Enhancing the performance of organic light-emitting devices by selective thermal treatment

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Abstract

Joule heat generated during device operation has been considered the important factor causing device degradation. We hence fabricated two devices composing indium–tin-oxide (ITO)/N,N-bis-(1-naphthy)-N,N-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB)/tris-(8-hydroxyquinoline) aluminum (Alq3)/aluminum (Al) and ITO/NPB/Alq3/lithium-fluoride/Al to investigate the effect of heat on device performance by annealing the whole devices at different temperatures or by selectively annealing the desired layer(s) at a certain temperature. The devices annealed at an appropriate temperature, such as 120°C, showed marked improvement in luminescent efficiency, brightness, and operating stability. Thermal annealing the NPB and Al electrode layers, especially the latter one, greatly improved the performance. The enhancements may be attributed to better electron injection and higher electron/hole recombination efficiency upon appropriate annealing.

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1. Introduction

Since the first report of a high efficiency bilayer organic light-emitting device (OLED) by Tang and Van Slyke [1] special interest has been paid to OLEDs for their potential in numerous display applications. Progress in this field has led to the realization of OLEDs with higher efficiency, lower drive voltage, and a range of colors that are adequate for commercialization [2–6]. However, operational stability remains a problem of much concern. Factors that affect the lifetime and performance of OLEDs must be investigated further.

OLED degradation is largely attributed to the formation and growth of dark spots [7–13]. Device degradation caused by crystallization [10] and interdiffusion [11] of the organic molecules has drawn much attention. Organic materials with higher glass transition temperatures have therefore been synthesized [14]. However, some reports have indicated that the devices with purposely prepared crystalline organic layers exhibit better performance in luminescent efficiency and brightness [15–18].

Hence, OLEDs were fabricated and annealed at various temperatures to investigate the effect of heat on some typical organic molecules and their effect on device performance. Most OLEDs are composed of at least two organic layers, so whether thermal annealing differently affects each organic layer must be determined.

2. Experimental details

The studied green organic bilayer devices were composed of a 50 nm N,N-bis-(1-naphthy)-N,N-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) as the hole-transporting layer and a 50 nm tris-(8-hydroxyquinoline) aluminum (Alq3) as the electron-transporting and light-emitting layer, sandwiched between a 150 nm indium–tin-oxide (ITO)-coated glass substrate with a sheet resistance of 20 Ω/square and a
150 nm aluminum (Al) cathode. Some OLEDs were also fabricated using a 0.5 nm lithium fluoride (LiF) as the electron-injecting layer before the deposition of Al. The organic layers, LiF, and Al cathode were prepared in a vacuum chamber at 2.5 \times 10^{-3} \text{ Pa}. The deposition rates of the NPB, Alq3, LiF, and Al were 0.1, 0.1, 0.01, and 1 nm/s, respectively. Thermal annealing of the resultant devices was performed in an electrical furnace at 6.5 Pa at 100, 120, 140, or 160 °C for 1 h. OLED luminance was measured using a Minolta LS-110 luminance meter. A Keithley 238 high-current source meter was used to measure the current–voltage characteristics. The morphological property of Al electrode at the Alq3/Al interface was studied by atomic force microscopy (AFM) (Nanoscope III, Digital Instruments, USA) and the scan area was 5 × 5 \mu m².

Some of the ITO/NPB/Alq3/Al devices were selectively annealed to explore further the effect of thermally annealing each layer on device performance. Device A was a standard device that did not undergo any thermal annealing; device B was the device whose NPB layer was thermally annealed before the depositions of Alq3 and Al, which were not further annealed; device C was the device with the NPB and Alq3 layers thermally annealed before the depositions of Al, which was not further annealed; and device D was the device of which each layer was thermally annealed. Thermal annealing was performed always at 120 °C for 1 h.

### 3. Results and discussion

Table 1 shows the effect of thermal annealing on the performance of ITO/NPB/Alq3/Al. Except when annealed at 160 °C, these devices exhibited obvious improvement in luminescent efficiency, brightness, and operational stability. For example, maximum brightness of the devices annealed at 100, 120, and 140 °C was improved from 3650 cd/m² for the unannealed device to 4870, 6240, and 5830 cd/m², respectively; the maximum efficiency was improved from 1.9 cd/A to 2.5, 3.5, and 3.3 cd/A. As a result, the thermal annealing temperature of these devices are higher than the glass transition temperatures (T_g) of NPB (T_g = 95 °C) and, according to the common belief, these devices would exhibit deleterious effects on the performance of OLEDs. However, our results demonstrated that performances of devices with appropriate thermal annealing were better than those of unannealed device.

In order to further explore the origin of these enhancements, the device was selectively annealed to explore further the effect of thermally annealing each layer on device performance. Table 2 shows the effect of selective annealing on the performance of the ITO/NPB/Alq3/Al device. The performance of device B whose NPB was thermally annealed was significantly better than that of the totally unannealed device A. The maximum luminescence efficiency and brightness of device B were 3.0 cd/A and 4730 cd/m², whereas those of device A were 1.9 cd/A and 3650 cd/m², respectively. On the other hand, device C with NPB and Alq3 annealed exhibited almost the same luminescent efficiency and brightness as compared with those of device B. This indicated that thermal annealing the Alq3 layer did not have any effect on device performance at 120 °C.

Fig. 1(a) reveals that the current–voltage curves of devices B and C shifted to higher voltages as compared with those of device A, implying that annealing NPB or NPB/Alq3 would impede or slow the transport of holes. In contrast, the current–voltage curve of device D, in which all the layers were annealed, shifted to lower voltages as compared with those of devices B and C.

As seen in Fig. 1(b), compared with device A, devices B, C, and D exhibited higher luminance at a given current density. Device B, with only NPB annealed, showed

<table>
<thead>
<tr>
<th>Layer(s) annealed</th>
<th>Voltage (V) at 100 cd/m²</th>
<th>Luminance (cd/m²) at 20 mA/cm²</th>
<th>Maximum efficiency (cd/A)</th>
<th>Maximum luminance (cd/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A None</td>
<td>8.8</td>
<td>280</td>
<td>1.9</td>
<td>3650</td>
</tr>
<tr>
<td>B NPB</td>
<td>9.8</td>
<td>570</td>
<td>3.0</td>
<td>4730</td>
</tr>
<tr>
<td>C NPB/Alq3</td>
<td>9.7</td>
<td>560</td>
<td>2.8</td>
<td>4790</td>
</tr>
<tr>
<td>D NPB/Alq3/Al</td>
<td>9.5</td>
<td>670</td>
<td>3.5</td>
<td>6240</td>
</tr>
</tbody>
</table>

The chosen temperature was 120 °C.
improvement in luminescent efficiency, brightness, and operational stability; these results were the same as those obtained using high substrate temperature to induce crystallization of NPB during deposition, as reported by Gao et al. [15].

It is widely known that the transport of holes in a standard bilayer NPB/Alq3 device is faster than that of electrons, leading to poor electron/hole recombination efficiency at NPB/Alq3 interface. This makes electrons the minority carriers, which in turn control the efficiency of the device. Therefore, when introducing a thin LiF as an electron-injection layer to increase electron injection or slow hole transport [15–17], the device efficiency can be greatly improved. Under these conditions, the density of electrons in the Alq3 layer adjacent to the NPB/Alq3 interface is relatively increased, leading to a more balanced electron/hole ratio. Thus, the better performance of device B can be attributed to the role of NPB with appropriate thermal annealing in achieving more balanced electron/hole ratio at NPB/Alq3 interface.

Fig. 1. Selective annealing effect on the characteristics of (a) current density–voltage and (b) luminance–current density of the studied ITO/NPB/Alq3/Al devices, where device A was a standard device without annealing, device B had the NPB annealed, device C had both NPB and Alq3 annealed, and device D had whole device annealed.

Fig. 2. Selective annealing effect on the characteristics of current efficiency–voltage–luminance of the studied ITO/NPB/Alq3/LiF/Al devices, where device E was a standard device without annealing, device F was a standard device without annealing (open circles), device F had the NPB annealed (solid squares), and device G had the whole device annealed (open triangles). Inset: Effect of selective annealing on the characteristics of green OLEDs (ITO/NPB/Alq3/LiF/Al).

Fig. 3. AFM images of the Al electrode at the Alq3/Al interface for the devices of ITO/NPB/Alq3/Al (a) without annealing, (b) with the NPB/Alq3 layers annealed before Al deposition, and (c) with the whole device annealed.
Fig. 2 shows the selective annealing effect on the characteristics of current efficiency–voltage–luminance of the ITO/NPB/Alq3/LiF/Al devices. The method of thermal annealing was the same as that mentioned previously. Device E was the device that underwent no thermal annealing; device F was that in which NPB was annealed; in device G, each layer was thermally annealed. The maximum brightness for devices E, F, and G was 21,900, 20,300, and 30,200 cd/m², respectively. The maximum luminance efficiency was 4.6, 4.8, and 6.2 cd/A, respectively, and the half-life was 14, 21, and 52 h, respectively. The half-life is defined as the time taken for the luminance of the device to drop to half of the original luminance at a driving current density of 10 mA/cm². All measurements were made in air on nonencapsulated devices.

The maximum brightness and luminance efficiency of device F with only NPB annealed did not show obvious improvement when compared with the unannealed device E. This could be attributed to the fact that introducing a thin LiF layer efficiently enhanced the electron injection, such that annealing NPB to decelerate the transport of holes would not help to create a better electron/hole recombination. In addition, device G in which all the layers were thermally annealed showed marked improvement. In particular, the half-life showed a substantial increase from 14 to 52 h.

The above results demonstrate that OLED performance indeed exhibits degradation at higher annealing temperature (i.e. 160 °C). However, if supplied an appropriate annealing temperature (i.e. 120 °C), OLED performance would show significant improvement in luminescence efficiency, brightness, and half-life. The device having NPB annealed exhibited marked improvement in half-life; however, the degree to which the annealing of NPB contributes to the improvement seems insufficient to explain the greater improvement in the device having the Al electrode annealed. A question arises with regards to whether or not the thermal treatment of the Al electrode plays a more important role in the enhancement mechanism, especially for device operating stability.

Fig. 1(a) shows device D having the Al electrode annealed to have a higher current density at a given applied voltage. Additionally, Fig. 1(b) shows device D yielding a greater brightness than devices A, B, and C at a given current density. These results reveal the annealing of the Al electrode to be more significant in enhancing the injection of electrons, leading to a better electron/hole recombination.

In order to investigate the thermal annealing effect of Al electrode on OLED performance, an AFM was used to observe the morphology of the Al electrode at the Alq3/Al interface of the device. Fig. 3 shows the AFM images of the morphologies of the Al electrodes at the Alq3/Al interfaces of devices A, C, and D. The roughness of devices A, C, and D were 5.1, 3.7, and 2.1 nm, respectively. The Al electrode of device D was even more than that of device A or C. Annealing of the Al electrode sufficed to even out the partial undulation of Al film and eliminated spikes that might cause the device to be electrically short and the damage of organic layers due to Joule heating, which was caused by localized high electric field during device operation. The lifetime of the devices was thus greatly increased accordingly.

4. Conclusions

In conclusion, the effect of heat on OLED performance was not entirely negative. The OLEDs annealed at 120 °C showed marked performance improvement. Selectively annealing the NPB and Al electrode layers, especially the latter one, has shown to greatly improve the performance. The enhanced performance was attributable to the fact that annealing NPB slowed hole transport and annealing of Al electrode increased electron injection, leading to higher electron/hole recombination efficiency.

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References