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Improvement of Electroluminescence Properties in Polymer Light Emitting Devices by Post-Thermal Process

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Recently, polymer light emitting devices (PLED) are studied in flat panel display and illumination industry because it has potential utility such as brightness, flexibility, low power consumption, etc. However, its external quantum efficiency is still very low. So we proposed post-thermal annealing under temperature variation. This method makes contact between EML and cathode and it helps to improve the characteristics of the device without buffer layers such as EIL, ETL that demand the vacuum deposition. Our results show the increases over 2 times of luminance and 20 times of current efficiency comparing to the non-post annealing device.

Keywords Luminance; polymer light emitting devices; post-annealing; quantum efficiency

1. Introduction

Since the 1990s, organic light emitting diodes (OLEDs) have been shown by Brroughes group. In the last decades, OLED have attracted the interest of researchers and industry due to potential use as integrated light sources with applications in different areas, from display technologies and solid state illumination to medical applications, not to mention manufacturing simplicity, low costs of fabrication, wide range of emission colors, and ability to work with low voltage and low power [1–3].

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Nevertheless, OLEDs still remain objective with poor structural stability resulting from several degradation processes and low conversion efficiency. So many researchers focused in enhanced efficiency. First, in terms of materials, Q. Sun *et al.* reported inorganic quantum dot LED with high external quantum efficiency [4] and S.Y. Ryu *et al.* reported combination LED has a multiple structure with a quantum dot and polymer interfacial layer [5]. It has very high current efficiency, but it need complex structure. Next, there is a research on additional structure formation as well, for instance, microlens array. This microlens array method can reduce the total inter-reflection loss at the interface of substrate and air by changing the difference of reflective index [6,7]. Previous mentioned methods are very efficient but not good for OLED market share because require low cost and simple structure. In short, these methods improved current efficiency according to structure design but had not thrown up PLED merits. In order to improve PLED efficiency using easier process, in contrast, the post-thermal treatment also has been studied. Liu *et al.* 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 photoluminescence efficiency [8]. In addition, Niu *et al.* demonstrated that by thermal annealing after cathode deposition just under the T_g of polyfluorene polymer [9]. Its device performance was greatly enhanced. However, the annealing variations were restrictive condition and dependent on time.

Therefore, we tried to systematically investigate the optimum post-annealing condition for the most efficient PLED. Specifically, we studied the effect of characteristics that there is not only film morphology but also luminance, current efficiency according to annealing variation under the T_g of conjugated polymer (copolymer). Finally, we were able to confirm the probability of high luminance and efficiency by the fabricated device that has only 5-layer structure. Our results show the increases over 2 times of luminance and 20 times of current efficiency comparing to the non-post annealing device.

2. Experimental Methods

In this study, we fabricated the PLED and performed post-annealing for increasing the efficiency of the device. Figure 1 shows our device structure and band diagram with five-layer, which consists of anode, hole injection layer (HIL), hole transport layer (HTL), copolymer as the emitting layer and cathode [10]. This device has merits of solvent process and simple structure.

Indium tin oxide (ITO), a typical anode material, was deposited on a glass substrate to a thickness of 150 nm and patterned through the photolithography process. We performed cleaning procedure of IPA, acetone, methanol and DI (Deionized Water) using ultra-sonic cleaner for 5 min. Then, we formed a HIL with PEDOT: PSS (poly (ethylenedioxythiophene): polystyrene sulphonate, Baytron VP AI 4083, H. C. Starck) on ITO to a thickness about 25 nm. After, we did thermal annealing process at 150°C for 10 min on plate. It was used as the buffer layer on the anode to increase the work function of anode from 4.7 eV (ITO) to 5.0 eV and reduce the surface roughness of the anode to obtain stable and pin-hole-free electrical conduction of the device. Next, we formed HTL with poly-TPD (poly(N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)benzidine), ADS 254BE, American Dye Source) dissolved in the chlorobenzene of 2 wt% to thickness of 50 nm. After spin-coating

poly-TPD on PEDOT:PSS, we did thermal treatment in vacuum oven for 30 min [11]. Its highest occupied molecular orbital (HOMO) level is 5.2 eV, which is very close to the work function of the ITO/PEDOT:PSS anode. Its low energy barrier helps hole to move more easily and inject into emitting layer, so it fully functions as HTL. The EML was spin-coated with light emitting copolymer (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1′,3}-thiadiazole)], ADS 233YE, American Dye Source) dissolved in toluene solvent of 1 wt% on poly-TPD layer. It is not a problem that poly-TPD has proven to be a good resistor to non-polar organic solvents such as toluene and xylene [4]. The copolymer has emitting characteristic with maximum photoluminescence of 528 nm that means green light emitting device when it used active layer. It also has molecular structure as shown in Figure 2.

The Al metal layer for cathode was deposited on EML through thermal evaporation. The area of emission layer perpendicular to anode and cathode electrode is 9 mm^2.

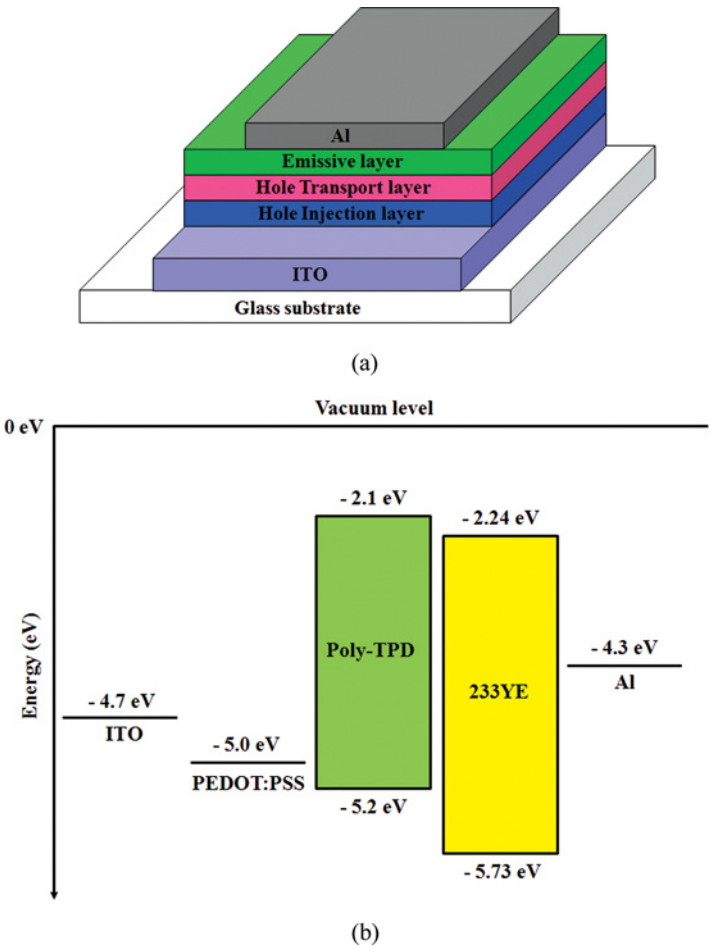

Figure 1. Schematic diagram of fabricated PLED: (a) structure and (b) energy band diagram. (Figure appears in color online.)

3. Results and Discussion

We performed post-annealing process at 90, 120, 150 and 180°C during 10 min in N_2 glove box for stability of interface characteristic in device [12]. And then, we measured the characteristics such as efficiency and luminance by a LS-100 (Minolta, Japan).

In the PLED, the majority carriers of the emissive copolymers are often holes, and the electron-hole collision area is located at the interface between the emissive copolymer and the cathode. Therefore, uniformity of the emissive copolymer is very important factor even if post annealing temperature changes in PLED. In order to confirm the morphology of the copolymer layer depending on annealing temperature, we performed the AFM analysis at each annealing condition as shown in Figure 3. As increasing the annealing temperature on the copolymer layer, there is not a great difference in surface morphology on active layer. Based on the AFM results, the surface morphology of copolymer is homogeneous on a narrow scale.

Figure 4 shows luminance curves with each temperature condition as a function of applied voltage. The maximum luminescence of 5,314 cd/m^2 is obtained in the reference device. The PLED devices with post annealing exhibit maximum luminance of 7,168 cd/m^2 at 90°C, 9,742 cd/m^2 at 120°C, 12,040 cd/m^2 at 150°C and 8,738 cd/m^2 at 180°C, respectively. The luminance is improved as the temperature increases by 150°C post-annealing temperature, but the above of the 150°C, this value decreases. The maximum luminance of PLED with 150°C annealing condition is 12,040 cd/m^2 and it is 2 times of the luminance of reference device, 5,314 cd/m^2.

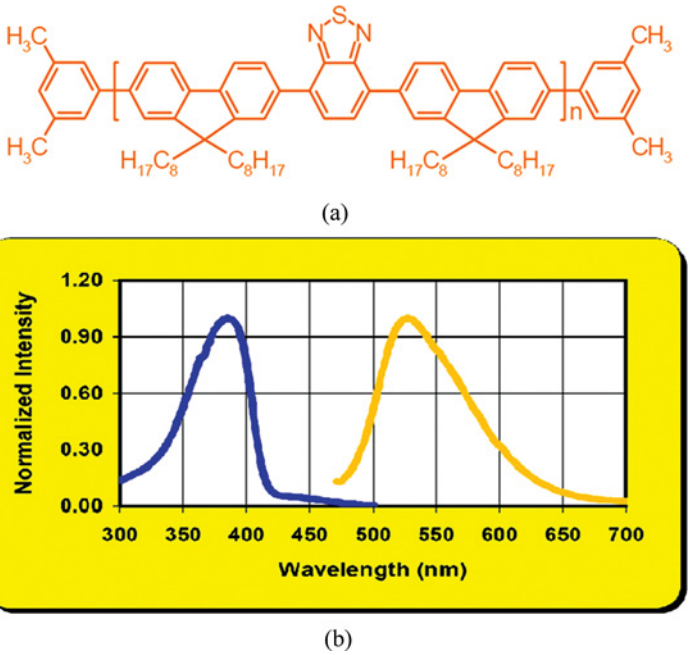

Figure 2. The characteristics of emissive copolymer: (a) chemical structure, (b) optical characteristic of absorption and photoluminescence spectra. (Figure appears in color online.)

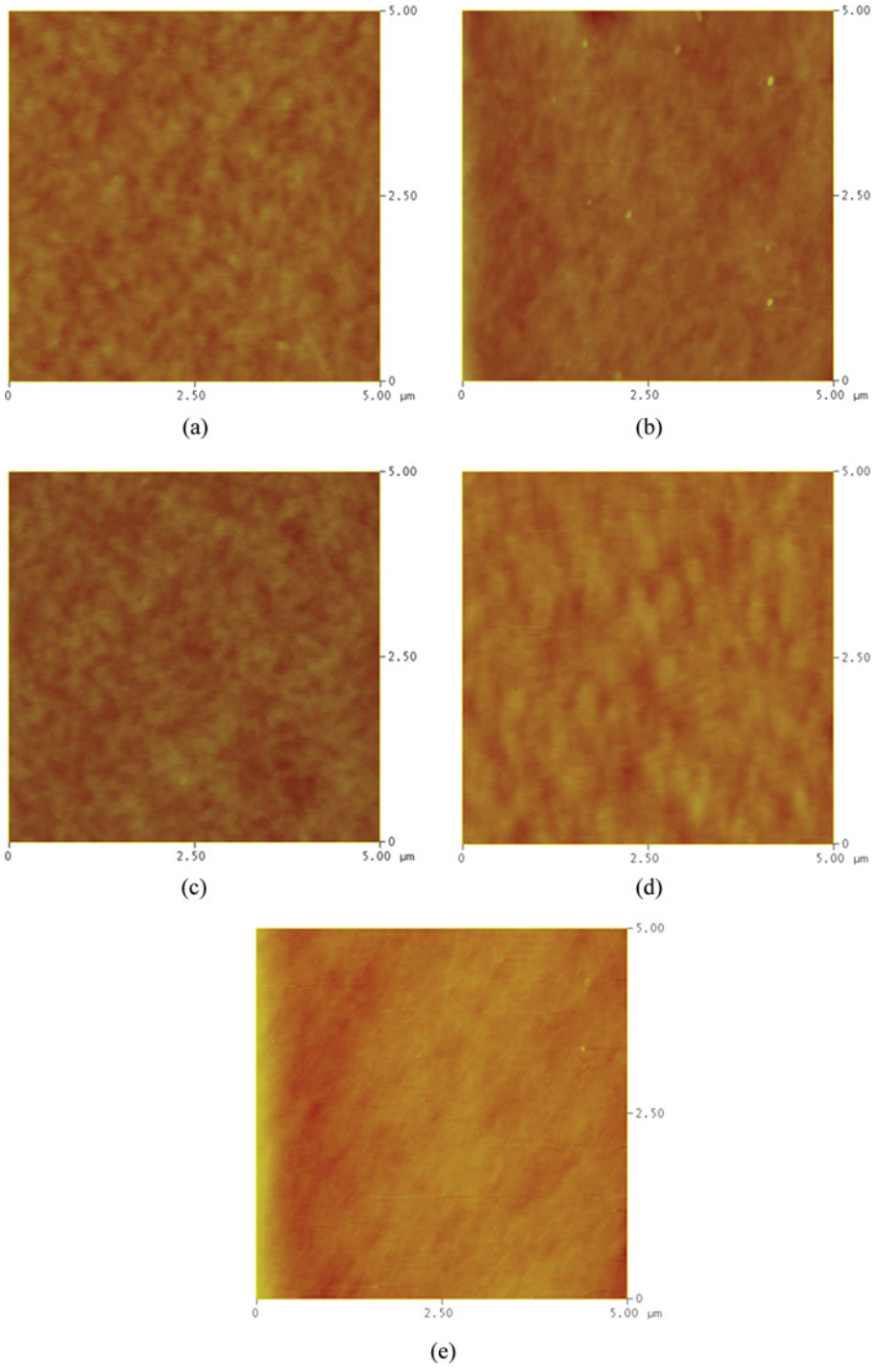

Figure 3. AFM analysis of emissive copolymer surface morphology: (a) reference surface without post-annealing, (b) post-annealed surface at 90°C condition, (c) post-annealed surface at 120°C condition, (d) post-annealed surface at 150°C condition and (e) post-annealed surface at 180°C condition. (Figure appears in color online.)

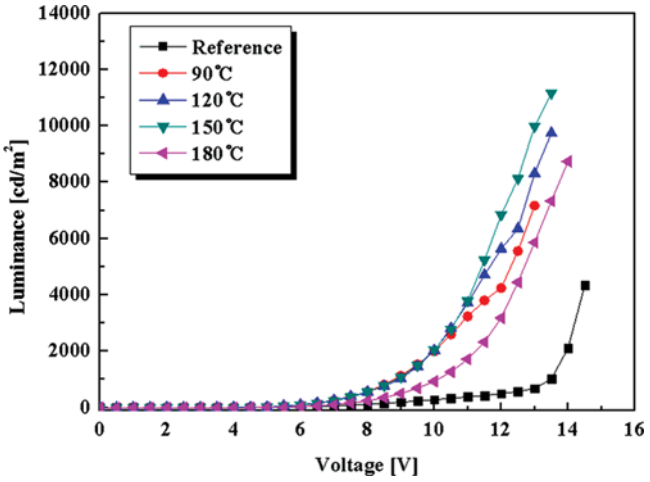

Figure 4. Luminance characteristic according to voltage of fabricated PLED.

Figure 5 shows the current efficiency according to the current density on each temperature. Under 400 mA/cm^2 current density, the efficiency of 90°C and 120°C post-thermal device are 1.0 and 1.5 cd/A. Also, that of 150°C and 180°C post-thermal device are 2.0 cd/A, which is the highest value, and 1.5 cd/A, respectively. The efficiency of the 150°C post-annealed device is 20 times to that of none post-annealed device, 0.1 cd/A.

As the results of our experiment, we confirmed that the luminance and current efficiency are dependent on the post-thermal temperature, and the characteristics of 150°C post-annealed device are more superior to that of the others. To explain the

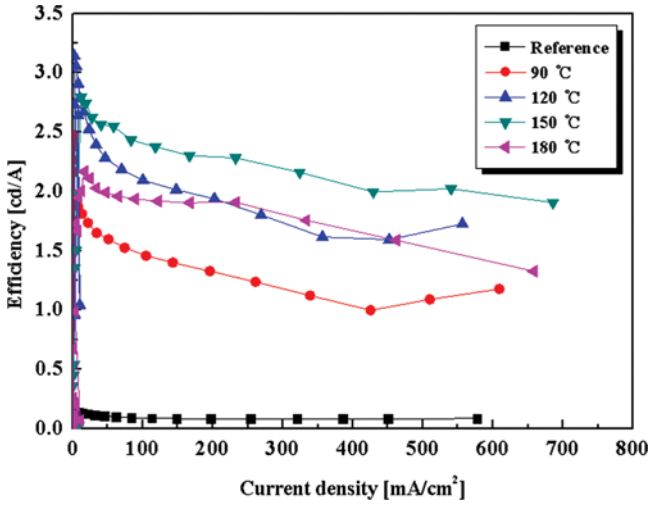

Figure 5. External current efficiency characteristic according to injection current of fabricated PLED.

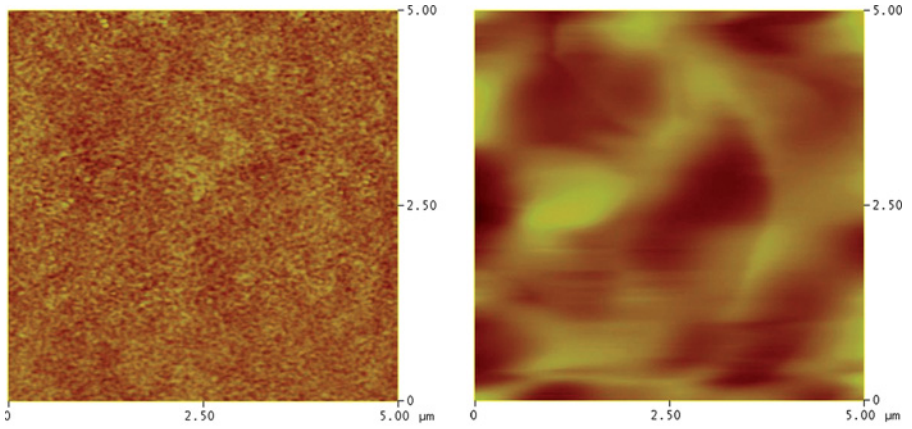

Figure 6. AFM analysis of Al layer surface morphology: (a) reference surface without post-annealing and (b) post-annealed surface at 150°C condition. (Figure appears in color online.)

phenomenon that the characteristic of the device increases as rely on the post-thermal temperatures, it is required to consider the relation between Al layer and emissive copolymer layer. Al deposition does not avoid to the vacuum thermal evaporation process, and this causes a bad contact to the emitting layer [13]. The bad contact has facilitated a degradation and imbalanced injection of carriers. When, it is possible to induce the molecule combinations between Al metal and C (carbon) included in organic emitting material, and Al-C covalent bond formation improves the interfacial adhesion between both [12,14]. It is explained through Figure 6. Above all, as shown in Figure 3, the values of roughness is similar to about 1 nm, without taking effect of post-annealing. In the contrast, Al morphology of 150°C post-annealed device shown in Figure 6 increased about 1 nm comparing to that of none post-thermal device. It verifies that the distance between both interfacial layers was shortened and the contact density was increased. Also, shown in Figure 5, the current density was increased because it is easy for the electrons to inject into emitting layer, as the contact density increases. In our experimental results, the injection current of post-thermal devices is 700 mA/cm^2 that is increased by 100 mA/cm^2, comparing to that of none post-thermal device.

However, if you heat up the device over the specific temperature to improve the interface characteristic, it is rather degenerated. In our device, the melting point of poly-TPD as ETL is near 170°C, and thus doing post-annealing process on 180°C may cause degradation phenomenon of poly-TPD and the optimum thickness of ETL layer changes as the material consisting of the layer is melted. So, ETL does not function their whole roles and the characteristic of device decreases.

4. Conclusions and Perspectives

After manufacturing organic electro-luminescent device using polymer, we confirmed that the efficiency under same current density was improved from 0.1 cd/A to 2.0 cd/A as a result of post-annealing treatment in nitrogen atmosphere. The

fabricated device had characteristics that turn-on voltage was 3.5 V and maximum luminance was 12,040 cd/m^2. The post annealing greatly enhances the EL efficiency. This improvement of PLED performance could be due to the charging of traps located interface between the uniform copolymer as an emissive layer and electrode as Al layer of penetrated into copolymer, lead to the charge injection easily. This post-annealing treatment is an attractive way to achieve efficiency enhancements, as it is a simple low-cost process. So, thermal post annealing can be applied to other polymer device such as the organic photo voltaic device.

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