

# Improving the Performance of Organic Light-Emitting Diodes Containing BCP/LiF/Al by Thermal Annealing

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**Abstract**—In this paper, we examined the effect of post-packaging annealing on the performance of organic light-emitting diodes containing tris-(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ ) or 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) in direct contact with a LiF–Al bilayer cathode. The detailed electroluminescent (EL) characteristics were compared before and after annealing at 70 °C for 5 hrs. It was found that better luminous efficiency as well as greater power efficiency could be achieved for devices with BCP/LiF/Al structure. However, other devices consisting of  $\text{Alq}_3$ /LiF/Al were less affected. It is believed that the thermal treatment helps to enhance the electron injection for the former, and less helpful for the latter.

**Index Terms**—Annealing, light-emitting diodes (LEDs), organic.

## I. INTRODUCTION

ORGANIC light-emitting diodes (OLEDs) have been widely investigated since Tang and VanSlyke [1] reported the first high-brightness and low-voltage heterojunction device. Tremendous efforts have been directed toward improving the performance of OLEDs [2]–[5]. One of the conditions of achieving high emission efficiency in OLEDs is a balance of the hole–electron injection [6], [7]. It is not trivial since, in general, there is a big difference in the hole and electron mobilities [8]. One solution is to use materials with higher electron affinity (e.g., silole derivatives) as the electron transport layer and make use of a composite hole transport layer (c-HTL) [9], [10].

Apart from the above, thermal treatment during or after deposition of the functional layers of OLEDs seems to be an additional way to further enhance device performance. Annealing of organic thin films of such as  $\text{Alq}_3$ -based devices has been investigated. Noticeably different results were obtained due to the different annealing conditions used among these reports [11]–[16]. In this paper, we report the effect of post-packaging annealing on various OLEDs. It was found that higher luminous efficiency and power efficiency could be achieved by post-packaging annealing at 70 °C for 5 hours in OLEDs containing 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) in direct connection

with LiF–Al. However, annealing was found to be not so helpful for other devices with  $\text{Alq}_3$ /LiF/Al. Improvement in the case of BCP–LiF–Al is believed to be due to the enhancement of electron injection by thermal treatment. Secondary ion mass spectrometry (SIMS) and X-ray photoemission spectroscopy (XPS) measurement were performed to characterize the Li diffusion and/or doping in these two organic thin films.

## II. EXPERIMENTS

In this study, we fabricated three devices, denoted as devices A, B, and C, with the structures of the equation shown at the bottom of the next page.

All devices were fabricated in the same run in order to eliminate different operation errors. They were all green emission devices with  $\text{Alq}_3$  as the emitter. Before testing, all the devices were encapsulated in a glove box filled with argon. Oxygen and water concentrations are kept below 0.1 ppm. Aluminum metal cover, thin film desiccant tape, and UV-curable epoxy were used for encapsulation. Half lifetime of  $\geq 10\,000$  hours of device A (initial luminance of 100  $\text{cd}/\text{m}^2$ , under constant current driving) could be easily achieved using the above encapsulation equipment even though organic materials were used as received and normal ITO glass substrates were used. Thus it is believed that any change of device performance of our encapsulated devices is intrinsic in the device itself and not due to extraneous factors.

ITO coated glass with the sheet resistance of  $25\Omega/\square$  were used as the starting substrates. The substrates were first soaked in ultra-sonic detergent for 30 min, then spray cleaned with deionized (DI) water for 10 min. They were then soaked in ultra-sonic DI water again for 30 min and oven-bake dried for 1 h. Organic materials, including NPB (N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine),  $\text{Alq}_3$  and BCP, were all purchased without further purification for device fabrication. All the films were prepared in a high vacuum chamber with a base pressure of less than  $1 \times 10^{-6}$  torr. The evaporation rate was typically 1–2 Å/s, 0.2–0.3 Å/s and 3–4 Å/s for organic materials, LiF and Al, respectively. A quartz crystal monitor was used for determining the thickness of films *in situ*. All the devices were transferred to glove box for encapsulation without exposure to atmosphere. Annealing of the samples was performed in digitally-controlled oven at 70 °C for 5 h.

The luminance-current density-voltage ( $L$ - $J$ - $V$ ) characteristics of the encapsulated device with and without annealing were recorded simultaneously by a semiconductor parameter

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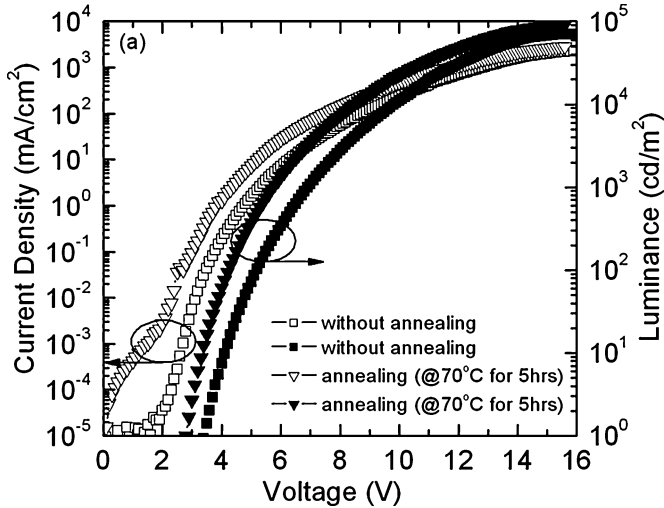


Fig. 1.  $J$ - $V$ - $L$  characteristics of device B with/without post-packaging annealing.

analyzer (HP4145B) combined with a calibrated silicon photodiode. The electroluminescence (EL) spectra were obtained from the PhotoResearch PR650 spectrometer. SIMS analysis was used to examine the diffusion of dissociated Li into the organic thin films. SIMS depth profiling was performed by sputtering and analysis of 8-keV Cs ion beam. XPS measurements were done using the Al  $K\alpha$  line at 1486.6 eV as the light source. The samples used in surface analysis were fabricated on ITO coated glass with organic layers and LiF (1 nm) on top of it. They were not packaged and annealed at the same condition with those encapsulated devices.

### III. RESULTS AND DISCUSSION

For device A, comparing the EL performance with and without post-packaging annealing, it was found that there were no noticeable changes in terms of the turn-on voltage, maximum luminance as well as luminous efficiency. This result does not agree with those in [16], [17]. Different thermal treatment conditions may account for this difference. In our experiment, post-packaging annealing was carried out at 70 °C for 5 h. However, for device B, the situation is different. Fig. 1 shows the  $J$ - $V$ - $L$  characteristics of device B with and without annealing. It can be observed that current density increases significantly especially at higher luminance, the turn-on voltage required for the luminance of 1  $\text{cd}/\text{m}^2$  was decreased from 3.4 to 2.8 V correspondingly due to annealing. The maximum luminance was improved from  $\sim 70\,000\ \text{cd}/\text{m}^2$  to  $\sim 90\,000\ \text{cd}/\text{m}^2$  at the driving voltage of 15.5 V. The luminous and power efficiencies curves are shown in Figs. 2 and 3. The luminous efficiency and, especially, the power efficiency were much improved after annealing. For instance, the luminous efficiency

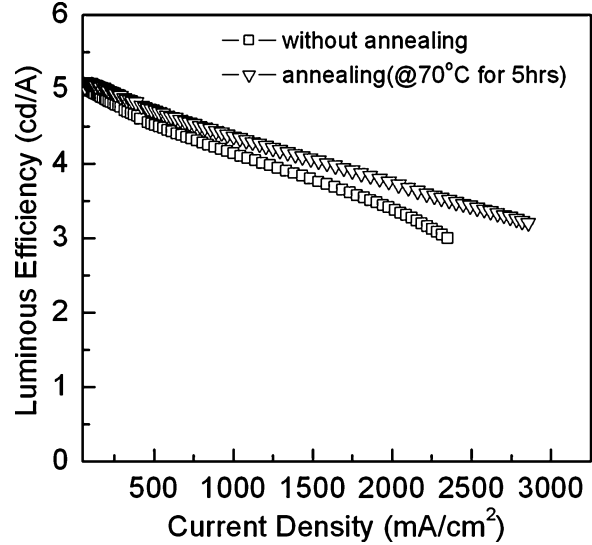


Fig. 2. Luminous efficiency curves of device B before and after annealing.

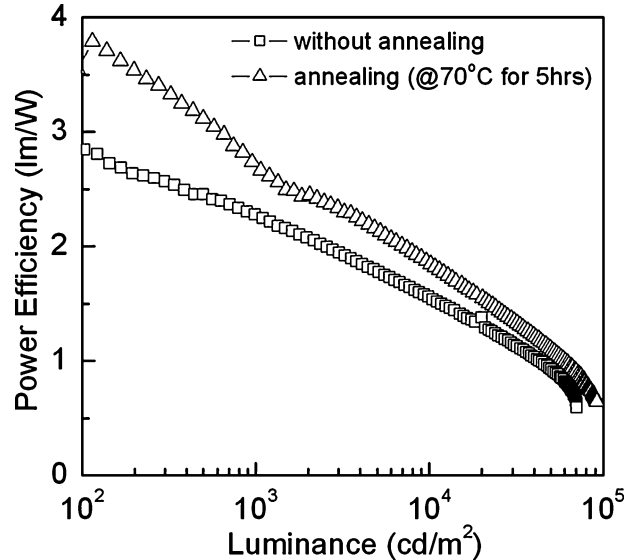


Fig. 3. Power efficiency curves of device B before and after annealing.

at 100  $\text{mA}/\text{cm}^2$  was improved from 4.9 to 5.1  $\text{cd}/\text{A}$ ; the power efficiency at 100  $\text{cd}/\text{m}^2$  was increased from 2.85 to 3.67  $\text{lm}/\text{W}$ .

Based on the different results for devices A and B in our experiment, the annealing effect on the ITO/NPB/Alq<sub>3</sub> can be neglected considering that they are the same for two devices. Additionally, we have measured the EL spectra of devices A and B (not shown here); they remain unchanged after annealing. This implies that annealing induced optical effect is absent. Obviously, the improved EL performance for device B is caused by the addition of BCP in-between the Alq<sub>3</sub> layer and LiF-Al cathode.

Device A : ITO/NPB(50 nm)/Alq<sub>3</sub>(60 nm)/LiF(1 nm)/Al(150 nm)

Device B : ITO/NPB(50 nm)/Alq<sub>3</sub>(60 nm)/BCP(20 nm)/LiF(1 nm)/Al(150 nm)

Device C : ITO/NPB(50 nm)/Alq<sub>3</sub>(30 nm)/BCP(20 nm)/Alq<sub>3</sub>(30 nm)/LiF(1 nm)/Al(150 nm)

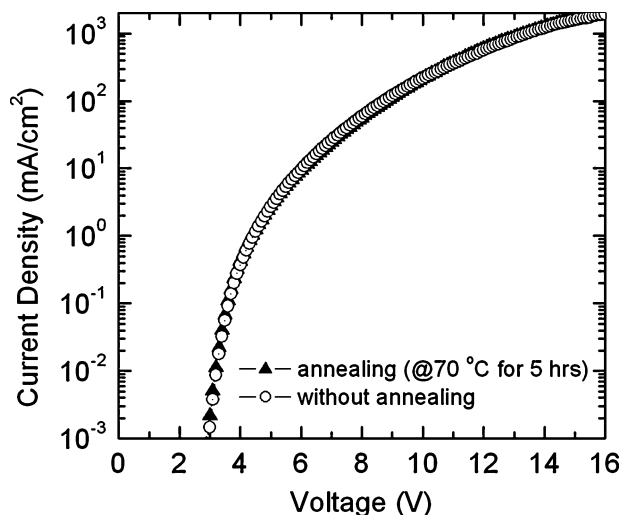


Fig. 4.  $J$ - $V$  curves comparison of device C before and after annealing.

The annealing temperature ( $70\text{ }^{\circ}\text{C}$ ) is rather close to the glass transition temperature ( $T_g$ ) of BCP ( $\sim 80\text{ }^{\circ}\text{C}$ ). It is expected that significant molecular movement is possible. Since the annealing duration is quite long, interdiffusion between organic layers may occur. This interdiffusion was reported to be helpful for the elimination of heterointerface and, therefore, improves the overall performance of OLED [18]–[20]. To check this possibility, we further fabricated device C with a structure of ITO/NPB/ $\text{Alq}_3$ /BCP/ $\text{Alq}_3$ /LiF/Al. There are two BCP/ $\text{Alq}_3$  heterointerfaces within this device. Using the same thermal treatment with device A and B, it was found that the  $J$ - $V$  curves shown in Fig. 4 remain unchanged after annealing. This may be due to the thicker BCP used here, which is 20 nm instead of 10 nm in [20]. It can be inferred that interdiffusion does not contribute to the improved performance of device B. This observation further shows that the device with  $\text{Alq}_3$ /LiF/Al cannot be improved by our annealing.

We suggest that the improvement of EL performance of device B is due to the enhancement of electron injection induced by thermal annealing. One possible reason is surface morphology change and better contact of organic/metallic layers after annealing, resulting in an increase of injected current [14]. Another explanation is that under thermal annealing, more dissociated Li diffuse into and doping the BCP layer resulting in better electron injection. However, for  $\text{Alq}_3$ , current annealing does not cause more Li diffusion into it. Shown in Fig. 5 are the Li counts versus depth of Li in BCP and  $\text{Alq}_3$ , with the organic layers thickness identified by the carbon signature. The thickness of BCP and  $\text{Alq}_3$  is 30 and 25 nm, as shown in (5a) and (5b), respectively. It is clearly seen that for the case of BCP/LiF, the dissociated Li diffusing into BCP was much increased after annealing. However, for  $\text{Alq}_3$ /LiF, the situations before and after annealing are almost the same. Furthermore, the XPS spectra, as shown in Fig. 6, indicate that the N(1s) core level of BCP shift to higher binding energy and broaden a little after annealing, which is similar with other reports on BCP/Li system when increasing Li incorporation [21]. This shift and broadening also verify the enhancement of Li diffusion into

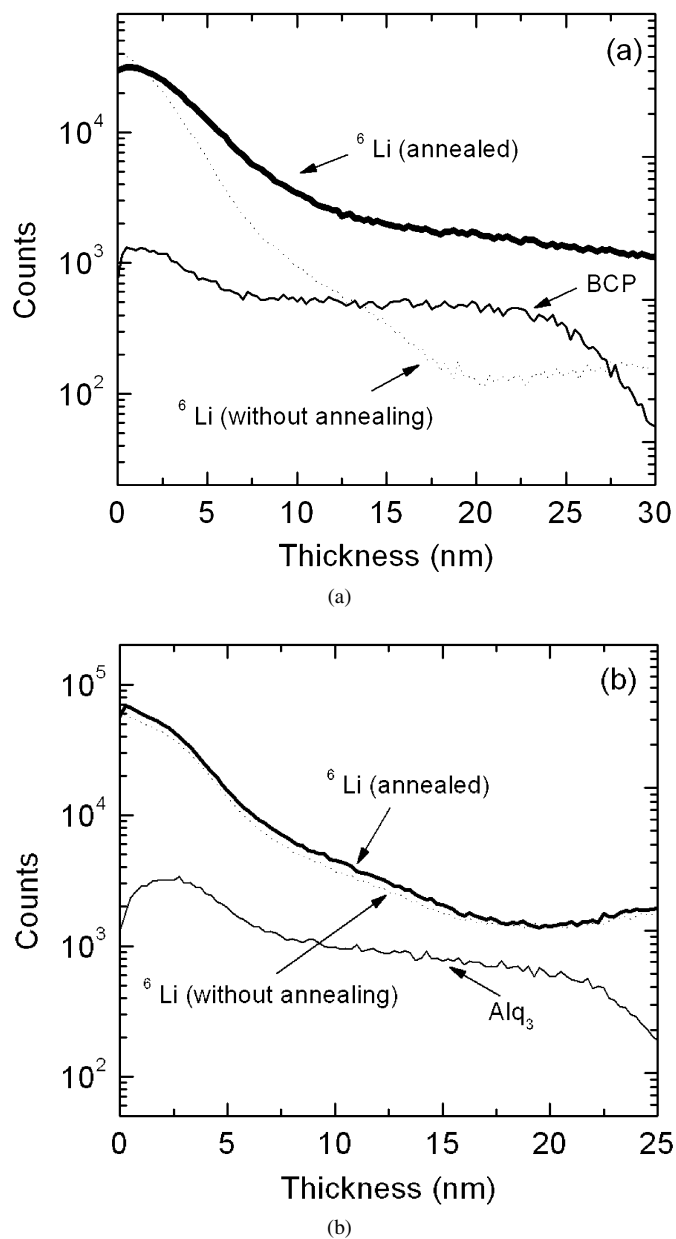


Fig. 5. (a) SIMS profile showing Li counts versus depth for BCP(30 nm)/LiF(1 nm). (b) Li counts versus depth for  $\text{Alq}_3$ (25 nm)/LiF(1 nm).

BCP layer due to our annealing. Lithium diffusion and doping of the organic thin films shall increase the transparency of the barrier to electron injection from the cathode contact [21] and, therefore, improve the overall EL performance of our device B with annealing.

Finally, we measured and compared the lifetime of device B with and without annealing under constant current driving. The preliminary results are depicted in Figs. 7 and 8. It can be seen that the device after annealing at  $70\text{ }^{\circ}\text{C}$  showed a slower decay of initial luminance ( $\sim 1200\text{ cd/m}^2$ ) and the increase of driving voltage was also somewhat smaller. It has a better luminous efficiency and greater power efficiency due to annealing. This results also in a longer lifetime. These results are consistent with those reported recently [22]. Indeed, compared with other thermal treatment, e.g., *in situ* post-growth annealing in

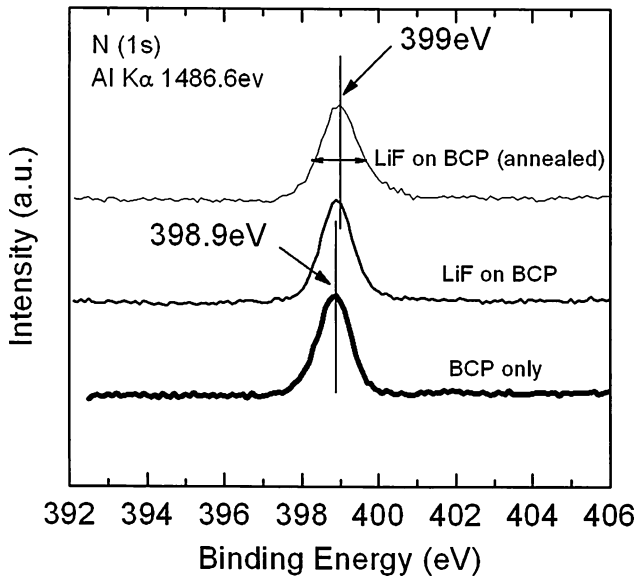


Fig. 6. XPS spectra showing the broadening and shift in the N(1 s) core level of BCP after annealing.

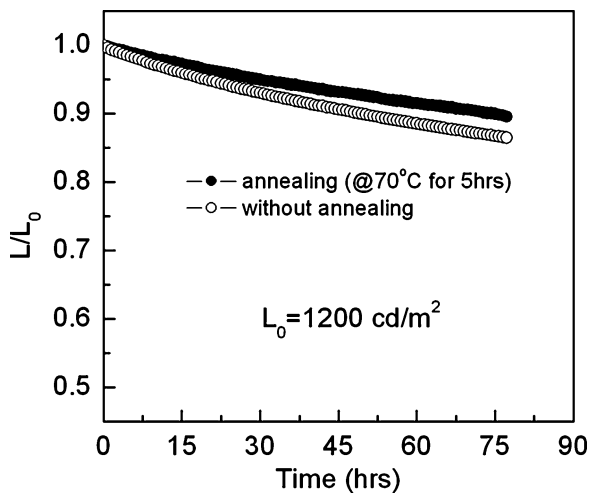


Fig. 7. Normalized EL intensity versus time curves of device B with/without post-packaging annealing.

vacuum or *ex situ* post-deposition annealing in nitrogen environment, the post-packaging annealing is quite easy to carry out. This post-packaging annealing may be a new way to improve the stability of OLED involving a BCP layer.

#### IV. CONCLUSION

In summary, we have examined the effect of post-packaging annealing on the EL performance of OLEDs with BCP/LiF-Al and Alq<sub>3</sub>-LiF/Al structures. Better efficiency and lower turn-on voltage can be achieved through this thermal treatment for the former. We further characterized and analyzed the dissociated Li diffusion and doping of BCP and Alq<sub>3</sub> thin films by SIMS as well as XPS. We believe that more doping of BCP after annealing lowered the electron injection barrier and increase the electron injection, resulting in the overall EL performance improvement of BCP/LiF containing devices. BCP was intensively

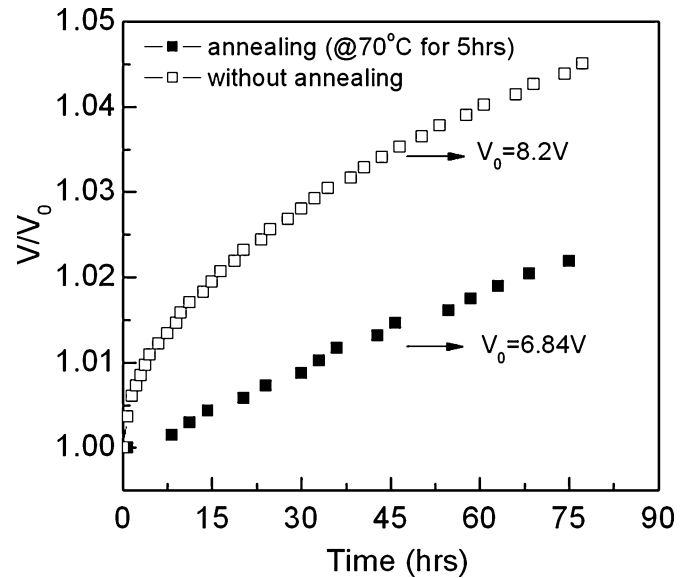


Fig. 8. Normalized voltage versus time curves of device B with/without post-packaging annealing.

used in OLED especially in phosphorescent OLEDs as the hole blocking layer (HBL). It is believed that this post-packaging annealing suggest a simple and economical way to further increase the already extremely high efficiency of phosphorescent OLEDs [23]. We also show that the same treatment can improve the device lifetime as well.

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