

Stacked metal cathode for high-contrast-ratio polymeric light-emitting devices

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An extremely high optical absorbing film made of alternating aluminum–silver layers was used as cathode in polymeric light-emitting devices (PLEDs). Physical properties of the cathodes were characterized by I – V measurement, atomic force microscopy, and x-ray photoemission spectroscopy. As a result of the slow evaporation rate, each pair of the aluminum–silver layer was shown to be in the form of aluminum–aluminum oxide nanoclusters embedded in an amorphous charge conducting network of silver. The nanoclusters helped to absorb and scatter the ambient light effectively. The use of four alternating layers structure in conventional PLEDs demonstrated 126% enhancement of contrast under 1000 lx ambient illumination. The I – V characteristics of the black cathode PLEDs remained intact when compared with reference PLEDs. This technology offers precise control of the cathode quality in terms of its reflectivity and conductivity. © 2005 American Institute of Physics. [DOI: 10.1063/1.1897440]

The fabrication of polymeric light-emitting diodes (PLEDs) with high brightness and efficiency has been shown feasible during the last decade and some device prototypes are being considered for market entry. An additional and possibly more important advantage is the availability of a broad range of substrates and device structures which can be used to further enhance the device performance. The cathode evaporated onto the device is usually a low work function metal or metal alloy, such as aluminum (Al), magnesium–silver (Mg–Ag), lithium–aluminum (Li–Al), and lithium fluoride–aluminum (LiF–Al) to reduce operating voltage and enhance device performance.^{1–3} The ambient light, however, after transmitting through the polymer layer, will be reflected by the metal cathode and coupled out of the device through the ITO coated substrate. As a result, the contrast ratio of PLEDs will be significantly reduced by reflected ambient light, and thus prohibiting the PLEDs for outdoor applications. There are many attempts to enhance the contrast ratio by inserting an absorption and conductive inorganic layer between the polymer layer and the cathode.^{4,5} However, the need of sputtering process for deposition brings about damage on the polymer layer. Recently, a black cathode consisting of a silicon monoxide doped Al film and an overlaid Al layer has been developed for organic light-emitting diodes, and exhibited superior device performances.⁶ However, in practice, the proposed technique causes the black conductive films porous even with precise control of the Al–silicon monoxide ratio during coevaporation. In this letter we demonstrate an evaporation technique and cathode structure, with primary focus being on the physical properties of Al–Al oxide nanoclusters which forms the essential element for the unique light absorbing ability. Since only one more type of metal is introduced in the material system, this technology requires no modification of the existing evaporation system.

The inset of Fig. 1(a) illustrates the black cathode device with a structure of glass/ITO/poly(3,4-ethylene-dioxythiophene) (500 Å)/green fluorine-containing copoly-

mer (5BTF8) (800 Å)/calcium(2) acetylacetonate ([Ca(acac)₂]/×4 Al (40 Å)–Ag (40 Å)/Ag (280 Å)). The readers are referred to Ref. 7 for fabrication details. It will be shown later that each pair of the Al–Ag layer is used to provide sufficient absorption of the ambient illumination, while maintaining good electron injection to the polymeric layer. The merit of using black cathode for PLEDs was com-

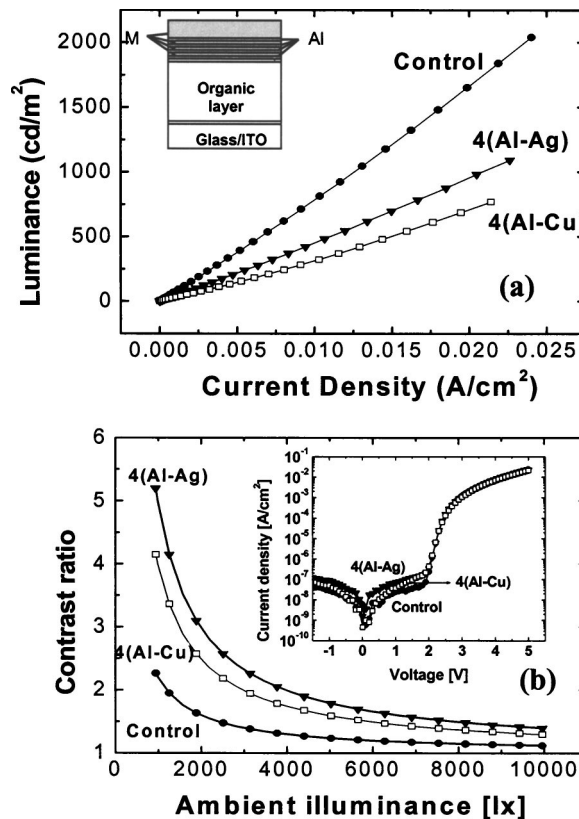


FIG. 1. (a) Electroluminescence of the black cathode PLEDs and the control device. Inset shows the device configuration of the black cathode PLEDs (M is either Al or Ag) and (b) contrast ratio of the black cathode PLEDs and the control device under different ambient illumination. The inset shows the current–voltage characteristics of the PLEDs.

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pared with a reference device using Al (600 Å) as a cathode. The thickness of both the Al and Ag were 40 Å. The evaporation rates of Al and Ag were 0.2 and 0.5 Å/s, respectively. The base pressure of the chamber was maintained at $\sim 1 \times 10^{-6}$ Torr. The current–voltage characteristics and electroluminescence were measured by a Keithley 2400 source measure unit with calibrated silicon photodiode and a Photo Research PR650 spectrophotometer. The contrast ratio measurement was achieved by putting the PLED inside a Newport 6 in. integrating sphere with a Thermo Oriel 150 W solar simulator as a standard light source. The contrast ratio C was then calculated as

$$C = \frac{I_r + I_{\text{on}}}{I_r + I_{\text{off}}}, \quad (1)$$

where I_r is the reflected ambient light from the device, and I_{on} and I_{off} are the device luminance when it is switched on and off, respectively. At ambient condition, I_{off} should be zero for devices. The background was calibrated by measuring the luminance from a rough piece of white paper placed in the integrating sphere.

Atomic force microscopy was performed by a Digital Instruments multimode scanning probe microscope. The scan size is $1 \mu\text{m}$ and scan rate is 2 Hz. For x-ray photoelectron spectroscopy measurement, the sample was prepared by evaporating Al at 0.2 Å/s on a silicon substrate and subsequently covered by fast evaporation of Al at 1.0 Å/s. 5 keV Ar^+ ion sputtering was first utilized to remove the covered Al and then the evolution of the spectrum was recorded. The fresh surface was analyzed using Omicron Nanotechnology multiprobe surface science system, with monochromatic Al $K\alpha$ radiation.

The black cathode PLEDs displayed black color in the background when the devices were turned off as compared with the control device. Figure 1(a) shows the electroluminescence (EL) of the black cathode PLEDs with four alternating layers of Al–Ag and Al–copper (Cu) [labeled as 4(Al–Ag) and 4(Al–Cu)] with respect to the control device. A luminance of 1300 cd/m^2 was achieved by the control device at a current density of 15 mA/cm^2 , while the black cathode PLEDs with the stacked Al–Ag and Al–Cu had a luminance of 640 and 450 cd/m^2 , respectively. The EL of the Al–Ag stacked black cathode PLED is about 50% lower than the control device. This one-half reduction of the EL is an indication of the strong optical absorbance of the black cathode. The EL from the black cathode PLED could not be reflected by the cathode layer as in the case of the control device. In our case, the Al–Cu material system brings less attention due to the relatively weak optical absorption.

Figure 1(b) presents the contrast ratios of the black cathode PLEDs and the control device under different ambient illumination. During the measurements, both the stacked black cathode PLEDs and the control device were maintained at a luminance of 300 cd/m^2 . Again the contrast ratio of the Al–Cu stacked black cathode PLED is shown for amenity. The contrast ratio of the Al–Ag stacked PLED is ~ 5.2 under 1000 lx ambient illumination, which corresponds to a 126% increase in contrast higher than the control device. It is worth noting that, the improvement of the contrast is about 25% under 10 000 lx ambient lighting. The black cathode PLEDs show sufficient brightness level which are suitable for outdoor applications. The inset of Fig. 1(b) shows the

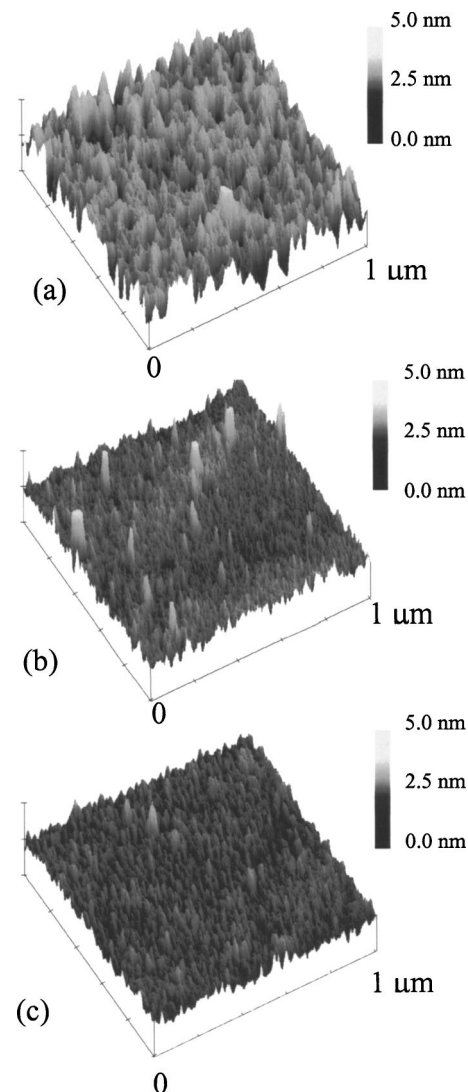


FIG. 2. Images of the atomic force microscopy on the (a) $[\text{Ca}(\text{acac})_2]$ surface, (b) Al surface with $[\text{Ca}(\text{acac})_2]$ underneath, and (c) the successive Ag surface. All the image size is $1 \mu\text{m}$ square.

I – V characteristics of the PLEDs with different metal combinations. The turn-on voltages ($\sim 2 \text{ V}$) and the I – V characteristics of the black cathode PLEDs are the same as that of the control device. It is strongly indicative that the integration of the black cathodes with PLEDs only changes their optical absorbance. The technique was proven to be able to form electrical conducting paths for the electrons migrating to the polymeric layer which was in principle, a different approach to the black cathode structure proposed by Wong *et al.*⁶

Figure 2 shows the atomic force microscopy (AFM) images of (a) the $[\text{Ca}(\text{acac})_2]$ surface, (b) the Al surface after the film (40 Å) was evaporated on the $[\text{Ca}(\text{acac})_2]$ layer, and (c) the Ag surface after the film (40 Å) was successively evaporated on the Al surface. From AFM software calculation, the surface roughness of the $[\text{Ca}(\text{acac})_2]$ and the Al surface were ~ 16.5 and ~ 6.7 Å, respectively, indicating that Al was able to smooth the $[\text{Ca}(\text{acac})_2]$ surface underneath. There are two scenarios; either the residue oxygen in the chamber acted like surfactant that allowed the high surface free-energy Al to wet the low surface free-energy organic film⁸ or the Al reacted with oxygen and formed other compounds that could wet the $[\text{Ca}(\text{acac})_2]$ surface. It will be

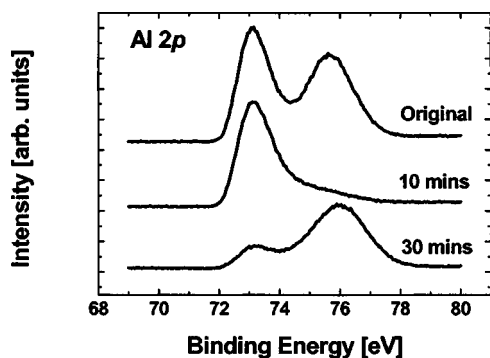


FIG. 3. XPS core level spectra immediately taken from the Al clusters covered with Al after evaporation (labeled as original) and their evolution (labeled as 10 and 30 min). Both the spectra labeled as original and 10 min have been vertically displaced for clarity.

shown later that the Al is in fact composed of Al and Al oxides. The subsequent Ag film, however, provided a relatively smooth surface as shown in Fig. 2(c) (roughness ~ 5.2 Å), due to the wetting ability of Ag was lower than that of the material underneath. We observed that the evaporation rate of Ag must be at least 0.5 Å/s or the cathodes were not conducting.

Last, it remains the issue of why the Al clusters are black in color. In order to probe the physical properties of the unaltered Al clusters, the sample was covered by a thick Al layer before transporting into the x-ray photoelectron spectroscopy (XPS) chamber. Figure 3 shows the XPS data from the Al clusters covered with Al (labeled as original). The two unique features at ~ 73.1 and ~ 75.5 eV Al $2p$ binding energies, belong specifically to the metallic Al and the most common Al native oxides.⁹ It is well known that Al reacts with oxygen and water to form protective surface oxides under ambient environment. The Al $2p$ core level spectrum confirms that the outermost Al surface is covered by Al native oxides. Following the Ar^+ ion sputtering to remove the native oxides, the spectrum showed only the characteristic peak of metallic Al after 10 min, indicating that the native oxides had been removed. With increasing sputtering time, another feature at ~ 76.0 eV Al $2p$ binding energy appeared with intensity higher than that from the metallic Al. The spectrum suggested that primary element of the Al clusters was a mixture of Al and Al oxides (different from the common native oxides). It was reported that Al oxides formed from Al under oxygen deficient ambient condition were: (i) not pure alumina but with chemical formula, $\text{Al}_2\text{O}_{x<3}$, (ii) light absorbing was strongly dependent on the degree of oxygen deficiency.⁶ It is then fair to mention that: (i) the exact chemical constituent of the Al oxides is still unclear, but presumably mainly composed of $\text{Al}_2\text{O}_{x<3}$ and (ii) the nanoscale clusters as shown in Fig. 2(b) can be considered as Al embedded in Al oxides by the intuition that the Al left the crucible and interacted strongly with the residue oxygen before reaching the target. As mentioned before, the Al and Ag evaporation rates are critical for the nanoclusters formation which dictates the cathode color and the overall conductivity. Similar phenomenon was observed by Han *et al.*¹⁰ They report that *the size of Al islands increases with increasing Al concentration, which leads to a dramatic reduction in resistivity and optical transmittance.* Although the material system used in Ref. 10 is different, but the work emphasized on the importance of the evaporation rates which could bring

about the opposite effect on the physical properties of the combined system. Our results suggested that the Al oxides were responsible for the light absorption, and will further enhanced the scattering of ambient light when they are in the form of nanoclusters.

The evaporation of Ag on the Al clusters not only smoothed their surface as shown in Fig. 2(c), but also took the role of charge transporting medium which enhanced the overall conductivity of the paired Al–Ag layers. It is possible to picture that the metallic Al clusters are separated by non-conducting $\text{Al}_2\text{O}_{x<3}$ and conducting Ag. Tunneling conduction between the metallic Al clusters reported by Abeles *et al.*^{11,12} is assumed to occur. It is considered that with such high conductivity in Ag, the anomalous skin effect could be present. This is the case when the electron mean free path becomes comparable with the skin depth. The collisions of the electrons within the Ag surface are now the dominating factor accounts for the optical properties¹³ of the metal. The electrons are accelerated and decelerated many times within the skin layer. On average, they absorb no energy from the field unless they undergo a collision. Since collisions with the lattice are unlikely in the anomalous regime, surface scattering is significant. This in turn, contributes to the overall black color of the cathode.

In closing, high optical contrast black cathodes have been integrated in PLEDs by successive thermal evaporation of alternating common metals. The primary chemical constituent and conduction mechanism in the cathodes have been characterized and addressed. The black cathode PLEDs demonstrate extremely high optical absorbance whilst maintaining no potential drop across the cathode layers. Illuminating at a brightness of 300 cd/m², the Al–Ag stacked black cathode PLEDs have contrast improved by 126% under 1000 lx ambient illumination. This fabrication technology not only offers black cathode PLEDs with a superior brightness level for outdoor applications, but also provides a mean to stabilize and standardize the optical and electrical properties of cathodes used in PLEDs.

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¹C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).

²M. Stossel, J. Staudigel, F. Steuber, J. Simmerer, and A. Winnacker, Appl. Phys. A: Mater. Sci. Process. **68**, 387 (1999).

³L. S. Hung, C. W. Tang, and M. G. Mason, Appl. Phys. Lett. **70**, 152 (1997).

⁴J. A. Dobrowolski, B. T. Sullivan, and R. C. Bajcar, US Patent No. 5,049,780 (1990).

⁵L. S. Hung and J. Madathil, Adv. Mater. (Weinheim, Ger.) **23**, 1787 (2001).

⁶F. L. Wong, M. K. Fung, X. Jiang, and C. S. Lee, Thin Solid Films **446**, 143 (2004).

⁷Q. Xu, J. Ouyang, and Y. Yang, Appl. Phys. Lett. **83**, 4695 (2003).

⁸J. Ivanco, B. Winter, F. P. Netzer, and M. G. Ramsey, Appl. Phys. Lett. **85**, 585 (2004).

⁹J. van den Brand, P. C. Snijders, W. G. Sloof, H. Terryn, and J. H. E. de Wit, J. Phys. Chem. B **108**, 6017 (2004).

¹⁰S. Han, D. Grozea, C. Huang, and Z. H. Lu, J. Appl. Phys. **96**, 709 (2004).

¹¹B. Abeles, P. Sheng, M. D. Coutts, and Y. Arie, Adv. Phys. **24**, 407 (1975).

¹²B. Abeles, RCA Rev. **36**, 594 (1975).

¹³T. Holstein, Phys. Rev. **88**, 1427 (1952).