Top-emitting organic light-emitting devices using surface-modified Ag anode

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A high-reflectivity bottom anode is essential for high-performance top-emitting organic light-emitting devices (OLEDs). Ag has the highest reflectivity for visible light among all metals, yet its electronic properties are not ideal for anodes of OLEDs. In this letter, we report that by inducing a thin silver oxide at the surface of Ag, hole injection from Ag anodes into OLEDs is largely enhanced yet with rather high reflectivity retained. Top-emitting devices using such surface-modified Ag anode show device characteristics competitive with those of a bottom-emitting device using the indium tin oxide anode. © 2003 American Institute of Physics.
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Advances in technologies of organic light-emitting devices (OLEDs) and displays in recent years have imposed substantial demands in efficient top-emitting OLEDs,^{1–6} i.e., OLEDs that emit light from the top surface of devices. Top-emitting OLEDs render feasible fabrication of OLED displays on opaque substrates such as Si wafers.¹ They also permit use of more complicated pixel circuits in active-matrix OLED displays for higher display quality yet without sacrificing aperture ratios of pixels.² In top-emitting OLEDs, high reflectivity of the bottom anode is essential for achieving high luminance efficiency. Among various metals, Ag has the highest reflectivity for visible light. Ag, however, is generally not considered as an ideal hole-injecting anode for OLEDs due to its rather low work function (~ 4.3 eV),⁷ not matching well the ionization potentials of organic materials commonly used in OLEDs. In this letter, we report that by inducing a thin silver oxide at the surface of the Ag anode, hole injection from Ag into OLEDs is substantially enhanced yet with rather high reflectivity retained. Top-emitting OLEDs fabricated on such surface-modified Ag anodes exhibit device performance competitive with that of a conventional bottom-emitting device using an indium tin oxide (ITO) anode.

Silver oxide (Ag_2O) is conventionally used as electrode materials in batteries or as catalytic substances in materials science.⁸ Yet, there are also studies showing that thin films of Ag_2O exhibit semiconducting properties.^{9–12} Various techniques had been used in preparing thin films of Ag_2O ,^{9–15} including sputtering or evaporation of Ag (or Ag_2O) in an oxygen atmosphere, and oxidation of Ag films with reactive oxygen species, such as oxygen plasma, oxygen radicals, or ozone, etc. Previous investigations of electronic structures and optical properties of Ag_2O films reveal that Ag_2O has a band gap of ~ 1.3 eV, an ionization potential of ~ 1.0 eV below the work function of Ag (i.e., ~ 5.3 eV).^{9,15} Ag_2O films in general were reported to show *p*-type semiconduct-

ing properties with the Fermi level ranging from 4.8 to 5.1 eV.^{9–12} These properties appear to match those of organic hole-transport materials and render Ag_2O a possible anode contact for OLEDs. In this study, Ag with a thin silver oxide induced at the surface by the UV-ozone treatment is investigated as a composite hole-injection and reflective anode for top-emitting OLEDs.

The UV-ozone treatment of Ag films was performed in an UV-ozone (UVO) chamber, in which the UV emission is generated from low-pressure quartz mercury vapor lamps and the UV intensity at the wavelength of 254 nm is ~ 28 mW/cm² at a distance of 6 mm from the lamps. In such system, the UV radiation is absorbed by atmospheric oxygen, changing it to ozone and atomic oxygen. Previous studies have shown that exposure to ozone largely facilitates oxidation of Ag through the reaction of $2\text{Ag}_{(s)} + \text{O}_{3(g)} \rightarrow \text{Ag}_2\text{O}_{(s)} + \text{O}_{2(g)}$.¹³ The oxidation otherwise would not readily take place under ambient conditions.¹³ To confirm the formation of Ag_2O at the Ag surface, x-ray photoelectron spectroscopy (XPS) was performed on treated Ag films. XPS spectra were collected using a VG Scientific ESCALAB 250 instrument equipped with an analytical chamber pumped to a base pressure $\sim 10^{-10}$ Torr, a twin-anode x-ray source, and a spherical sector analyzer with multichannel detectors. For analysis, samples were mounted on stainless steel stubs using double-sided adhesive tape. Spectra were excited using $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV). All XPS data were corrected for sample charging during x-ray irradiation using adventitious hydrocarbon referencing (C 1s at ~ 285 eV).

Figure 1 shows the core-level O 1s XPS spectra of an as-deposited Ag film and the treated Ag film (UVO treatment time: 1 and 2 min). The spectrum of the as-deposited Ag film shows a broad feature around 531 eV, which is presumably associated with the oxygen and CO_2 adsorbed on Ag during the preparation of samples for XPS.^{13,15,16} The spectra of the treated samples exhibit an additional narrower peak around 529.7 eV. This additional feature is a typical signature of oxygen associated with Ag_2O ,^{13,15,16} and confirms the formation of silver oxide using the room-temperature UVO treat-

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FIG. 1. Core-level O 1s XPS spectra of an as-deposited Ag film and a UV-ozone-treated Ag film. The as-deposited Ag thickness was 80 nm for both.

ment. Treating the Ag film with longer time (>3 min) resulted in substantially reduced reflectivity and a yellowish to brownish color for the sample surface, indicating an Ag_2O thickness over $100 \text{ \AA}$. Nevertheless, under the treatment conditions for device preparation (1–2 min), the sample surface retained metallic and highly reflective appearance of Ag with the estimated Ag_2O thickness on the order of tens of $\text{\AA}$. Figure 2 compares the reflection spectra of the as-deposited Ag film and the treated Ag films (UVO treatment time: 1 and 2 min) measured with a Shimadzu UV-1601PC spectrophotometer. It shows that the briefly treated Ag film for device fabrication (usually 1 min treatment) retains a high reflectance of 82%–91% over the visible range, only slightly lower than that of an as-deposited Ag film.

The device structure of top-emitting OLEDs employing the surface-oxidized Ag anode is shown in Fig. 3(a). The devices were built on glass substrates precoated with Ag (80 nm), which was used as deposited or was treated with UV ozone (1 min) before following deposition. The organic multilayer structure sequentially consists of 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA, 30 nm) as the hole-injection layer,¹⁷ α -naphthylphenylbiphenyl diamine (α -NPD, 20 nm) as the hole-transport layer,¹⁸ tris-(8-hydroxyquinoline) aluminum (Alq, 50 nm) as the electron transport and emitting layer.¹⁸ The cathode is composed of multiple functional layers to achieve both optical transmission and effective electron injection. Ultrathin layers of LiF (0.5 nm) and Al (1 nm) are deposited in sequence as the electron-injecting contact.⁵ A thin layer (20 nm) of Ag, which has relatively low optical absorption and the highest conductivity among all metals, then overlays the LiF/Al contact for reducing sheet resistance of the composite cathode.⁵ A 20-nm-thick Ag film gives a sheet resistance of $\sim 1 \text{ } \Omega/\square$, which is one-order lower than that of thick (hundreds of nm) ITO. The multilayer cathode is further capped with a high-refractive-

FIG. 2. Reflection spectra of an as-deposited Ag film and a UV-ozone-treated Ag film.

FIG. 3. Device structures of (a) the top-emitting device, and (b) the bottom-emitting device.

index dielectric layer as an index-matching (or antireflection) layer to enhance the optical transmission of the thin metal cathode.^{3,5} Figure 4 shows the measured transmission spectrum of the multilayer cathode. TeO_2 is used as the dielectric capping layer for its high refractive index ($n \sim 2.2$ – 2.3), its transparency in the visible range, and its convenience in deposition with thermal evaporation.¹⁹ The last gives TeO_2 the processing compatibility with material layers underneath. The thicknesses of organic layers and the TeO_2 dielectric layer (40 nm) had been optimized for colors and efficiency of devices. For comparison, control devices [i.e., conventional bottom-emitting devices, Fig. 3(b)] with the same organic multilayer structure sandwiched between the ITO anode and the LiF/Al cathode were also fabricated.

All the material layers in devices, including TeO_2 , were deposited by thermal evaporation in a multiple-source vacuum chamber. The deposition system is equipped with a specially designed shutter and mask mechanism, so that a few complete devices with independently controlled structures can be fabricated in a single vacuum pumpdown, permitting reliable side-by-side comparison of various devices.^{20–21} After the device deposition, the devices were encapsulated with a cover glass under dry nitrogen atmosphere. The current–voltage–brightness (I – V – L) characteristics of devices were measured with a source measurement unit and a Si photodiode calibrated with a Photoresearch PR650 spectroradiometer. The electroluminescence (EL) spectra were taken with a calibrated CCD spectragraph.

Figure 5(a) shows the EL spectra at viewing angles of 0° , 30° , and 60° off the surface normal for the top-emitting device using the treated Ag anode. EL spectra of the device using the as-deposited Ag anode are similar to those in Fig. 5(a). EL of the top-emitting device shows more saturated colors in comparison with photoluminescence (PL) of Alq (and EL of the bottom-emitting device) due to the stronger microcavity effect.^{3,22,23} The stronger microcavity effect usually would also lead to large variation of colors with viewing

FIG. 4. Transmission spectrum of the multilayer cathode on quartz with the structure of quartz/Alq (40 nm)/LiF (0.5 nm)/Al (1 nm)/Ag (20 nm)/ TeO_2 (40 nm).

FIG. 5. (a) EL spectra (0°, 30°, and 60° off the surface normal) of the top-emitting device in comparison with the PL spectrum of Alq. (b) I - V characteristics, and (c) L - V characteristics of the top-emitting device using the as-deposited Ag anode, the top-emitting device using the UV-ozone-treated Ag anode, and a bottom-emitting device using the ITO anode: (a) the angular distribution of EL intensity for the bottom-emitting device and the top-emitting device using the treated Ag anode. All intensities are normalized relative to the 0° intensity of the bottom-emitting device; (c) comparison of efficiency characteristics of the three devices.

angles.^{22,23} Nevertheless, the layer thicknesses in the present device structure could be optimized to nearly eliminate such color shift, as demonstrated in the case of Fig. 5(a). The inset of Fig. 5(a) shows the angular distribution of relative EL intensity for the top-emitting device and the bottom-emitting device. The emission pattern of the bottom-emitting device is close to a Lambertian distribution, while that of the top-emitting device shows enhancement in the forward direction again due to the stronger microcavity effect.^{22,23} Such enhancement leads to increased forward-direction cd/A efficiency of the top-emitting device in comparison with that of the bottom-emitting device [6 cd/A vs 4.5 cd/A, inset of Fig. 5(c)].

Figures 5(b) and 5(c) compare the current-voltage (I - V) and emission characteristics (along the surface normal) of a conventional bottom-emitting device and the top-emitting devices with the as-deposited or treated Ag anodes.

Compared to the device using the as-deposited Ag anode, the device using the treated Ag anode exhibits a substantially lower operation voltage and a higher EL efficiency [6 cd/A vs. 4.5 cd/A, inset of Fig. 5(c)]. Furthermore, the treated Ag anode gives nearly identical operation voltage as the ITO anode. Both achieve brightnesses over 17 000 cd/m² at 10 V. These results indicate that the UV-ozone treatment of the Ag electrode substantially enhances hole injection into the device, and that the effectiveness of the treated Ag as an anode is competitive with that of a conventional ITO.

In summary, we report the UV-ozone treated Ag electrode as the effective reflecting anode for the top-emitting OLEDs. The UV-ozone treatment is used to induce a thin layer of silver oxide at the Ag surface as confirmed by XPS. In comparison with the as-deposited Ag, the surface-modified Ag anode shows largely enhanced hole injection and reduced operation voltage in devices, yet retaining relatively high reflectivity. The top-emitting devices using the surface-modified Ag anode have been shown to give device characteristics competitive with those of a bottom-emitting device using the ITO anode.

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