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Polymeric tandem organic light-emitting diodes using a self-organized interfacial layer

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The authors have demonstrated efficient polymeric tandem organic light-emitting diodes (OLEDs) with a self-organized interfacial layer, which was formed by differences in chemical surface energy. Hydrophilic poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT:PSS) was spin coated onto the hydrophobic poly(9,9-dyooctylfluorene) (PFO) surface and a PEDOT:PSS bubble or dome was built as an interfacial layer. The barrier heights of PEDOT:PSS and PFO in the two-unit tandem OLED induced a charge accumulation at the interface in the heterojunction and thereby created exciton recombination at a much higher level than in the one-unit reference. This effect was confirmed in both the hole only and the electron only devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894072]

Organic light-emitting diodes (OLEDs) have long been touted as a next generation display and as a light source. However, even though they have many advantages over current devices as displays and illuminations, the degradation of organic materials due to overflow currents shortens these devices' lifetimes. To address this problem, stacked tandem OLEDs¹⁻⁵ were created to produce high brightness and efficiency with low current density in small molecule devices. However, such structures need an interfacial layer,¹⁻⁵ which acts as both anode and cathode, to spout both holes and electrons and to generate intrinsic carriers in order to overcome the requirement of high operating voltage.

Power consumption is a key factor in many OLED applications, including those of tandem OLEDs. Lower power consumption is especially needed for their application to mobile phones and laptop computers. Therefore, improving luminance efficiency is highly desirable. Generally, electroluminescence (EL) is generated by the recombination of holes and electrons flowing between electrodes. However, some carriers do not combine for the exciton and pass through to the opposite electrode by potential difference. This means that there are so-called surplus holes and electrons that consequently are not used in the luminescence. It is, therefore, essential to use up these surplus holes and electrons through charge accumulation in order to increase luminous efficiency; this is the one of various methods⁶⁻¹⁸ used to raise current efficiency. Kim and Lee^{6,7} reported that the quantum well structure can confine excitons within an emitting layer to enhance luminance efficiency for surplus holes and electrons with the carriers' accumulation. It also has been reported that a phase separated mixture of two polymers can produce EL from a micron sized phase-separated guest poly-

mer, which also increases efficiency.⁸⁻¹² Karthaus and Adachi⁹ and Karthaus¹⁰ reported that utilizing a dewetting process formed a patterned monochrome EL device with luminescent domains, with a diameter of 0.5–2 μm . It is known that by casting from a dilute solution, polymers and low molar mass compounds dewet and form circular droplets with a diameter of one to several micrometers on substrates.^{9,10}

In our present work, we have fabricated a polymeric tandem OLED with an interfacial layer. Three types of OLEDs, with different structural conditions, were prepared for comparison: (a) a one-unit reference, (b) a double-structured poly(9, 9-dyooctylfluorene) (PFO) emitting layer device, and (c) a two-unit tandem OLED. "Double-structured PFO" simply means that the PFO is double spin coated successively in the device. For preparation, ITO glass substrate was cleaned and organic materials, 40 nm poly(styrene sulfonate)-doped poly(3,4-ethylene dioxythiophene) (PEDOT:PSS) and 60 nm PFO thin films, were spin coated on the ITO glass and baked. A polymeric tandem OLED was also prepared by spin coating on the one-unit device. A second PEDOT:PSS film was spin coated onto the first PFO emitting layer, and baked at 110 °C for 30 min to vaporize the water solution, taking into consideration the PFO's low glass transition temperature. Metal cathodes (LiF 1.2 nm/Al 100 nm) were then sequentially deposited onto the organic layer by thermal evaporation.

Figure 1(a) shows the tandem OLED's structure. The contact angles of the PEDOT:PSS layer on the ITO glass, the PFO emitting layer on the ITO glass, and the PEDOT:PSS layer on a PFO layer are shown in Figs. 1(b)–1(d), respectively. It is well known that the PEDOT:PSS and PFO layers have both hydrophilic and hydrophobic surfaces, which tend to have low and high contact angles, respectively, and are equivalent to high and low polar surface energies, respec-

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FIG. 1. (Color online) (a) Schematic structure of two-unit tandem OLEDs. Contact angle data measured on the ITO glass, (b) as spin coated PEDOT:PSS layer, (c) PFO layer, and (d) PEDOT:PSS on PFO layer.

tively. Before spin coating the second PEDOT:PSS, the water contact angle of the as-prepared PFO layer was around 99.8° , indicating a highly hydrophobic surface. The formation of a PEDOT:PSS thin film on the PFO layer reduced the PFO/PEDOT:PSS film's contact angle to around 94.2° . This indicates that a PEDOT:PSS thin film or dot shape was formed on the one-unit PFO layer. The difference between the hydrophobic and hydrophilic surface energies^{9,10} induced the formation of a thin interfacial layer on the PFO layer. The force that drives the film's formation is interfacial tension between the hydrophobic PFO and the hydrophilic PEDOT:PSS.^{9,10}

Figure 2 shows transmittance electron microscopic (TEM) images of organic layers. Figure 2(a) shows the PEDOT:PSS layer on ITO glass, while Figs. 2(b) and 2(c) show the PEDOT:PSS layer on a PFO layer. Two regions

FIG. 2. (Color online) TEM images of various organic films deposited onto ITO glass (a) as spin coated PEDOT:PSS layer, [(b) and (c)] PEDOT:PSS on PFO layer in two different regions, SEM and AFM images of various organic films deposited onto ITO glass, (d) SEM image of spin coated PEDOT:PSS layer on PFO layer, (e) AFM image of PFO layer, and (f) AFM image of PEDOT:PSS on PFO layer.

FIG. 3. (Color online) (a) V - I characteristics of devices, (b) V - L characteristics of devices, (c) current efficiency-voltage characteristics of devices, and (d) power efficiency-voltage characteristics for one-unit reference, double-structured PFO device and two-unit device.

were selected for examination. They show obvious self-organized dot formations, which indicate *nanosize*. The TEM image of the PEDOT:PSS layer shows a flat surface and there are two sizes of PEDOT:PSS layers on the hydrophobic PFO layer. Karthaus and Adachi⁹ and Karthaus¹⁰ reported that various sizes of droplets are generated and the droplets' patterns and spacing change over a few orders of magnitude. This formation depends on the self-organization of molecules and organic molecules tend to assemble into large aggregates.^{9,10} Intermolecular interactions, originating from van der Waals forces, can affect self-assembly, as can the hydrophilic material's effect on hydrophobic material, electrostatic interactions, and hydrogen bonding.^{9,10} Consequently, chemical potential induces structural formation, which helps thermodynamic equilibrium.^{9,10}

Figure 2 also shows images from the scanning electron microscopy (SEM) and atomic force microscopy (AFM) of organic layers. Figure 2(d) is a SEM image of the PEDOT:PSS layer on the PFO layer. Fig. 2(e) shows an AFM image of the PFO emitting layer, and Fig. 2(f) is an AFM image of the PEDOT:PSS layer on the PFO layer. Self-organized dot formations are obvious here, which indicate *microsize*. The SEM image's bubbles are much bigger than those in the AFM images, indicating various patterns of self-organized interfacial layers of PEDOT:PSS; self-organization is thought to be due to the formation of molecular aggregates,^{9,10} and depends on intermolecular interactions for self-assembly. Polymer concentration and the decreasing the spin coating speed determine the size of the droplets' size;^{9,10} the higher the concentration and the lower the speed, the larger the domes. Consequently, the solvent's temperature and volatility are quite important for the droplets' formation.^{9,10}

Figure 3 displays the electrical properties of the variously structured devices. Figure 3(a) is voltage-current density (V - I), Fig. 3(b) is voltage-luminance (V - L), Fig. 3(c) is voltage-current efficiency, and Fig. 3(d) is voltage-power efficiency. The current injections of the double-structured PFO and two-unit tandem devices are much poorer than that of the one-unit device, because of their thicker PFO and stacked structure. Carriers of both holes and electrons are significantly delayed due to the potential barrier height between

FIG. 4. (Color online) (a) Hole only device plot, (b) electron only device plot for one-unit reference, double-structured PFO device and two-unit device, and (c) schematic diagram of the tandem OLED with dot formed interfacial layer.

PFO and PEDOT:PSS. The luminance of the double-structured PFO and two-unit tandem devices is also lower than that of the one-unit reference device, because of poor current injection, and their turn-on and operating voltages are higher. However, the current and power efficiencies of the double-structured PFO and two-unit tandem devices are higher than those of the one-unit device, possibly because of charge accumulation between the PFO layers and the PEDOT:PSS layers for both holes and electrons. That would induce a high probability of exciton recombination to reduce surplus carriers of both holes and electrons, thereby increasing current and power efficiency.

In small molecule tandem OLEDs, many researchers have tried to adapt electric field-assisted bipolar charge carriers to the spouting zone, which is an anode-cathode layer, to cope with high operating voltages due to the stacked tandem structure.¹⁻⁵ A strong electric field from an externally applied voltage assists with generating a number of free charge carriers of both electrons and holes from the bounded electron-hole pairs by the Onsager theory,² to reduce the potential barrier between the stacked structures.¹⁻⁵ The chemical charge transfer between alkali or alkaline earth metals and organic material can also create free charge carriers in the interfacial layer.¹⁻⁵ However, in polymeric tandem OLEDs, the performance enhancement mechanism seems to be quite different from that in stacked small molecule tandem OLEDs. The dot-formed interfacial layer's role is just charge blocking and accumulation of both holes and electrons, not the spouting zone. Moreover, the polymeric tandem device's structure is hardly an exact tandem structure because the second PEDOT:PSS' film deforms to a bubble or dome, as shown in Fig. 4(c). Consequently, due to the interfacial layer, polymeric tandem OLEDs perform better than any of the other devices. The double-structured PFO device has a thicker PFO emitting layer than the one-unit reference device, which is more effective for charge accumulation.

However, two-unit tandem devices are most effective for charge accumulation; the double-structured PFO has a carrier mobility delay only through the thick PFO emitting layer, which is not as effective as the two-unit tandem OLED method.

Figure 4 shows the data plots. Figure 4(a) is a hole only device, with a structure of ITO/PEDOT:PSS/PFO/PEDOT:PSS interfacial layer/PFO/Au and Fig. 4(b) is an electron only device, with a structure of Al/PFO/PEDOT:PSS interfacial layer/PFO/LiF/Al. Both types effectively demonstrated a desirable majority of the carrier's characteristics. However, the number of two-unit tandem electrons in the electron only device was much lower than the number of two-unit tandem holes in the hole only device, confirming that electron accumulation is much higher than hole accumulation because the potential barrier for electrons between the first PFO layer and the PEDOT:PSS dot formed interfacial layer is much higher than that for holes between the interfacial and second PFO layers. The potential difference between the lowest unoccupied molecular orbital of PFO and that of PEDOT:PSS is 0.9 eV and the difference between the highest occupied molecular orbital of PEDOT:PSS and that of PFO is 0.4 eV. Consequently, hole and electron accumulation between the dot-formed, self-organized PEDOT:PSS interfacial layer and the PFO emitting layer enhances the two-unit tandem device's current efficiency, as shown in Fig. 4(c).

In summary, we demonstrated the current efficiency of tandem OLEDs with a dot-formed interfacial layer and the charge accumulation of both electrons and holes. The surface energy difference was used to generate the dot formation of a hydrophilic PEDOT:PSS layer on the PFO layer's hydrophobic surface. Consequently, modification of the PFO surface with a PEDOT:PSS coating improved the tandem OLED's properties regarding the accumulation of carriers.

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