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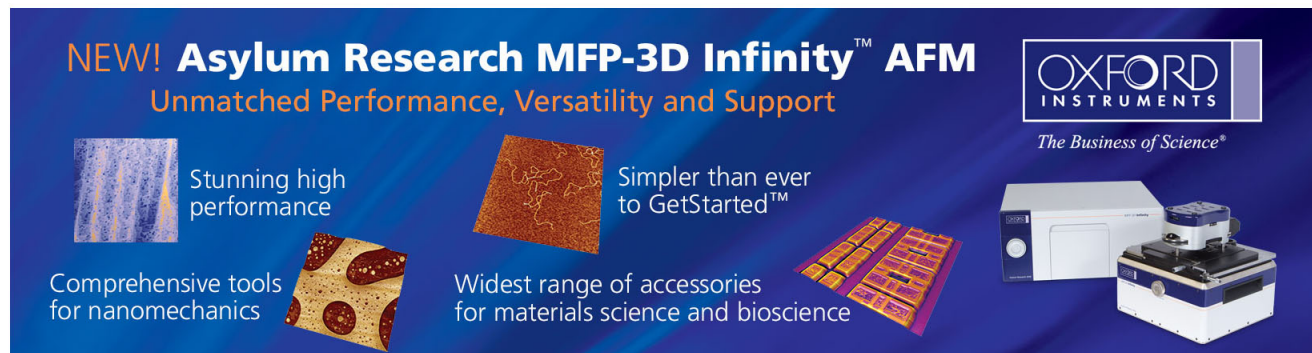
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## Stable inverted bottom-emitting organic electroluminescent devices with molecular doping and morphology improvement

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Stable inverted bottom-emitting organic light-emitting diodes (IBOLEDs) have been investigated by inserting *n*-type Cs<sub>2</sub>O dopant between indium-tin oxide bottom cathode and Alq<sub>3</sub>, the combination of which not only improved the morphology of organic layer but enhanced the lifetime of the IBOLED. This *n*-type doped IBOLED achieved efficiencies of 5.2 cd/A and 2.0 lm/W at 20 mA/cm<sup>2</sup>. The 20% decay lifetime (*t*<sub>80</sub>) of Cs<sub>2</sub>O doped IBOLED is 270 h which is about 1.7 times more stable than that of the conventional OLED (160 h) and 2.5 times of Li doped IBOLED (104 h). © 2006 American Institute of Physics. [DOI: 10.1063/1.2335374]

Organic light-emitting devices (OLEDs) have been developed for many years emerging as one of the main contenders of the next-generation information flat displays. Typical OLEDs have a transparent electrode indium-tin oxide (ITO) with high work function deposited on glass for anode and have an opaque metal for cathode such as Mg: Ag (Ref. 1) and Al/LiF (Ref. 2) from which light is reflected and emitted through the bottom ITO glass. To take advantage of the *n*-channel *a*-Si thin film transistor (TFT) which gives better uniform brightness for large display, it is highly desirable for active-matrix organic light-emitting diode (AMOLED) to employ an inverted OLED (IOLED) device which has the inverted structure with the bottom contact as the cathode. There have been several inverted top-emitting OLEDs (ITOLEDs) reported in the literature which need a reflective cathode as the base substrate and a transparent ITO sputtered above the organic layers as anode. However, the intense radiation energy created by sputtering would damage the organic layer and induce more nonradiative relaxation of the injected carriers.<sup>3,4</sup> The inverted bottom-emitting OLED (IBOLED) on the other hand is free from such problem. As a result, IBOLED will likely become more important in the future, particularly for large AMOLED displays such as future TV applications where large sized *a*-Si TFT is readily available and free from uniformity problems of the rival low temperature polysilicon TFT. Usually, structure of IBOLED has an ITO bottom cathode and an opaque and reflective top metal as anode to allow light to escape from ITO glass at the bottom. Since the transparent ITO has a high work function, efficient electron injection from ITO into organic has been a dogged issue to be resolved in IBOLED. We had proposed earlier that the barrier between ITO and

Alq<sub>3</sub> can be reduced by interfacial charge-transfer dipole by evaporating an ultrathin layer of magnesium (Mg) onto ITO which produced IBOLED with a luminous and current efficiencies of 1.51 lm/W and 4.66 cd/A, respectively, at a driving voltage of 8.9 V and current density of 20 mA/cm<sup>2</sup>.<sup>5</sup>

It has also been reported that doping can increase the mobility of carriers and lead to generation of very thin space-charge layers at the contacts associated with efficient injection.<sup>6-8</sup> For examples, Zhou *et al.* had reported *n-i-p* structure using Li doping in transparent inverted OLED (Ref. 9) to reduce drive voltage. However, the small atom of Li is prone to diffuse into organic layer which can cause nonradiative recombination<sup>10-12</sup> and ultimately leads to reduced device stability. In previous studies, the small atom of Li has been replaced by the larger atom of Cs to serve as the *n*-type dopant.<sup>13</sup> But, pure, low melting Cs source is rather difficult to handle and deposit by thermal process because it is extremely reactive in air. Often a specially designed and expensive Cs dispenser is needed to accomplish the trick in a vacuum chamber. Therefore, there is a continuing need to develop molecular *n* dopant for OLED. In this letter, we report the molecular Cs<sub>2</sub>O doping to enhance electron injection in IBOLED. Additionally, this Cs<sub>2</sub>O dopant will also improve the morphology of the electron injection layer with which significantly enhanced lifetime can be achieved.

In our study, the thickness and sheet resistance of ITO glass were 100 nm and 35 Ω/□, respectively. Prior to deposition, the ITO coated glass substrates were sequentially cleaned in acetone, isopropyl alcohol, and de-ionized water and these materials were then deposited by thermal evaporation in an ULVAC Solciet OLED coater at a vacuum of 10<sup>-7</sup> torr. *n* doping of Cs<sub>2</sub>O decomposed by cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) can be easily handled in the fabrication processes.<sup>14</sup> Further, Wakimoto *et al.*<sup>15</sup> has reported that

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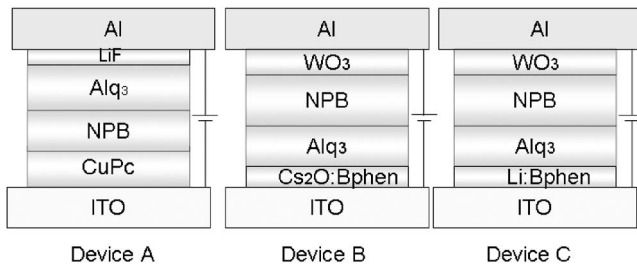
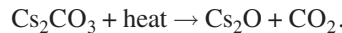


FIG. 1. Structure of inverted bottom-emitting OLED and conventional OLED.

$\text{Cs}_2\text{CO}_3$  will decomposed into  $\text{Cs}_2\text{O}$  according to the following reaction:



But, recently, Wu *et al.* reported that  $\text{Cs}_2\text{CO}_3$  deposited on the Au substrate measured with x-ray photoemission spectra (XPS) found that  $\text{Cs}_2\text{CO}_3$  did not decompose during the evaporation.<sup>16</sup> However, contrary to the observation of Wu *et al.*, we found that during thermal evaporation, the pressure in the vacuum chamber had increased rapidly near the decomposition temperature of  $\text{Cs}_2\text{CO}_3$  which we believe was due to the formation of  $\text{Cs}_2\text{O}$  and gaseous  $\text{CO}_2$ . The transition metal oxides, such as  $\text{V}_2\text{O}_5$ ,<sup>17</sup>  $\text{MoO}_3$ ,<sup>18</sup> and  $\text{WO}_3$  (Refs. 19 and 20) have been used to enhance the hole injection in the literatures. We opted to use  $\text{WO}_3$  as the hole-injection layer. The OLED structures of the conventional OLED and IBOLED are shown in Fig. 1, ITO/CuPc/NPB/Alq<sub>3</sub>/LiF/Al (device A), ITO/Cs<sub>2</sub>O:Bphen//Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device B), and ITO/Li:Bphen/Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device C), and designated as Figs. 1(a)–1(c), respectively. The current-density–voltage–luminance ( $J$ - $V$ - $L$ ) characteristics of the devices were measured by using a Photo Research PR650 spectrophotometer and a computer-controlled programmable dc source (Keithley 2400). Atomic force microscopy (AFM) was used in an attempt to correlate these characteristics of the surface morphology. The lifetime was measured in a glove box at a constant driving current density of 20 mA/cm<sup>2</sup>.

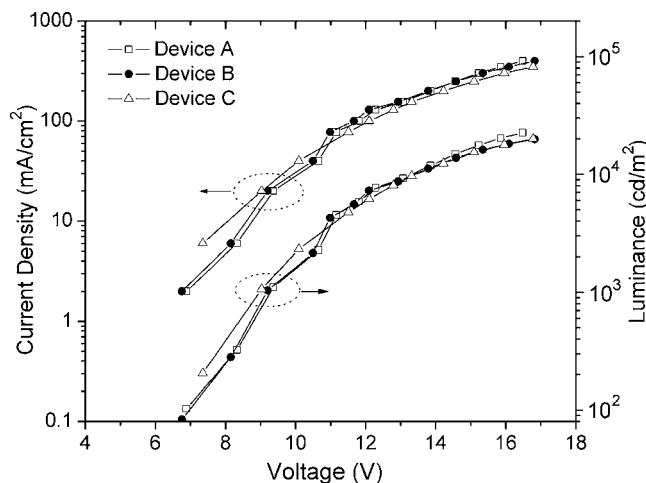


FIG. 2. Current-density–voltage–luminance characteristics of ITO/CuPc/NPB/Alq<sub>3</sub>/LiF/Al (device A), ITO/Cs<sub>2</sub>O:Bphen/Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device B), and ITO/Li:Bphen/Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device C).

TABLE I. Characteristic performances of the inverted bottom-emitting OLED (IBOLED) and conventional OLED driven at 20 mA/cm<sup>2</sup>.

Device	Voltage (V)	Brightness (cd/m <sup>2</sup> )	Lum. yield (cd/A)	Power efficiency (lm/W)
A	8.32	1106	5.53	2.09
B	8.15	1038	5.19	2.00
C	9.60	1078	5.39	1.85

The dependency of the voltage on current density and luminance is shown in Fig. 2. We find at the same current density that the performance of the Cs<sub>2</sub>O doped IBOLED is comparable with that of the conventional OLED in brightness, but its voltage is lower with 8.32, 8.15, and 9.62 V at 20 mA/cm<sup>2</sup> for devices A–C, respectively. The maximum brightness of Cs<sub>2</sub>O-doping device achieved 22 061 cd/m<sup>2</sup> at 450 mA/cm<sup>2</sup>. Wu *et al.*<sup>16</sup> has found that there were extra states above the Alq<sub>3</sub> highest occupied molecular orbital when Alq<sub>3</sub> was doped with Cs<sub>2</sub>CO<sub>3</sub>. We would like to propose instead that Cs<sub>2</sub>O-doping Bphen layer between ITO and Alq<sub>3</sub> could provide certain trap states which would enhance electron injections from ITO to the Alq<sub>3</sub>. Table I summarizes the performance of the devices at a drive current density of 20 mA/cm<sup>2</sup>. In previous studies, Cs atom which is larger than Li has been exploited as the  $n$  dopant to reduce the probability of metal diffusing into emission layer and quenching the excitons.<sup>21</sup> We propose that molecular Cs<sub>2</sub>O is even better for alleviating the problem of diffusion into organic layer which causes nonradiative recombination. Furthermore, the electron-transporting Bphen which is known to be morphologically unstable has been found to induce device degradation.<sup>22</sup> Figure 3 shows the AFM surface morphology of films deposited on glass substrates with the same thickness. The average surface roughnesses (root mean square average) are 4.3, 18.9, 2.94, and 2.3 nm for Bphen without or with annealing and Cs<sub>2</sub>O doped Bphen without or with annealing, respectively (Fig. 3). Compare Fig. 3(a) with 3(b),

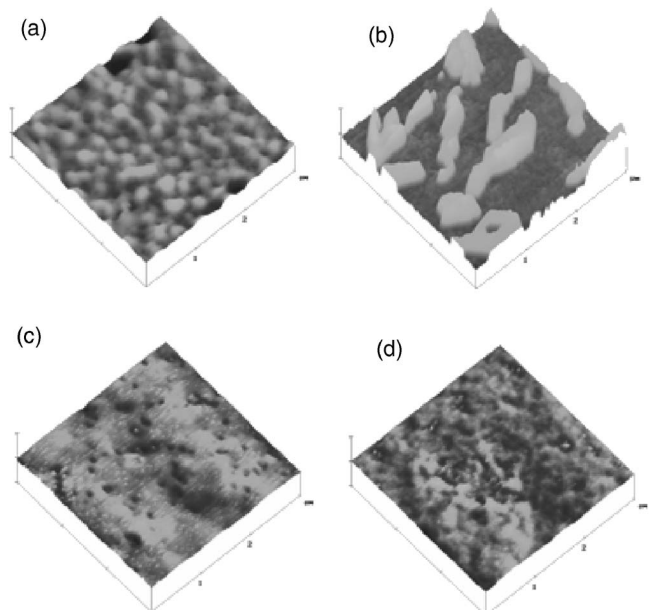


FIG. 3. Surface morphology of Bphen and Cs<sub>2</sub>O doped Bphen by AFM. (a) Bphen without anneal, (b) Bphen with annealing, (c) Cs<sub>2</sub>O doped Bphen without annealing, and (d) Cs<sub>2</sub>O doped Bphen with annealing.

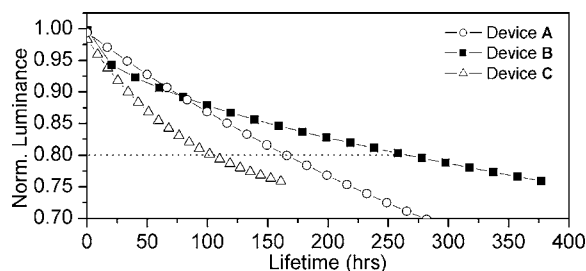


FIG. 4. Lifetime of ITO/CuPc/NPB/Alq<sub>3</sub>/LiF/Al (device A), ITO/Cs<sub>2</sub>O:Bphen/Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device B), and ITO/Li:Bphen/Alq<sub>3</sub>/NPB/WO<sub>3</sub>/Al (device C).

crystallization is evident in Bphen films after annealing at 80 °C for 20 min. However, by doping Bphen film with Cs<sub>2</sub>O, the phenomenon of crystallization after annealing under the same condition is clearly suppressed. We expect therefore that the Cs<sub>2</sub>O doped Bphen should improve device operational stability under thermal stress.

Figure 4 shows the lifetime for IBOLED in comparison with the conventional OLED which was measured in a glove box at a constant drive current density of 20 mA/cm<sup>2</sup>. Although the efficiencies of Li doped device can reach 5.39 cd/A and 1.85 lm/W, its lifetime was rather short due to the diffusion of the Li atom. On the other hand, the Cs<sub>2</sub>O doping of IBOLED device is observed to have much longer lifetime than both the convention OLED and Li doping of IBOLED devices with the  $t_{80}$  of devices A–C 160, 270, and 104 h, respectively, at a constant current density of 20 mA/cm<sup>2</sup>.

To conclude, Cs<sub>2</sub>O doping of IBOLED has excellent performance, including high efficiency, low voltage, and long lifetime. We suggest that thin Cs<sub>2</sub>O doped Bphen layer can provide trap states to enhance electron injection. In addition, the molecular Cs<sub>2</sub>O will eliminate the diffusion of Cs atom into the organic layer to create the nonradiative recombination. We also find that Cs<sub>2</sub>O doped Bphen layer has good morphological stability which is likely to reduce nonemissive dark spot growth. As a result, Cs<sub>2</sub>O doped IBOLED is 1.7 times more stable than the conventional OLED and 2.5 times than Li doping of IBOLED at the 20% decay lifetime ( $t_{80}$ ).

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