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I.-Ching Chen, Shiao-Wen Hwang, and Chin H. Chen

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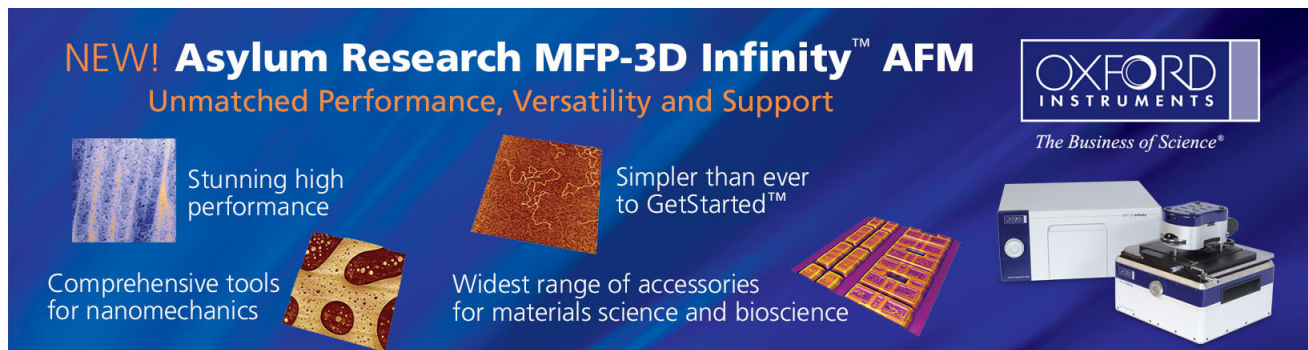
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# Improved performance and stability of organic light-emitting devices with Al–Cu alloy cathode

I.-Ching Chen

Department of Applied Chemistry, National Chiao Tung University, Hsinshu, Taiwan 300, Republic of China

Shiao-Wen Hwang and Chin H. Chen<sup>a)</sup>

Display Institute, Microelectronics and Information Systems Research Center, National Chiao Tung University, Hsinshu, Taiwan 300, Republic of China

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We have developed a stable green organic electroluminescent (EL) device by using an Al–Cu alloy as a cathode, which has better performance and reliability than the device with an Al cathode. The device with an Al–Cu alloy cathode achieved an EL efficiency of 3.78 cd/A (2.18 lm/W) at 20 mA/cm<sup>2</sup> and the operating voltage was 5.46 V, while device with Al cathode had an EL efficiency of 3.1 cd/A (1.34 lm/W) and 7.3 V at the same drive condition. The Al–Cu device achieved a 20% decay lifetime ( $t_{80}$ ) of 1234 h at an initial brightness of 756 cd/m<sup>2</sup>, which is twice the lifetime of conventional device with the state-of-the-art LiF/Al cathode. © 2005 American Institute of Physics. [DOI: 10.1063/1.1879103]

Since the discovery of efficient organic light-emitting devices (OLEDs), there has been considerable interest in developing them with high brightness, high efficiency, and long lifetime for display applications.<sup>1,2</sup> Cathodes play an important role in the overall performance of OLEDs. A cathode in the OLED is expected to have not only good electron-injecting ability but also good corrosion resistance. Generally, the structures of metal cathodes are separated into two types: Bilayer structures and alloy composite structures. Previous literature has shown the application of a bilayer cathode consisting of reactive low and high work function metals, e.g., Ca/Al, Mg/Ag, Li/Al, Gd/Al.<sup>3–6</sup> Insertion of low work function metals helps to lower the injection barrier between the cathode and organic layer, while high work function metals intrinsically have more robust properties to reduce the corrosion rate. Some metal alloys are used as cathode in OLEDs for the purpose of improving the adhesion property or electron-injecting ability, such as Mg:Ag, Al:Li, Al:Mg, and Al:Ca.<sup>7–9</sup> Metal alloys which contain at least one kind of low work function metal are still subject to corrosion under ambient conditions. Most research focuses on the electron-injecting ability but the corrosion problem due to the reactive low work function metals could often be problematic.

Recently, Liao and Tang at Kodak introduced the so-called “high work function metal alloy cathode”—Al:Ni to enhance corrosion resistance and reduce the dark edge growth rate of the emitting area in the OLEDs.<sup>10</sup> Application of Al:Ni alloy did prolong device lifetime at the expense of electroluminescent (EL) efficiency.

As is known, alloying two or more high work function metals can enhance the corrosion resistance of the alloy. Therefore, high work function metal alloy cathodes are expected to improve the long-term performance of OLEDs. In this letter, we propose a cathode composition for the fabrication of significantly improved stability; moreover, it also significantly elevates the efficiency and brightness of OLEDs.

This cathode is achieved by codeposition of Al and Cu, and both Al (4.2 eV) and Cu (4.6 eV) are high work function metals. Al:Cu alloy is well known in the semiconductor industry, thus its properties are also well understood. One of the advantages of the Al:Cu alloy is its ability to withstand high thermal stress during operation; the other is its good resistance to corrosion. We have found that the green EL device with an Al:Cu cathode has both better luminous efficiency and a longer lifetime than that of Al. The device with an Al:Cu cathode achieved an EL efficiency of 3.78 cd/A at 20 mA/cm<sup>2</sup> and 5.46 V, while the device with an Al cathode had an EL efficiency of 3.1 cd/A and 7.3 V. The device with an Al:Cu cathode had a 20% decay lifetime of  $t_{80}$ =1234 h, but the device with Al cathode only achieved 9 h which is more than 100 times shorter.

The device structure is depicted in Fig. 1, where CF<sub>x</sub>, *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl, 1,1'-biphenyl-4,4'-diamine (NPB), *tris*(8-quinolinolato)aluminum (Alq<sub>3</sub>), and lithium acetate (CH<sub>3</sub>COOLi) were used as the hole-injection material,<sup>11</sup> hole-transport material, light-emitting material, and electron-injection material, respectively. CH<sub>3</sub>COOLi was used by Fujihira *et al.*<sup>12</sup> as the electron-injection material.<sup>12</sup> Its temperature for thermal evaporation is about 300 °C at a base pressure of about 10<sup>-6</sup> Torr, which is more easily adapted in our thin-film evaporation system

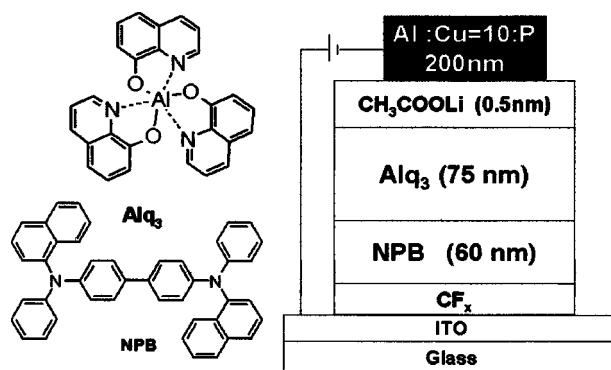


FIG. 1. Configuration of the OLED and molecular structures of the materials used.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: fredchen@mail.nctu.edu.tw

TABLE I. EL performances of devices with different composition cathodes driven at 20 mA/cm<sup>2</sup>. (Al:Cu ratio=10:P).

P (Al:Cu=10:P)	Voltage (V)	Luminance yield (cd/A)	CIE		Efficiency (lm/W)
			X	Y	
0	7.3	3.10	0.33	0.56	1.34
0.1	6.24	3.42	0.33	0.56	1.72
0.3	6.11	3.48	0.33	0.56	1.79
0.4	5.46	3.78	0.33	0.56	2.18
0.6	6.43	3.24	0.33	0.56	1.58
1	7.52	3.06	0.36	0.56	1.28

than the commonly used electron-injection material—LiF—which has a much higher evaporation temperature.

The detailed EL performances are summarized in Table I. The voltage, luminance yields, color coordinates, and power efficiencies were measured at 20 mA/cm<sup>2</sup>. After a routine cleaning procedure, the indium-tin-oxide (ITO)-coated glass was loaded onto the ground electrode of a parallel-plate plasma reactor, pretreated by oxygen plasma, then coated with a polymerized fluorocarbon film.<sup>12</sup> Devices were fabricated under the base vacuum of about 10<sup>-6</sup> Torr in a thin-film evaporation coater following a published protocol.<sup>13</sup> A multilayer structure of NPB/Alq<sub>3</sub>/CH<sub>3</sub>COOLi/Al:Cu was deposited on the substrate by resistive heating with a thickness of 60, 75, 0.5, and 200 nm for NPB, Alq<sub>3</sub>, CH<sub>3</sub>COOLi, and Al:Cu, respectively. The cathode was deposited by thermal coevaporating Al:Cu at a ratio of 10:0.1 to 10:1 by volume. All devices were hermetically sealed prior to testing. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 9 mm<sup>2</sup>. The current-voltage-luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled programmable dc source. The device lifetime measurements were performed in a glove box at a constant drive current density of 20 mA/cm<sup>2</sup>. X-ray diffraction (XRD) analysis was used to probe the composition of thin-film Al:Cu cathode by depositing about 200 nm of an

Al:Cu alloy of a different composition onto an *n*-type Si wafer in a thermal evaporation coater.

The current-voltage (*J-V*) and brightness-voltage (*B-V*) curves for cathodes of different compositions are shown in Figs. 2(a) and 2(b), respectively. With the addition of Cu into the Al cathode, the driving voltage is found to decrease until the ratio of Al:Cu reaches 10:0.4, then increase again when the Cu concentration is higher. The device with a Cu cathode has the highest driving voltage for largest electron-injection barrier, thus we attribute the profile of driving voltage within the Al:Cu devices to be influenced by the electron-injection ability of the cathode. The profile of EL efficiency with respect to Cu concentration has just the opposite effect. The addition of Cu initially enhances the luminous yield but the yield drops as Al:Cu ratio is beyond 10:0.4. The plot of luminance efficiency versus current density for all devices is shown in Fig. 3. Detailed EL performances are summarized in Table I in which the voltage, luminance yields, color coordinates, and power efficiencies were measured at 20 mA/cm<sup>2</sup>. The optimum performance of devices is at the Al:Cu ratio of 10:0.4, providing an EL efficiency of 3.78 cd/A and 2.18 lm/W at 5.46 V; while the device performance of the Al device is 3.10 cd/A and 1.34 lm/W at 7.3 V. The chromaticity of all the devices remains unchanged at CIE<sub>x,y</sub>=0.33, 0.56. It is apparent that the application of an Al:Cu alloy cathode enhances the EL efficiency of devices and also significantly lowers the driving voltage (by 30%) without impacting the emissive color.

In all of the devices studied, the magic ratio of Al:Cu seems to be around 10:0.4, which we attribute to the electron-injection ability of cathode. In attempt to understand the relationship between the coevaporated ratio of Al:Cu and the electron-injection ability of cathode, we study the XRD analysis of an Al:Cu thin film of different compositions

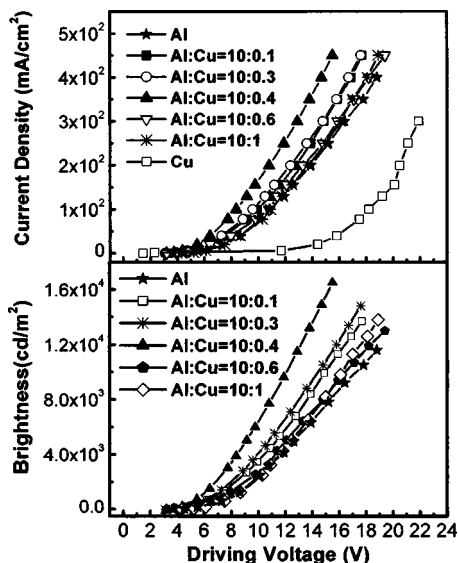


FIG. 2. *J-V* and *B-V* characteristics for devices with different cathode compositions.

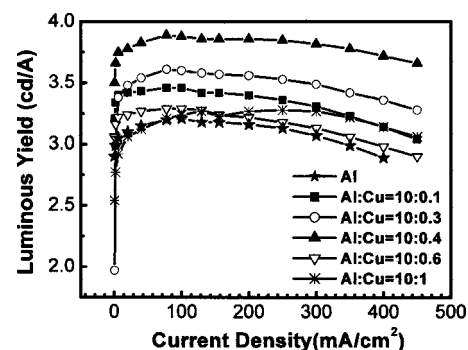


FIG. 3. The dependency of the EL efficiency on the drive current density for devices with different cathode compositions.

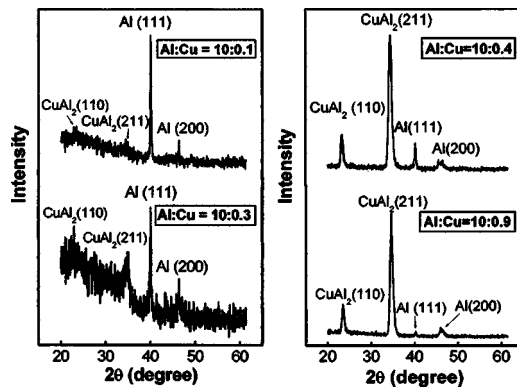


FIG. 4. XRD results of Al:Cu thin films with different compositions.

whose crystallographic planes are depicted in Fig. 4. As the ratio of Al:Cu is 10:0.1 and 10:0.3, Al (111) and Al (200) are easily discernible and to the left-hand side of which, notable small peaks of  $\text{CuAl}_2(211)$  and  $\text{CuAl}_2(110)$  are also detected. The gross baseline in the spectra of 10:0.1 and 10:0.3 is considered to be the effect of the disturbance of Cu. When the ratio of Al:Cu is close to 10:0.4, the peaks of  $\text{CuAl}_2(211)$  and  $\text{CuAl}_2(110)$  rise dramatically and are considerably more intense than the peaks of Al surface planes. Compared to the other XRD spectra in Fig. 4, the one of the ratio 10:0.9 has the relatively lowest intensity of Al (111). As no peak of any crystallographic planes of Cu is observed, we conclude that all of the evaporated Cu has been transformed into  $\text{CuAl}_2$ , thus the Al:Cu thin-film codeposited as a cathode in our devices is, for the most part, a composite of Al and  $\text{CuAl}_2$ .

In general, metals display anisotropy in their work function.<sup>14</sup> The origin of this anisotropy is believed to be the difference in atomic packing density along the various crystallographic planes. Densely packed crystallographic surfaces display high work functions, since these surfaces are relatively inert with fewer broken planes. Open crystallographic surfaces display lower work functions owing to a greater number of broken bonds. Amorphous metal films can thus be expected to have lower work functions than their corresponding crystalline counterparts.<sup>15,16</sup> The work function of the cathode is the average of all crystallographic planes. In our XRD analysis, the composition of different crystallographic planes were found to change with the co-evaporated ratio of Al:Cu. Thus, the work function of the cathode could be varied at different evaporating conditions. We further surmise that the change in the driving voltage at different ratios of Al:Cu may simply be due to change of the work function. At the optimum ratio of 10:0.4, the composition of crystallographic planes has the relatively lower work function and the barrier for electron injection is close to the lowest in the compositional ratio of Al:Cu from 10:0.1 to 10:1.

The device operational stability for devices with Al:Cu (10:0.4) cathode is shown in Fig. 5 with an initial brightness of  $756 \text{ cd/m}^2$  and an initial drive voltage of 5.46 V. Compared to devices with an Al cathode (9 h), the lifetime at 20% decay in luminance for an Al:Cu cathode is 1234 h, which is >100 times better. To benchmark against the state-of-the-art LiF/Al cathode which was clocked at  $t_{80} \sim 600 \text{ h}$  at the same operational condition with an initial brightness of  $682 \text{ cd/m}^2$ , our device lifetime with a  $\text{CH}_3\text{COOLi}/\text{Al}:\text{Cu}$  cathode is also nearly twice as robust as that of the LiF/Al

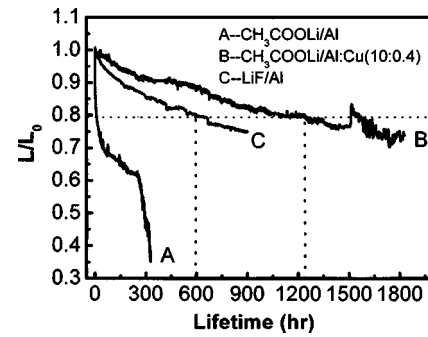


FIG. 5. Comparison of operational stability among devices with different composition of Al:Cu cathode.

device which represents a significant improvement over current OLEDs.

In summary, we have introduced a composition of a cathode, which is composed of two high work function metals: Al and Cu—whose alloy possesses both good corrosion resistance and electrical conductivity. We found that the device with an Al:Cu cathode has much better overall EL performance than the device with the common Al cathode. An optimum alloy composition is found at the Al:Cu ratio of 10:0.4. In XRD analysis, we found that the composition of different crystallographic planes in an Al:Cu thin film varies with the ratio of Al:Cu, thus the work function of the cathode may become relatively low in the ratio of about 10:0.4, which leads to the lower barrier of electron injection and optimum device performance. We also found that the reliability of device is considerably enhanced when an Al-Cu alloy is utilized as the cathode in our device structure that is twice as good as the state-of-the-art LiF/Al cathode.

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