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High-efficiency flexible white organic light-emitting diodes†

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A high-efficiency flexible white organic light-emitting diode (OLED) was fabricated using effective device structure on high glass-transition plastic substrate with a thin silicon dioxide pre-coat and highly conductive indium tin oxide (ITO) deposited by radio frequency magnetron sputtering at elevated temperature. Sputtering ITO at 200 °C on a 150 Å SiO_2-modified polyethersulfone yielded a high power efficiency of 6.5 lm/W at 800 cd m^{-2} and a maximum external quantum efficiency of 3.2% with a pure-white emission of (0.321, 0.339). Besides device structure, the power efficiency of the flexible OLEDs depends strongly on the conductivity of ITO, which in turn depends on its surface topology, which can be most effectively improved by adding a SiO_2 pre-coat of optimal thickness.

White organic light-emitting diodes (OLEDs) have attracted considerable attention because of their great potential for use in high-quality full-color displays and area illumination.[1,2] Extension to bendable, wearable or roll-up devices would make them even more attractive in numerous fields.[3–5] However, serious difficulties have been encountered in the fabrication of flexible white OLEDs with bright and efficient emission on plastics, although numerous high-efficiency emissive device architectures are available.[1,6,7] For instance, the greatest power efficiency of white emission on plastics is 4.3 lm/W at 100 cd m^{-2}.[4] That on glass at 100 cd m^{-2} is 17.1 lm/W from fluorescent white OLEDs,[8] or 53 lm/W from phosphorescent OLEDs.[6] Recently, the power efficiency of phosphorescent white OLEDs reached 90 lm/W with improved light out-coupling technology.[1] Beside the difference in electro-luminescent type, fluorescent or phosphorescent, the marked efficiency difference is mainly due to the difference in conductivity of the transparent conductive oxides (TCO) on the different substrates.[3] TCO deposited on plastic substrates frequently possesses poor conductivity because most plastics have a low glass transition temperature and are soft, preventing TCO being formed at high temperatures, and making the surface smooth. Ironically, polymers with high glass transition temperatures are commonly colored and exhibit a low transmittance.[3] Hence, limited progress in the development of bright and efficient flexible white OLEDs has been made.

To improve this, a high-transmittance plastic with high T_g is required to enable the chosen TCO to be deposited at elevated temperatures. Silicon dioxide (SiO_2) is frequently introduced between TCO and plastic substrates to improve their interfacial adhesion or enhance resistance to the diffusion of moisture.[9] Only a relatively thin SiO_2 layer is required to enhance adhesion, while a thick SiO_2 layer is preferred for passivation. However, it is still unknown as to whether the addition of SiO_2 and its thickness profoundly affect the resulting power efficiency. Further investigation seems necessary.

Here we report the fabrication of efficient flexible white OLEDs with effective emissive device architecture on SiO_2 modified polyethersulfone (PES) substrate with highly conductive indium tin oxide (ITO) obtained by radio frequency magnetron sputtering at elevated temperatures. Sputtering the ITO at 200 °C on a 150 Å-thick SiO_2-pre-coated PES yields record-breaking pure white emission with a power efficiency of 6.5 lm/W at 800 cd m^{-2} and a maximum external quantum efficiency of 3.2%, obtained using blue host 1-butyl-9,10-naphthalene-anthracene (BANE) doped with 0.05 wt% red dye 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-yl-vinyl)-4*H*-pyran (DCM2) in a single emissive layer sandwiched between an electron-blocking effective hole-transporting-layer of *N*,*N*′-bis-(1-naphthy)-*N*,*N*′diphenyl-1,1′-biphenyl-4-4′-di-amine (NPB) and a hole-blocking effective electron-transporting-layer of 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl)benzene (TPBi).

Fig. 1 shows the schematic illustration of the device structure and a photograph of the BANE host composing flexible pure-white device at emission. The device comprises 175 μm PES/50-500 Å SiO_2/500 Å ITO/450 Å NPB/300 Å white emissive layer/400 Å TPBi/10 Å lithium fluoride/1500 Å aluminium. The white emissive layer was obtained by vapor deposition of a solution-premixed compound of the blue light-emitting host with the red dye. The experimental details are presented in the literature.[10]

Fig. 2(a) shows the electro-luminescent (EL) spectra of the white OLEDs with the use of blue host BANE, doped with red dye DCM2, on PES and glass substrates. By doping 0.05 wt% DCM2 into a blue BANE host on glass yields a device with pure white emission with Commission International de L'Eclairage (CIE) coordinates

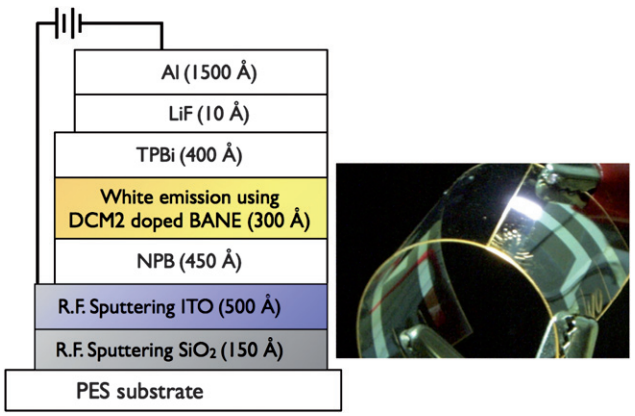

Fig. 1 A schematic illustration of the structure of the flexible white OLED. The inset shows the photograph of the resultant device at emission under bending.

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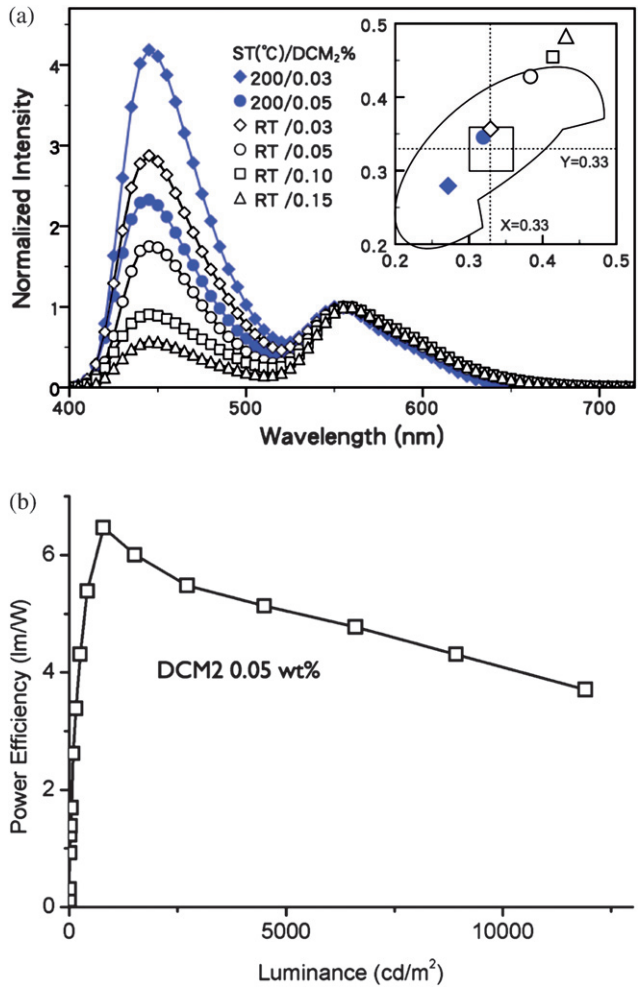

Fig. 2 (a) The effect of ITO sputtering temperature on the electroluminescent spectra of DCM2 doped blue BANE which compose white OLEDs at 100 cd m^{-2} on PES and the resultant emissions in terms of CIE coordinates for the devices with ITO films sputtered at various different temperatures (inset), where ST denotes the sputtering temperature and RT room temperature. (b) The power efficiency–luminance characteristics of the device with 0.05 wt% DCM2 doping and ITO sputtering temperature of 200 °C.

(0.314, 0.317) with a power efficiency of 5.5 lm/W at 52 cd m^{-2}. Surprisingly, fabricating the same emissive structure on the PES substrate with ITO deposited at room temperature yields emission that deviates strongly from the pure-white region, with CIE coordinates of (0.380, 0.430). To obtain pure-white emission on PES, the DCM2 concentration was reduced to 0.03 wt%, and the resulting CIE coordinates were (0.331, 0.355) with a power efficiency of 3.7 lm/W at 200 cd m^{-2}, which is lower than that on glass (5.5 lm/W). This finding may be attributed to the lower conductivity of the ITO on PES, whose surface resistivity is 9.1×10^{-4} Ω cm, while that on glass is 1.6×10^{-4} Ω cm. To improve efficiency, the ITO on PES was then sputtered at 100, 150, 200 and 220 °C, and the respective resulting power efficiency was 3.8, 3.9, 4.1 and 3.8 lm/W, at corresponding luminance of 300, 500, 200, and 200 cd m^{-2}, respectively. At 250 °C, no film can be made without great distortion, due to the viscoelastic deformation of the PES substrate at temperatures above its T_g (230 °C). The power efficiency was higher for ITO sputtered at higher temperatures, but not at 220 °C, which is too close to the T_g of PES, and at which temperature material softening may take place.

Interestingly, the emission changes markedly from pure-white to bluish-white for ITO sputtered at 200 °C or above. Such blue-shift enables more red dye DCM2 to be added, to keep the emission pure-white. Adding 0.05 wt% DCM2 to the blue BANE device on PES yields pure-white emission of (0.321, 0.339) with a high power efficiency of 6.5 lm/W with 800 cd m^{-2} at 8.5 V. Its maximum brightness was 12,000 cd m^{-2} with 670 A m^{-2} at 11.5 V, as presented in Fig. 2(b) and Table 1. The device exhibits excellent colour stability, *i.e.* that its CIE coordinates change only from (0.320, 0.331) to (0.314, 0.327) for brightness changing from 100 to 1,000 cd m^{-2}.

Fig. 3(a) shows the effect of the sputtering temperature of ITO on the surface resistivity and carrier concentration of the ITO films on PES. Both the resistivity and carrier concentration were directly measured using Van der Pauw techniques at room temperature by using a Hall-effect measurement system (Accent HL 5500 PC). Prior to the measurements, each ITO sample was ultrasonically cleaned with methanol and blown dry with high-purity nitrogen gas, and ohmic-contact between the ITO sample surface and the four metallic probes was secured to minimize imperfect-contact-resulting electronic noise. The lower resistivity of the ITO films sputtered at high temperatures may be attributed to their better film crystallinity,[11] as revealed by the X-ray diffraction pattern of the ITO films deposited at various temperatures in Fig. 3(b). The fact that the resistivity measured in the ITO film sputtered at 200 °C was lowest explains why the device has the highest power efficiency. At 220 °C, the ITO surface is slightly rougher and a slightly higher resistivity is detected, explaining why the power efficiency becomes lower.

As also shown in Fig. 3(a), the ITO films sputtered at 200 and 220 °C exhibit carrier concentrations of 7.4×10^{20} and 1.7×10^{20} cm^{-3},

Table 1 ITO sputtering temperature effects on the electroluminescent characteristics of the flexible white OLEDs with the blue host BANE doped with 0.03 wt% red dye DCM2 on PES substrate

ITO sputtering T/°C	Turn-on voltage[a]/V	Maximum luminance/cd m^{-2}	Maximum power efficiency/the corresponding brightness (lm/W)/(cd/m²)	CIE (x,y) at 100/1000 cd m^{-2}
RT	6.1	4,000	3.7/200	(0.331, 0.355)/(0.325, 0.348)
100	5.2	4,800	3.8/300	(0.321, 0.349)/(0.316, 0.340)
150	4.6	5,500	3.9/500	(0.320, 0.342)/(0.311,0.336)
200	4.0	6,400	4.1/200	(0.262, 0.261)/(0.255, 0.266)
220	4.2	6,000	3.8/200	(0.284, 0.298)/(0.274, 0.288)
200[b]	4.0	12,000	6.5/800	(0.321, 0.339)/(0.319, 0.338)

[a] Turn-on voltage is defined as the value obtained at 1 cd m^{-2}. [b] The device composes 0.05 wt% DCM2, while the rest compose 0.03 wt%.

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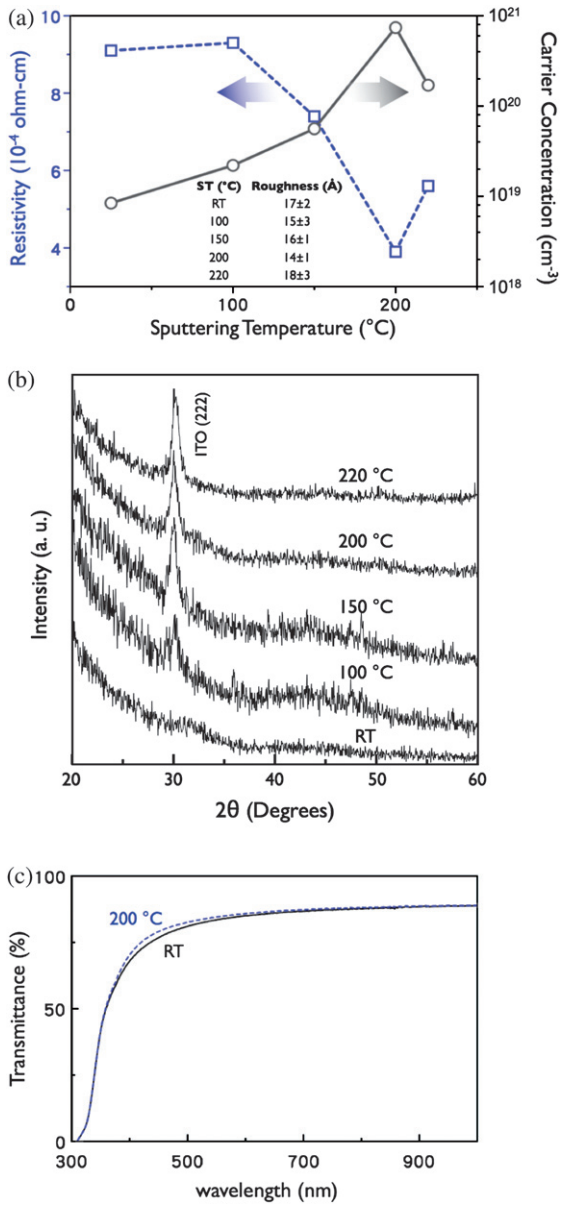

Fig. 3 (a) ITO sputtering temperature effects on the resistivity and carrier concentration of the 500 Å ITO films on 150 Å SiO_2 pre-coated PES. (b) An XRD pattern of the ITO thin films sputtered on SiO_2 pre-coated PES substrate at various temperatures. (c) Transmittance comparison of the ITO films sputtered at room temperature (RT) and 200 °C.

respectively, both of which are greater than the minimum carrier concentration required to cause the Burstein-Moss effect during the transmission of light through the ITO films.[12] As revealed by Burstein,[13] for semi-conducting materials, the increase in carrier concentration forces the excessive free electrons to fill the conduction band. Consequently, the energy required to excite an electron from the valence band to the unoccupied conduction band becomes higher. As a result, only light with high binding energy, such as ultraviolet, could then be absorbed thereby to trigger the excitement, which will cause a better transmittance at blue region for ITO films deposited at elevated temperature, as shown in the transmittance comparison of the ITO films deposited at room temperature and 200 °C (Fig. 3(c)). The blue light that was generated by the blue host BANE is then freely transmitted through the ITO film, resulting in a stronger blue emission. This result explains why the device with the 0.03 wt% DCM2 doped BANE on ITO sputtered at 200 or 220 °C showed a bluish-white emission. The Burstein-Moss effect is stronger at 200 °C since the carrier concentration is much higher.

Additionally, the ITO films sputtered at 200 °C exhibited a much higher conductivity, more than two times that at room temperature, which would consequently affect the injection of carriers and hence the recombination zone, and the shifting of which may also cause a change in micro-resonator length. Since the device structure, including layer thickness, and the materials used were kept the same, changing of the corresponding micro-resonator length may cause emission shift. To verify the effect of recombination zone shifting on the corresponding micro-resonator length and hence the resulting emission, further experiments are worth pursuing.

Although SiO_2 is known to be passivation effective[9] and thicker layers are preferred, its addition can positively or negatively affect the power efficiency, depending on its thickness. For example, the power efficiency of the device with 0.03 wt% DCM2 doped BANE on PES was 2.4 lm/W at 550 cd m^{-2} without SiO_2. The corresponding values were 1.3, 2.0, 4.1, 1.5, and 1.0 lm/W for SiO_2 layers of thickness 50, 100, 150, 300 and 500 Å, with corresponding luminance values of

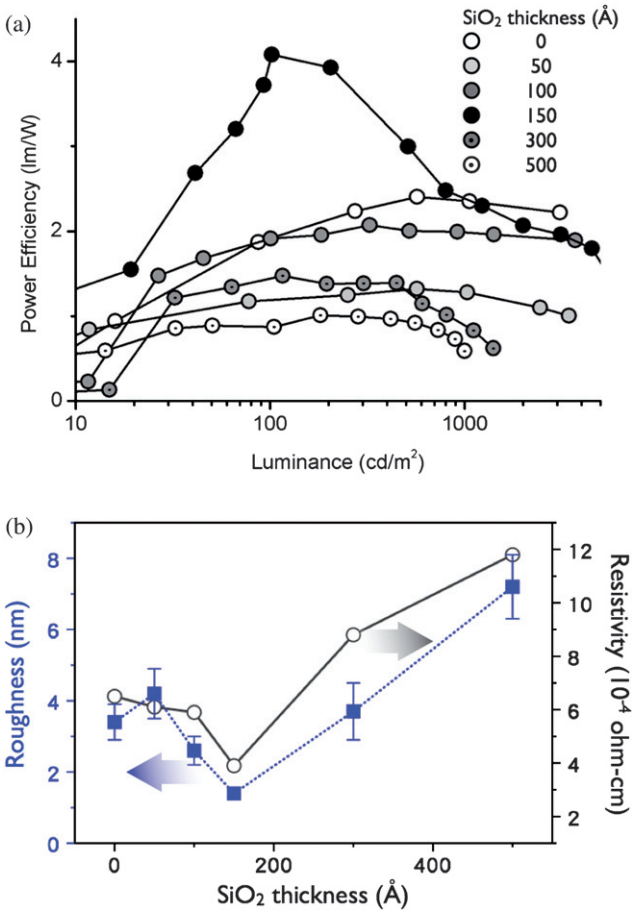

Fig. 4 (a) SiO_2 thickness effect on the resultant device efficiency. (b) SiO_2 thickness effects on the surface roughness and resistivity of the ITO films sputter on SiO_2 pre-coated PES, where the sputtering temperature and thickness of ITO is fixed at 200 °C and 500 Å.

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570, 330, 100, 120 and 180 cd m^{-2}, respectively (Fig. 4(a)). The power efficiency was increased only with the addition of 150 Å SiO_2, and decreased if much thinner or thicker than 150 Å. As shown in Fig. 4(b), the ITO film deposited on PES pre-coated with a 150 Å SiO_2 showed the smoothest surface structure, with a roughness of 14 ± 1 Å. A rougher surface was observed for SiO_2 much less than 150 Å due to discontinuous film structure. A rougher surface was also observed for SiO_2 much thicker than 150 Å due to the coarsening effect of SiO_2 grain growth.[14] For example, 300 Å and 500 Å thick layers of SiO_2 had surface roughnesses of 37 ± 8 Å and 72 ± 9 Å, respectively, greater than that of the bare substrate. As also shown in Fig. 4(b), the resistivity of ITO films depends strongly on the surface roughness. The smoothest film that was deposited on the 150 Å thick SiO_2 layer pre-coated PES exhibited a lowest resistivity of 3.9×10^{-4} Ω cm, explaining why its corresponding power efficiency was the highest among all.

In conclusion, this study demonstrated efficient flexible white OLEDs with effective emissive device architecture on a thin SiO_2 pre-coated PES substrate with highly conductive ITO sputtered at elevated temperature. With 0.05 wt% DCM2 doped in blue host BANE, a pure white emission with CIE coordinates of (0.321, 0.339) was obtained with a power efficiency of 6.5 lm/W at 800 cd m^{-2}.

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