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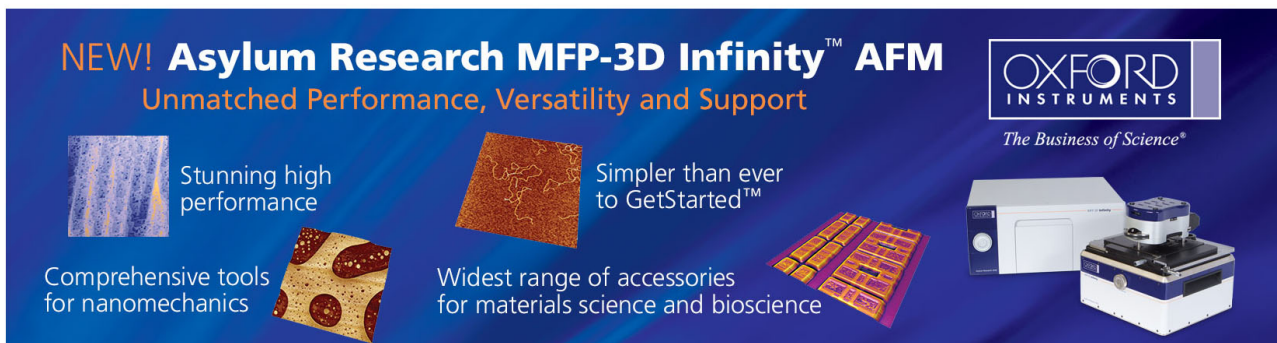
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Multilayer polymer light-emitting diodes by blade coating method

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Multilayer polymer light-emitting diodes fabricated by blade coating are presented. Multilayer of polymers can be easily deposited by blade coating on a hot plate. The multilayer structure is confirmed by the total thickness and the cross section view in the scanning electron microscope. The film thickness variation is only 3.3% in 10 cm scale and the film roughness is about 0.3 nm in the micron scale. The efficiency of single layer poly(*para*-phenylene vinylene) copolymer Super Yellow and poly(9,9-dioctylfluorene) (PFO, deep blue) devices are 9 and 1.7 cd/A, respectively, by blade coating. The efficiency of the PFO device is raised to 2.9 cd/A with a 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) hole-blocking layer and to 2.3 cd/A with a poly[(9,9-dioctylfluorenyl-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.[1–3] 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. However, the usage of materials is only 5% and the manufacturing throughput by spin coating is low for large areas, raising 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.[4–9] A liquid buffer method which completely prevents the dissolution was recently reported to achieve high-efficiency and stable PLEDs.[10] 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.[11] 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 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 to expel the solvent of the second polymer solution. So the second film is formed by solution but

quickly dried before dissolving the first polymer 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-dioctylfluorene) (PFO, purchased from American Dye Source) solution was blade coated on top of the S-Y layer to form a 70 nm thin film. The sample was placed on a 70 °C hot plate as the second layer was blade coated for rapid solvent evaporation. 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
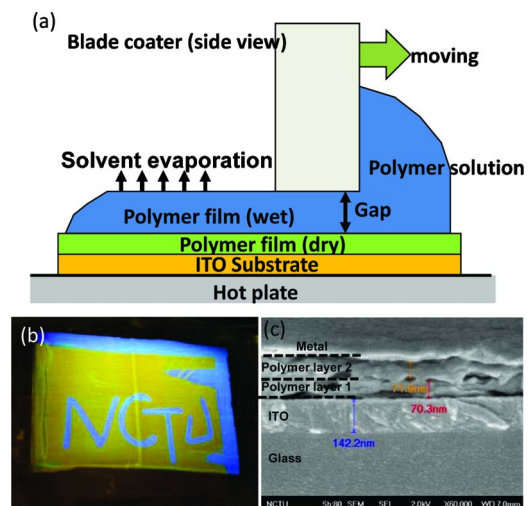

FIG. 1. (Color online) (a) Schematic working principle of multilayer structure by blade coating; the process of the second layer is on a hot plate. The solvent of the second layer is quickly evaporated without dissolving the first layer. (b) Double layer S-Y/PFO under ultraviolet illumination. The scratch pattern NCTU is made by a cotton stick on the S-Y thin film before blade coating the PFO thin film. (c) The lateral profile of the double layer polymer film by SEM. There is no dissolution between these two polymer layers by blade coating.

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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. The large scale uniformity in an area of 6×5 cm^2 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 polymer film roughness in a 0.5×1 μm^2 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/FEDOT: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-dioctylfluorenyl-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 2 shows the results of single layer devices. 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).[12]

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. 3. 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
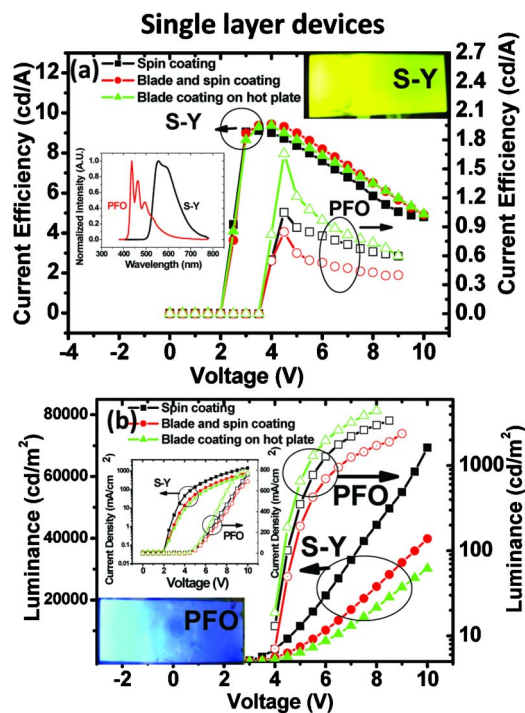

FIG. 2. (Color online) Device performance of single layer S-Y and PFO PLEDs by spin coating (square), blade and spin coating (circle), and blade coating on a hot plate (triangle). (a) The current efficiency. Inset is the electroluminescent spectra of S-Y and PFO devices by blade coating as well as the S-Y device in operation. The active area of the device is 4×7.5 cm^2. (b) The luminance. Inset is the current density and the PFO device by blade coating in operation. The active area of the device is 4×7.5 cm^2.

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/m^2 for the TFB/PFO device, about 2.5 times larger than that of the single layer PFO device (3371 cd/m^2). The maximum luminance is 4429 cd/m^2 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 basic transport and optical properties of films by various fabrication methods are investigated by the currents in hole-only and electron-only devices and by comparing the photoluminescence (PL) spectra. The structures are ITO/PEDOT/EML/Al for hole-only devices and Al/EML/CsF/Al for electron-only devices. The results are shown in Fig. 4. The electron currents of the blade coated and spin coated devices are almost the same. Due to the Ohmic contact with CsF/Al cathode the electron current follows space-charge-limited current behavior, $J_{SCLC} = (9/8)\varepsilon\mu_e[(V - V_{bi})^2/L^3]$. J is the current density, ε is the permittivity of the polymer, μ_e is the electron mobility, V is the driving voltage, V_{bi} is the built-in voltage, and L is the polymer thickness. The fitted electron mobility is 2.5×10^{-8} cm^2/V s for PFO (at 0.6 MV/cm) and 5
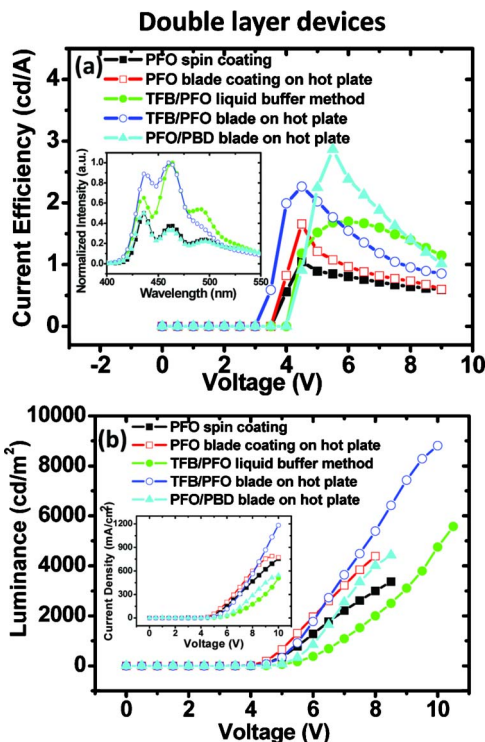
FIG. 3. (Color online) Device performance of single layer PFO PLEDs and double layer TFB/PFO and PFO/PBD PLEDs. (a) The current efficiency. Inset is the electroluminescent spectra of the devices. The spectra of single layer PFO and double layer PFO/PBD devices are almost the same and normalized to 0.5 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).
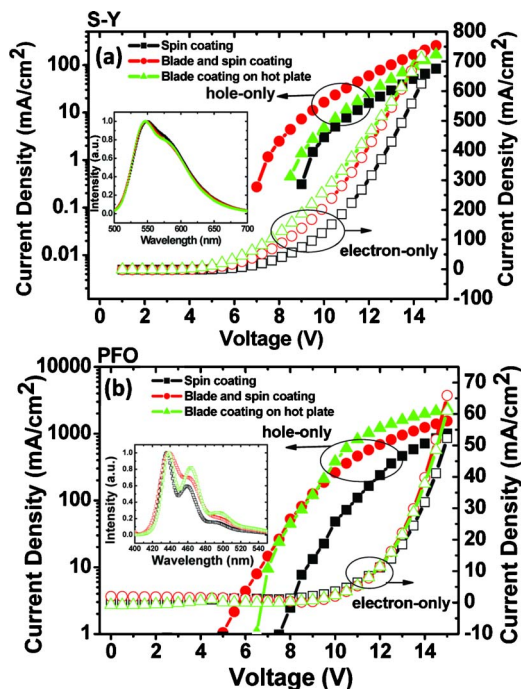

FIG. 4. (Color online) Hole-only and electron-only devices made by spin coating (square), blade and spin coating (circle), and blade coating on a hot plate (triangle). (a) S-Y devices: (b) PFO devices. Inset shows the PL spectra.

$\times 10^{-6}$ cm^2/V s for S-Y (at 0.6 MV/cm) with all fabrication methods. Strictly speaking the space-charge-limited formula is valid only for trap-free cases. Although there may be some overall correction due to the traps on the absolute values of the electron mobility, the relative magnitudes of the mobility for the fabrication processes are still meaningful. Such results provide the microscopic basis for the similarity in performances for blade and spin coated PLEDs. The hole currents of the blade coated devices are slightly higher than those of the spin coated ones. Because of the large hole injection barrier the current is dominated by defect levels in the energy gap.[13] The large hole current for blade coating may be due to the gap levels originated from the aggregates. In PLED the hole injection is no longer limited by the high barrier due to the higher field near the anode;[13] the aggregate levels may cause lower hole mobilities and lower luminances in blade coated PLED. However, in the PL spectra of PFO films, the shoulder peaks of 464 and 494 nm grow in blade coated films which may contain more aggregates and therefore stronger low energy emission due to exciton delocalization.[14]

In conclusion we have developed a way to simultaneously 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. 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.

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