# Thermal annealing for long-term stability of polymer light-emitting devices

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## Abstract

*Thermal annealing of a polymer light-emitting diode (PLED) is shown to result in a remarkable improvement in the long-term stability of the device. The best half-life is obtained at an annealing temperature above the $T_g$ of emitting polymer. It is shown that the annealing of the emitting polymer layer results in a more than an order of magnitude increase in the half-life in spite of a decrease in the efficiency of the device as the annealing temperature increases.[1]*

## 1. Introduction

Polymer light-emitting diodes (PLEDs) that are based on conjugated polymers have attracted much attention because of their potential applicability to large-area flat panel displays.[2] While various avenues have been explored to improve the device efficiency and its lifetime, one avenue that has only recently received attention is the thermal treatment of emitting polymer layers [3] and that of the device.[4,5,6] Liu et al.[3] reported that annealing before cathode deposition at a temperature higher than the glass transition temperature $(T_g)$ can improve the efficiency of hole injection at the expense of the PL efficiency, and *vice versa*. Lee and Park [4] found that thermal annealing at a temperature above the $T_g$ of the emitting polymer before metal deposition or pre-annealing increases maximum light output but lowers the quantum yield. However, they found that thermal annealing after Al deposition or post-annealing significantly enhances the device efficiency. They attributed the improvement to an altered polymer/Al interface. In contrast, Niu et al.[5] demonstrated that by thermal annealing after cathode deposition just below the $T_g$ of polyfluorene (PF) polymers the device performance was greatly enhanced. However, the effect of annealing on the lifetime of the device has not been well studied.

In this work, we present an effect of thermal treatment before cathode deposition for the purpose of achieving long-term stability of a PLED and demonstrate how annealing can be tailored to improve the lifetime of the device. A major disadvantage of PLEDs has to do with the instability under operating conditions and the lack of long-term reliability, that is, lifetime of the device.

## 2. Experiment

Substrates were indium-tin oxide (ITO) coated glass plates with a sheet resistance of ca. 20 $\Omega$ per square. To fabricate the device, ITO substrate was cleaned in succession by ultra-sonication in the acetone, isopropanol, and deionized water. The cleaned substrates were dried at 200 °C for 1 h. Then, the substrates were exposed to RF plasma for surface treatment using oxygen and argon for 30 sec at a power of 100 W. The flow rate of the $O_2$ and Ar were 20 sccm and 80 sccm, respectively. Onto this cleaned substrate, a 50 nm thick hole-injection layer (HIL) of poly(3,4-ethylenedioxythiophene)-poly(4-styrene sulfonate) (PEDT-PSS) was spin-coated and the film was annealed in a nitrogen environment at 200 °C for 10 minutes. Then LUMATION[*][7] Green 1300, purchased from The Dow Chemical Company, was spin coated on top of the PEDT-PSS layer, and subsequently annealed at different conditions in the glove box under nitrogen atmosphere. The polymer solution for film preparation was made by

dissolving 15 mg of polymer in 1 mL of xylenes. A bilayer cathode consisting of a 10 nm calcium (Ca) layer and a 170 nm aluminum (Al) layer were deposited by evaporation in a ultra-high vacuum with a base pressure less than $2\times10^{-6}$ Torr. The device structure we used for the purpose was: ITO/PEDT-PSS/LUMATION Green 1300/Ca/Al. Finally the device was packaged using a simple can cover fixed with an ultraviolet (UV) curing epoxy resin. The emitting area was defined by using a shadow mask to be $2\times2$ mm$^2$.

## 3. Results and Discussion

The applied voltage, current density, and photometric efficiencies at 1000 cd/m$^2$ as a function of annealing temperature for the emitting polymer layer are listed in Table I. The device annealed at 90 ℃, which is the temperature below the $T_g$ of LUMATION Green 1300, has the greatest efficiency for those temperatures studied. The results in Table I clearly indicate that the device efficiency decreases with increasing annealing temperature.

TABLE I. Applied voltage, current density, and efficiencies at 1000 cd/m$^2$ as a function of annealing temperature for the annealed device before the cathode deposition.

| Temp. (℃) | Applied voltage (V) | Current density (mA/cm$^2$) | Efficiency (cd/A) |
|---|---|---|---|
| 90 | 3.77 | 7.55 | 13.04 |
| 110 | 3.80 | 8.76 | 11.26 |
| 150 | 4.06 | 9.53 | 10.44 |

These decreases of the efficiency according to the increased annealing temperature are due to an interaction between the polymer chains by the change of the chain conformation.[4] The intermolecular interaction can be further reduced to enhance the exciton confinement.[8] Thermal annealing above the $T_g$, however, enhances

the polymer packing density of the polymer thin film. The enhanced packing was confirmed by the reduction of thickness. It can increase the thermal stability of the polymer thin film and its ability to endure the Joule heat generated during operation. The effect of the increased thermal stability of the device can play an important role in lengthening the lifetime. The half-life is measured at 50 % humidity and 25 ℃ with an initial brightness of 1000 cd/m$^2$ while keeping the current constant.

The results for the decay brightness with time are given in Fig. 1. As shown in Fig. 1, the half-life of the annealed devices at 90 ℃ (below $T_g$) and 110 ℃ ($T_g$) are 80 and 110 h, respectively. However, that of the device annealed at 150 ℃ is about 2000 h in spite of its lower efficiency.
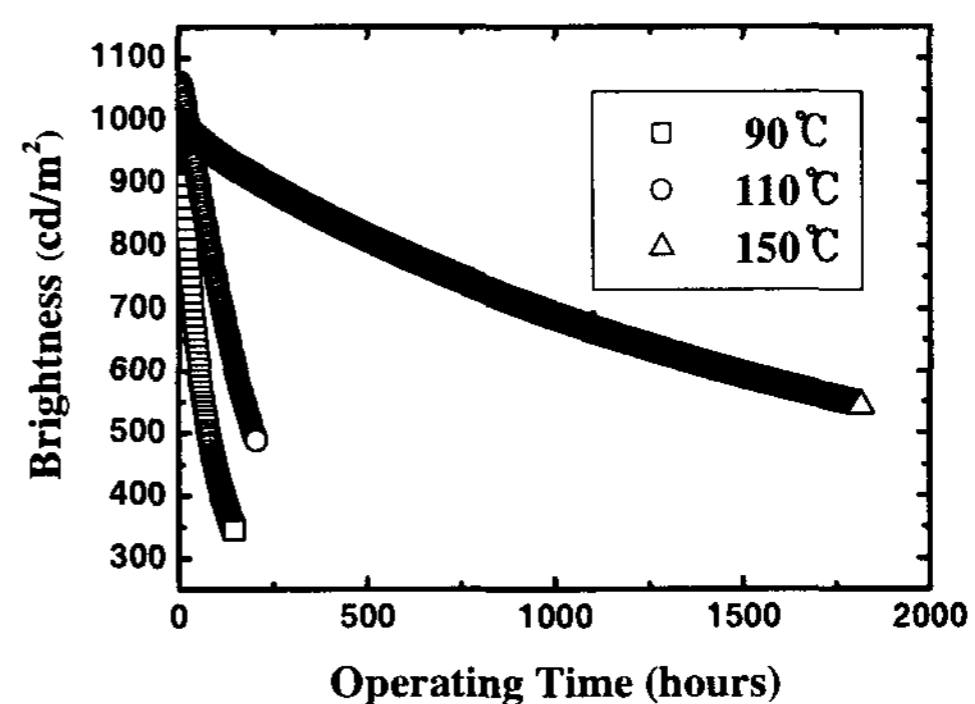


Figure 1: Brightness vs. operating time of the pre-annealed device at 90 ℃ (square), 110 ℃ (circle), and 150 ℃ (triangle) is shown. The measurement was carried out at 50 % humidity and 25 ℃ with an initial brightness of 1000 cd/m$^2$ under continuous driving at constant current.

This fact indicates that the enhancement of thermal endurance of the polymer film contributes to the long-term stability of the device in spite of its initial adverse effect. Similar annealing experiments were done on another LUMATION light emitting polymer (LEP) purchased from The Dow Chemical

Company. The lifetimes of those devices are not shown in this paper, however, the lifetime was also enhanced as annealing temperature increased too.

Annealing is a standard technique[9] used in the processing of inorganic semiconductors for fabrication of electronic circuits. Because of the nature of polymeric materials, care must be taken in applying annealing to organic devices such as PLEDs. These materials exhibit a fluid-like behavior above their $T_g$ and the thermal expansion coefficients are much larger than those of the inorganic counterparts. When a metal is deposited onto a polymer layer at a high temperature and then cooled, buckling takes place to relieve the stress generated by the large difference in thermal expansion coefficient between the metal and the underlying organic layer. This buckling leads to the formation of a wavy metal surface.[10] Thermal stress is also generated when a bilayer consisting of a metal layer and a polymer layer is heated due to the difference in the thermal expansion coefficient. This stress also causes formation of wavy metal surface,[11] much like the ripple-like morphology of the metal electrode surface that is usually observed when organic LEDs fail to function after a thermal breakdown.[12]

The formation of a wavy metal surface is caused by the thermal stress generated in the emissive polymer layer that has the lowest $T_g$. When the device is heated by Joule heating or external heating a compressive stress sets in, which is relieved by buckling that leads to the wave formation.[11] This formation of a wavy metal surface can be prevented if a proper annealing is applied to the layer of the lowest $T_g$ prior to metal deposition. When a polymer film on a substrate is heated and cooled, a tensile stress is generated that can be retained in the film. As long as this tensile stress is larger than the compressive stress generated by heating, no wave structure forms.[11] Otherwise, the wave structure forms. Thus, the wavelength and/or roughness of the wave indicate the thermal stability of the multi-layered device structure.

Shown in Fig. 2. are atomic force microscopy (AFM) images of an aluminum surface of ITO/PEDT-PSS/LUMATION Green 1300/Al (40nm) externally heated at $250\,^\circ C$ for 24 h. All devices were annealed before Al deposition at different temperatures. From these images, the effects of thermal treatment of LUMATION Green 1300 at the different temperatures are clearly observed. The root mean square (RMS), which represented the degree of the surface roughness, gradually decreases from 24 nm to 15 nm. In addition to, the wavelength of the wave tends to decrease as the annealing temperature increases,[11] so a higher annealing temperature would generate a higher tensile stress and thus the layer becomes more resilient to severer external heating conditions. Therefore, it is seen that the wavy metal surface results when the device is post-annealed. It was found that the performance of the post-annealed device above $T_g$ is much worse than that of the device pre-annealed. Another important reason for the lower performance would be accelerated the diffusion between polymer/metal that takes place when the device is post-annealed. The metal diffusion into polymers has been proposed as causes leading to the formation of dark spot and device failure. Recently, Chua et al.[13] reported that by inserting another parylene layer in between the polymer and cathode layers, the probability of formation of nonemissive areas is further reduced.
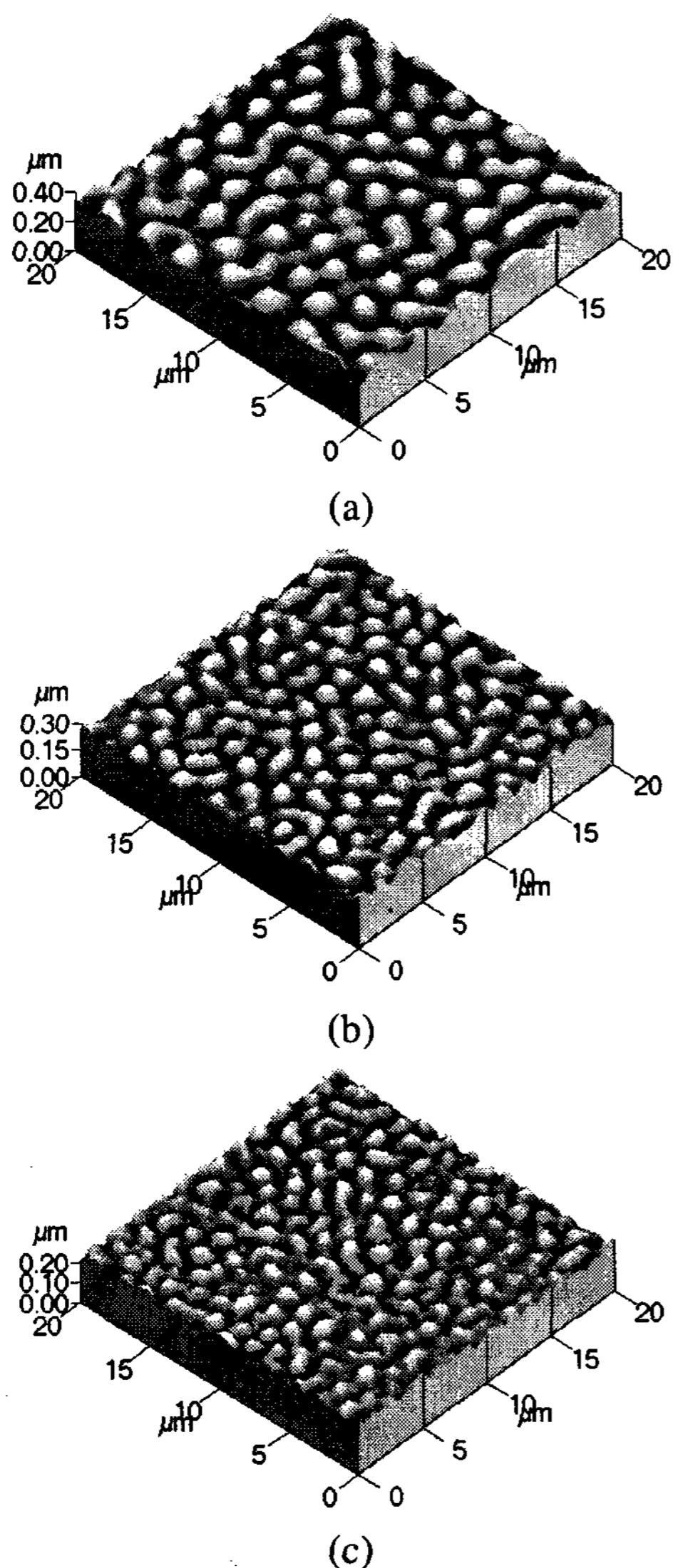
(a)



(b)



(c)

Figure 2: AFM images of the Al surface in the ITO/PEDT-PSS/LUMATION Green 1300/Al structure after external heating in an oven maintained at 250 °C for 1day. (a) pre-annealed at 90 °C , (b) 110°C, and (c) 150°C. RMS is 24 nm, 18 nm, and 15 nm, respectively.

## 4. Summary

It has been found that a proper annealing of a PLED leads to a more than an order of magnitude improvement in the half lifetime of the device in spite of a decrease in the efficiency of the device as annealing temperature is increased. Annealing has to be layer-specific in that the annealing should center on the layer with the lowest $T_g$. Through thermal stress experiments, the stiffness of the annealed polymer film improves with increasing temperature. The pre-thermal annealing method provides a practical way to obtain PLED with better long-term stability.

## 5. Acknowledgement

## 6. References

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