Dye-Doped Mesostructured Silica as a Distributed Feedback Laser Fabricated by Soft Lithography**

By *Brian J. Scott*, *Gernot Wirnsberger*, *Michael D. McGehee*, *Bradley F. Chmelka*, and *Galen D. Stucky**

Self-assembled block co-polymer templated mesostructured silica (nanocomposites) produced under acidic conditions have recently attracted attention as potential optical materials.[1–10] They have several desirable properties such as easy processing that allows for a variety of useful structures for optical applications such as thin films,[3,4,11–15] fibers,[16,17] monoliths,[18–20] hierarchical ordering,[21] and micropatterns produced by soft lithography.[5,9,22] Further, these materials can be readily doped with a wide range of components such as organometallic complexes,[23] semiconducting nanocrystals,[24,25] semiconducting polymers,[26,27] and dyes.[5,7,8,28] Such host/guest nanocomposites combine the high stability of the inorganic host framework with the diversity of guest dopants, leading to versatile properties that are currently being explored to produce novel optical materials.

Previously, dye-doped mesostructures have demonstrated their utility as potential laser materials by displaying amplified spontaneous emission (ASE).[5,8] Further, their unique architectures, e.g., organic/inorganic phase separation on the nanometer scale, has allowed for higher active dye doping by suppressing concentration quenching.[29]

While characterizing ASE is a useful way to demonstrate that a material can amplify light, to make a laser it is necessary to incorporate the gain material into a cavity with resonant feedback. A simple way to produce a high Q laser cavity is to dip-coat an optical fiber or form a microdisk through photolithography.[6] Although these structures are easy to fabricate, they have the disadvantage that they emit light into a ring instead of a well-defined beam.[30] One way to make an in-plane laser with a well-defined output beam is to reflect light in a waveguide through the incorporation of a periodic modulation of refractive index or gain so that light is Bragg reflected. Lasers that operate by this type of grating-induced coupling are known as distributed feedback (DFB) lasers.[31,32] The lasing wavelength of a DFB laser is close to the Bragg wavelength, $\lambda_{Bragg} = 2n_{eff}\Lambda$ (n_{eff} is the effective refractive index of the waveguide and Λ is the period of the grating), and can be tuned by changing either n_{eff} or Λ. Single-mode DFB lasers are made when light is reflected through modulation of gain or by incorporating a phase shift. Dual-mode DFB lasers are obtained when Bragg reflection occurs through modulation of the refractive index with one mode just below and the other just above λ_{Bragg}.

Recently, DFB lasers have been made by etching gratings into a low-refractive-index substrate and then spin casting a conjugated polymer or evaporating small luminescent molecules over the grating.[30,33] The gratings were made by holographic lithography or precision photolithography and reactive ion etching, techniques that require expensive optical and clean room equipment. Over the past several years, alternative techniques to traditional lithography that are much less expensive and easier to perform, such as embossing, ink jet printing,[34] and soft lithography,[35,36] have been developed. Soft lithography uses elastomeric molds (stamps) to pattern materials. This technique can be used to make patterned structures with dimensions ranging in size from ~30 nm to over a centimeter and can be performed on non-planar substrates. Conventional lithography is used to make the mold, but once the mold is made many replica structures can be made from it. In this letter we report the use of soft lithography to fabricate an optically pumped rhodamine-6G-doped mesostructured silica DFB laser that has a moderately low lasing threshold (~55 kW/cm^2) and emission linewidths with a full width at half maximum (FWHM) of only 0.3 nm.

Figure 1 illustrates the fabrication steps for the DFB resonators. A typical master was fabricated by first spin-coating a standard photoresist, e.g., AZ 4110 (Clariant), onto a silicon wafer. The photoresist was first exposed in a conventional mask aligner through a photomask with a waveguide stripe pattern on it. Then, the photoresist was exposed to a holographic grating pattern that was generated by interfering two beams from a 325 nm wavelength He:Cd laser. The grating

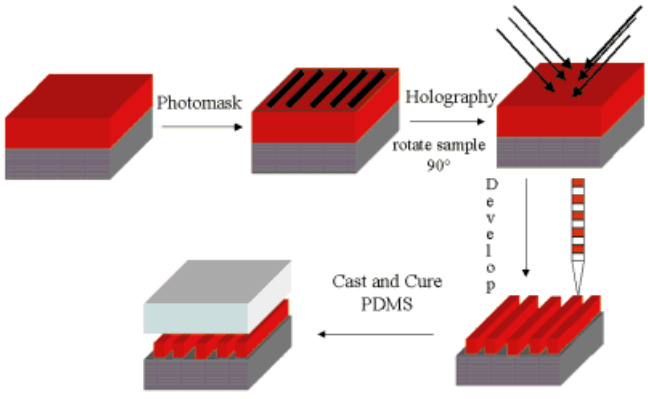

Fig. 1. Fabrication steps for DFB resonators.

[*] Prof. G. D. Stucky, B. J. Scott, Dr. G. Wirnsberger[+]
Department of Chemistry, University of California, Santa Barbara
Santa Barbara, CA 93106 (USA)
E-mail: stucky@chem.ucsb.edu
Dr. M. D. McGehee[++]
Department of Materials Science
University of California, Santa Barbara
Santa Barbara, CA 93106 (USA)
Prof. B. F. Chmelka
Department of Chemical Engineering
University of California, Santa Barbara
Santa Barbara, CA 93106 (USA)
[+] Current address: Department of Chemistry, Inorganic Chemistry, Karl-Franzens-University Graz, A-8010 Graz, Austria.
[++] Current address: Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305–2205, USA.

[**] This work was supported by the U.S. National Science Foundation under grant DMR 95–20971 and the U.S. Army Research Office under grant DAAH04–96–1-0443. It made use of the central facilities of the UCSB Materials Research Laboratory supported by the NSF under award DMR-9632716. G.W. is on leave from the Karl-Franzens-University Graz and acknowledges the Fonds zur Förderung wissenschaftlicher Forschung for an Erwin-Schrödinger scholarship (J1634-CHE). We thank Vojislav I. Srdanov for fruitful discussions.

 © WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 0935-9648/01/1608-1231 $ 17.50+.50/0

ADVANCED MATERIALS

grooves were arranged to be perpendicular to the waveguide stripes. The grating periods were set between 190–210 nm by varying the angle between the interfering laser beams. This wavelength regime was chosen so that first order reflections would occur in the waveguides. Due to the differences in photoresist sensitivities for the different wavelengths used in the two exposures, the holographic exposure was generally over 10 times longer. After the two exposures, the photoresist was developed. Grating depths were controlled through a combination of exposure and development times and could be varied between 4–40 nm (Fig. 2). Deeper gratings are principally possible but were not explored. From these photoresist patterns (masters), stamps were made by casting and curing polydimethylsiloxane (PDMS) onto the relief structures.[35,36]

The mesostructure precursor solution was made as follows: 3.5 g tetraethylorthosilicate (TEOS) was hydrolyzed by reaction with 1.3 g water (pH 1.3 with HCl) until the solution was homogenous. Separately, 1 g P123 [poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), ($EO_{20}PO_{70}$-EO_{20})] was dissolved in 10 g ethanol. The solutions were mixed, 20 mg rhodamine 6G was added, and stirred for an hour prior to use. The final molar composition TEOS/EtOH/H_2O/HCl/P123/dye was 1:18.2:6:0.005:0.014:0.0035.

For waveguiding in a thin film of a gain material to occur, the refractive index of the substrate, which acts as a cladding, should be lower than that of the gain layer. Ideally it should be much lower so that the light is well confined in the gain medium. Since the refractive index of our mesostructured films is between 1.4 and 1.5, we chose to use mesoporous silica, which has a refractive index of ~1.2, as a cladding layer to support the gain layer. The claddings, which were typically 1 μm thick, were deposited onto silicon wafers as described previously.[5]

When structures were made by MIMIC (micromolding in capillaries), both ends of a PDMS stamp were cut open and the stamp was placed in conformal contact with the substrate. A drop of the previously described sol–gel block copolymer dye solution was placed at one end and allowed to fill the microchannels by capillary flow. While gelation of the mesostructure precursors normally occurs within a few hours, the molds were generally left undisturbed overnight to allow for increased cross-linking and condensation of the silica framework. Finally, the stamp was removed and the substrate cleaved to produce smooth edges for optimal output and to remove thick film areas that occur where the substrate was not covered by the stamp.

The width of the waveguide stripes was controlled by the photomask and ranged in size from 2.5–50 μm. The length of the stripes was determined by the wafer cleaving and varied from several millimeters to over 1 cm. The heights of the ridge waveguide DFBs were controlled by choice of photoresist, in combination with spinning speed, and were varied from 0.9–2.5 μm. When wide short structures, e.g., 50 μm width by 1.1 μm tall, where made, sagging of the stamp occurred, causing the tops to be U-shaped. When structures are made with the proper aspect ratio, no sagging occurred.[35,36] However, even in the sagging structures, the Bragg reflector was successfully transferred and lasing was observed.

Previously, it has been demonstrated that mesostructures prepared by combining soft lithography and block copolymer templating results in long-range hexagonal order with the mesostructured channels lying parallel to the surface and along the direction of capillary flow.[5,22] Mesoscopic ordering was characterized by low angle X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD pattern (Fig. 3) shows only (*h*00) reflections consistent with a hexagonal mesophase, whose channels are aligned parallel to the substrate. The hexagonal mesophase is further confirmed by TEM of the calcined samples (Fig. 4), which shows free-standing cylinders viewed normal to the cylinder axis in the plane of the substrate.

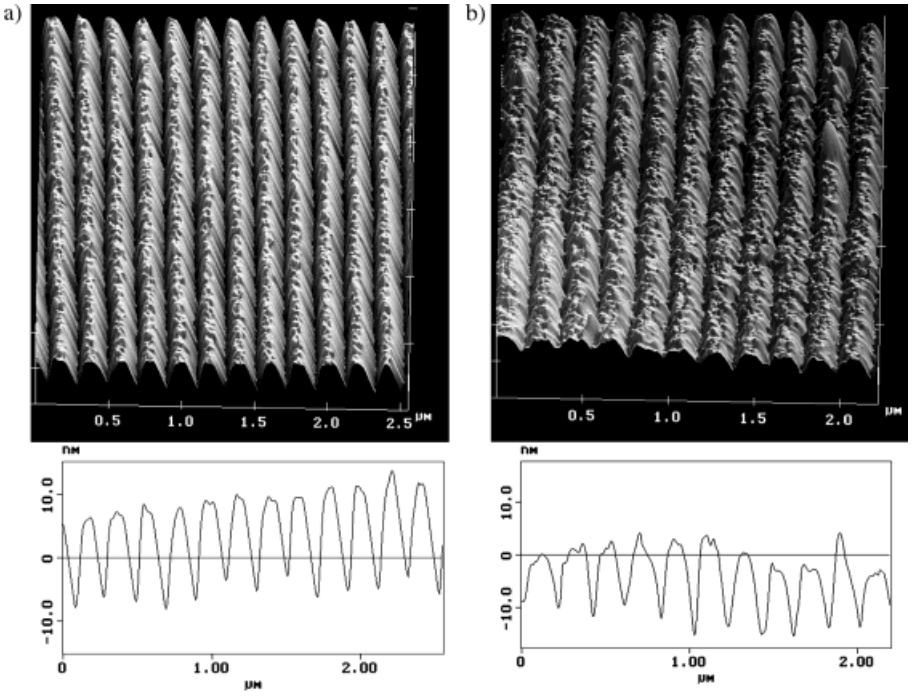

Fig. 2. a) AFM image and cross-sectional analysis of Bragg grating of photoresist DFB master. b) AFM image and cross-sectional of Bragg grating of rhodamine 6G doped mesostructured silica ridge DFB waveguide.

Samples were optically pumped with a frequency-doubled neodymium–yttrium–aluminum–garnet (Nd:YAG) laser at 532 nm, 10 Hz pump frequency, and 10 ns pulse widths. The energy of the pulses was controlled using a set of calibrated neutral density filters. An adjustable slit and cylindrical lens were used to shape the beam into a stripe 1.5 mm × 0.5 mm. Samples were pumped at

 © WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 0935-9648/01/1608-1232 $ 17.50+.50/0

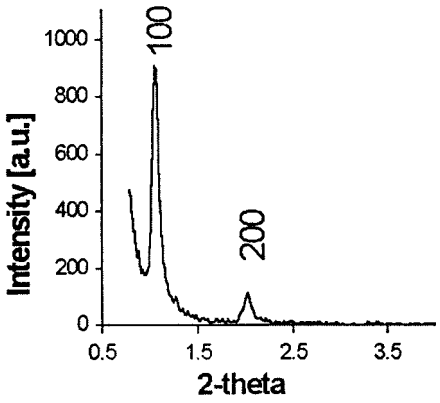

Fig. 3. X-ray diffraction pattern of rhodamine 6G doped mesostructured silica ridge DFB waveguide.

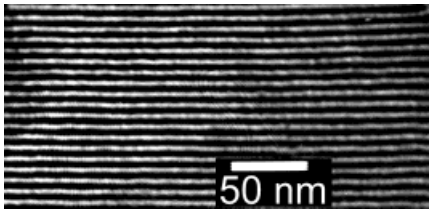

Fig. 4. TEM micrograph of calcined rhodamine 6G doped mesostructured silica ridge DFB waveguide.

normal incidence with the long direction of the stripe perpendicular to the grooves in the ridge waveguides. The light emitted from the edge was detected with a monochromator (600 grooves/mm) and liquid-nitrogen cooled charge coupled device (CCD) detector. Scattered light from the pump laser was suppressed by a 532 nm notch filter.

The edge emission intensity versus the pump intensity, along with the corresponding spectrum are shown in Figure 5a, for a hexagonal mesostructured silica waveguide containing 1 wt.-% rhodamine 6G. Below the threshold, the emission is characteristic of spontaneous emission and broad, ~60 nm. Once the threshold is reached, ~55 kW/cm^2, the emission is dominated by a few lines that have FWHM of 0.3 nm. The n_{eff} of the waveguides can be calculated from the Bragg equation and atomic force microscopy (AFM) measurements of the grating period. For the sample shown in Figure 5a, whose period is 200 nm, n_{eff} is calculated to be ~1.40 and compares well to the measured value of 1.43.[5]

Although we observed spectra with as few as three lasing modes, in most samples, 4 to 5 modes occur (Fig. 5b). Multimode behavior most likely results for one of two possible phenomena. The first is that slight distortions may occur in the grating period over the pumped region from either the master/stamp reproduction or from the transfer of the pattern by the stamps to the mesostructure. To produce the first-order Bragg grating used to provide feedback in these samples, a small period is required, ~200 nm. While soft lithography has successfully fabricated structures smaller than 200 nm, single-mode lasing places stringent requirements on exact periodicity and small deformations associated with soft lithography could change the grating period enough to observe this

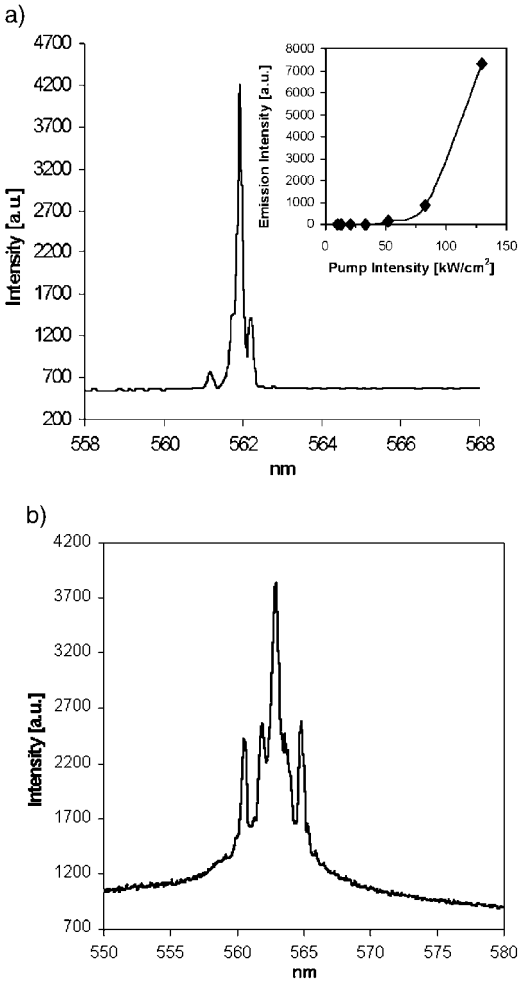

Fig. 5. a) DFB lasing spectrum of a 1% rhodamine 6G doped mesostructured silica ridge waveguide with power dependence as a function of pump intensity shown in the inset. b) DFB lasing spectrum of a typical sample.

behavior.[37] For example, a grating variation from 200 nm to 202 nm could produce the range of peaks observed in Figure 5b. Previous studies on stamped organic DFBs used higher order gratings, and therefore longer periods, and still observed multimode mode behavior in many samples.[38,39] Secondly, the large size of the excitation beam simultaneously excites multiple waveguides. For example, in Figure 5b each waveguide is 3 μm wide and separated by 4 μm so a 0.5 mm wide excitation strip would excite ~72 DFBs. Therefore, if there is a small difference between each waveguide DFB, then multiple emission peaks would be observed.

In summary, we have demonstrated a simple technique to produce dye-doped mesostructured DFB lasers. The lasers exhibited multimode lasing with FWHM < 0.3 nm and had a threshold of ~55 kW/cm^2. The technique employs low-cost stamping methods that are capable of replicating features of only a few hundred nanometers, a requirement for producing a first-order grating. Furthermore, the masters were fabricated through hierarchically patterning photoresist that does not require etching or metal depositions.

Received: March 30, 2001
Final version: April 4, 2001

 © WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 0935-9648/01/1608-1233 $ 17.50+.50/0

ADVANCED MATERIALS

[1] D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.
[2] D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
[3] D. Y. Zhao, P. D. Yang, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Chem. Commun.* **1998**, 2499.
[4] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380.
[5] P. D. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto, G. D. Stucky, *Science* **2000**, *287*, 465.
[6] G. Wirnsberger, G. D. Stucky, *Chem. Mater.* **2000**, *12*, 2525.
[7] G. Wirnsberger, B. J. Scott, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **2000**, *12*, 1450.
[8] F. Marlow, M. D. McGehee, D. Y. Zhao, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1999**, *11*, 632.
[9] H. Y. Fan, Y. F. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, V. Perez-Luna, G. P. Lopez, C. J. Brinker, *Nature* **2000**, *405*, 56.
[10] D. A. Doshi, N. K. Huesing, M. C. Lu, H. Y. Fan, Y. F. Lu, K. Simmons-Potter, B. G. Potter, A. J. Hurd, C. J. Brinker, *Science* **2000**, *290*, 107.
[11] C. J. Brinker, Y. F. Lu, A. Sellinger, H. Y. Fan, *Adv. Mater.* **1999**, *11*, 579.
[12] R. Ryoo, C. H. Ko, S. J. Cho, J. M. Kim, *J. Phys. Chem. B* **1997**, *101*, 10 610.
[13] M. Ogawa, *Chem. Commun.* **1996**, 1149.
[14] H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *Nature* **1996**, *381*, 589.
[15] H. Yang, A. Kuperman, N. Coombs, S. Mamicheafara, G. A. Ozin, *Nature* **1996**, *379*, 703.
[16] P. D. Yang, D. Y. Zhao, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **1998**, *10*, 2033.
[17] Q. S. Huo, D. Y. Zhao, J. H. Feng, K. Weston, S. K. Buratto, G. D. Stucky, S. Schacht, F. Schuth, *Adv. Mater.* **1997**, *9*, 974.
[18] N. A. Melosh, P. Lipic, F. S. Bates, F. Wudl, G. D. Stucky, G. H. Fredrickson, B. F. Chmelka, *Macromolecules* **1999**, *32*, 4332.
[19] P. Y. Feng, X. H. Bu, G. D. Stucky, D. J. Pine, *J. Am. Chem. Soc.* **2000**, *122*, 994.
[20] G. S. Attard, J. C. Glyde, C. G. Goltner, *Nature* **1995**, *378*, 366.
[21] P. D. Yang, T. Deng, D. Y. Zhao, P. Y. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244.
[22] M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides, I. A. Aksay, *Nature* **1997**, *390*, 674.
[23] M. Ogawa, T. Nakamura, J. Mori, K. Kuroda, *J. Phys. Chem. B* **2000**, *104*, 8554.
[24] V. I. Srdanov, I. Alxneit, G. D. Stucky, C. M. Reaves, S. P. DenBaars, *J. Phys. Chem. B* **1998**, *102*, 3341.
[25] O. Dag, G. A. Ozin, H. Yang, C. Reber, G. Bussiere, *Adv. Mater.* **1999**, *11*, 474.
[26] T. Q. Nguyen, J. J. Wu, V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652.
[27] J. J. Wu, A. F. Gross, S. H. Tolbert, *J. Phys. Chem. B* **1999**, *103*, 2374.
[28] C. E. Fowler, B. Lebeau, S. Mann, *Chem. Commun.* **1998**, 1825.
[29] G. Wirnsberger, P. D. Yang, H. C. Huang, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, *J. Phys. Chem. B*, in press.
[30] A. Dodabalapur, M. Berggren, R. E. Slusher, Z. Bao, A. Timko, P. Schiortino, E. Laskowski, H. E. Katz, O. Nalamasu, *IEEE J. Sel. Top. Quantum Electron.* **1998**, *4*, 67.
[31] L. A. Coldren, S. W. Corzine, *Diode Lasers and Photonic Integrated Circuits*, Wiley, New York **1995**.
[32] H. Kogelnik, C. V. Shank, *Appl. Phys. Lett.* **1971**, *18*, 152.
[33] M. D. McGehee, M. A. DiazGarcia, F. Hide, R. Gupta, E. K. Miller, D. Moses, A. J. Heeger, *Appl. Phys. Lett.* **1998**, *72*, 1536.
[34] T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, J. C. Sturm, *Appl. Phys. Lett.* **1998**, *72*, 519.
[35] Y. N. Xia, G. M. Whitesides, *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.
[36] Y. N. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 551.
[37] J. A. Rogers, K. E. Paul, G. M. Whitesides, *J. Vac. Sci. Technol. B* **1998**, *16*, 88.
[38] J. A. Rogers, M. Meier, A. Dodabalapur, *Appl. Phys. Lett.* **1998**, *73*, 1766.
[39] J. A. Rogers, M. Meier, A. Dodabalapur, E. J. Laskowski, M. A. Cappuzzo, *Appl. Phys. Lett.* **1999**, *74*, 3257.

Modification of Indium Tin Oxide for Improved Hole Injection in Organic Light Emitting Diodes**

By *Yulong Shen*, *Daniel B. Jacobs*, *George G. Malliaras*,* *Goutam Koley*, *Michael G. Spencer*, and *Andronique Ioannidis*

Organic light emitting diodes (OLEDs) represent a very promising technology for flat panel displays and are already appearing in consumer electronics products such as car stereos and cell phones. The ease of fabrication, robustness, high efficiency, and small weight and thickness are major advantages over competing technologies, such as liquid crystals. A large research effort in both academia and industry is focused on understanding the device physics and improving their efficiency and lifetime.

In its simplest case, an OLED consists of one or more organic semiconductor layers sandwiched between two metal electrodes, one with a high (anode) and one with a low (cathode) work function. Upon application of forward bias, electrons and holes are injected from the cathode and the anode respectively and recombine inside the organic layer(s) producing light emission.[1] The process of charge injection is of fundamental importance, as it can control the electrical characteristics and/or the efficiency of the device.[2] A great deal of contemporary research addresses various aspects of metal/organic interfaces, such as morphology,[3,4] energetics,[5–11] and charge transport.[12–15] Modification of interfaces has also received considerable attention; especially on the cathode side of the device where the need to replace low work function metals, such as Ca, with more stable ones, such as Al, is pressing. The bulk of the work has been carried out on ultrathin layers of LiF, CsF, and low work function metals inserted between the organic and Al to produce OLEDs with higher efficiency than those with Al cathodes alone.[16–19]

On the anode-side of the device, indium tin oxide (ITO) seems to be the electrode of choice. Although it comes with its own set of problems, such as a large variation in properties depending on preparation,[20,21] release of indium and oxygen into the organic layer,[22] and poor compatibility with some organic materials,[4] it offers a combination of transparency and conductivity that is hard to replace. Modification of ITO

[*] Prof. G. G. Malliaras, Y. Shen, D. B. Jacobs
Materials Science and Engineering, Cornell University
Ithaca, NY 14853 (USA)
E-mail: george@ccmr.cornell.edu
G. Koley, Prof. M. G. Spencer
School of Electrical and Computer Engineering, Cornell University
Ithaca, NY 14853 (USA)
Dr. A. Ioannidis
Corporate Strategic Services, Xerox Corporation
800 Phillips Road, Webster, NY 14580 (USA)

[**] This work was supported by the Cornell Center for Materials Research (CCMR), a Materials Research Science and Engineering Center of the National Science Foundation (DMR-9632275).

 © WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 0935-9648/01/1608-1234 $ 17.50+.50/0