Effects of thermal annealing on the performance of polymer light emitting diodes

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Thermal annealing plays an important role in controlling morphologies of polymer thin films and consequently the device performance, such as emission spectra, turn-on voltages, quantum efficiency of photoluminescence (PL) and electroluminescence (EL). In thermal annealing there is a tradeoff between hole-injection efficiency and PL efficiency. Annealing at a temperature higher than the glass transition temperature can improve the efficiency of hole injection at the expense of the PL efficiency, and vice versa. Optimizing the annealing conditions can improve the overall EL efficiency. The high efficiency of poly(2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene) based polymer light-emitting diodes is demonstrated: 2.7 cd/A at a luminescence of 1000 cd/m². © 2002 American Institute of Physics. [DOI: 10.1063/1.1427435]

I. INTRODUCTION

Polymer light-emitting diodes (PLEDs) fabricated from semiconducting polymers, such as poly(2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), have potential use in display technology.1–3 Typical PLEDs fabrication involves: (1) preparing polymer solutions, (2) spin-coating the solutions on precleaned indium–tin–oxide (ITO)/glass substrates, (3) removing the solvents in a vacuum at room temperature,4 or annealing the films at a relative high temperature in an inert gas environment,5 and (4) depositing metal cathodes.

It was recently found that the morphology of MEH-PPV films can be manipulated by using different organic solvents, concentrations, and spin speeds, thereby varying optical and electrical properties of the polymer films and PLEDs:5–7 however, the effects of annealing have not been well studied. For amorphous polymers, thermal treatment can play a very important role in changing the morphology. If the temperature is lower than the glass transition temperature Tg, the polymer chains are mainly immobile, thereby maintaining the existing morphology; however, if the annealing temperature is greater than the Tg, the polymer chains will relax. It has been found that the morphology can be modified upon annealing at a temperature higher than the Tg, thus changing the physical properties of the films.7

In this work the effects of thermal annealing on morphologies of MEH-PPV films and consequently the device performances are investigated. The dependence of photoluminescence, electroluminescence as well as efficiency of hole injection is discussed. Highly efficient PLEDs have been made by controlling the annealing.

II. EXPERIMENT

The Tg was determined by a differential scanning calorimeter. MEH-PPV, having a Tg around 75 °C, was dissolved in different organic solvents: p-xylene, dichlorobenzene, chlorobenzene, toluene, cyclohexanone, tetrahydrofuran, and chloroform. Polymer films were prepared by spin coating MEH-PPV solutions on precleaned ITO/glass substrates and then annealed. The temperatures were 50, 70, 90, 110, and 140 °C, and the annealing was carried out in an inert gas environment. Also films dried at room temperature and under vacuum (RT + Vac). The thickness of the films was 60–75 nm as determined by an alpha-step profilometer. The effects of annealing on the photoluminescence (PL) spectra of poly(2,5-bis(chelestranoxy)-1,4-phenylene vinylene) (BCHA-PPV) were also studied.

Typical PLEDs used in this study were an ITO/PEDOT/MEH-PPV/Ca/Al. A conducting polymer layer, 3,4-polyethylenedioxythiophene-polystyrene-sulfonate (PEDOT), was spin coated onto a precleaned ITO glass substrate and then baked at 120 °C for 2 h. Then MEH-PPV was spun on top of the PEDOT layer, and subsequently annealed at different conditions. A bilayer cathode consisting of a 50 nm calcium (Ca) layer and a 100 nm aluminum (Al) layer were thermally evaporated in a vacuum less than 6 × 10⁻⁶ Torr. The active area of the device is approximately 0.12 cm².

PL spectra of polymer films were measured using a Spex Fluorolog-3 double grating spectrophotometer. Polymer films were positioned such that the emission was detected at 22.5° from the incident beam. The excitation wavelength was 480 nm for both MEH-PPV and BCHA-PPV. Relative fluorescence quantum yields were estimated by integrating the PL spectra.

In order to further confirm the polymer morphology, the reflective absorption Fourier Transfer infrared (RA-FTIR) spectrum was recorded for each film. Reflective absorption infrared spectroscopy is a very useful method of determining the orientations of dipole moments. At a large incident angle (to the normal of the polymer surface) and a p-polarized light source, only the dipole moments oriented perpendicular to the mirror plane give the enhanced absorbances.8 The intensity of absorption is then a function of the transition dipole of

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a molecular chain or of the dipole moment orientation. Therefore, the average orientation of the molecular chains can be estimated from the corresponding transition dipole moment absorption in the FTIR spectra.5

The RA-FTIR spectra were recorded by a Midac M2200 spectrometer equipped with a mercury–cadmium–telluride detector. A Seagull stage (Harrick Scientific Corp.) was used as the reflection stage. The p- polarized infrared was employed as the light source for the grazing-angle experiment. Chrome plated steel plates (Doran Enterprises Inc.) were used as both reference and sample substrates. The substrate was cleaned with a Bunsen burner, and then washed with acetone before the spin coating. In addition, the transmission FTIR were also recorded by using sodium chloride pellets as substrates.

Current–voltage characteristics were determined by a Hewlett Packard 4155B semiconductor parameter analyzer. The light output of the PLED was converted to a photocurrent output using a photomultiplier tube (PMT) in order to determine device turn-on voltages (defined as the onset voltage at which the light intensity starts to increase rapidly in a semilog light versus voltage plot). Electroluminescence (EL) spectra and luminescence were measured with a Spectra-scan PR 650 spectrometer.

III. RESULTS AND DISCUSSION

A. PL and EL spectra

Figure 1 shows the PL spectra of MEH-PPV films annealed under different conditions. Figure 1(a) gives the normalized PL spectra of different MEH-PPV films fabricated with the same polymer solution and the same spin speed, while Fig. 1(b) shows PL spectra of the same MEH-PPV film after being annealed under different conditions. As can be seen, varying annealing conditions can dramatically change the PL spectra. For the MEH-PPV film annealed at RT+Vac, a yellowish PL spectrum with a main peak at 575 nm and a shoulder at 610 nm, is observed. Increasing the annealing temperature significantly changes the shape of the PL spectra: a reduction in intensity of the main peak, an increase in intensity of the shoulder peak, and a redshift of the overall spectrum [Fig. 1(a)]. For example, after a film is annealed at 140 °C for 2 h, the strongest peak appears at 630 nm; the emission color becomes reddish rather than yellowish. The same phenomena are also observed in EL spectra (Fig. 2).

Furthermore, relative PL quantum efficiency decreases dramatically with an increase of the annealing temperature [Fig. 1(b)]. For example, the relative quantum yield of the film annealed at 140 °C is less than one third that of the film annealed under RT+Vac. Dependence of EL quantum efficiency on the annealing conditions will be discussed further on.

It has been reported that for MEH-PPV films the yellowish peak at ~575 nm originates from intrachain (or single chain) exciton emissions;10 the reddish peak at ~630 nm is related to emissions from interchain species, such as aggregates or excimers.5 It was found that during spin coating, MEH-PPV chains can be extended or stretched in the direction of the centrifugal force.5,6 The solvents most likely dried during the first few seconds of the 1 min spin-coating period. Therefore, it is anticipated that polymer chains and the corresponding morphology were “locked” during the spin coating. Unless the postannealing temperature is above the Tg of MEH-PPV films, the extent of aggregation of as-prepared or low-temperature annealed polymer films is expected to be small, thereby developing a yellowish emission dominated by emissions from the less aggregated polymer chains or single chain excitons.

It is interesting to note that the temperature dependence of the PL spectra is also observed when MEH-PPV films are baked at a temperature below the Tg, e.g., 50 °C. It is well known that the Tg is not a well-defined physical parameter
and depends on experimental conditions, such as how the sample is prepared and its thermal history. In addition, several groups\textsuperscript{11,12} have reported that the actual \( T_g \) of a polymer thin film can be much lower than that of the bulk material due to interface properties and/or substrate–film interactions. Furthermore, it is also possible that during the spin coating the fast evaporation of solvents creates lots of empty spaces or free volumes in the films. These empty spaces facilitates the motion of chains, thereby lowering the onset temperature for the glass transition of spin-coated polymer films. Meanwhile, residues of the solvent after spin coating may also contribute to the relaxation of polymer chains.

The interpretation of the changes in PL spectra by the formation of interchain species in MEH-PPV films upon annealing is further supported by the lower temperature dependence of PL characteristics of BCHA-PPV (Fig. 3). As shown in the inset of Fig. 3, BCHA-PPV is also a derivative of poly(\( \pi \))-phenylene vinylene, which has the same phenyl–vinyl conjugated backbone as MEH-PPV, but much bigger side groups. In BCHA-PPV films, the formation of interchain interactions is most unlikely because of the separation of conjugated backbones by those bulky rigid side groups.\textsuperscript{13,14} Due to the absence of interchain interactions, or if any, very low density of the interchain species, the PL characteristics of BCHA-PPV films, which are unlike the MEH-PPV films, are less sensitive to the annealing temperature.

Figure 1 also reveals that the conformational states formed during the spin coating are thermodynamically unstable when subjected to changes of the external environment, such as annealing at high temperatures.\textsuperscript{15} When a film is annealed at a temperature beyond the \( T_g \) of MEH-PPV, e.g., 140 °C, the polymer chains start to relax and tend to form aggregates. The increased interchain interactions cause the changes in the PL spectra;\textsuperscript{5,7} emissions from those interchain species probably outweigh emissions from intrachain...
excitons, thus changing the emission color from yellowish to reddish. In addition, the quenching of the PL efficiency indicates low emissive species have been formed during the annealing process.

**B. FTIR spectra**

The relaxation of polymer chains is further confirmed by the FTIR spectra shown in Fig. 4. As can be seen in Fig. 4, characteristic groups of MEH-PPV chains have different absorption intensities when the films are annealed at different temperatures. For example, the ratio of the absorption intensity at 968 cm$^{-1}$ to that at 1042 cm$^{-1}$ is 0.91, 1.04, and 1.31 for the film annealed at RT, 70 °C, and 140 °C, respectively. In reflection mode (RA-FTIR), the stepwise increase in absorption intensity indicates the vibration direction of out-of-plane wagging for trans vinyl C–H and phenyl C–H become oriented more normal to the reflection plane, i.e., the substrate surface, with increasing annealing temperatures. Because of the $sp^2$ hybrid of C atoms within the benzene ring and the double bond, the phenyl C–H’s and vinyl C–H’s are in plane with the phenyl ring and the double bond. The enhanced intensity of the phenyl and vinyl C–H out-of-plane wagging reveals that both the double bonds and phenyl rings become more in plane, i.e., more parallel to the substrate plane, upon annealing at high temperatures.

Furthermore, unlike the reflection spectra, transmission spectra show no significant changes with varying annealing temperature, thus indicating that chemical reactions are unlikely to occur. Therefore the changes in absorption intensity in RA-FTIR spectra are due mainly to changes in dipole orientations.

**C. Device performance**

Light versus voltage curves of devices annealed under different conditions are shown in Fig. 5. As can be seen, increasing annealing temperatures can lower the turn-on voltages of MEH-PPV-based PLEDs. For example, the turn-on voltage for the device (p-xylene as the solvent) annealed under RT+Vac, 70 °C and 140 °C is 1.79, 1.73, and

![FIG. 5. Light–voltage curves of MEH-PPV based PLEDs fabricated with different solvents: (a) p-xylene and (b) tetrahydrofuran. The turn-on voltages decrease as the annealing temperatures increase from RT+Vac, 70–140 °C. Light outputs of the PLEDs were converted to photocurrents using a PMT.](image1)

![FIG. 6. Current–electric field curves of MEH-PPV based PLEDs. The magnitude of current injections under the same electrical field increases as the annealing temperatures increase from RT+Vac, 70–140 °C.](image2)

**TABLE I.** The turn-on voltages for devices annealed at different conditions.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>RT+Vac</th>
<th>50 °C</th>
<th>70 °C</th>
<th>90 °C</th>
<th>140 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-xylene</td>
<td>1.82</td>
<td>1.77</td>
<td>1.74</td>
<td>1.70</td>
<td>1.62</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>1.79</td>
<td>1.76</td>
<td>1.73</td>
<td>1.71</td>
<td>1.62</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.82</td>
<td>1.79</td>
<td>1.76</td>
<td>1.74</td>
<td>1.65</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.80</td>
<td>1.77</td>
<td>1.74</td>
<td>1.70</td>
<td>1.62</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>1.81</td>
<td>1.78</td>
<td>1.75</td>
<td>1.70</td>
<td>1.63</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>1.93</td>
<td>1.85</td>
<td>1.81</td>
<td>1.79</td>
<td>1.69</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.92</td>
<td>1.86</td>
<td>1.82</td>
<td>1.77</td>
<td>1.71</td>
</tr>
</tbody>
</table>
1.62 V, respectively [Fig. 5(a)]. A similar phenomenon is observed if other solvents are used [Fig. 5(b) and Table I].

The device turn-on voltage for the emission of photons is associated with the minority carrier injection; the turn-on voltage becomes smaller indicating that efficiency of minority carrier injection is improved by increasing the annealing temperature. It is believed that holes are the minority carriers for MEH-PPV based PLEDs with ITO/PEDOT and calcium as the anode and the cathode, respectively. This means the new morphology of polymer films and/or the polymer–metal contact formed by the annealing process has improved hole injection. As a result, devices annealed at a higher temperature show a greater current under the same magnitude of electrical field (Fig. 6), especially within low fields where the current is controlled by the injection.

The overall influence of high temperature annealing of MEH-PPV shows a tradeoff between the enhancing of minority carrier injection at the cost of reducing the thin film PL efficiency.

Based on the above understandings, two approaches have been used to fabricate PLEDs with high efficiency. The first approach is to optimize the annealing temperature to enhance the EL efficiency. Figure 7 shows efficiency versus current and luminescence versus current curves for devices treated under different annealing conditions. The device annealed at 70 °C, which is slightly less than the $T_g$ of MEH-PPV, has the greatest efficiency for those temperatures studied. At a luminescence of 1000 cd/m², its efficiency is about 2.3 cd/A. At the same luminescence level, the efficiency of a device annealed at RT+Vac and 140 °C is only 1.7 and 1.1 cd/A, respectively.

The second approach is to construct a “double layer” device consisting of a better hole-injection polymer thin film (the MEH-PPV film treated by a high temperature annealing) and a higher PL efficiency polymer thin film (the MEH-PPV film treated by a low temperature annealing). First, a very thin layer of MEH-PPV was spin coated on top of the PEDOT/ITO substrate and then annealed at 140 °C, which is much higher than the $T_g$ of MEH-PPV. Then the second layer of MEH-PPV was spin coated on top of the first layer and then annealed at 70 °C. The thinner bottom layer polymer serves as a hole-transporting layer to improve the hole-injection efficiency, while the “thicker top layer” with greater PL efficiency serves as the light emissive layer.

At low electrical fields where currents are in injection-controlled regimes, the “double layer” device has a much greater current than the device annealed at 70 °C due to the enhanced hole-injection efficiency (Fig. 8). At high fields, where currents are in bulk-controlled regimes, these curves overlap, thus indicating that the current is dominated by the top MEH-PPV film that was annealed at 70 °C. The balance of dual charge injection is improved, thus yielding much higher EL efficiency. The efficiency of the “double layer” device is 2.7 cd/A at a luminescence of 1000 cd/m², respectively.

FIG. 7. Efficiency–current curves (a) and luminescence–current (b) curves of MEH-PPV based PLEDs. MEH-PPV films were thermally annealed at RT+Vac, 50 °C, 70 °C, 90 °C, and 140 °C, respectively.
which is much higher than that of the single layer devices annealed at 70 or 140 °C as shown in Fig. 9.

IV. CONCLUSION

During annealing the polymer morphologies, such as the orientation of dipole moments and the degree of interchain interactions, are subjected to change, thereby varying the optical and electrical properties of polymer thin films as well as device performance. The effects of annealing show a tradeoff between hole-injection efficiency and PL efficiency. Two approaches have been demonstrated to yield high performance PLEDs. The first one is to optimize the annealing temperatures, i.e., annealing the polymer film at a temperature close to but slightly less than the $T_g$, can dramatically increase the EL efficiency for the single layer device. In the second approach a very thin MEH-PPV film, annealed at a temperature much higher than the $T_g$, improves hole-injection efficiency. Due to a more balanced charge injection, a highly efficient PLED is obtained with an efficiency of 2.7 cd/A (1000 cd/m²) by the "double layer" device. Constructing a hole-transporting layer provides a convenient way for improving the performance of PLEDs, especially when the device quantum efficiency is limited by hole injection.

FIG. 9. Efficiency–current curves (a) and luminescence–current curves (b) for a double layer device and devices annealed at 70 and 140 °C, respectively.