APPLIED PHYSICS LETTERS **86**, 143501 (2005)

Efficiency enhancement of an organic light-emitting diode with a cathode forming two-dimensional periodic hole array

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(Received 23 November 2004; accepted 22 February 2005; published online 28 March 2005)

We fabricated an organic light-emitting diode using a π-conjugated polymer emissive layer sandwiched between two semitransparent electrodes: an optically thin gold film anode, whereas the cathode was in the form of an optically thick aluminum (Al) film with patterned periodic subwavelength two-dimensional hole array that showed anomalous transmission in the spectral range of the polymer photoluminescence band. At similar current densities, we obtained a sevenfold electroluminescence efficiency enhancement with the patterned Al device compared with a control device based on unperforated Al electrode. © *2005 American Institute of Physics*.
[DOI: 10.1063/1.1895481]

In the simplest form of organic light-emitting diodes (OLEDs) the active organic semiconductor is sandwiched between two metallic electrodes.[1,2] Since such electrodes are usually opaque in the visible spectral range unless very thin, this type of geometry prevents efficient surface emission. This difficulty can be finessed by using a semitransparent electrode such as indium tin oxide as the hole-injecting anode. However, for the electron-injecting cathode, opaque metallic electrodes such as aluminum (Al) are still being used.[3] In this OLED configuration, due to the relatively high refractive index of the organic active layer, a considerable fraction of the emitted radiation remains trapped in the device as waveguide modes that eventually couple to surface plasmons (SP) excitations on the anode surface, which consequently decay nonradiatively.[4] If nothing is done to recover this trapped waveguided light, then the device efficiency remains always low.[5] In this letter we demonstrate an efficient way to extract more electroluminescence (EL) out of an OLED device using a semitransparent perforated electron-injecting cathode, due to the anomalous transmission caused by its patterned periodic two-dimensional (2D) subwavelength hole array that is comprised of a 2D metallo-dielectric photonic crystal.

On a smooth metal-dielectric interface, light cannot efficiently couple to the SP excitations, which are the elementary excitations of the metal surface, because conservation of energy, E, and momentum, k, is not obeyed.[6] But in a metal film that is perforated with a 2D periodic array of holes, the periodicity allows grating coupling of the SP to light;[7] this coupling results in surface plasmon polariton (SPP) excitations. Indeed it was recently found[7–18] that the optical transmission through subwavelength hole arrays fabricated on optically thick metallic films is enhanced at resonance wavelengths (or maxima), where light couples to the film's SPP excitations. If these maxima overlap with the photoluminescence (PL) band of the active organic layer of an OLED, then it might be possible to extract more EL light out of the device[5,19–21] without compromising the current injection capability of the patterned electrode.

Here we report our study of the optical transmission, PL emission, OLED fabrication and electronic properties of an organic semiconductor polymer [a soluble derivative of poly-p-phenylene vinylene (PPV)] sandwiched between an optically thin gold anode, and an optically thick Al film perforated with a periodic hole array used as a cathode. We found that the extraordinary transmission resonances in the Al optical spectra match the PL band of the organic active layer, and thus more EL light could be extracted from the device.

The Al cathode hole array was in the form of a square 5×5 mm^2 in area that was fabricated by Nanonex Corp. (Princeton, NJ) using a nano-imprint method. The periodic hole array with square symmetry consisted of an 80-nm-thick Al film on a glass substrate with subwavelength hole size of about 150 nm and lattice constant periodicity, a_0, of about 300 nm [Fig. 1(a) inset]. An unperforated Al film used for the control OLED was fabricated by evaporating Al on glass, with the same thickness as that of the Al hole array sample. The active layer of both OLEDs was a soluble derivative of PPV, namely poly (2-5 methoxy-ethyl-hexyloxy) [MEH-PPV] of which repeat unit is shown in Fig. 2 inset. The optical transmission and PL spectra were measured at room temperature using a homemade spectrometer.

The OLEDs were fabricated by the "inverted method,"[22] in which first the active layer is spin coated on the cathode followed by deposition of the anode [Fig. 3(a)]. All procedures were done in a homemade glovebox, having 1 ppm of oxygen. A thin layer (2 nm thick) of barium (Ba) was first evaporated onto the perforated Al and control Al films, for enhancing their electron-injection capability. We then spin coated a 130-nm-thick film of MEH-PPV onto the Al electrodes. The devices were completed by capping a 70 nm gold (Au). The *I-V* characteristics and the external EL quantum efficiencies (ELQE) of the devices were measured in a glovebox that was purged with dry nitrogen using a computer-controlled Keithley 236 source and measure unit, and an integrated sphere[23] with a silicon photodiode. The ELQE was calibrated using OLEDs with known EL efficiency, which were obtained from another laboratory.

The zeroth order optical transmission, $T(\lambda)$, through the Al hole arrays in the visible/near-infrared spectral range is shown in Fig. 1(a) for an incident angle $\theta=0$. The spectrum is composed of several transmission resonances, $\lambda_{\max}$, and

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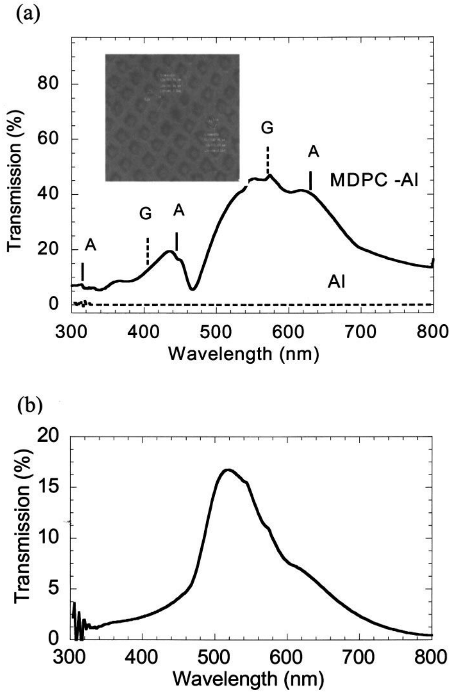

FIG. 1. The optical transmission spectra, $T(\lambda)$, of the OLED metallic electrodes; (a) 80-nm-thick Al cathode, and (b) 70-nm-thick Au anode. In (a) we compare $T(\lambda)$ of the perforated Al electrode in the form of metallic dielectric photonic crystal—MDPC as shown in the inset, to that of an unperforated Al film. The anomalous transmission bands are assigned to the SPP excitations at the air-Al (A) or glass-Al (G) interfaces by vertical full lines and dashed lines, respectively.

transmission minima, $\lambda_{\min}$. The features at $\lambda_{\max}$ are due to extraordinary transmission resonances that are formed as the result of light coupling to SPP[7–18] giving $T > 25\%$ (which is the area covered by the holes in the perforated film). This could be verified from the angular dependence of $T(\lambda)$, where a redshift in $\lambda_{\max}$ was measured at $\theta > 0$. The transmission minima at $\lambda_{\min}$, on the contrary, are due to Wood's anomalies.[24] Importantly, T is maximum in the spectral range of MEH-PPV PL emission band (Fig. 2), and thus the perforated film may be efficiently used to couple EL emission from the OLED.[25] For comparison we plot in Fig. 1(a) $T(\lambda)$ of the control Al film; T is very low, less than 1% in the spectral range of interest. We also plot in Fig. 1(b) $T(\lambda)$ of the semitransparent 70-nm-thick gold electrode that was used as a cathode for the OLED devices. $T(\lambda)$ peaks at 15%, but T at 600 nm, which is the PL emission maximum of the PPV-MEH polymer (Fig. 2) is only about 7%.

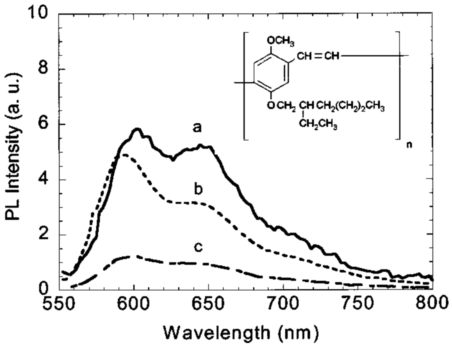

FIG. 2. The PL spectra of a MEH-PPV polymer film spin coated on the unperforated Al (full line), and perforated Al electrodes, which are measured in reflection geometry (dashed line), and transmission geometry through the film (dotted-dashed line). The inset shows the MEH-PPV polymer repeat unit.

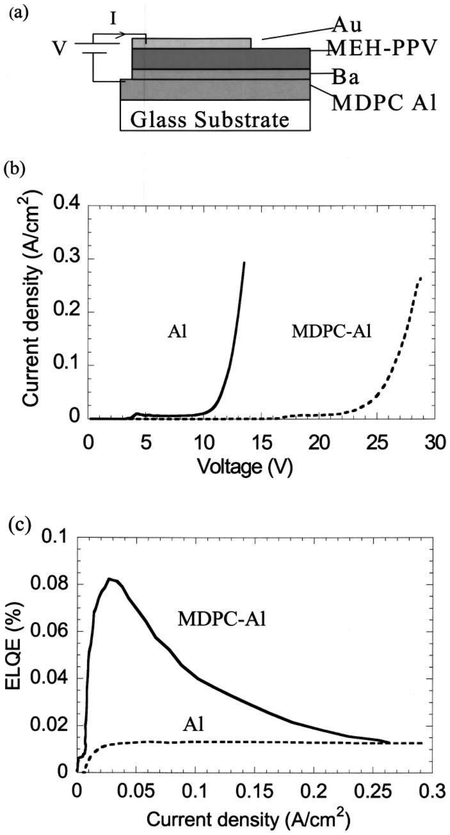

FIG. 3. Color online. (a) The inverted OLED configuration that consists of three layers: an Al cathode coated with a thin Ba film for enhanced electron injecting, the active MEH-PPV polymer layer, capped by a gold anode. The OLED device operates at forward bias, V. (b) The I-V characteristics of the two OLEDs; dashed (full) line is for the device based on the perforated (unperforated) Al cathode. (c) The EL quantum efficiency of the two OLEDs measured as a function of the current density, dashed and full lines as in (b).

In the standard aperture theory of Bethe,[26] the transmission through a subwavelength aperture follows $(d/\lambda)^4$ dependence due to diffraction, where d is the hole diameter. However, $T(\lambda)$ through the Al subwavelength array of holes shows "anomalous" behavior, with significant transmission at wavelengths much longer than d [Fig. 1(a)]. The perforated metallic surface allows coupling between the incident light and SPP excitations on both sides of the film. The conservation of momentum in this case can be written as[7]

$$\mathbf{k}_{\mathrm{sp}} = \mathbf{k}_x \pm m\mathbf{u}_x \pm n\mathbf{u}_y, \tag{1}$$

where $|\mathbf{k}_x| = (2\pi/\lambda)\sin\theta$ is the component of incident wave vector of light in the plane of the hole array, $\mathbf{u}_x$ and $\mathbf{u}_y$ are the reciprocal lattice vectors (for a square lattice as in our case we have $|\mathbf{u}_x| = |\mathbf{u}_y| = 2\pi/a_0$), and m and n are integers. From the conservation of energy we get for the SP wave-vector k_{sp} on a smooth metallic film

$$|\mathbf{k}_{\mathrm{sp}}| = \frac{\omega}{c}\left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}\right)^{1/2}, \tag{2}$$

where ε_m and ε_d are the real parts of the dielectric constants for the metal and substrate (glass or air), respectively. At normal incidence ($\theta = 0$) Eqs. (1) and (2) can be reduced to

$$\lambda_{\max} = \frac{a_0}{\sqrt{m^2+n^2}}\left(\frac{\varepsilon_m\varepsilon_d}{\varepsilon_m+\varepsilon_d}\right)^{1/2}. \qquad (3)$$

Using Eq. (3) the positions of transmission maxima $\lambda(n,m)$ can be associated with the SPP modes on the different interfaces. The calculated transmission maxima are in good agreement with the spectrum shown in Fig. 1(a) despite the simple model used here. The transmission minimum at $\lambda = 460$ nm is due to Wood's anomaly,[24] and thus cannot be described by coupling to SPP excitations.

The PL spectra of MEH-PPV spin casted on the two Al films are shown in Fig. 2 in transmission and reflection geometries, respectively. The PL spectra show typical phonon replicas $(0-n)$, and indicate that a good match exists with the transmission maxima of the perforated Al film [Fig. 1(a)],[25] and that of the Au top electrode [Fig. 1(b)]. The PL intensity measured in transmission is relatively strong for the perforated Al electrode due to the match with the anomalous $T(\lambda)$. On the contrary, the PL intensity measured through the control Al film (not shown) is much smaller (by about two orders of magnitude).

The measured responses of the two OLEDs are shown in Fig. 3. Figure 3(b) shows *I-V* characteristics; both devices show an abrupt onset to EL mode of operation. It is evident that the device onset biasing voltage V for the perforated Al ($V \approx 20$ V) is higher compared with that of the unperforated Al electrode ($V \approx 10$ V). Nevertheless, the *I-V* curves indicate that the perforated Al electrode, in principle, can deliver as high current densities in spite of the many holes that decorate the electron-injecting cathode. Figure 3(c) shows the ELQE of the two OLEDs measured as a function of V. Admittedly the ELQE is low compared with the best values in the literature.[3] However, we note that our devices do not have hole and electron intermediate transport layers, which, due to electron-hole balancing currents,[3] can increase the ELQE by at least an order of magnitude. Importantly, at similar current densities, J the OLED based on the perforated Al cathode shows a substantial ELQE enhancement over that based on the unperforated Al film, of up to a factor of 7 at small J. At high J the enhancement is smaller, probably due to the patterned electron current density in the device that is injected by the hole arrays Al cathode.

The EL enhancement in the device based on the perforated cathode, in principle, can be due to an enhanced PL efficiency close to the holes in the cathode, where the electric field is much higher,[18,19] or simply due to the enhancement of EL transmission through the perforated Al cathode.[20] From the transmission spectra shown in Fig. 1, however, it is obvious that the latter reason is more viable. Since there is practically no transmission through the Al cathode in the unperforated OLED, then the EL emission is collected only through the Au anode with 7% transmission at 600 nm. In the perforated OLED, on the contrary, there is extra transmission of ~45% at 600 nm[25] due to the anomalous transmission of the patterned Al cathode, so that the overall transmission of the OLED may reach 52% at 600 nm. This represents about a sevenfold enhancement in the potential for EL collecting efficiency of the device, in good agreement with the data [Fig. 3(c)].

In conclusion, we fabricated an OLED based on a perforated Al cathode in the form of a periodic 2D hole array, and compared its performance to that of a control device based on an unperforated Al electrode. The anomalous transmission through the patterned Al electrode can be well explained by resonant coupling of the incident light to SPP excitations on the two cathode interfaces, and matches the PL emission spectrum of the active polymer, MEH-PPV. At similar current densities we obtained up to a sevenfold increase in the EL collection efficiency from the perforated device compared to the control device. This demonstrates that the method of patterning the electrodes into 2D hole arrays is very efficient, and can be used in the future for extracting more EL in practical device applications.

This work was supported in part by the ARO Grant No. DAAD 19-03-1-0290; the NSF- NIRT Grant No. 0102964; and the DOE Grant No. FG-02-04ER46109.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] J. H. Borroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 799 (1990).
[3] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlung, and W. R. Salaneck, Nature (London) **397**, 121 (1999).
[4] P. A. Hobson, J. A. E. Wasey, I. Sage, and W. L. Barnes, IEEE J. Sel. Top. Quantum Electron. **8**, 378 (2002).
[5] W. L. Barnes, P. A. Hobson, S. Wedge, J. A. E. Wasey, and I. Sage, Adv. Mater. (Weinheim, Ger.) **14**, 1393 (2002).
[6] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* (Springer, Berlin, 1988).
[7] T. W. Ebbesen, H. J. Lezec, H. F. Gaemi, T. Thio, and P. A. Wolff, Nature (London) **391**, 667 (1998).
[8] H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, and H. J. Lezec, Phys. Rev. B **58**, 6779 (1998).
[9] T. Thio, H. F. Ghaemi, H. J. Lezec, P. A. Wolff, and P. A. Ebbesen, J. Opt. Soc. Am. B **16**, 1743 (1998).
[10] T. J. Kim, T. Thio, T. W. Ebbesen, D. E. Grupp, and H. J. Lezec, Opt. Lett. **24**, 256 (1999).
[11] I. Avrutsky, Y. Zhao, and V. Kochergin, Opt. Lett. **25**, 595 (2000).
[12] D. E. Grupp, H. J. Lezec, T. W. Ebbesen, K. M. Pellerin, and T. Thio, Appl. Phys. Lett. **77**, 1569 (2000).
[13] L. Martin-Moreno, F. J. Garcia-Vidal, H. J. Lezec, K. M. Pellerin, T. Thio, J. B. Pendry, and T. W. Ebbesen, Phys. Rev. Lett. **86**, 114 (2001).
[14] L. Salomon, F. Grillot, A. V. Zayats, and F. de Fornel, Phys. Rev. Lett. **86**, 1110 (2001).
[15] A. M. Dykhne, A. K. Sarychev, and V. M. Shalaev, IEEE J. Quantum Electron. **38**, 956 (2002).
[16] S. Enoch, E. Popov, M. Nevier, and R. Reinisch, J. Opt. A, Pure Appl. Opt. **4**, S83 (2002).
[17] A. Krishnan, T. Thio, T. J. Kim, H. J. Lezec, T. W. Ebbesen, P. A. Wolff, J. Pendry, L. Martin-Moreno, and F. J. Garcia-Vidal, Opt. Commun. **200**, 1 (2002).
[18] Y. Liu and S. Blair, Opt. Lett. **28**, 507 (2003).
[19] S. Gianordoli, R. Hainbrerger, A. Kock, N. Finger, E. Gornik, C. Hanke, and L. Korte, Appl. Phys. Lett. **77**, 2295 (2000).
[20] D. K. Gifford and D. G. Hall, Appl. Phys. Lett. **81**, 4315 (2000); **80**, 3679 (2002).
[21] H. Ichikawa and T. Baba, Appl. Phys. Lett. **84**, 457 (2004).
[22] T. Dobbertin, O. Werner, J. Meyer, A. Kammoun, D. Schneider, T. Riedl, E. Becker, H.-H. Joannes, and W. Kowalski, Appl. Phys. Lett. **83**, 5071 (2003).
[23] N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, Chem. Phys. Lett. **241**, 89 (1995).
[24] R. W. Wood, Philos. Mag. **4**, 396 (1902); Proc. R. Soc. London, Ser. A **18**, 269 (1902).
[25] As a matter of fact, $T(\lambda)$ changes slightly after the polymer deposition; however, when the angular dependence of the first maximum is taken into account, then it efficiently covers the entire PL spectrum.
[26] H. A. Bethe, Phys. Rev. **66**, 163 (1944).