules, but also from the rearrangement of the chains in the film, which reduces the vacant volume, as well as helping the chains to be packed against each other. Also, the Nile red was dissolved in the emitting Alq$_3$ layer (ITO/PDPMA/dye doped Alq$_3$/Al) and in the PDPMA layer (ITO/dye doped PDPMA/Alq$_3$/Al). The lifetimes of the devices were compared, and the stability was found to be better in the dye doped PDPMA case.

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