Hybrid inorganic/organic microstructured light-emitting diodes produced using photocurable polymer blends

Sun, Handong; Dawson, M. D.; Mackintosh, A. R.; Gu, E.; Zhang, H. X.; Kuhne, A. J. C.;
Pethrick, R. A.; Belton, C.; Bradley, D. D. C.

2007

Gu, E., Zhang, H. X., Sun, H. D., Dawson, M. D., MackIntosh, A. R., Kuhne, A. J. C., et al. (2007).
Hybrid inorganic/organic microstructured light-emitting diodes produced using
photocurable polymer blends. *Applied Physics Letters*.

<https://hdl.handle.net/10356/91712>

<https://doi.org/10.1063/1.2431772>

Applied Physics Letters @ copyright 2007 American Institute of Physics

Downloaded on 26 Apr 2023 22:54:27 SGT

Hybrid inorganic/organic microstructured light-emitting diodes produced using photocurable polymer blends

E. Gu,^{a)} H. X. Zhang, H. D. Sun, and M. D. Dawson

Institute of Photonics, University of Strathclyde, 106 Rottenrow, Glasgow G4 0NW, United Kingdom

A. R. Mackintosh, A. J. C. Kuehne, and R. A. Pethrick

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

C. Belton and D. D. C. Bradley^{b)}

The Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2BZ, United Kingdom

(Received 1 October 2006; accepted 11 December 2006; published online 19 January 2007)

Light-emitting diodes (LEDs) in the form of a one-dimensional array of microstrips emitting at 370 nm were fabricated from AlInGa_N inorganic semiconductor. These microlight sources were then used to “directly write” microstructures in photocurable blends of organic light-emitting polymers (LEPs) spin coated onto the LED surface. In this way, thin microstrips of LEP as narrow as 50 μm have been fabricated and integrated with the micro-LEDs. These “self-aligned” polymer microstrips serve as wavelength downconverters under further excitation by the UV micro-LEDs, producing hybrid inorganic/organic microstructured LEDs. © 2007 American Institute of Physics. [DOI: 10.1063/1.2431772]

Inorganic group III-nitride semiconductor materials are showing great promise for development of compact solid-state light sources capable of operating from wavelengths in the green and blue down to as short as 210 nm in the deep ultraviolet (UV).¹ Using these materials, several groups including ours have fabricated micropixelated light-emitting diodes (micro-LEDs) in various formats, including two-dimensional arrays of microdisks and one-dimensional arrays of microstrips.^{2–7} Such devices, consisting of individual emitter elements of diameter/width typically $\sim 20\ \mu\text{m}$, on a typical pitch of 30–40 μm , are pattern-programmable microlight sources offering wide applicability in areas including miniature chemical and biological sensors and lab-on-a-chip devices.

In parallel to the development of AlInGa_N devices, tremendous progress has been made in organic electronic materials and devices such as light-emitting polymers (LEPs) and organic LEDs.⁸ These low-cost organic materials can be easily processed from solution and can be molecularly engineered to achieve different functionalities. It is anticipated that hybrid inorganic/organic optoelectronic devices will take full advantage of the optical and electronic properties of both inorganic and organic materials and offer a promising route to development of a range of low-cost and highly efficient light sources for scientific and instrumentation applications.

We have recently demonstrated hybrid inorganic/organic light-emitting devices showing full coverage of the visible spectrum and white-light emission.⁹ However, the polyfluorene organic component of these hybrid devices is in the form of an unpatterned film, which puts restrictions on the device miniaturization and functionality. Due to the recognized incompatibilities between the vast majority of functional organics such as LEPs and the chemicals used in conventional photolithography,¹⁰ fabricating microstructures in chemically sensitive organic materials presents a consider-

able technical challenge. In this work, we address this problem by blending the polyfluorene LEPs with host divinyl monomers that can be photoactivated with ultraviolet light, thus producing a blend which is photocurable and may also serve to isolate the LEP component from environmental effects. This offers the capability of forming LEP microstructures by “direct writing” from a scanned or microstructured UV illumination beam. The technique demonstrated here allows self-aligned fabrication of integrated hybrid devices, but is potentially widely applicable to the micropatterning of LEPs. Furthermore, it does not require the development of custom photocurable LEPs.¹¹

The inorganic component of our hybrid devices comprises a LED array, consisting of 120 individually addressable, parallel microstripe elements.⁶ These stripe micro-LEDs were fabricated from UV (370 nm) LED wafers containing InGa_N/AlGa_N quantum wells.^{5,6} A representative emission pattern (not true color) for such a UV microstripe LED device is shown in Fig. 1(a). By using a confocal microscope to take optical sections through the beam at successive distances from the emitter,^{12,13} the emission characteristics of individual micro-LED stripes can be determined. A measured beam profile of a microstripe LED taken in this way is shown in Fig. 1(b). The position of the LED stripes in cross section is indicated schematically in the figure. This image shows LED vertical emission both into the ambient downwards and up through the sapphire substrate. It can be seen that the LED ambient emission is concentrated at the LED surface and propagates directionally in an emission cone (full divergence angle of $\sim 80^\circ$), which facilitates the polymer direct writing.

To fabricate the hybrid inorganic/organic LED devices, the blue light-emitting poly(9,9-dioctylfluorene) (PFO) (Ref. 14) conjugated polymer in a 20 mg/ml solution of toluene was mixed with a divinyl functionalized monomer in solution. A concentration of PFO equivalent to 0.3 wt % (including solvent) relative to the monomer was found to achieve high curing definition. Other LEPs including blue-emitting

^{a)}Electronic mail: erdan.gu@strath.ac.uk

^{b)}Electronic mail: d.bradley@imperial.ac.uk

FIG. 1. (Color online) (a) Plan-view optical micrograph of an UV (370 nm) microstripe LED array, showing a pattern of one stripe on/three stripes off (not true color). (b) The vertical light emission profile of one of the microstripe LED elements.

poly(9,9-dioctylfluorene-*co*-9,9-di(4-methoxy) phenylfluorene) (F8DP) and the green-emitting poly(9,9-dioctylfluorene-*co*-benzothiadiazole) were also used to make photocurable blends for hybrid device fabrication. The polyfluorene LEP materials were selected for their high solid-state photoluminescence quantum efficiencies and their ability together to cover the entire visible spectrum.¹⁵

The polyfluorene/divinyl monomer mixture blend was spin coated (2000 rpm) directly on the surface of the UV microstripe LED device. Polymer microstructures were then formed by local photocuring using the individual micro-UV beams generated from the microstripe LED elements underneath the blend layer. For a single LED stripe, an injection current of 5.0 mA was used, which gave an optical output power of 18 μW. It was found that the definition of the polymer microstructure depends strongly on the curing time and overcuring can result in structure broadening. In this work, an optimized curing time of 0.5 s was used and under these conditions, the energy dose for polymer curing is estimated to be 15.7 mJ/cm². The unexposed regions of the blend layer were then removed by washing in toluene to leave a single integrated polymer stripe. The polymer microstructure fabricated in this way had a thickness of 20 μm.

During the photocuring process, the divinyl monomer undergoes cationic polymerization, induced by a strong Brønsted acid generated by photodecomposition of a photoacid generator (PAG). The PAG used here is a diaryl iodonium hexafluoroantimonate, with an optimal initiation wavelength of 251 nm. The optimal level of PAG incorporation in the PFO/divinyl monomer mixture was found to be 0.05 wt % relative to the monomer. The PFO has a strong

FIG. 2. (Color online) (a) Schematic diagram and (b) optical micrograph of a polymer microstripe directly "written" on top of an UV microstripe LED.

absorption peaking at around 390 nm. In this wavelength range, mixtures of either divinyl monomer/PAG or divinyl monomer/PFO do not undergo polymerization even with prolonged exposure. However, we find that the PFO/divinyl monomer/PAG mixture readily cures under 370 nm microstripe LED illumination, indicative of an interaction between PFO and PAG. This is considered to be a significant finding. The fast polymerization process (<1.0 s) in the blend has the advantage of restricting photoacid diffusion and thus enabling high-resolution curing. Furthermore, due to the low number of UV-absorbing polar and aromatic groups in the polymerized host polymer, quenching and solvatochromic effects on the LEP are minimized.¹⁶

A schematic diagram and micrograph of a polymer microstripe directly "written" on top of a LED stripe are shown in Figs. 2(a) and 2(b), respectively. Figure 2(b) shows that the resulting polymer stripe has a width of ~50 μm. This image also shows that the UV LED stripe which "wrote" the stripe pattern into the blend film is fully covered by the polymer stripe, demonstrating the capability of direct writing and self-alignment.

The automatically aligned polymer microstripes serve as wavelength converters, absorbing photons from the InGaN/AlGaIn quantum wells and then reemitting photons at longer wavelength (with the characteristic LEP spectrum), thus forming a hybrid inorganic/organic microstripe LED device. With PFO and F8DP light-emitting polymers, the hybrid microstripe LEDs emit in the blue spectral region. An image of an operating hybrid inorganic/organic microstripe LED is shown in Fig. 3 (not true color). Three adjacent microstripe LEDs are visible in the image. The uppermost is a turned on bare UV stripe LED, the middle one is a turned off bare UV stripe LED, and the lowest is a turned on hybrid

FIG. 3. (Color online) Optical micrograph (not true color) of an operating hybrid inorganic/organic microstripe LED device, showing a turned on bare stripe LED (top), a turned off bare stripe LED (center), and a turned on hybrid stripe LED (bottom).

FIG. 4. (Color online) (a) Normalized absorption spectrum (dash dot line) of a poly(9,9-dioctylfluorene) (PFO) film and emission spectrum (solid line) of an UV microstripe LED. (b) Emission spectra of a hybrid microstripe LED (solid line), a PFO film (dash dot line), and of the vinyl ether polymer (short dash line).

LEP blend/UV stripe LED. It is evident that the hybrid stripe produces a bright color-shifted emission, which is well defined (limited to the area defined by the underlying UV stripe LED). The uniformity of the color-shifted emission indicates that there is no gross phase separation during curing of the LEP/divinyl monomer blend.

The emission spectrum of a typical UV microstripe LED and the absorption spectrum of a PFO film were measured and are shown in Fig. 4(a). The narrow LED emission falls within the broad absorption band of PFO (peak at 390 nm), indicating that downconversion should be effective for this combination of materials. The small absorption peak of PFO at 435 nm is characteristic of chains in the β -phase conformation.¹⁷ The absorption spectrum of a cured PFO/divinyl monomer/PAG blend was also measured and was found to show the same absorption characteristics as the PFO film. The resulting emission spectrum for the hybrid microstructured LED device was measured and is shown in Fig. 4(b) together with the photoluminescence spectra of pure PFO excited at 390 nm and the vinyl ether polymer, produced by curing the divinyl monomer. The pure PFO emission spectrum contains photoluminescence from both the glassy and β phase,¹⁷ resulting in the shoulder at 424 nm from glassy PFO matrix and the observed peaks at 440, 468, 500, and 533 nm from β -phase chains.¹⁷ It is evident that the vinyl polymer alone shows negligible photoluminescence and that the emission characteristics of the hybrid micro-

stripe LED in the visible region closely match those of the pure PFO layer. The blending and photocuring processes do not, therefore, substantially alter the emission characteristics of the PFO within the organic microstripe of the hybrid device. Due to the low concentration of the PFO in the organic microstripe, combined with the high UV transparency of the vinyl ether polymer, the transmitted 370 nm emission is clearly seen in the emission spectrum of the hybrid LED device. This UV emission would allow further writing, for example, to create a multilayer microstructure for white light emission. Otherwise it would be possible to filter it with a variety of conventional polymer coatings.

In summary, we have demonstrated that well-defined microstructures of LEP wavelength conversion materials can be fabricated by self-aligned direct writing with an UV micro-LED light source. This technique provides an attractive approach to developing hybrid inorganic/organic micro-optoelectronic devices, for example, microscale light sources that can emit at wavelengths across the entire visible spectrum and that can generate programmable dynamic emission patterns by spatially and temporally selective pumping. The approach of self-aligned direct writing takes full advantage of the tunable chemical properties of polymer blend systems and offers the potential of dramatically reducing fabrication time while increasing complexity.

This research work is supported by the Research Councils UK Basic Technology Research Programme. The authors thank the Sumitomo Chemical Co. for supplying the polyfluorenes they have used.

- ¹Y. Taniyasu, M. Kasu, and T. Makimoto, *Nature (London)* **441**, 325 (2006).
- ²H. X. Jiang, S. X. Jin, J. Li, J. Shaky, and J. Y. Lin, *Appl. Phys. Lett.* **78**, 1303 (2001).
- ³I. Ozden, M. Diagne, A. V. Nurmikko, J. Han, and T. Takeuchi, *Phys. Status Solidi A* **188**, 139 (2001).
- ⁴S. Wu, S. Chhajed, L. Yan, W. H. Sun, M. Shatalov, V. Adivarahan, and M. Asif Khan, *Jpn. J. Appl. Phys., Part 2* **45**, L352 (2006).
- ⁵C. W. Jeon, H. W. Choi, E. Gu, and M. D. Dawson, *IEEE Photonics Technol. Lett.* **16**, 2421 (2004).
- ⁶H. X. Zhang, E. Gu, C. W. Jeon, Z. Gong, M. D. Dawson, M. A. A. Neil, and P. M. W. French, *IEEE Photonics Technol. Lett.* **18**, 1681 (2006).
- ⁷C. W. Jeon, E. Gu, and M. D. Dawson, *Appl. Phys. Lett.* **86**, 221105 (2005).
- ⁸R. 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. Logdlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).
- ⁹G. Heliotis, P. N. Stavrinou, D. D. C. Bradley, E. Gu, C. Griffin, C. W. Jeon, and M. D. Dawson, *Appl. Phys. Lett.* **87**, 103505 (2005).
- ¹⁰J. A. DeFranco, B. S. Schmidt, M. Lipson, and G. G. Malliaras, *Org. Electron.* **7**, 22 (2006).
- ¹¹C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhorn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, and K. Meerholz, *Nature (London)* **421**, 829 (2003).
- ¹²E. Gu, H. W. Choi, C. Liu, C. Griffin, J. M. Girkin, I. M. Watson, and M. D. Dawson, *Appl. Phys. Lett.* **84**, 2754 (2004).
- ¹³C. Griffin, E. Gu, H. W. Choi, C. W. Jeon, G. McConnell, J. M. Girkin, and M. D. Dawson, *Appl. Phys. Lett.* **86**, 041111 (2005).
- ¹⁴G. Heliotis, D. D. C. Bradley, G. A. Turnbull, and I. D. W. Samuel, *Appl. Phys. Lett.* **81**, 415 (2002).
- ¹⁵R. Xia, G. Heliotis, Y. B. Hou, and D. D. C. Bradley, *Org. Electron.* **4**, 165 (2003).
- ¹⁶D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 5th ed. (McGraw Hill, London, 1995), p. 5–7.
- ¹⁷M. Ariu, M. Sims, M. D. Rahn, J. Hill, A. M. Fox, D. G. Lidzey, M. Oda, J. Cabanillas-Gozalaz, and D. D. C. Bradley, *Phys. Rev. B* **67**, 195333 (2003).