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High-contrast top-emitting organic light-emitting diodes with $AlO_{1.086}$ dark-and-conductive electrodes

Shuming Chen *, Jianning Yu

Department of Electrical and Electronic Engineering, South University of Science and Technology of China, Shenzhen, Guangdong 518055, PR China

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ABSTRACT

To improve the poor contrast of conventional organic light-emitting diodes (OLEDs) resulting from highly reflective metal electrode, a dark-and-conductive electrode with an average reflectance of 28.1% and a resistivity of 4.6×10^{-4} Ω/cm was fabricated by fine-tuning O_2/Ar flow ratio on aluminum electrode sputtering. X-ray photoelectron spectroscopy analysis indicates pure aluminum and aluminum oxide coexist in the fabricated dark-and-conductive electrodes. With the proposed dark-and-conductive $AlO_{1.086}$ electrodes, top-emitting OLEDs exhibit significantly improved contrast, whereas maintain moderate luminous efficiency. The demonstrated $AlO_{1.086}$ dark-and-conductive electrodes can potentially replace the circular polarizers for high-contrast OLED display applications.

1. Introduction

Display technologies based on organic light-emitting diodes (OLEDs) have been attracting increasing attention in recent years due to their advantages of fast response, wide viewing angle, vivid color, thin and flexible form factors. In conventional OLEDs, metal thin films with low work function and high reflectance, such as calcium (Ca), lithium-fluoride/aluminum (LiF/Al), and magnesium–silver (Mg:Ag) are commonly employed as cathodes. Various reflective metal layers benefit the out-coupling efficiency of OLEDs because the back emission from the organic layers can be reflected forward and finally escapes from the structures. However, the metal electrodes degrade the contrast ratio (CR) of OLED displays due to the reflection of ambient light by the highly reflective electrodes, which becomes particularly serious for outdoor display applications [1].

Many approaches have been developed to improve the CR of OLED displays. The most common method is using the circular polarizers, which are integrated onto the outside surface of OLEDs [2–4], to reduce the ambient reflection. Though effective, the utilization of circular polarizers reduces the emission efficiency of OLEDs and increases the cost of OLED displays. Direct replacement of highly reflective metals by dark metals such as chromium (Cr) [5], molybdenum (Mo) [6], Sm:Ag [7,8] and copper (Cu) [9] can also improve the CR of OLEDs. However, the reflectance of these dark metals is still too high and therefore the improvement on CR is very limited. Recently, black layers based on destructive-optical-interference emerged as promising technologies to be incorporated into OLEDs to enhance CR. Black layer structure consists of thin semi-transparent metal layer, a phase-tuning organic layer, and a thick reflective metal layer [10–12]. The low reflection is realized by the cancellation (destructive interference) of two reflected light waves, one from the front thin metal layer and another one with a π-phase difference from the rear thick metal layer. According to this principle, a contrast-enhancing stack (trademarked Black Layer™) has also been invented by Luxell Technologies Co., Ltd [13]. How-

* Corresponding author.
E-mail address: chen.sm@sustc.edu.cn (S. Chen).

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ever, the multilayer structure complicates the fabrication process. Besides, there are few demonstrations on black layer for top-emitting OLEDs applications.

In this work, we propose a very simple and cost-effective method that reduce the ambient reflection effectively and thus improve the CR of top-emitting OLEDs significantly. It is widely recognized that energetic Al is very easily oxidized to AlO_x even in a high vacuum environment [14]. If Al is fully oxidized, the resultant oxide film (Al_2O_3) is optically transparent and electrically insulated. However, if Al is partially oxidized, the resultant oxygen-deficient AlO_x films, with x ranging from 0 to 1.5, become optically absorptive and electrically conductive. With this understanding, Yang's group had fabricated a dark electrode by evaporating Al with a very slow rate of 0.2 Å/s at a pressure of $\sim 10^{-6}$ Torr [14]. At such slow rate, a part of the Al atoms are oxidized by the residue oxygen. However, the proposed method has a very narrow processing window, as the reflectance and conductivity of the resultant films are very sensitive to the evaporation rate and the amount of the residue oxygen. Moreover, the evaporated films with poor adhesion cannot withstand various physical/chemical treatments and thus cannot serve as pixel electrodes for top-emitting OLEDs. In this work, dark-and-conductive films are fabricated by fine-tuning O_2/Ar flow ratio during Al electrode sputtering. The proposed method has a wide processing window and the resultant films can serve as pixel electrodes for top-emitting OLEDs. The optimized $AlO_{1.086}$ films exhibit an average reflectance of 28.1% and a resistivity of $4.6 \times 10^{-4}\ \Omega$/cm. With the proposed dark-and-conductive $AlO_{1.086}$ electrodes, top-emitting OLEDs exhibit significantly improved contrast, whereas maintain moderate luminous efficiency.

2. Results and discussion

The proposed dark-and-conductive AlO_x electrodes were fabricated by intentionally introducing oxygen during sputtering of Al. To tune the value of x, O_2 with different flow of 0, 1.0, 1.2, 1.4, and 1.8 sccm was introduced. Fig. 1(a) shows the photos of the samples fabricated at different O_2 flow. The pure Al films are highly reflective, whereas by introducing O_2 with flow 1.0–1.4 sccm to partially oxidize Al, the resultant AlO_x films look dark and opaque. Further increasing O_2 flow to 1.8 sccm, all Al atoms are oxidized completely and the resultant films become transparent.

To ascertain the difference in ambient reflection between pure Al and oxygen-deficient AlO_x films, the reflectance of the films in the spectral range of 380–780 nm was measured. As shown in Fig. 1(b), the average reflectance of AlO_x films rapidly decreases from 91.7% to 28.1% when the O_2 flow increases from 0 to 1 sccm. The remarkably reduced reflectance is mainly due to the formation of oxygen-deficient AlO_x, which absorbs the light effectively [15–17]. As part of the Al atoms are oxidized, the resistivity of the films increases from 3.2×10^{-6} to $4.6 \times 10^{-4}\ \Omega$/cm. Further increasing O_2 flow to 1.2 and 1.4 sccm, more Al atoms are oxidized, resulting in a significantly increased resistivity of 8.4×10^{-3} and $1.6 \times 10^{-1}\ \Omega$/cm, respectively. However, the reflectance of corresponding AlO_x films only slightly decreases to 25.7% and 24.7%, respectively. To serve as dark electrodes for top-emitting OLEDs, the films should have low reflectance as well as low resistivity. Though there is trade-off between reflectance and resistivity, the optimal AlO_x films fabricated at an O_2 flow of 1 sccm exhibit a low reflectance of 28.1% and a low resistivity of $4.6 \times 10^{-4}\ \Omega$/cm simultaneously. For comparison, Fig. 1(c) shows the calculated reflectance of various dark metal films such as Cr, Cu, Mo, Ni, Ti, and W, which are commonly employed as dark electrodes for top-emitting OLEDs [5,6,9]. It is obvious that the reflectance of the demonstrated dark-and-conductive AlO_x electrodes is far lower than that of conventional dark metals, and therefore enhanced CR can be expected by using proposed AlO_x electrode.

To investigate the origins account for the low reflectance and the low resistivity, the composition of the AlO_x films was characterized by X-ray photoelectron spectroscopy (XPS). The binding energy for Al 2p electrons in pure Al and Al_2O_3 is 72.9 eV and 76.4 eV, respectively [14]. As shown in Fig. 2(a), without introducing O_2, only Al peak can be observed, whereas by introducing excess O_2 with a flow of 1.8 sccm, all Al atoms are completely oxidized as evidenced by the sole Al_2O_3 peak shown in Fig. 2(c). At a milder O_2 flow of 1–1.4 sccm, both Al and Al_2O_3 peaks can be observed, indicating part of the Al atoms are fully oxidized whereas the others remain intact. Therefore, the resultant AlO_x films are a mixture of Al and Al_2O_3, in which Al is responsible for the electrical conduction, whereas the doping of Al_2O_3 into Al matrix, reduces the reflectance of the Al. Such phenomenon has also been observed by doping SiO or organic to Al host [16,17]. The concentration of Al and Al_2O_3 in the blended films can be calculated by integrating their corresponding XPS spectra. At an O_2 flow of 1 sccm, 73% Al atoms are oxidized and hence the atomic ratio of the blended film is $AlO_{1.086}$. Further increasing the O_2 flow, reduces the Al concentration and thus increases its resistivity. The thickness, sheet resistance, resistivity, reflectance, atomic ratio and Al concentration of the fabricated films are summarized in Table 1.

Encouraged by their low reflectance and low resistivity, $AlO_{1.086}$ films were employed as anodes for top-emitting OLEDs for improving the CR. To enhance the hole injection, a 8 nm MoO_3 layer was employed. For comparison, top-emitting OLEDs with pure Al anodes were also fabricated. Fig. 3(a) shows the photos of the devices. It is obvious that with $AlO_{1.086}$ electrodes, the devices look pretty dark even under strong illumination. Interestingly, the devices are substantially darker than the $AlO_{1.086}$ electrodes, as can be observed from the photos. For example, the devices exhibit a reflectance of $\sim$1.6% at the wavelength of 470–620 nm, which is significantly lower than $\sim$28% for the $AlO_{1.086}$ electrodes. The reduced reflectance is mainly due to the destructive interference of two reflected light waves, one from the front thin Ag electrode and another one with a π-phase difference from the rear $AlO_{1.086}$ electrodes [10–13]. The organic layers sandwiched between two metal electrodes serve as a phase tuning media. By optimizing the thickness of the phase tuning layers, minimum reflectance can be achieved. The n, k values of $AlO_{1.086}$ measured by

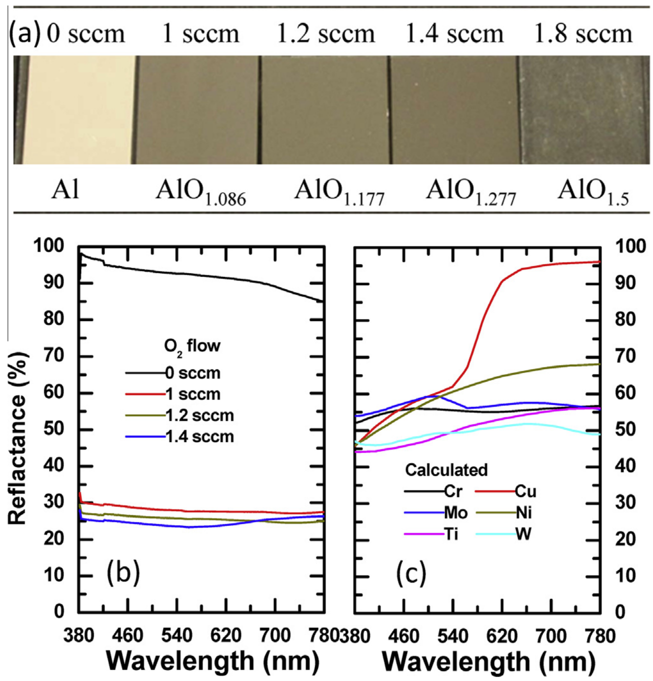

Fig. 1. (a) Photos of the fabricated films. O_2 with different flow of 0, 1.0, 1.2, 1.4, 1.8 sccm was introduced during deposition of Al. (b) Measured reflectance of the fabricated films. (c) Calculated reflectance of conventional dark metal films.

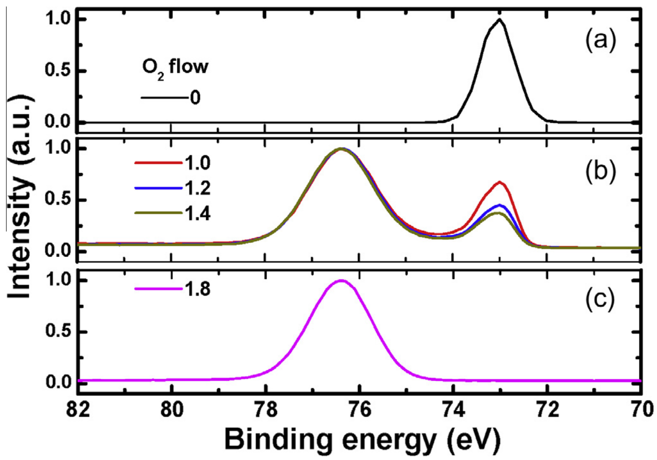

Fig. 2. XPS spectra of the AlO_x films fabricated at an O_2 flow of 0 sccm (a), 1.0–1.4 sccm (b) and 1.8 sccm (c). The binding energy for Al 2p electrons in pure Al and Al_2O_3 is 72.9 eV and 76.4 eV, respectively.

Table 1
Key parameters of the AlO_x films fabricated at various O_2 flow.

O_2 flow (sccm)	Thickness (nm)	Sheet resistance (Ω/□)	Resistivity (Ω/cm)	Average reflectance (%)	Atomic ratio	Al concentration (%)
0	200	0.16	3.2×10^{-6}	91.7	AlO_0	100
1.0	220	21	4.6×10^{-4}	28.1	$AlO_{1.086}$	27
1.2	240	350	8.4×10^{-3}	25.7	$AlO_{1.177}$	21
1.4	240	6860	1.6×10^{-1}	24.7	$AlO_{1.277}$	14
1.8	250	–	–	–	$AlO_{1.5}$	0

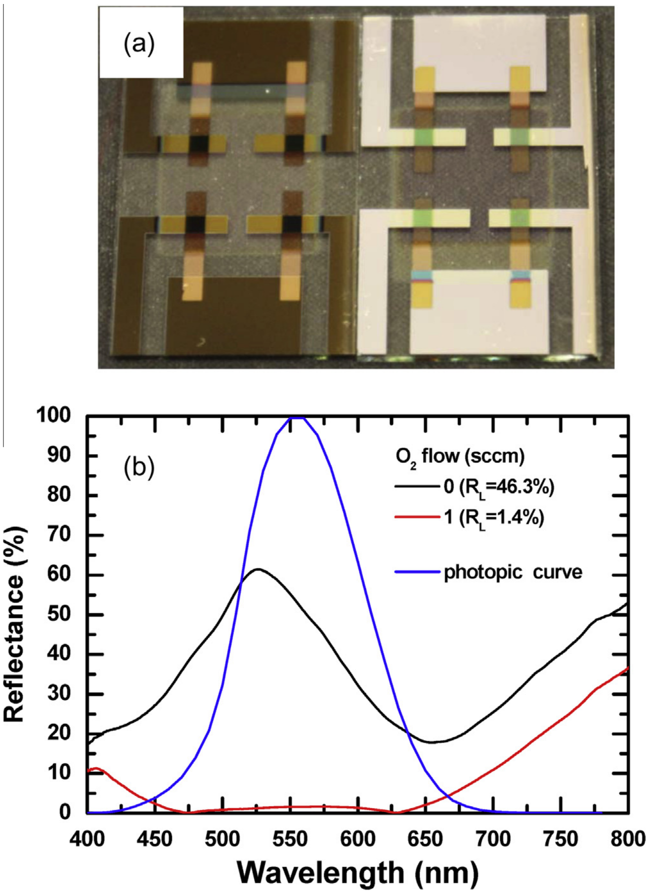

Fig. 3. (a) Photos of the TOLEDs with $AlO_{1.086}$ and Al anodes. (b) Measured reflectance of the TOLEDs. With $AlO_{1.086}$ anodes, TOLEDs look very dark and exhibit an average luminous reflectance of 1.4%.

spectroscopic ellipsometer and the calculated reflectance of the devices can be found in Supporting Information Fig. S1. As shown in Fig. 3(b), the reflectance of the devices with $AlO_{1.086}$ is significantly lower than that with pure Al, especially at the wavelength of 470–620 nm, where human eye is most sensitive to the reflective photons as reflected in the human photopic curve. The calculated luminous reflectance (R_L) to human eyes under a light source D65 is 1.4% for the devices with $AlO_{1.086}$, which is remarkably lower than 46.7% for the devices with pure Al, and is among the lowest reported values [5–12,14–19]. Due to the low R_L, devices with $AlO_{1.086}$ exhibit extremely high CR even under strong illumination, as shown in Fig. 4(a). For example, at an indoor ambient illumination of 140 l×, the CR for the devices with $AlO_{1.086}$ is 496:1, which is 31-fold higher than 16:1 for the devices with Al. Even under strong illumination of 10000 l×, which is close to the outdoor illuminance in a sunny day [1], the devices with $AlO_{1.086}$ can still maintain a moderate CR of 8:1, whereas the devices with Al almost lose its CR with a value of 1.2:1. The proposed dark-and-conductive $AlO_{1.086}$ electrode is an ideal candidate for outdoor display applications and can potentially replace the circular polarizers without increasing material or fabrication cost.

Fig. 4(b) shows the current density–voltage–luminance (*J–V–L*) characteristics of the devices. Due to relatively higher resistance of $AlO_{1.086}$, the devices with $AlO_{1.086}$ electrodes exhibit smaller current and higher turn on voltage compared to those with pure Al electrodes. However, it should be noted that the area for the experimental devices is 4 mm^2, whereas for typical display pixels, the area is in the order of $100 \times 100\ \mu m^2$. Typically, the pixel resistance is in the order of MΩ (assuming pixel size $250 \times 250\ \mu m^2$, driving voltage 6 V and current efficiency 20 cd/A for a luminance of 1000 cd/m^2), which is several orders higher than that of the electrodes, and therefore the resistance of the electrodes almost has not impact on the *J–V–L* characteristics of the pixels. For practical applications, a thin ITO layer can be deposited on top of $AlO_{1.086}$ electrodes to further reduce the resistance and improve the hole injection. The Fig. 4(c) shows the current efficiency–luminance–current density characteristics of the devices. The efficiency and luminance for the devices with $AlO_{1.086}$ electrodes are approximately 42% of those with Al electrodes, and are comparable to those with circular polarizers as the transmission of the circular polarizers is 40% [2,18]. The low efficiency is mainly due to the low reflectance as well as weak microcavity effect resulting from the $AlO_{1.086}$ dark electrodes. The spectra of the devices are shown in Fig. 4(d), due to weaker microcavity effect, devices with $AlO_{1.086}$ exhibit broader spectrum.

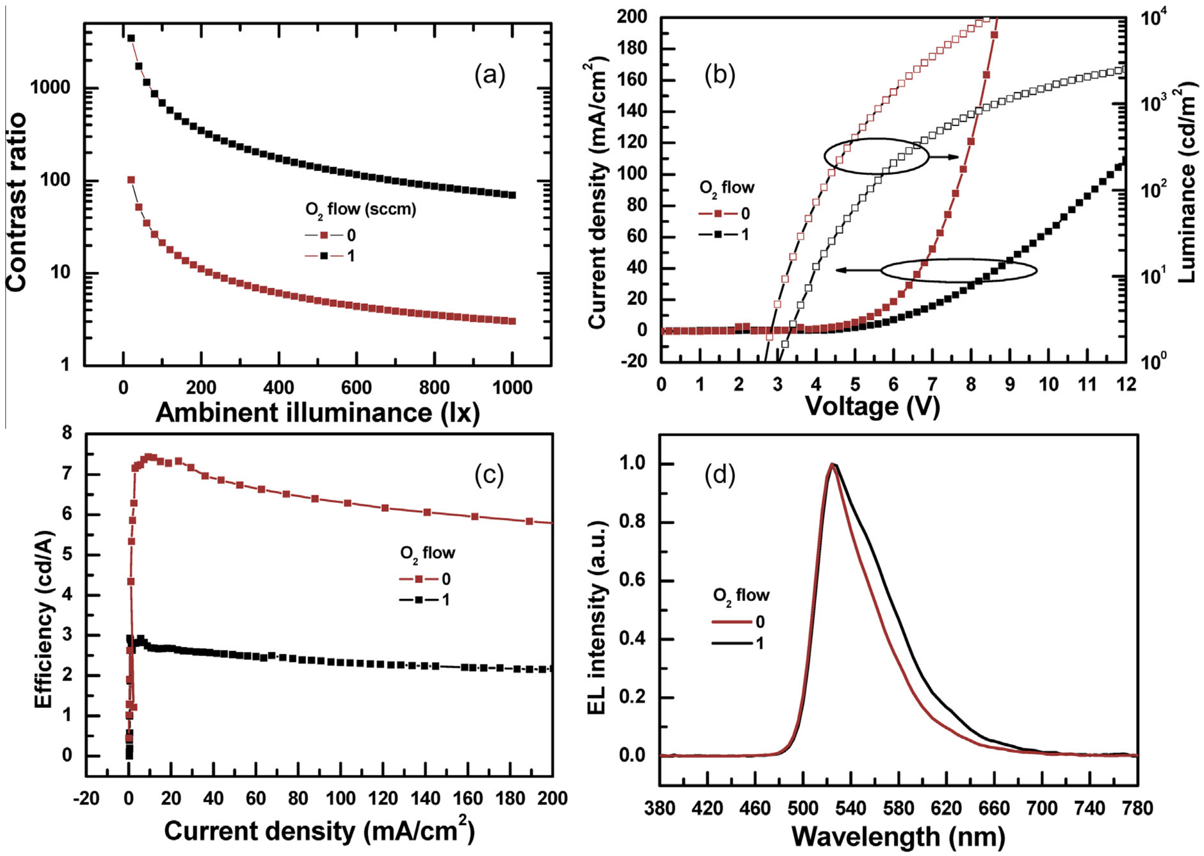

Fig. 4. (a) Calculated CR for the TOLEDs with $AlO_{1.086}$ and Al anodes, (b) current density–voltage–luminance, (c) current efficiency–current density characteristics and (d) spectra of the TOLEDs. With $AlO_{1.086}$ anodes, TOLEDs exhibit extremely high CR and moderate efficiency.

3. Conclusion

In summary, we have prepared dark-and-conductive oxygen-deficient $AlO_{1.086}$ electrodes by introducing 1 sccm O_2 flow during Al sputtering process. Due to the coexistence of pure Al and Al_2O_3, the resultant $AlO_{1.086}$ films simultaneously exhibit low reflectance and low resistivity. Top-emitting OLEDs with $AlO_{1.086}$ anodes demonstrate an extremely high CR of 496:1 under on-state luminance of 300 cd/m^2 and ambient illuminance of 140 l×, whereas maintain moderate luminous efficiency. The proposed dark-and-conductive $AlO_{1.086}$ electrode is an ideal candidate for high CR display applications and can potentially replace the circular polarizers currently used in OLED displays without increasing material or fabrication cost.

4. Experimental section

AlO_x films were deposited on glass substrate at room temperature by direct current (DC) magnetron sputtering, using a 2-inch-diam Al target (99.99% purity) with a power of 200 W and time of 18 min. The deposition chamber was initially evacuated to 1×10^{-5} Torr. During the deposition process, Ar processing gas with flow of 20 sccm was introduced into the chamber to maintain a constant pressure of 2.5 mTorr. In order to form oxygen-deficient AlO_x and find the best configuration for dark-and-conductive metal layers, O_2 with different flow of 0, 1, 1.2, 1.4, and 1.8 sccm was introduced. The sheet resistance of the fabricated AlO_x films was measured by four point probes. The reflectance of the AlO_x film was measured by UV–Vis spectrophotometer. The composition of the AlO_x films was characterized by XPS.

$AlO_{1.086}$ or Al films were patterned by photolithography and etched by phosphoric acid. Top-emitting OLEDs with $AlO_{1.086}$ anodes or pure Al anodes with structures: glass/$AlO_{1.086}$ or Al 200–250 nm/MoO_3 8 nm/NPB 35 nm/Alq:C545T 1 wt.%, 20 nm/Alq 30 nm/Yb 5 nm/Ag 15 nm/NPB 35 nm were fabricated. All organic layers and Yb/Ag layers were thermally evaporated sequentially in a multisource vacuum chamber at a base pressure of about 5×10^{-7} Torr. The current efficiency–current density–luminance characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer and a calibrated UDT PIN-25D silicon photodiode.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.10.002.

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