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High contrast flexible organic light emitting diodes under ambient light without sacrificing luminous efficiency

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ABSTRACT

We demonstrate a polarizer free high contrast ratio (CR) flexible top emitting organic light emitting diode (TOLED) using a periodic metal/dielectric anti-reflection (AR) cathode structure. The AR cathode was designed to have an asymmetric reflectance for the inward (low reflectance) and outward (high reflectance) directions of the OLED. The flexible AR-TOLED showed a sufficiently low luminous reflectance (6%), very high efficiency (86% of the TOLED without the AR structure), 1.75 times higher than the TOLED employing a circular polarizer, and extremely high durability upon repeated bending with a bending radius of 0.7 cm up to 10,000 times.

1. Introduction

Top emission organic light emitting diodes (TOLEDs) are widely used in mobile displays for portable media players (PMPs) and smart phones. TOLEDs, which are composed of semi-transparent and thick counter metal electrodes, emit light not through a substrate but through a semi-transparent metal electrode. One of the limiting performances of TOLEDs is their visibility in high luminous environments. Organic light emitting diodes (OLEDs) are self-emitting devices so that the contrast ratio of the devices in a dark environment is in principle infinite. Unfortunately, in a luminous environment, ambient light significantly degrades the contrast ratio (CR) of OLEDs due to a strong reflection of ambient light by the reflective metal electrode of OLEDs. Therefore, suppressing the reflection from the OLEDs is a key technology required to fabricate high contrast TOLEDs. For this reason, commercial OLEDs use a circular polarizer (CP), which is composed of a quarter wavelength plate and a linear polarizer [1]. The CP has sufficiently low reflectance (4–6%), is easy to apply and does not require any absorbing layer in the OLED. However, adoption of the CP in OLEDs has a few drawbacks [2]. Firstly, the output power of the OLEDs is reduced to less than half by the CPs, which is a critical disadvantage for fabricating high performance OLEDs. Secondly, CPs are difficult to integrate in the conventional OLED fabrication process because the CP cannot be applied to the fabrication of OLEDs by evaporation or solution process methods. Moreover, CPs are generally thick, expensive and not very flexible.

For these reasons, various approaches have been reported up to now to replace CPs. These techniques can be classified into four groups: insertion of an absorbing layer between the active layer and an electrode [3–6]; use of low reflective multilayered structures (a so called 'black electrode') [7–10]; use of a low reflectance material as an electrode [11–13]; and adoption of an anti-reflection (AR) coating [14,15]. However, most of these methods either failed to get low enough luminous reflectance below 5–6% or resulted in a large reduction of efficiency of over 40%. Most of the methods used absorptive materials in the devices to reduce the reflection of ambient light.

Here we report a high contrast flexible TOLEDs with little reduction in efficiency by integrating a multilayer dielectric-metal AR structure on the top semi-transparent

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cathode. By rigorous optical simulation, we designed the AR structure consisting of two stacks of very thin metal/dielectric layer and one dielectric layer. Cr and LiF were used as the thin metal and the phase change/phase compensation dielectric layers, respectively. The AR structure reduced the reflectance of ambient light by the combination of absorption by the thin metal layers and the destructive interference by the dielectric layer. Moreover, the AR structure combined with the semitransparent Ag cathode maintained high internal reflectance giving the microcavity effect to enhance light emission of OLEDs due to an asymmetric reflectance for the inward (low reflectance) and outward (high reflectance) direction of the OLEDs. Based on the design principle, we successfully demonstrate high contrast top emission OLEDs having both a low enough luminous reflectance and only a little reduction of efficiency. This structure has several advantages over previously reported structures for a high contrast ratio under ambient light: (1) a low average luminous reflectance of 6% over the whole visible wavelength, (2) a high efficiency of nearly 90% of the original device without the AR structure corresponding to 1.75 times higher than the TOLED with a CP, (3) no deterioration of the electrical characteristics of the underlying TOLED since the AR structure is integrated on top of the TOLED (outside of the original TOLED) and the process temperature is low, (4) a weak viewing angle dependence, and (5) very the flexible with no change in efficiency after the 10,000 times bending test with a bending radius of 0.7 cm. If proper materials are selected, the AR structure can be utilized for thin film encapsulation, which is very important technology for the realization of flexible OLEDs.

2. Brief description about theoretical approach and experiment

Our goal is to design and fabricate a TOLED with a high contrast ratio and a high external efficiency at the same time. The contrast ratio of OLEDs under ambient light is expressed as in the following equation [2]:

$$\text{Contrast ratio (CR)} = \frac{L_{\text{on}} + R_L L_{\text{ambient}}}{L_{\text{off}} + R_L L_{\text{ambient}}} \tag{1}$$

where L_{on} and L_{off} are the luminance of on and off pixels of OLEDs, respectively, and L_{ambient} is the luminance of ambient light. R_L is the luminous reflectance of OLEDs defined as

$$R_L = \frac{\int_{\lambda_1}^{\lambda_2} V(\lambda)R(\lambda)S(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} V(\lambda)S(\lambda)d\lambda} \tag{2}$$

where $V(\lambda)$ is the spectral eye sensitivity and $R(\lambda)$ is the reflectance at the surface of the OLEDs. $S(\lambda)$ is the spectrum of ambient light. Eq. (1) indicates that R_L is the only parameter related to the device structure, while L_{on} and L_{ambient} are controlled by an operating condition.

The schematic diagram of the device structures used for the simulation is displayed in Fig. 1. The AR structure has two stacks of thin metal and dielectric layers and one dielectric layer. The thin metal layers reflect and absorb the incident light. The dielectric layers adjust the phase of the incident and reflected light. Therefore, the AR structure reduces the reflectance of ambient light by the combination of absorption by the thin metal layers and the destructive interference by the dielectric layers. The role of each layer in the AR structure is illustrated in Fig. 1c. The absorptive thin metal layer is important to reduce the reflectance of ambient light because it is not easy to achieve low enough reflectance over wide spectrum by the effect of the destructive interference only. Based on the consideration, LiF and Cr were selected as the dielectric and thin metal layers to fabricate the dielectric-metal AR structure, since LiF shows a low refractive index with a small dispersion over the visible wavelength (n = 1.4027 at 350 nm and n = 1.3887 at 750 nm) [20] and Cr possesses low reflectance and high absorption. Two thin (3 nm) Cr layers were used in the AR structure instead of one thicker Cr layer to increase the effect of the destructive interference by adding one more stack of metal/dielectric layers. If only one thicker absorptive metal layer is used, the thickness of the metal layer must be thicker than the twice of the thin metal layer to sufficiently reduce the reflectance due to the reduction of the interference effect of the dielectric layer. However, the thicker metal layer absorbs the emitted light from OLEDs at the same time resulting in lower performance of the OLEDs. Through rigorous optical simulation, we designed the AR structure consisting of two stacks of very thin Cr/dielectric layers and one dielectric layer.

The optical constants of all organic layers for the optical modeling were measured using a spectroscopic ellipsometer (Woollam M2000D). The refractive indices of the metals including Al and Ag are referred to elsewhere [21]. The green emitting TOLED structure without an AR was first optimized using classical electromagnetic theory and then the AR structure was optimized to have a low R_L and a high luminous efficiency without modifying the already optimized TOLED. The transfer matrix method was used to calculate the reflectance spectra and R_L [16]. A standard light source, D65, was selected as the ambient light source to calculate R_L. Changes of the electroluminescence (EL) spectra and relative luminance with the varying AR structures were also simulated using classical electromagnetic theory under the assumptions of randomly oriented sheet dipoles in the layered structures [17–19]. The relative luminance of AR-TOLEDs for various thicknesses of the dielectric layers (i.e. x, y, and z in Fig. 1b) are normalized by the luminance of the optimized reference devices (i.e. Fig. 1a). The thickness of the dielectric layers giving the maximum relative luminance can be extracted from the simulation under a fixed R_L. By repeating the calculation for different R_L, we were able to obtain the information on the optimum device structure to get maximum luminance under a certain R_L. The calculation results are displayed in Supplementary Fig. 1 where corresponding x, y and z values are displayed in parentheses by the data points. The thickness of the Cr layers was fixed at 3 nm in the calculation, which is the optimized thickness to get a sufficiently low R_L and high light emission/luminous efficiencies. The achievable maximum luminance ratio linearly increases with R_L. The AR structure with (x, y, z) = (60 nm, 142.5 nm, 112.5 nm) results in a maximum relative luminance of 78% when R_L is 7%.

The TOLEDs were fabricated on Al pre-coated (70 nm) glass substrates by successively depositing an 8 wt.% rhenium oxide (ReO_3)-doped 1,1-bis((di-4-toly1amino)-

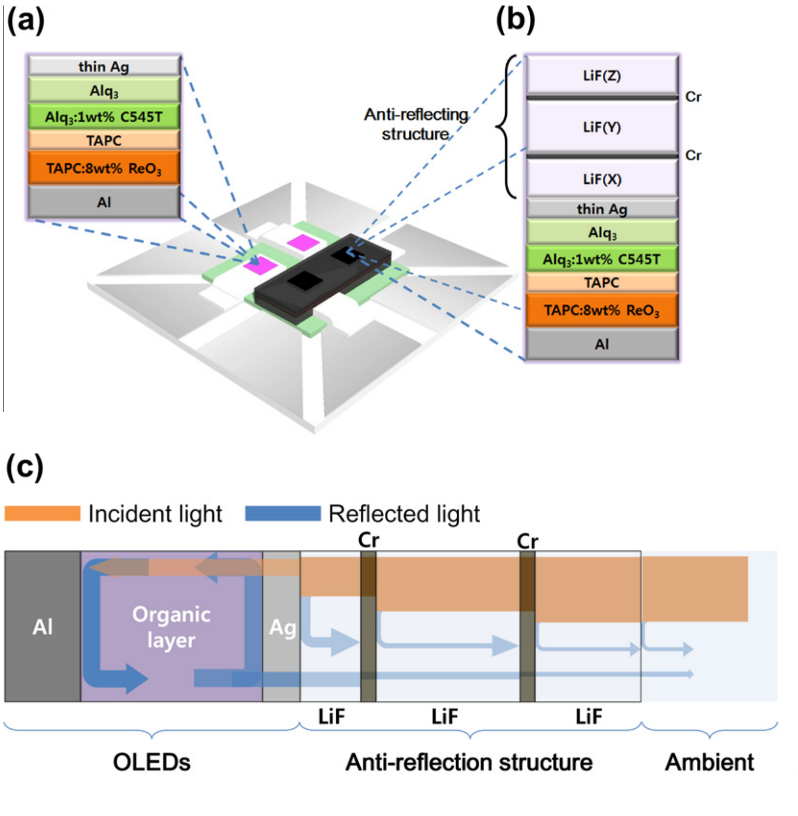

Fig. 1. Schematic diagrams of the device structure, (a) control TOLED, (b) AR-TOLED (x, y, and z in b are the thicknesses of the LiF as a phase change layer for 1st and 2nd periodicity and a phase compensation layer, respectively.), and (c) schematic diagram of distribution of incident light to describe the reduction of reflectance.

phenyl) cyclohexane (TAPC) p-hole transporting layer (p-HTL) (52 nm), undoped TAPC HTL (15 nm), an emitting layer (EML) of 1 wt.% green fluorescent dye C545T-doped tris(8-hydroxyquinoline)aluminum (Alq_3) (20 nm), an undoped Alq_3 electron transporting layer (ETL) (24 nm), and LiF (1 nm)/Al (1 nm) as an injection contact between ETL and semi-transparent Ag (15 nm) cathode. The device structure is the optimized one for TOLEDs. After the fabrication of TOLEDs, the AR structure was deposited on the semi-transparent cathode composed of two periodic LiF/Cr layers and one LiF layer as the phase compensate layer. The thicknesses of the LiF layers were varied (x, y and z in Fig. 1) while the thicknesses of the Cr layers were fixed to 3 nm. The LiF and Cr layers were deposited by thermal evaporation without breaking the vacuum. The current density–voltage–luminance (J–V–L) characteristics of the devices were measured by a Keithley 2400 source meter and a Photo Research PR-650 spectrophotometer. The reflectance spectra of all devices were measured by a Cary 5000 UV–Vis-NIR spectrophotometer. All devices were encapsulated prior to the measurement except for measuring reflectance.

3. Results and discussion

Three different types of TOLEDs were fabricated for comparison: a control device without the AR structure (Fig. 1a), an AR-TOLED (Fig. 1b), and a TOLED with a CP film. The AR-TOLED has layer thicknesses of $x = 60$ nm, $y = 142.5$ nm, and $z = 112.5$ nm, respectively. The CP film was simply attached onto the encapsulation glass of the TOLED. The reflection spectra of the TOLEDs are displayed in Fig. 2a. The photographs of the TOLEDs are also shown in Fig. 2b–d for the control device, the TOLED with a CP, and the AR-TOLED, respectively. The experimental reflectance spectra of the control TOLED and the AR-TOLED agrees very well with the simulated spectra. The control TOLED has one reflectance minimum at 553 nm, showing a typical spectrum of a Fabry–Perot interferometer [22]. The control device shows a large reflectance close to 80–90% at the red and blue color parts of the spectrum. In contrast, the AR-TOLED shows a much lower reflectance below 10% in the wavelength range between 450 nm and 650 nm. The reflection spectrum resembles a typical metal-dielectric band pass filter, exhibiting asymmetric reflectance [23]. The luminous reflectances of the control TOLED, the AR-TOLED, and the CP-TOLED are 40.8%, 6.0%, and 4.4%, respectively, which were calculated from the experimental spectra using Eq. (2). The luminous reflectance of the AR-TOLED is almost one seventh of the control TOLED, and comparable with the CP-TOLED. Even though the luminous reflectance of the AR-TOLED is a little higher than that of the CP-OLED, the higher efficiency of the AR-OLED enables getting a higher CR than the CP-OLED with lower power

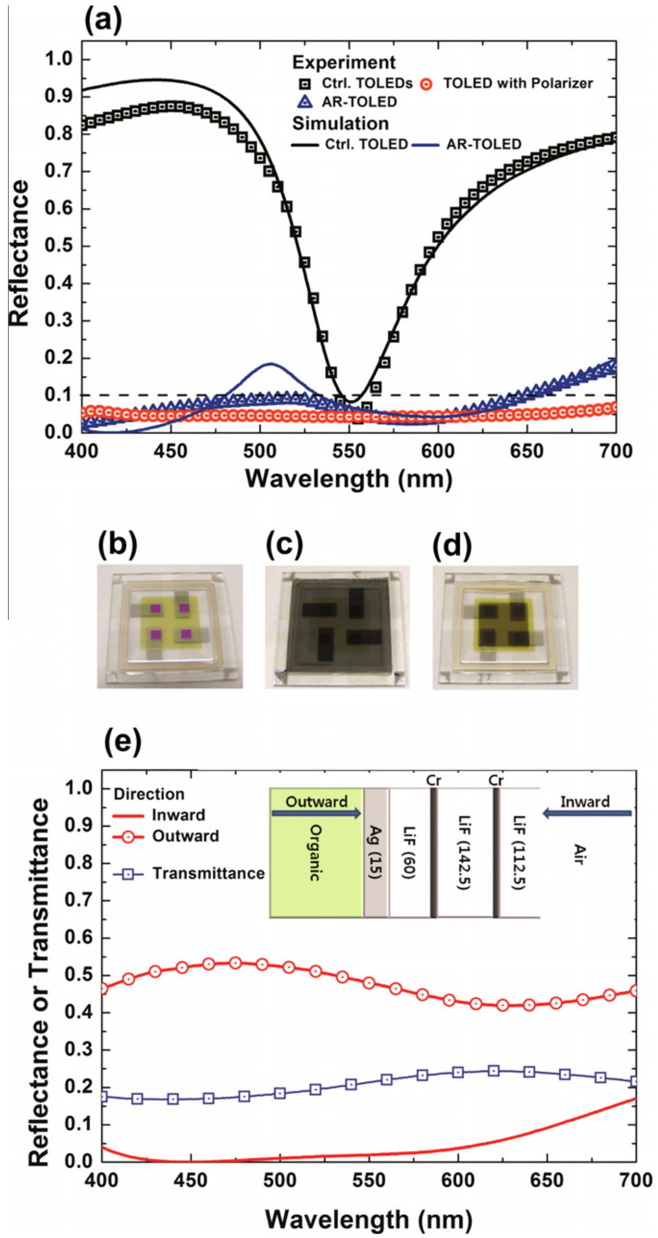

Fig. 2. (a) Experimental results of the reflectance spectra for the control TOLED (square), CP-TOLEDs (circle), and AR-TOLED (triangle). Solid lines are simulated reflection spectra of the control TOLED (black) and AR-TOLEDs (blue). (b–d) Photograph of fabricated devices for the experiment: (b) control TOLED; (c) CP-TOLED; and (d) AR-TOLED. (e) Simulated reflectance spectra for the inward (red solid line) and outward (red empty circle with line) directions for the AR cathode structure. Blue opened square is simulated transmittance spectrum of AR cathode structure. (Inset is a schematic diagram of the AR-cathode used for the simulation.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

consumption. To characterize the asymmetric reflectance of our electrode structure, the reflectance and transmittance spectra of the AR cathode structure are simulated and are shown in Fig. 2e. The inset of Fig. 2e shows the schematic diagram of the AR cathode structure used for the simulation. Fig. 2e clearly displays that the reflectance of the AR cathode is much higher in the outward direction than in the inward direction in the entire visible range. Therefore, a strong microcavity effect inside of the AR-TOLED is maintained and it is expected that the AR-TOLED shows a high luminous efficiency, even though it has an R_L value similar to the CP-TOLED. This asymmetric reflectance obtained from the metal/dielectric multi-layered structure is very powerful to realize efficient opto-electronic devices such as semi-transparent organic photovoltaic cells due to easy modulation of optical properties of the devices [24].

The current density–voltage (J–V) characteristics of the devices are identical while their luminances are different from each other, as shown in Fig. 3a. These results indicate that the fabrication procedure of the AR structure does not

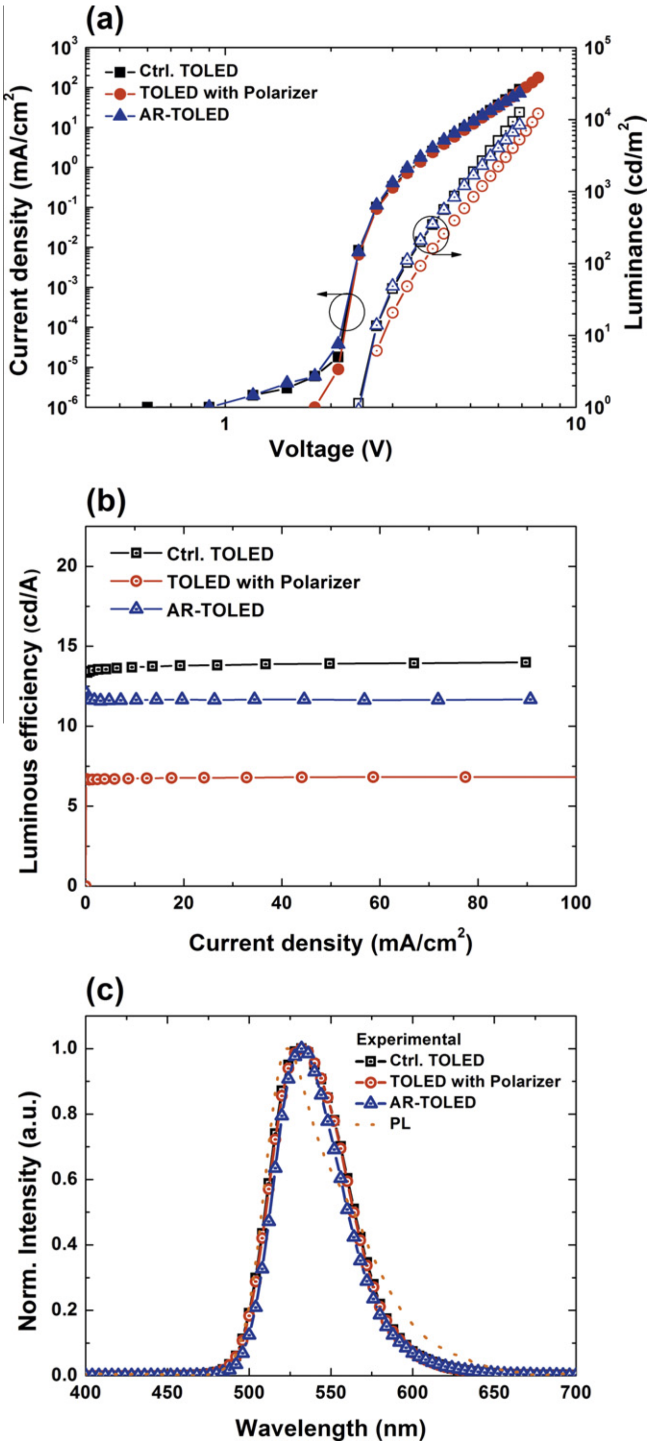

Fig. 3. Experimental results of (a) *J–V–L*, (b) *J*-luminous efficiency, and (c) EL spectra for control TOLED, CP-TOLED, and AR-TOLED. The thicknesses of *x*, *y*, and *z* for the AR-TOLED are the same as illustrated in Fig 2.

cause any damage to the underlying TOLED. Therefore, the differences in luminance output among the devices originate from purely optical effects. The luminous efficiency of the devices are plotted as a function of the current density in Fig. 3b. The luminous efficiencies of all the devices were almost constant up to 10,000 cd/m^2 in the normal direction with little roll-off. The control device without the AR structure or the CP shows the efficiency of 14 cd/A and red-shifted spectrum compared with photoluminescence (PL), indicating that the device structure is optically

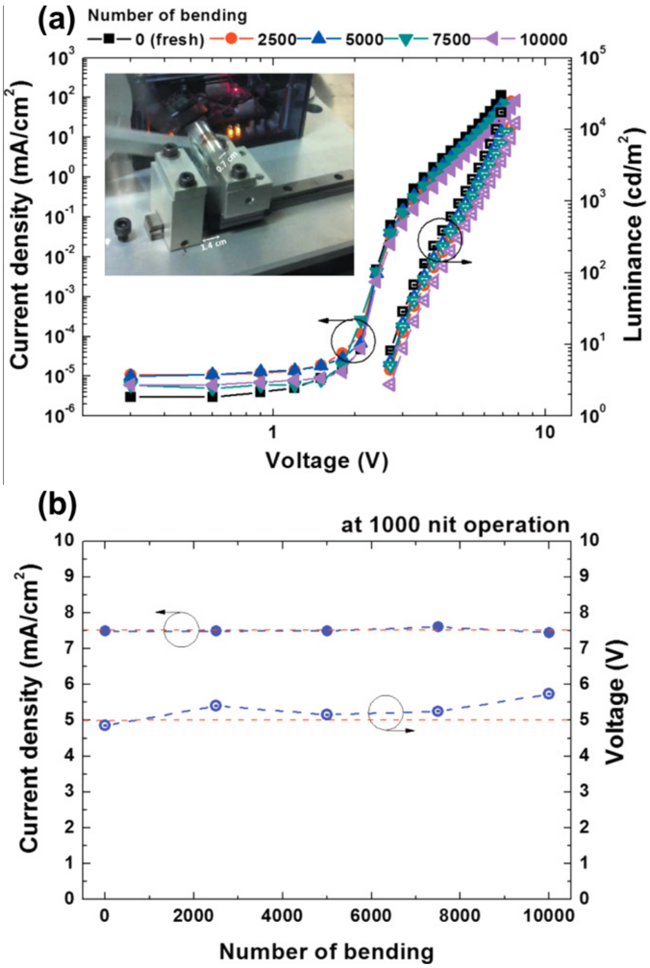

Fig. 4. Experimental results of flexible AR-TOLEDs. (a) *J–V–L* (Inset is a still picture of the video for the bending test.), (b) J and Voltage with the number of bending cycles for an under 1000 nit operation.

optimized for the top emisstion structure [25]. The AR-TOLED exhibits a luminous efficiency of 12.1 cd/A corresponding to 86.4% of the control device, while the CP-TOLED shows a luminous efficiency of 6.8 cd/m^2 corresponding to 49.3% of the control device. AR-TOLEDs achieve an enhancement by a factor of 1.75 compared with the CP-TOLED. Moreover, the enhancement was achieved with only a little modification of the electroluminescence spectrum of the control device, as shown in Fig. 3c. The normalized EL spectra of all devices did not change with the current density (not shown) and their spectra (the peak of EL spectrum for each device is at 532 nm) are a little red-shifted from the PL spectrum of C545T due to the optical microcavity effect. The AR-TOLED shows a slightly narrow EL spectrum coming from a higher internal reflectance (outward direction in the inset of Fig. 2e) in the cathode side than seen in the control device due to the AR structure (50.0% for the AR-TOLED, and 40.3% for the control TOLED at 532 nm). The higher internal reflectance from the Ag/AR structure than the Ag only cathode is coming from the reflections at the interfaces of the metal/dielectric layers. This is the reason why the AR-TOLED shows a very high efficiency compared with the CP-TOLED, although the AR layer is directly integrated on the cathode.

The direct integration of the AR structure on TOLEDs allows for easy fabrication of flexible TOLEDs. We have fabricated an AR-TOLED on a plastic substrate to demonstrate the feasibility. Polyethylenenaphthalate (PEN film, Teonex® made by Teijin-Dupont Film Japan Ltd.) was used as the substrate and the device structure and fabrication procedure are the same as for a device on a glass substrate. To test the durability of the flexible AR-TOLED under mechanical stress, the *J–V–L* characteristics of the flexible AR-TOLED were measured at every 2500 bending cycles up to 10,000 times. A homemade bending tester shown in the inset of Fig. 4a was used for the experiment (a moving picture is in Supporting information). The bending radius and rate were about 0.7 cm and 67 revolutions/min, respectively. The *J–V–L* characteristics of the device before and after the bending tests are displayed in Fig. 4a, exhibiting only small changes even after the 10,000 bending cycles. The luminous efficiency was unaffected with the bending cycles, as shown in Fig. 4b. The driving voltage marginally increased by less than 1 V at a luminance of 1000 cd/m^2.

Fig. 4a and b clearly demonstrate that our AR structure is sufficiently durable to be applied to a flexible device, and the processing temperature of the AR structure is low enough not to deteriorate the device characteristics.

4. Conclusion

We demonstrated a polarizer free high contrast flexible TOLED with only a little reduction of efficiency by employing a periodic dielectric-metal AR structure integrated on the top semi-transparent cathode. Cr and LiF were used as the thin metal and the phase change/phase compensation layer, respectively. Since the AR structure is integrated on top of the TOLEDs (outside of the original TOLEDs) and the process temperature is low, no deterioration of the electrical characteristics of the underlying organic device took place. The flexible AR-TOLED showed a sufficiently low luminous reflectance (6%), high efficiency (86% of the TOLED without the AR structure, 1.75 times higher than the CP-TOLED) and extremely high durability upon repeated bending up to 10,000 times for the bending radius of 0.7 cm. Further enhancement is expected if the AR structure is fully optimized through experiments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2012.01.015.

References

[1] V. Vaenkatesan, R.T. Wegh, J.-P. Teunissen, J. Lub, C.W.M. Bastiaansen, D.J. Broer, Improving the brightness and daylight contrast of organic light-emitting diodes, Advanced Functional Materials 15 (2005) 138–142.
[2] D. Poitras, C.-C. Kuo, C. Py, Design of high-contrast OLEDs with microcavity effect, Optics Express 16 (2008) 8003.
[3] L.-S. Hung, J. Madathil, Reduction of ambient light reflection in organic light-emitting diodes, Advanced Materials 13 (2001) 1787.
[4] H. Aziz, Y.-F. Liew, H. Michelle Grandin, Z.D. Popovic, Reduced reflectance cathode for organic light-emitting devices using metalorganic mixtures, Applied Physics Letters 83 (2003) 186.
[5] S.H. Li, H. Liem, C.W. Chen, E.H. Wu, Z. Xu, Y. Yang, Stacked metal cathode for high-contrast-ratio polymeric light-emitting devices, Applied Physics Letters 86 (2005).
[6] W.F. Xie, Y. Zhao, C.N. Li, S.Y. Liu, Contrast and efficiency enhancement in organic light-emitting devices utilizing high absorption and high charge mobility organic layers, Optics Express 14 (2006) 7954.
[7] O. Renaulta, O.V. Salatac, M. Etchellsa, P.J. Dobsona, V. Christoub, A low reflectivity multilayer cathode for organic light-emitting diodes, Thin Solid Films 379 (2000) 195.
[8] A.N. Krasnov, High-contrast organic light-emitting diodes on flexible substrates, Applied Physics Letters 80 (2002) 3853.
[9] X.D. Feng, R. Khangura, Z.H. Lu, Metal-organic-metal cathode for high-contrast organic light-emitting diodes, Applied Physics Letters 85 (2004) 497.
[10] Y.C. Zhou, L.L. Ma, J. Zhou, X.D. Gao, H.R. Wu, X.M. Ding, X.Y. Hou, High contrast organic light-emitting devices with improved electrical characteristics, Applied Physics Letters 88 (2006) 233505.
[11] K.C. Lau, W.F. Xie, H.Y. Sun, C.S. Lee, S.T. Lee, Contrast improvement of organic light-emitting devices with Sm:Ag cathode, Applied Physics Letters 88 (2006) 083507.
[12] W.F. Xie, H.Y. Sun, C.W. Law, C.S. Lee, S.T. Lee, S.Y. Liu, High-contrast and high-efficiency top-emitting organic light-emitting devices, Applied Physics A 85 (2006) 95–97.
[13] S.M. Chen, Y.B. Yuan, J.R. Lian, X. Zhou, High-efficiency and high-contrast phosphorescent top-emitting organic light emitting devices with p-type Si anodes, Optics Express 15 (2007) 14644.
[14] C.-J. Yang, C.-L. Lin, C.-C. Wu, Y.-H. Yeh, C.-C. Cheng, Y.-H. Kuo, T.-H. Chen, High-contrast top-emitting organic light-emitting devices for active-matrix displays, Applied Physics Letters 87 (2005) 143507.
[15] B. Lee, Y. Cho, M. Oh, S. Lee, J. Lee, D. Zang, Characteristics of contrast of active-matrix organic light-emitting diodes containing a black matrix and antireflection layers, Materials Chemistry and Physics 112 (2008) 734–737.
[16] H.A. Macleod, Thin-Film Optical Filters, third ed., Institute of Physics Pub., Bristol, 2001.
[17] R.R. Chance, A. Prock, R. Silbey, Molecular Fluorescence and Energy Transfer Near Interfaces, John Wiley & Sons, Inc., 1978.
[18] J.A.E. Wasey, W.L. Barnes, Efficiency of spontaneous emission from planar microcavities, Journal of Modern Optics 47 (2000) 725–741.
[19] S.Y. Kim, J.J. Kim, Outcoupling efficiency of organic light emitting diodes and the effect of ITO thickness, Organic Electronics 11 (2010) 1010–1015.
[20] H.H. Li, Refractive index of alkali halides and its wavelength and temperature derivatives, Journal of Physical and Chemical Reference Data 5 (1976) 329–528.
[21] E.D. Palik, G. Ghosh, Handbook of Optical Constants of Solids, Academic Press, San Diego, 1998.
[22] O.S. Heavens, Optical Properties of Thin Solid Films, Dover Publications, New York, 1991.
[23] J.A. Dobrowolski, L. Li, R.A. Kemp, Metal/dielectric transmission interference filters with low reflectance. 1. Design, Applied Optics 34 (1995) 5673–5683.
[24] D. Han, H. Kim, S. Lee, M. Seo, S. Yoo, Realization of efficient semitransparent organic photovoltaic cells with metallic top electrodes: utilizing the tunable absorption asymmetry, Optics Express 18 (2010) A513–A521.
[25] C.L. Lin, H.C. Chang, K.C. Tien, C.C. Wu, Influences of resonant wavelengths on performances of microcavity organic light-emitting devices, Applied Physics Letters 90 (2007).