Multilayer polymer light-emitting diodes by blade coating method

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Multilayer polymer light-emitting diodes fabricated by blade coating are presented. Multilayer of the spin coated one. The bilayer PLED is even better than the one by liquid buffer method.

The working principle of multilayer fabrication process by blade coating is shown in Fig. 1(a). A heater is needed for multilayer process. The second layer was blade coated for rapid solvent evaporation. The solvent of the second layer is quickly evaporated without dissolving the first layer. A 70 nm poly(para-phenylene vinylene) copolymer Super-Yellow (S-Y, supplied by Merck OLED Materials GmbH) thin film was first formed by blade coating in toluene solution with a scratch pattern “NCTU” made by a cotton stick with solvent toluene. Then poly(9,9-dioclylfluorenyl-2,7-diyl)-co-(4,4’-(N-(4-sec-butylphenyl)diphenylamine)] electron-blocking layer added by blade coating. © 2008 American Institute of Physics.

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Small molecule organic light-emitting diodes (OLEDs) and polymer light-emitting diodes (PLEDs) have generated great interest in the past decade. Due to its low cost solution process PLED has the potential to be more competitive than OLED in many future applications. In addition to display technology, PLED can be used as a flexible light integrated on any surface. It can be applied in the lighting for interior design, clothes, purses, cars, and even the art works. The most common fabrication process for PLED is spin coating with the advantage of good film uniformity. However, the usage of materials is only 5% and the manufacturing throughput by spin coating is low for large areas. This raise dramatically the cost of PLED. More importantly, it has been proved difficult to make multilayer polymer structures by spin coating because the solvent of the second layer will dissolve the first. The multilayer structure including carrier transport, emission, and carrier blocking layers is known to be necessary for high efficiency. The incompatibility between spin coating method and multilayer device design is the main reason that the performance of PLED is so far below that of the thermally evaporated OLED. In the past few years many strategies were developed to overcome the dissolution problem and make multilayer PLEDs by spin coating. Most of these methods involve synthesizing cross-linkable or water/methanol-soluble materials which often compromise the semiconductor quality. A liquid buffer method which completely prevents the dissolution was recently reported to achieve high-efficiency and stable PLEDs. Material waste is, however, still a problem and it is nontrivial to scale up to very large areas. Blade coating is a common method to form large-area polymer films with micrometer thickness such as photoresists and color filters. Unlike spin coating the area can be easily scaled up and the material usage is almost 100%. Furthermore, not only single layer but also multilayer can be deposited without a buffer liquid. The single layer PLED performance is as good as that of the bilayer PLED.
The total thickness of the S-Y/PFO bilayer was 150 nm as measured by a Kosaka ET4000 surface profiler, which was the same as the sum of the thickness of the individually blade coated S-Y and PFO layers. The NCTU pattern of the first S-Y layer is not damaged by the second PFO solution at all as shown in Fig. 1(b) under ultraviolet illumination, implying that the mutual dissolution is minimal. The pattern will be completely destroyed if the PFO layer is deposited by spin coating. The lateral profile was checked by scanning electron microscope (SEM, JEOL JSM-6390LV). The result is shown in Fig. 1(c). It is clear that there exists an interface between the two polymer layers. The uniformity was verified by comparison with the standard spin coated films. PFO thin films made by three processes have been compared, including spin coating, blade and spin coating, and blade coating on a hot plate. In the blade and spin coating process the polymer wet film was first blade coated then spun immediately to form the polymer dry thin film. This process is ideal for the first layer as it combines the advantages of fast drying for spin coating and high material usage of blade coating. On the other hand blade coating on a hot plate is ideal for the second layer. The large scale uniformity in an area of 6×5 cm² is 60±3 nm for spin coating, 60±2 nm for blade and spin coating, and 60±10 nm for blade coating on a hot plate at 70 °C. The microscopic uniformity was checked by SEM and atomic force microscope (AFM). The results are shown in Fig. 2. There is no obvious difference among these three processes. The polymer film roughness in a 0.5 ×1 μm² area is 5.5 Å for spin coating, 3.6 Å for blade and spin coating, and 3.1 Å for blade coating on a hot plate. The single layer polymer thin film by blade coating is almost the same as that by spin coating in both macroscopic and microscopic scales. Blade coating therefore combines the advantages of multilayer deposition and efficient material usage without sacrificing the film quality.

Now we turn to PLED performance. Single layer PLEDs of the structure ITO/PEDOT:PSS/EML/CsF/Al were fabricated. PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate). S-Y and PFO were used for the emissive layer (EML). Both S-Y and PFO were dissolved in toluene. Bilayer PFO devices were made with the structures ITO/PEDOT:PSS/TFB/PFO/CsF/Al and ITO/PEDOT/PFO/PBD/CsF/Al. TFB is poly[(9,9-diocetylfluorenyl-2,7-diyl)-co-(4,4’-(N-(4-sec-butylphenyl)diphenylamine)] purchased from American Dye Source. PBD is 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole purchased from Sigma Aldrich. TFB acts as the electron blocking layer and PBD as the hole blocking layer. Both TFB and PBD were dissolved in toluene. The indium tin oxide (ITO) substrates were cleaned and the surfaces were treated by oxygen plasma followed by spin coating 50 nm of PEDOT:PSS. The PEDOT:PSS film was baked at 200 °C for 5 min in vacuum environment (10⁻³ torr). The TFB film (30 nm) was spin coated on the PEDOT:PSS film and annealed at 180 °C in vacuum for 40 min. PFO was blade coated on top of the TFB layer on a hot plate at 70 °C. PBD was blade coated on the PFO layer on a hot plate at 100 °C. The thickness of PFO is about 80 nm in single layer devices and 70 nm in bilayer devices. S-Y was blade coated on PEDOT:PSS. The PFO and S-Y thin film were annealed at 120 °C in vacuum (10⁻³ torr). All the devices were coated with CsF(2 nm)/Al(100 nm) cathode and packaged in a glove box.

Figure 3 shows the results of single layer devices with...
The device structure of ITO/PEDOT/EML/CsF/Al. The values of the maximum efficiency of S-Y PLEDs are almost the same (about 9 cd/A at 3.5 V). Surprisingly the performance of PFO PLED by blade coating on a hot plate is the best. Since the uniformity is almost the same for all PFO films, we speculate that the chain entanglement of PFO in the nanometer scale by blade coating on a hot plate is stronger than that of the other methods. Such entanglement enhancement is important for the low molecular weight (MW) PFO (MW below 100,000) but not so for the high MW S-Y (MW about 1,000,000).

Bilayer PFO devices with structures of TFB/PFO and PFO/PBD were made by blade coating on a hot plate for the second layer. The results are shown in Fig. 4. The maximum efficiency is raised to 2.3 cd/A for TFB/PFO as compared to 1.05 cd/A for the single layer PFO device. The TFB/PFO made by liquid buffer has the efficiency of 1.7 cd/A which is lower than that of the same structure made by blade coating. This is probably because TFB and PFO are more in contact with each other in blade coating on a hot plate than in the liquid buffer process. Moreover the device efficiency is raised to 2.9 cd/A in the PFO/PBD device. The maximum luminance is 8807 cd/m² for the TFB/PFO device, about 2.5 times larger than that of the single layer PFO device (3371 cd/m²). The maximum luminance is 4429 cd/m² for the PFO/PBD device. The enhancement in the TFB/PFO bilayer devices is due to the fact that the electrons in PFO are blocked by TFB, which induces more holes to be injected and achieves higher efficiency and luminance. As for the PFO/PBD device the holes are blocked by PBD. The efficiency is enhanced by separating the recombination zone from the cathode to reduce metal quenching. The performances of all the devices are listed in Table I. S-Y and PFO are just two examples to demonstrate this fabrication method. Apparently blade coating can be applied to any kind of semiconducting polymer.

The basic transport and optical properties of films by various fabrication methods are investigated by the currents of semiconducting polymer.

<table>
<thead>
<tr>
<th>Label</th>
<th>Max. current efficiency (cd/A)</th>
<th>Max. EQE (%)</th>
<th>Max. luminance (cd/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-Y (spin coating)</td>
<td>9.1 (at 3.5 V)</td>
<td>3.36</td>
<td>69,330 (at 10 V)</td>
</tr>
<tr>
<td>S-Y (blade and spin coating)</td>
<td>9.4 (at 3.5 V)</td>
<td>3.55</td>
<td>39,830 (at 10 V)</td>
</tr>
<tr>
<td>S-Y (blade on a hot plate)</td>
<td>9.4 (at 3.5 V)</td>
<td>3.8</td>
<td>30,190 (at 10 V)</td>
</tr>
<tr>
<td>PFO (spin coating)</td>
<td>1.1 (at 4.5 V)</td>
<td>0.69</td>
<td>3,371 (at 8.5 V)</td>
</tr>
<tr>
<td>PFO (blade and spin coating)</td>
<td>0.9 (at 4.5 V)</td>
<td>0.61</td>
<td>2,370 (at 9 V)</td>
</tr>
<tr>
<td>PFO (blade on a hot plate)</td>
<td>1.7 (at 4.5 V)</td>
<td>1.14</td>
<td>4,390 (at 8 V)</td>
</tr>
<tr>
<td>TFB/PFO (liquid buffer method)</td>
<td>1.7 (at 5.5 V)</td>
<td>1.34</td>
<td>5,575 (at 10.5 V)</td>
</tr>
<tr>
<td>TFB/PFO (blade on a hot plate)</td>
<td>2.3 (at 4.5 V)</td>
<td>2.2</td>
<td>8,807 (at 10 V)</td>
</tr>
<tr>
<td>PFO/PBD (blade on a hot plate)</td>
<td>2.9 (at 5.5 V)</td>
<td>1.83</td>
<td>4,429 (at 8.5 V)</td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) Device performance of single layer PFO PLEDs and double layer TFB/PFO and PFO/PBD PLEDs. (a) The current efficiency. Inset is the electroluminescent spectra of the devices. The spectra of single layer PFO and double layer PFO/PBD devices are almost the same and normalized to 0.5 for clarity. (b) The luminance. Inset is the current density. Single layer PFO devices by spin coating (solid square) and by blade coating on the hot plate (empty square). Double layer TFB/PFO devices by liquid buffer method (solid circle) and by blade coating on a hot plate (empty circle). Double layer PFO/PBD device by blade coating on a hot plate (solid triangle).

FIG. 5. (Color online) Hole-only and electron-only devices made by spin coating (square), blade and spin coating (circle), and blade coating on a hot plate (triangle). (a) S-Y devices; (b) PFO devices. Inset shows the PL spectra.
The current is dominated by defect levels in the energy gap.\textsuperscript{13} Because of the large hole injection barrier the ionization potentials of S-Y and PFO are 5.5 and 5.8 eV coated ones. The workfunction of PEDOT:PSS is 5 eV while coated devices are slightly higher than those of the spin blade and spin coated PLEDs. The hole currents of the blade microscopic basis for the similarity in performances for determined by the electron mobility. Such results provide the known that the charge balance and efficiency of PLED are for the fabrication processes are still meaningful. It is well scales. There is no need to design functional materials. The polymer devices in potentially very large areas up to meter talline packing tendency and lower MW. The lack of centrifugal force in blade coating may favor the formation of the aggregates of ordered structures during drying. The PL spectrum of PFO is more sensitive to fabrication methods than S-Y probably because PFO has a liquid crys-

In conclusion we have developed a way to simulta-

neously reduce the cost of PLED and prevent the dissolution between two polymer layers by blade coating. This is a very simple method to fabricate all-solution-processed multilayer polymer devices in potentially very large areas up to meter scales. There is no need to design functional materials. The film uniformity is about the same as standard spin coated films in both large and small scales. The performance of the single layer PLED by blade coating is the same as that of spin coated ones. For bilayer PLED made by blade coating the efficiency is more than double compared with the single-

layer spin coated PLED. This method can be applied to not only PLED but also other solution-processed multilayer polymer devices such as solar cells.

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References

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