High-brightness top-emissive polymer light-emitting diodes utilizing organic oxide/Al/Ag composite cathode

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This work presents the fabrication of high-brightness (over 30 000 cd/m\(^2\)) top-emissive polymer light-emitting diodes (PLEDs) using a hybrid semitransparent cathode capable of efficient injection of electrons. The composite cathode is comprised of the organic oxide/Al complex as the injection buffer layer covered by a thin Ag overlayer. The anode is made of Ag:Ag\(_2\)O coated on the glass substrate. The electroluminescence (EL) efficiency of 8.9 cd/A for phenyl-substituted poly(\textit{para}-phenylene vinylene) copolymer based top-emissive PLED markedly exceeds that of 4.3 cd/A for the control device with the bottom-emissive configuration. The high performance is attributed to the balanced injection of charge carriers and the effective extraction of EL emission from the top cathode. The optical microcavity effect significantly promotes the EL emission in the direction along the surface normal. © 2006 American Institute of Physics.

The top-emissive organic and polymer light-emitting diodes (T-OLEDs and T-PLEDs) emit light from the top surface of devices, which have many favorable features than the bottom-emissive O/PLEDs in active-matrix (AM) flat panel display applications.\(^1\)\^-\(^4\) These diodes can be fabricated on opaque substrates, including rigid Si wafers and flexible steel foils,\(^5\)\(^,\)\(^6\) and can function at a lower bias voltage or current, while still exhibiting the same luminescence as bottom-emissive devices. The AM panels made of top-emissive O/PLEDs are expected to present a much more vividly colored image and increased operating lifetime.

The configurations of typical T-O/PLEDs comprise several organic layers with different functionalities sandwiched between the highly reflective bottom anode and the semitransparent top cathode. Ag is commonly adopted as a conductive bottom anode, because of its highest reflectivity of light in the visible region and its ability of efficient injection of holes after the appropriate surface treatment.\(^7\)\^-\(^8\) In the semitransparent cathode, an ideal top electrode should be highly conductive of charges, support the efficient injection of electrons, be highly transparent to light, have a high emission out-coupling efficiency, and have a long-term operating stability. However, no single material satisfies all of the requirements of the top cathode simultaneously. Many research groups have applied an ultrathin layer of the low work function metals, LiF/Al, or copper phthalocyanine covered with a thin Ag or indium-tin-oxide (ITO) overlayer to fabricate the top cathodes.\(^9\)\^-\(^11\) The performance of T-O/PLEDs thus obtained was favorable.\(^12\)\^-\(^16\) A composite electrode is required to develop the multifunctional cathode structure. In this letter, an organic oxide/Al/Ag composite cathode is reported for the fabrication of high-brightness and high-performance top-emissive PLEDs.

The configurations of the top-emissive PLEDs here in this study are plotted in the inset of Fig. 3. The Ag:Ag\(_2\)O electrode on the glass substrate, reported by Chen et al.,\(^3\) is used as a highly reflective anode and supports the efficient injection of holes in a top-emissive device. The thin layer of Ag:O is prepared by UV-ozone treatment of the Ag/glass substrate. The device configuration is comprised of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Bayer Corp. 4083) as the hole transport layer, “high-yellow” phenyl-substituted poly(\textit{para}-phenylene vinylene) copolymer (HY-PPV; electroluminescence (EL) emission centered at 560 nm) film as the light-emissive layer, and the hybrid organic oxide/Al/thin Ag as the semitransparent cathode. The organic-oxide film is deposited by thermally evaporating a thin polymer layer, 15 Å, of poly(ethylene glycol) dimethyl ether (PEGDE) (Aldrich, Mn ca. 2000) on the surface of HY-PPV film inside a vacuum chamber (10\(^{-5}\)torr). The semitransparent metal electrode, 15 Å thick Al layer and Ag of different thicknesses, is evaporated on the substrates sequentially without breaking the vacuum. No dielectric capping layer is utilized for the hybrid cathode in this study. The active pixel area of the device is 0.06 cm\(^2\). The details of the fabrication procedure and the current-brightness-voltage \((I-L-V)\) measurement can be found elsewhere.\(^17\)\(^,\)\(^18\)

The usage of the organic oxide, PEGDE, as the cathode buffer layer enables the efficient injection of electrons through the Al cathode and blocks the metal-induced quenching sites in the EL layer.\(^17\)\(^,\)\(^18\) In addition, the enhanced performance is limited only to the use of Al metal.\(^18\)\^-\(^20\) The device configurations of the bottom-emissive devices...
with organic oxide/Al cathodes with Al metal layers of different thicknesses are glass/ITO/PEDOT:PSS/HY-PPV/PEGDE(15 Å)/Al(x Å)/Ag(1200 Å), with x=5, 15, 50, and 100 Å. Ag is used as the covering layer on the organic oxide/Al composite cathode to retain the conductivity of the electrode. The maximum efficiency is 10.7 cd/A at 6.70 V and 5142.0 cd/m² for the device with the PEGDE(15 Å)/Al(100 Å)/Ag(1200 Å) cathode (which has a thick Al middle layer), but only 3.4 cd/A at 6.20 V and 2831.9 cd/m² for the device with the PEGDE(15 Å)/Al(5 Å)/Ag(1200 Å) cathode structure (which has a thin Al middle layer). The luminous efficiencies are 9.1 cd/A at 6.70 V, 4824.8 cd/m² and 4.3 cd/A at 6.80 V, 5186.2 cd/m² for the devices with PEGDE(15 Å)/Al(50 Å)/Ag(1200 Å) and PEGDE(15 Å)/Al(15 Å)/Ag(1200 Å) cathode structure, respectively. The higher performance of the devices with thicker Al middle layers follows from the balanced injection of charge carriers, according to our previous investigations.13,14 Optimizing the thickness of the organic oxide/Al complex layer is critical to the injection of electrons through the cathode as well as the improvement in the performance of the device.

Figure 1 plots the I-L-V curves of the top- and the control bottom-emissive devices with the structures of glass/Ag:Ag2O/PEDOT:PSS/HY-PPV/PEGDE(15 Å)/Al(15 Å)/Ag(70 Å) and glass/ITO/PEDOT:PSS/HY-PPV/PEGDE(15 Å)/Al(15 Å)/Ag(1200 Å), respectively. The light intensity of the top-emissive device exceeds 30 000 cd/m² in the direction along the surface normal when biased at 8.80 V. The turn-on voltage of the light emission is under 3.0 V. As shown in the inset in Fig. 1, the maximum luminous efficiency of the top-emissive device is 8.9 cd/A (6677.3 cd/m², EL emission centered at ~560 nm) when the device is biased at 6.60 V (74.98 mA/cm²), in which the efficiency markedly exceeds that of 4.3 cd/A (5186.2 cd/m²), biased at 6.80 V (120.40 mA/cm²), for the control device with the bottom-emissive configuration. Since the cathode parts of the top- and control bottom-emissive devices are comprised of the same composition of the organic oxide/Al complex [PEGDE(15 Å)/Al(15 Å)] as the injection buffer layer for electrons, the superior luminous efficiency for the top-emissive device is presumed to be related to the enhanced spontaneous emission and the modified emission distribution of the optical microcavity effect.12,21,22 The preferential direction of EL emission between the highly reflective Ag:Ag2O anode and the semitransparent organic oxide/Al cathode is tuned from the internal reflection toward the out-coupling regime. Hence, the device with the top-emissive configuration exhibits a substantially enhanced EL intensity in the forward direction, with a higher luminous efficiency along the direction of surface normal than that of the control bottom-emissive device without the cavity effect.

The internal reflections of the light that propagates between the highly reflective Ag:Ag2O anode and the semitransparent composite cathode are expected to have strong optical microcavity effects on both the spectral and the spatial distributions of the EL emission.21,22 Figure 2 presents the normalized EL spectra of the control bottom-emissive device, glass/ITO/PEDOT:PSS/HY-PPV/PEGDE(15 Å)/Al(15 Å)/Ag(1200 Å), and the top-emissive devices made of Ag overlayers of various thicknesses, glass/Ag:Ag2O/PEDOT:PSS/HY-PPV/PEGDE(15 Å)/Al(15 Å)/Ag(70 Å), Y=70, 150, and 300 Å. The full width at half maximum (FWHM) of the control bottom-emissive device is ~92 nm, but that of the top-emissive device with the PEGDE(15 Å)/Al(15 Å)/Ag(70 Å) cathode structure is ~52 nm. The shift in the λmax toward the shorter wavelength (from ~560 to ~548 nm) and the decline in the FWHM (from ~52 to ~24 nm) of the EL emissions were also observed for the top-emissive devices with the thick and uniformly covered Ag overlayers.

The approximate calculation of the Fabry-Pérot cavity theory is as follows:12,21,23

\[
G_{\text{cav}}(\lambda) = \frac{|E_{\text{out}}|^2}{|E_0|^2} \times \frac{\tau_{\text{cav}}}{\tau_{\text{non-cav}}}, \quad S_{\text{cav}}(\lambda) = S_0(\lambda) \times G_{\text{cav}}(\lambda),
\]

where \(G_{\text{cav}}(\lambda)\) is the emission enhancement factor associated with the optical cavity at a single wavelength \(\lambda\), \(E_{\text{out}}\) and \(E_0\) are the out-coupled and the free-space electric-field intensities of the emissions, respectively. \(\tau_{\text{cav}}\) and \(\tau_{\text{non-cav}}\) are the...
radiative lifetimes of the excited molecules in the cavity and in free space, respectively. $S_0(\lambda)$ is the intrinsic emission spectrum of an emitter and is assumed to be Gaussian. $S_{\text{car}}(\lambda)$ represents the emission spectrum under the influence of the optical microcavity effect. The inset in Fig. 2 shows the simulated EL emission, $S_{\text{car}}(\lambda)$, determined by the calculation based on Fabry-Pérot cavity theory and the EL spectrum obtained in the direction along the surface normal of the top-emissive device with the cathode structure PEGDE(15 Å)/Al(15 Å)/Ag(300 Å). The simulated EL spectrum overlaps substantially with the experimental result. The shift of $\lambda_{\text{max}}$ from 560 nm (for the top-emissive device with a 70 Å thick Ag covering layer) toward 548 nm (with a 300 Å thick Ag covering layer), as observed in Fig. 2, is probably caused by the change in the reflectivity of the composite cathode, which forms a complete cavity structure, and thus, multiply reflects the EL emission and moves the $\lambda_{\text{max}}$ toward the resonance wavelength of the optical cavity.

The simulation of FWHM is determined from Eq. (1) as follows:\textsuperscript{23}

$$\text{FWHM}(\lambda) = \frac{\lambda^2}{2L} \left[ \frac{1 - \sqrt{R_1R_2}}{\pi (R_1R_2)^{1/4}} \right],$$

where $\lambda$ is the resonance wavelength and $L$ is the effective channel length in the cavity. $R_1$ and $R_2$ are the reflectivities of the anode (Ag:Ag$_2$O) and the composite cathode (organic oxide/Al/Ag), respectively. The reflectivity ($R_2$) is higher for the composite cathode with a thicker Ag overlay. Therefore, the FWHM of the EL emissions is narrowed and the color of the top-emissive device is changed from orange-yellow to a saturated green-yellow as the thickness of the Ag covering layer is increased.

Figure 3 illustrates the EL spectra of the top-emissive device, with the cathode structure PEGDE(15 Å)/Al(15 Å)/Ag(70 Å), measured at viewing angles of 0°, 30°, and 60° from the surface normal. The EL intensity is maximal in the forward direction of the substrate (0°), but decreases to 60% and 45% of the maximum intensity at the viewing angles of 30° and 60°, respectively. The net out-coupling efficiencies of the EL emissions (or the external quantum efficiencies) for the top- and control bottom-emissive devices, as presented in Fig. 1, are compared by measuring the intensities of photocurrents through a photodiode inside an integrated sphere, which are approximately identical for both devices. Depositing an additional index matching layer onto the structure of the composite cathode is expected to increase the net EL out-coupling efficiency of the top-emissive devices.

In summary, the organic oxide/Al/Ag composite electrode was disclosed as an appropriate cathode structure in the fabrication of high-performance and high-brightness top-emissive PLEDs. The optical microcavity effect is responsible for the redistribution of EL emissions, in which the top-emissive devices exhibit saturated color emission and enhanced luminous intensity in the direction of the surface normal.

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