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## Addressable, Large-Area Nanoscale Organic Light-Emitting Diodes\*\*

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Advances in the fabrication and processing of macroscale organic light-emitting diodes (OLEDs) for full-color displays have created interest in generating OLEDs at the nanoscale.<sup>[1,2]</sup> Reducing the size of an OLED can produce higher device densities per unit area, which allows the manufacture of higher resolution displays that are more defect tolerant and viewable at close range.<sup>[3]</sup> Furthermore, nano-OLEDs (those whose active area is on the order of 100 nm) could potentially be used as subwavelength light sources for high-resolution imaging techniques<sup>[4]</sup> and for nanooptical lithography.<sup>[5]</sup> Although serial approaches such as electron-beam lithography (EBL) have been used to fabricate arrays of nano-OLEDs, drawbacks of these prototype-only methods include small patterned areas ( $\leq 0.2 \text{ mm}^2$ ) and low densities ( $1 \times 10^4$  pixels per  $\text{mm}^2$ ).<sup>[6,7]</sup>

Here we report the fabrication of nano-OLED arrays over large areas ( $\approx \text{cm}^2$ ) and with higher pixel densities than those prepared using serial techniques. We have used soft nanolithography—parallel patterning methods that can routinely produce feature sizes less than 500 nm using composite poly(dimethylsiloxane) (PDMS) stamps<sup>[8–10]</sup>—to generate arrays of 250-nm-diameter holes in negative photoresist supported on a transparent conducting substrate. Electroluminescent molecules were then assembled within these holes to produce nano-OLEDs. We achieved pixel densities exceeding  $10^5$  pixels per  $\text{mm}^2$  with defect densities that depended only on imperfections in the PDMS mask. Moreover, we have demonstrated that these nano-OLEDs are addressable in one dimension.

Progress toward nano-OLEDs has largely been achieved by defining the area of the electrical contacts. Nanosphere lithography has been used to fabricate sub-100-nm pixels by reducing the active area of the indium tin oxide (ITO) anode.<sup>[11]</sup> Nanoscale holes (60–200 nm in diameter) within films of insulating materials such as  $\text{SiO}_2$ <sup>[6]</sup> or  $\text{Si}_3\text{N}_4$ <sup>[7]</sup> have been used to define nano-OLEDs based on polyfluorene<sup>[6]</sup> and poly-[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV).<sup>[7]</sup> Although EBL could confine the ef-

fective size of the anode, the nano-OLEDs could not be individually addressed because they were all patterned on the same electrical back plane. Other reports used soft-contact lamination to pattern the cathode into lines of gold electrodes with widths as small as 150 nm to produce MEH-PPV OLEDs.<sup>[18–20]</sup>

OLED devices based on the electroluminescent ruthenium bipyridyl complex  $\text{Ru}[(\text{bpy})_3]$  have received attention because this molecule is an efficient and bright emitter.<sup>[12–15]</sup> Addressable 1D arrays of  $\text{Ru}[(\text{bpy})_3(\text{ClO}_4)_2]$ -based OLEDs have been fabricated on glass substrates patterned with five 0.9- $\mu\text{m}$  lines or “finger electrodes” of ITO on a 1.1- $\mu\text{m}$  pitch.<sup>[16,17]</sup> Although individual lines were contacted, one drawback was that the wet-etching step used in this fabrication procedure generated small defects in the ITO lines. The ability to pattern addressable, nano-OLEDs over  $\text{cm}^2$  areas is critical for producing practical devices and for testing the possibilities of confining light emission to nanoscale dimensions.

Figure 1 shows our simple procedure to fabricate  $\text{Ru}[(\text{bpy})_3(\text{BF}_4)_2]$ -based nano-OLEDs. SU-8, an insulating

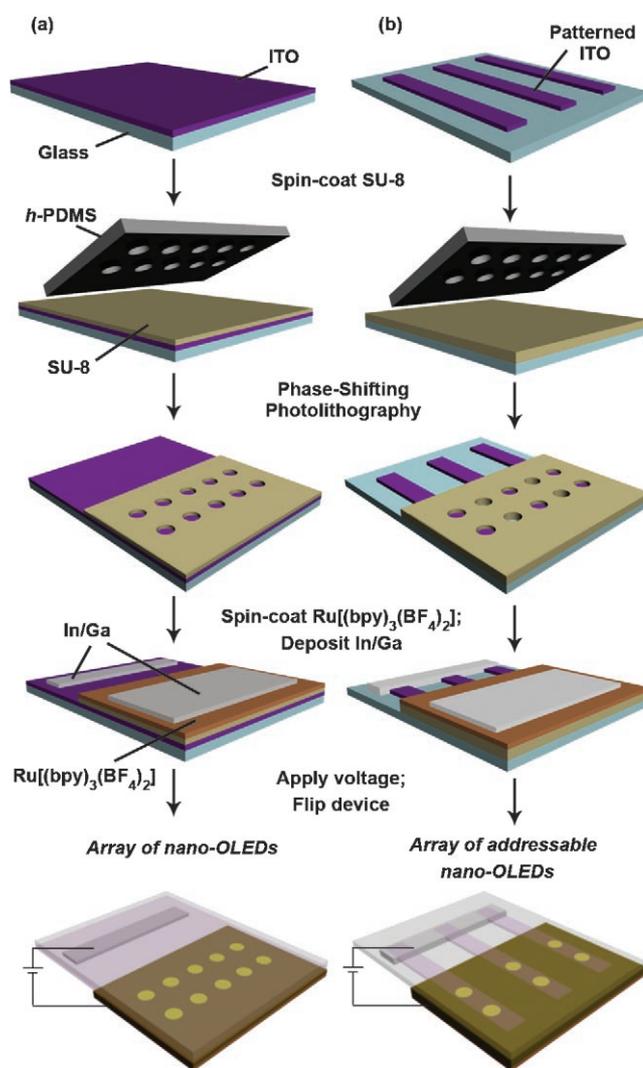


Figure 1. a) Scheme for defining the anode area for fabricating nano-OLEDs. b) Scheme for patterning addressable nano-OLEDs.

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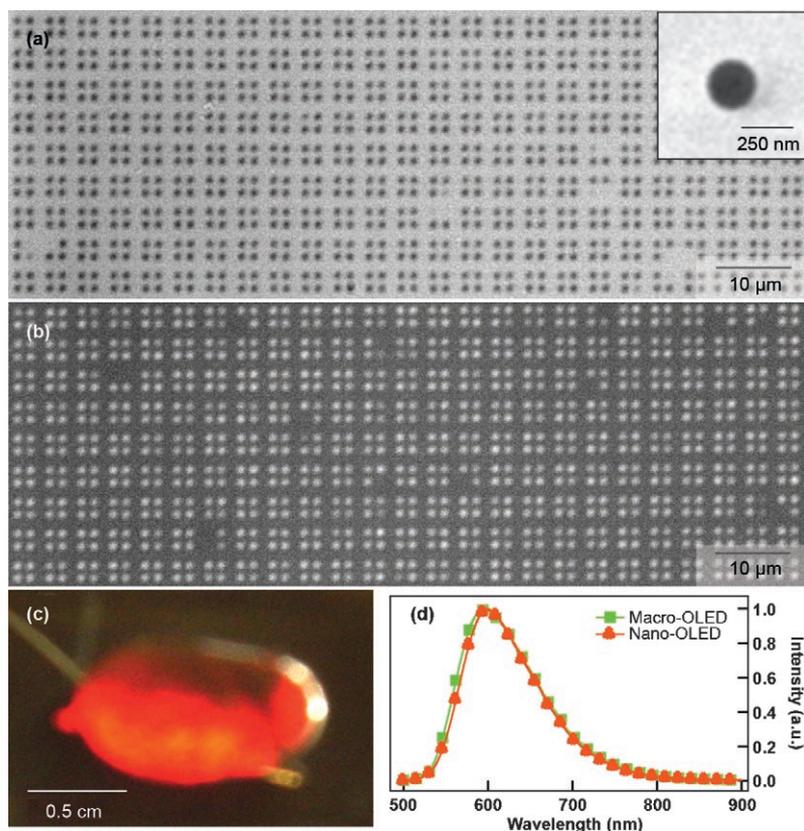
and transparent negative-tone photoresist, was first spin-cast onto ITO-coated glass slides. Arrays of 250-nm-diameter holes in SU-8, which defined the active area of the OLEDs, were then generated over a square centimeter using phase-shifting photolithography (PSP)<sup>[8–10]</sup> to construct a two-dimensional hole array. Addressable nano-OLEDs were fabricated following a similar procedure, except the ITO layer was first patterned into an array of 1D electrodes (Figure 1b). Devices were assembled by spin-coating a solution of Ru[(bpy)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>] onto the SU-8 nanohole arrays followed by a quick baking step and then placing an In/Ga eutectic cathode onto the Ru[(bpy)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>] layer.

A typical optical micrograph of the 250-nm circular openings in SU-8 indicates that some holes in the array are missing (Figure 2a). Upon examining the composite (h-PDMS) mask used in the PSP step, we found that the missing holes in SU-8 were a consequence of defects in the PDMS mask. We carried out statistics on ten areas of the patterned SU-8 layer (each covering 7200 μm<sup>2</sup>) and found that (1.8 ± 0.2)% of the holes were missing. Using PSP to define the hole sizes in SU-8 allows us to pattern arrays of holes simultaneously and with much higher densities (2.6 × 10<sup>5</sup> pixels per mm<sup>2</sup>) than holes that EBL has produced in SiO<sub>2</sub> (1 × 10<sup>4</sup> pixels per mm<sup>2</sup>).<sup>[6]</sup> Using an inverted optical microscope (TE-2000 Nikon), we imaged the electroluminescence (EL) from individual nano-OLEDs in a large-area array (Figure 2b). Only 2% of the nanopixels viewed in a 7200 μm<sup>2</sup> area did not exhibit EL. Importantly, the density

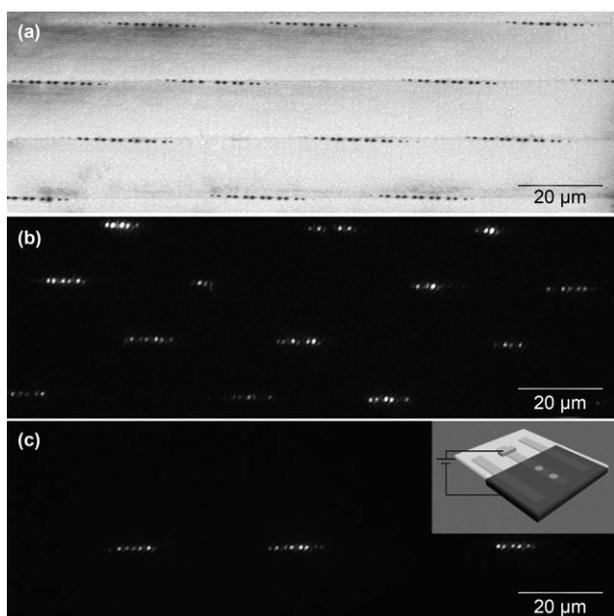
of defects matched the density of missing holes in the SU-8 pattern; thus, the number of defects in our arrays can be reduced to less than 2% simply by using a higher quality h-PDMS nanomask. Moreover, this defect density is significantly lower than the failure rate reported for nano-OLEDs prepared by EBL (10%),<sup>[6]</sup> where the primary cause of defects was incomplete etching of some of the holes. Figure 2c shows that EL can be observed over areas as large as 0.7 cm<sup>2</sup>, which contain ≈ 2 × 10<sup>7</sup> nano-OLEDs. The EL spectrum recorded from a 0.07 mm<sup>2</sup> area containing nearly 2 × 10<sup>4</sup> nano-OLEDs exhibited an emission peak at 600 nm with a full-width-at-half-maximum (FWHM) of 150 nm (Figure 2d); this nano-OLED emission spectrum was similar to that from a single macroscale OLED (≈ 5 mm<sup>2</sup>), as expected. Devices that were operated at 3.9 V in air showed bright EL that could be observed under ambient conditions for about two hours, a comparable lifetime to other reports of Ru[(bpy)<sub>3</sub>]-based devices patterned in air.<sup>[15,17]</sup>

To address a single row of nano-OLEDs, we patterned SU-8 hole arrays on 350-nm lines of ITO separated by 15 μm. Although the ITO lines could have been easily fabricated on the same pitch as the SU-8 holes, we prepared ITO lines with relatively large spacings so that each electrode could be individually addressed by hand using a sharpened aluminum wire. Figure 3a shows that a slight mismatch exists between the arrays of SU-8 holes and the ITO lines after patterning because of the challenge in manually aligning patterns with such small feature sizes. We were still able to observe EL from the nano-OLEDs in contact with the ITO even though the mismatch in alignment led to periodic discontinuities along each row (Figure 3b). By contacting a single ITO electrode, we observed EL only from nano-OLEDs in contact with this ITO line (Figure 3c). This row of nano-OLEDs is probably one of the smallest individually addressable light sources reported to date.

In summary, we have developed a simple procedure to fabricate low-defect, nano-OLED arrays containing up to ≈ 2 × 10<sup>7</sup> pixels over areas of 0.7 cm<sup>2</sup>. Our patterning method has several advantages, including 1) it is parallel, and thus can be scaled up to fabricate even larger-area arrays of nano-OLEDs; 2) defects can be easily controlled using higher quality PDMS photomasks; and 3) displays on flexible substrates are possible because



**Figure 2.** a) Optical micrograph of 250-nm circular openings in SU-8 (inset: SEM image of a single nano-hole). b) EL image of nano-OLEDs operated at 3.9 V. c) Photograph of large-area emission from the nano-OLED array. d) EL spectra of nano-OLEDs (▲, orange line) and macroscale OLEDs (■, green line).



**Figure 3.** a) SEM image of 250-nm circular openings in SU-8 patterned on 350-nm-wide ITO lines spaced by 15 μm. The dark spots indicate where the holes are in contact with the ITO lines. b) EL image of an array of addressable nano-OLEDs. c) EL image of an individually addressed row of nano-OLEDs (inset: scheme of how this single row was addressed).

our devices are fabricated in SU-8. One drawback is the difficulty in obtaining perfect registration between the patterned ITO lines and the SU-8 nanoholes when aligning the patterns by hand. This problem can be overcome by using more precise mechanical alignment techniques or by fabricating SU-8 hole arrays with larger spacings. Future applications of our patterning method include fully addressable nano-OLED arrays generated by patterning the cathode in addition to the anode. Fabrication of arrays with individually addressable pixels is an important step toward useful high-resolution devices.

### Experimental Section

**Synthesis of  $Ru[(bpy)_3(BF_4)_2]$ :** Tris(2,2'-bipyridyl) ruthenium(II) chloride (Sigma–Aldrich, Inc.) and sodium tetrafluoroborate (Sigma–Aldrich, Inc.) were dissolved in Millipore water in separate beakers and heated to 95 °C. The aqueous sodium tetrafluoroborate solution was then added dropwise into the tris(2,2'-bipyridyl) ruthenium(II) chloride solution and stirred for 15 min at 95 °C. As the reaction mixture was slowly cooled to room temperature over a one-hour period, tris(2,2'-bipyridyl) ruthenium(II) tetrafluoroborate ( $Ru[(bpy)_3(BF_4)_2]$ ) crystals formed. After cooling the reaction mixture for another 20 min over an ice bath, the crystals were isolated and collected by vacuum filtration. Crystals were washed with ice-cold Millipore water and stored in a vacuum desiccator until they were used in the devices. 10 mg mL<sup>-1</sup> stock solutions of  $Ru[(bpy)_3(BF_4)_2]$  were prepared in acetonitrile prior to device patterning.

**Phase-Shifting Photolithography (PSP) on SU-8:** Composite PDMS masks patterned with 250-nm recessed posts spaced by

2 μm were prepared for PSP according to a procedure reported elsewhere.<sup>[8,9]</sup> PSP using these masks produced arrays of 250-nm holes in 150-nm-thick films of SU-8. This procedure included 1) spin-coating SU-8 2000 (diluted 1:2 with cyclopropanone) on ITO-coated glass slides at 4000 rpm for 40 s; 2) pre-baking the SU-8 at 95 °C for 1 min; 3) exposing the SU-8 through the PSP mask for 1 s; 4) post-baking the sample at 95 °C for 1 min; and 5) developing the SU-8 in propylene glycol monomethyl ether acetate for 2 min.

**Fabrication of the ITO line array:** Shipley 1805 photoresist was spin-cast onto ITO-coated glass slides. Phase-shifting photolithography was performed using a PDMS mask patterned with 15-μm lines spaced by 15 μm. After development in 351 developer, 350-nm lines of photoresist spaced by 15 μm remained on the ITO. The photoresist acted as an etch mask in a  $CH_4/H_2$  plasma. The ITO was etched at a rate of 10 nm min<sup>-1</sup> using flow rates of 5/25 sccm  $CH_4/H_2$  at a pressure of 11 mTorr and an rf power of 100 W. The photoresist was then lifted off by sonicating the samples in acetone and treating the residual organics with oxygen plasma to reveal lines of ITO that were 350-nm wide. The ITO was then cleaned by sonicating the samples for 5 min in Millipore water, acetone, dichloromethane, and absolute ethanol.

### Keywords:

electroluminescence • light-emitting diodes • nanolithography • optoelectronics

- [1] Z. L. Shen, P. E. Burrows, V. Bulovic, S. R. Forrest, M. E. Thompson, *Science* **1997**, 276, 2009.
- [2] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **1992**, 357, 477.
- [3] W. E. Howard, O. F. Prache, *IBM J. Res. Dev.* **2001**, 45, 115.
- [4] A. Lee, P. J. B. Burke, J. P. Brody, *Proc. SPIE-Int. Soc. Opt. Eng.* **2004**, 5331, 13.
- [5] M. Granstrom, M. Berggren, O. Inganäs, *Science* **1995**, 267, 1479.
- [6] F. A. Boroumand, P. W. Fry, D. G. Lidzey, *Nano Lett.* **2005**, 5, 67.
- [7] H. Yamamoto, J. Wilkinson, J. P. Long, K. Bussman, J. A. Christodoulides, Z. H. Kafafi, *Nano Lett.* **2005**, 5, 2485.
- [8] T. W. Odom, V. R. Thalladi, J. C. Love, G. M. Whitesides, *J. Am. Chem. Soc.* **2002**, 124, 12112.
- [9] T. W. Odom, J. C. Love, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Langmuir* **2002**, 18, 5314.
- [10] J. Henzie, J. E. Barton, C. L. Stender, T. W. Odom, *Acc. Chem. Res.* **2006**, 39, 249.
- [11] J. G. C. Veinot, H. Yan, S. M. Smith, J. Cui, Q. L. Huang, T. J. Marks, *Nano Lett.* **2002**, 2, 333.
- [12] F. G. Gao, A. J. Bard, *J. Am. Chem. Soc.* **2000**, 122, 7426.
- [13] H. Rudmann, M. F. Rubner, *J. Appl. Phys.* **2001**, 90, 4338.
- [14] H. Rudmann, S. Shimada, M. F. Rubner, *J. Am. Chem. Soc.* **2002**, 124, 4918.
- [15] G. Kalyuzhny, M. Buda, J. McNeill, P. Barbara, A. J. Bard, *J. Am. Chem. Soc.* **2003**, 125, 6272.
- [16] C. Y. Liu, A. J. Bard, *J. Am. Chem. Soc.* **2002**, 124, 4190.
- [17] C. Y. Liu, A. J. Bard, *Appl. Phys. Lett.* **2005**, 87, 061110.
- [18] T. W. Lee, J. Zaumseil, Z. N. Bao, J. W. P. Hsu, J. A. Rogers, *Proc. Natl. Acad. Sci. USA* **2004**, 101, 429.
- [19] T. W. Lee, S. Jeon, J. Maria, J. Zaumseil, J. W. P. Hsu, J. A. Rogers, *Adv. Funct. Mater.* **2005**, 15, 1435.
- [20] J. A. Rogers, Z. Bao, L. Dhar, *Appl. Phys. Lett.* **1998**, 73, 294.

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