DOI: 10.1002/adma.200501158

Positive/Negative Arrays of Organic Light-Emitting Diodes by a Surface-Tension-Driven Approach**

By Ilenia Viola,* Marco Mazzeo, Alessandra Passabì, Stefania D'Amone, Roberto Cingolani, and Giuseppe Gigli

Patterning molecular materials is a challenge motivated by the recent development of organic optoelectronic and electronic devices, such as organic light-emitting diodes (OLEDs),^[1,2] field-effect transistors (FETs),^[3,4] and organic lasers.^[5] The size reduction of organic devices requires unconventional lithographic techniques that have to preserve the optical and conductive properties of the materials.^[6–10] The fabrication of micro/nanostructures thus becomes crucial in several applications, such as full-color displays, where improvement in resolution and efficiency requires an increase of the pixel integration,^[11] and in lighting panels, where the spread of dark spots in time strongly affects the device performance.^[12]

Two different approaches are possible for patterning organic compounds, namely the top-down and the bottom-up approaches. The former includes lithographic techniques such as nanoimprinting and soft embossing,^[13,14] which employ a stamp or a mould to transfer a prepatterned structure onto a bulk organic layer. Such techniques are characterized by a high resolution, which is limited by the size of the master structures, though they usually require high-temperature processes which, in combination with oxygen exposure, may affect the physical-chemical properties of the materials.^[15]

In order to avoid such problems, the imprinting procedures have to be carried out in a controlled atmosphere or under high vacuum, thus requiring expensive and complex experimental systems.^[16,17]

Techniques utilizing a bottom-up approach, such as dewetting^[18,19] and microcontact printing,^[20] exploit the peculiar characteristics of molecular materials, such as self-assembly and recognition capability, to allow the formation of molecular structures by spontaneous aggregation due to free-energy minimization-induced processes. Moreover, the combination

of external and internal forces with geometrical constraints can lead to well-defined pattern replication,^[21–24] which may find a wide range of strategic applications in optoelectronic or biological devices.^[25] Recent studies of Karthaus et al. have shown how a random microdome array of OLEDs can be fabricated by a controlled dewetting process.^[26]

In this paper, we present a surface-tension-driven technique to pattern molecular arrays of electroluminescent compounds by using a metallic grid to induce the geometrical confinement. Such a technique enables the controlled replication of the micrometer-scale template, thus allowing the fabrication of arrays of OLED pixels of a well-defined geometry. The principle of this approach is the controlled dewetting of the molecular compounds in the feature of the template, allowing us to realize either negative or positive patterns.

Dewetting occurs when a drop of liquid forms a finite contact angle with a substrate.^[27] In order to quantify a dewetting process, the spreading coefficient $S = \gamma_s - \gamma_l - \gamma_{ls}$ is usually introduced. It is a function of the surface tension, γ , where s , l , and ls label the surface tensions of the substrate, liquid, and liquid–solid interface, respectively. $S < 0$ indicates a dewetting process favored by long-range forces (such as van der Waals' forces) that enhance fluctuations at the liquid thickness. $S > 0$ occurs for wettable surface where the thickness fluctuations of the liquid film are restoring and the film is stable.^[19,28]

A liquid thin film on a non-wetting surface undergoes instability phenomena, mainly driven by polar (i.e., hydrogen bonds) and apolar forces (i.e., van der Waals' and dispersion forces), and by variations of the surface tension with temperature and/or liquid composition (Marangoni-type transport).^[29–31] In the case of volatile liquids, dewetting is initiated by solvent evaporation and the breaking of homogeneous thin films. This breaking is expected to occur both by heterogeneous nucleation and spinodal decomposition phenomena. The first starts almost immediately and acts as a mechanism for hole nucleation in the presence of substrate defects or spurious particles in the liquid film. After some time, the amplification of surface instabilities at the liquid interface proceeds with a spontaneous breaking of symmetry (spinodal dewetting), which is driven in thin films ($h < 100$ nm) by attractive van der Waals' interactions.^[18] These two nucleation events develop with a transport of materials towards the receding rims surrounding the holes, because of the pinning of the contact line in order to compensate for the evaporation.^[32]

It is known that the beginning of a dewetting process, as well as the morphology or the pattern roughness, are usually strongly influenced by several parameters such as surface tension, substrate polarity, solvent-evaporation rate, and solvent dipole moment.^[33,34] In the technique reported here, the selective control of these parameters, through a suitable choice of the solvent polarity and the evaporation rate, allows us to modify the pattern size and geometry of the final device, by selectively choosing the characteristics of the materials used.

Figure 1 displays the procedure for creating a molecular pattern by self organization, under dewetting experimental

[*] Dr. I. Viola, Dr. M. Mazzeo, Dr. A. Passabì, Dr. S. D'Amone, Prof. R. Cingolani, Prof. G. Gigli
National Nanotechnology Laboratory
Istituto Nazionale di Fisica della Materia and
Centro Nazionale delle Ricerche
Istituto Superiore Universitario di Formazione
Interdisciplinare-sezione Nanoscienze
via Arnesano, I-73100 Lecce (Italy)
E-mail: ilenia.viola@unile.it

[**] The authors gratefully acknowledge M. Cavallini and F. Biscarini (CNR-ISMN Bologna, Italy) for useful discussions.

Figure 1. Sketch of the surface-tension-driven procedure used for patterning a molecular layer: a drop of a dilute solution of volatile solvent (CHCl_3 or acetone) is placed in the centre of a template mesh set on a ITO/glass substrate (a); after solvent evaporation, the organic molecules (*N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine; TPD) move under the mesh for solutions of CHCl_3 (b), whereas by using the quite polar acetone the complementary array is obtained (c). The self-organized pattern reproduced on the substrate (d) was used to fabricate an array of OLEDs (e).

conditions, on indium tin oxide (ITO)-covered glass. We employed a copper grid with 40 μm wide square holes and 20 μm wide bars as the template. In addition, we chose two organic molecules, namely TPD and 8-hydroxyquinoline aluminium salt (AlQ_3), both of which are commonly used in light-emitting devices by virtue of their excellent hole-injecting and electron-transporting/emissive properties, respectively.

After fixing the grid onto the ITO/glass substrate, 1 μL of a chloroform solution of TPD was dropped onto the grid (see Fig. 1a). In order to avoid any distortion of the pattern from deformation of the template, the grid perimeter was fastened by a suitable metallic gasket to allow both the solution to be dropped in the center of the template and to keep it in position during evaporation. After complete evaporation of the solvent, the grid was removed and a TPD layer under the grid was obtained (see Figs. 1b,c). The confinement of the molecular material under the template mesh is due to the interplay between the characteristic parameters of the solution and the two solid interfaces (ITO and the Cu grid).^[23,24,33]

The molecular self-organized layer of TPD was characterized by optical microscopy in transmission mode, in order to check the geometrical assembly and the pattern reproducibility (see Fig. 2a). All the observed features are strongly connected to the solvent properties, namely surface tension, polarity, evaporation rate, and vapor pressure, which govern the behavior at the liquid–solid interface. For example, by using a quite polar solvent such as acetone, a complementary array with the materials confined inside the mesh squares is obtained (see Figs. 1c,2b). The different modulations of the patterned surface are shown diagrammatically in Figures 1b,c.

Figure 2. Optical images of the patterns on an ITO/glass substrate. Pattern (a) shows a template under the bar of TPD in CHCl_3 . In pattern (b) the polarity of acetone allows a complementary deposition to be obtained.

tained (see Figs. 1c,2b). The different modulations of the patterned surface are shown diagrammatically in Figures 1b,c.

The results indicate that our lithographic approach can be considered as the bottom–up alternative to the choice of a negative/positive resist in top–down photolithography.^[13] The role of the photoresist, i.e., its chemical properties and sensitivity to UV-light exposure, are played, in this case, by the liquid–solid interface characteristics.

Atomic force microscopy (AFM), in semicontact mode, was employed to characterize the morphology of the single structure (Fig. 3a). As shown in Figures 3a,b, the pattern made by the CHCl_3 solution reproduces the original template's grid, with a U-shaped homogeneous profile and an average height of about 400 nm. The U-shaped film profile is a result of the liquid flow towards the edges of the replicated structures to compensate for the volume reduction and to keep the liquid–solid contact line constant during solvent evaporation (Fig. 4).^[32,35] A remaining ring-like deposit of TPD, with a smaller maximum height of 100 nm, is also observed inside the grid holes.

More importantly, the self-organization procedures are not affected by heating, so the solid-state properties of the involved materials remain intact. As an example, the photoluminescence (PL) spectra of spin-coated TPD films and TPD structures after the dewetting process are reported: the differences are negligible (Fig. 5).

As a practical demonstration, we applied the deposition technique to the fabrication of two complementary OLED arrays, both positive and negative. To this aim, we thermally evaporated 50 nm of AlQ_3 onto the TPD negative/positive

Figure 3. a) AFM image of a TPD molecular array obtained with a chloroform solution under non-wetting experimental conditions; b) the structure reveals a U-shaped profile due to the confinement of material at the rims, and a shorter ring-like deposit of TPD, inside the grid holes.

Figure 4. During the evaporation flux of a liquid drop, the profile is reduced to prevent shrinkage of the drop by pinning the contact line. The consequent effect is an outward flow of the solute dispersed in the fluid and thus a U-shaped profile.

patterned layers, to act as an electron-transporting and active material (see Figs. 1d,e). Finally, electrodes were deposited by the subsequent evaporation of 50 nm of calcium and 150 nm of aluminum, respectively. Figure 1e represents a sketch of the complete device.

Figure 6 shows the resulting positive and negative microarrays of OLEDs in the on and off state. In Figure 6b, the green-light emission originates from areas delimited by

Figure 5. PL spectra of a TPD array (■), obtained by the dewetting process, and of an unpatterned TPD layer (continuous line), deposited by spin coating. It can be observed that patterning does not substantially modify the emission properties.

the grid, where 50 nm of AlQ_3 have been deposited on the 100 nm layer of TPD. No emission is detected from the grid regions, where the 400 nm thick TPD structure is present. The negative device, in Figure 6d, exhibits the electroluminescence (EL) intensity from the grid template. For both devices, low emission has been also detected from reference unpatterned areas where the AlQ_3 has been deposited directly onto the ITO substrate (data not reported).

A thin layer (50–100 nm) of TPD enhances the charge recombination between holes and electrons compared with a standard single-layer device. Nevertheless, since the OLED current density, J , is proportional to $d^{-(2n+1)}$ (where d is the thickness of the organic layers and $n > 1$), J will be drastically reduced if this layer is too thick. The profile of TPD in the positive pattern (see Figs. 3a,b) suggests that the bars of the grid act as electrically insulating spacers due to the greater thickness (400 nm) of the layer. Instead, in the middle of the holes of the grid, the less-thick layer of TPD (less than 100 nm) allows good charge recombination. On the other side, along the edges where the thickness of TPD is negligible, the brightness of the device is lower due to the poor hole injection and electron–hole recombination. This is confirmed by the EL intensity distribution. The maximum intensity is observed in the middle of the grid holes and decreases towards the edges (Fig. 6b), and no emission is observed from the grid bars. For the negative pattern, the light emission is strongly enhanced along the bars among the TPD-patterned squares (Fig. 6d).

In conclusion, an ordered and controlled microarray of isolated organic electroluminescent pixels fabricated by a surface-tension-driven technique is reported. The molecular TPD-patterned layer was realized by taking advantage of the combination of both liquid instability, following the dewetting phenomena, and geometrical confinement, induced by a template mesh.

The main advantages of this surface-tension-driven technique for OLED-array fabrication are the flexibility, the ease of realization, and the absence of any lithographic step that can damage the involved materials. Both the resolution and the geometry of the pattern can be modulated in a controlled

Figure 6. Optical images of the a,b) positive and c,d) negative OLED arrays; (a) and (c) are the images of the off device; (b) and (d) are the images of the devices switched on with a 10 V bias.

way by varying the solvent properties at the liquid–solid interface, and by using external constraints, such as elastomeric stamps with submicrometer features.

Experimental

Microstructure Fabrication: Molecular pixel microarrays were realized by using a micropipette (Pipet-Lite SL-2 Rainin) to deposit 1 μL of 0.1 % (w/v) of freshly prepared volatile solutions of TPD (Sigma–Aldrich) in chloroform (CHCl_3) and acetone ($\text{C}_3\text{H}_6\text{O}$) on a metallic template fixed onto an ITO-covered glass substrate (Vision Tek Systems LTD).

Before use, the substrates were cleaned in an ultrasonic bath by three different solvents, namely: acetone, isopropyl alcohol, and de-ionized water (10 min for each step). As the template for geometrical confinement, a transmission electron microscopy (TEM) calibration copper grid (400 mesh) with 40 μm wide square holes and 20 μm wide bars was used. The morphology of the molecular patterned structures were characterized by optical microscopy (Vanox AHMT3, Olympus) and by AFM (Solver Pro, NT-MDT) in a semicontact mode. PL measurements were performed on a spectrophotometer (Eclipse, Varian).

OLED Fabrication: AlQ_3 (50 nm) was deposited by thermal evaporation (rate = $3\text{--}5 \text{ \AA s}^{-1}$) on the patterned layer of TPD. Calcium (50 nm) was then deposited as a cathode followed by 150 nm of aluminum as a capping layer. All the layers were evaporated at a pressure of 10^{-6} mbar (1 mbar = 10^2 Pa). The OLED array was biased with

a direct current voltage of 10 V and the EL collected by a charge-coupled device (CCD) color camera coupled to a confocal laser scanning microscope (FluoView1000, Olympus).

Received: June 6, 2005

Final version: August 4, 2005

Published online: October 31, 2005

- [1] C. W. Tang, S. A. Van Slyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
- [2] C. W. Tang, S. A. Van Slyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3610.
- [3] F. Dinelli, M. Murgia, P. Levy, M. Cavallini, F. Biscarini, D. M. De Leeuw, *Phys. Rev. Lett.* **2004**, *92*, 116802.
- [4] M. L. Chabinyc, W. S. Wong, K. E. Paul, R. A. Street, *Adv. Mater.* **2003**, *15*, 1903.
- [5] N. Tessler, G. J. Denton, R. H. Friend, *Nature* **1996**, *382*, 695.
- [6] K. Kargupta, A. Sharma, *Langmuir* **2002**, *18*, 1893.
- [7] M. Cavallini, M. Murgia, F. Biscarini, *Nano Lett.* **2001**, *1*, 193.
- [8] M. Brinkmann, S. Graff, F. Biscarini, *Phys. Rev. B* **2002**, *66*, 165430.
- [9] J. T. Rantala, G. E. Jabbour, J. Vahakangas, S. Honkanen, B. Kippelen, N. Peyghambarian, *Jpn. J. Appl. Phys., Part 2* **1998**, *37*, 1098.
- [10] S. Noach, E. Z. Faraggi, G. Cohen, Y. Avny, R. Neumann, D. Davidov, A. Lewis, *Appl. Phys. Lett.* **1996**, *69*, 3650.
- [11] T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, J. C. Sturm, *Appl. Phys. Lett.* **1998**, *72*, 519.
- [12] H. Aziz, Z. Popovic, S. Xie, A. M. Hor, N. X. Hu, C. Trip, G. Xu, *Appl. Phys. Lett.* **1997**, *72*, 756.
- [13] Y. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 550.
- [14] M. Geissler, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 1249.

- [15] H. C. Scheer, H. Schulz, T. Hoffmann, C. M. S. Torres, *J. Vac. Sci. Technol. B* **1998**, *16*, 3917.
- [16] D. Pisignano, A. Melcarne, D. Mangiullo, R. Cingolani, G. Gigli, *J. Vac. Sci. Technol. B* **2004**, *22*, 185.
- [17] D. Pisignano, L. Persano, R. Cingolani, G. Gigli, *Appl. Phys. Lett.* **2004**, *84*, 1365.
- [18] A. Sharma, *Langmuir* **1993**, *9*, 861.
- [19] A. Faldi, R. J. Composto, K. I. Winey, *Langmuir* **1995**, *11*, 4855.
- [20] X. M. Zhao, Y. Xia, G. M. Whitesides, *J. Mater. Chem.* **1997**, *7*, 1069.
- [21] S. Harkema, E. Schäffer, M. D. Morariu, U. Steiner, *Langmuir* **2003**, *19*, 9714.
- [22] M. Cavallini, F. Biscarini, M. Massi, A. Farran-Morales, D. A. Leigh, F. Zerbetto, *Nano Lett.* **2002**, *2*, 635.
- [23] M. Cavallini, F. Biscarini, *Nano Lett.* **2003**, *3*, 1269.
- [24] M. Massi, M. Cavallini, S. Stagni, A. Palazzi, F. Biscarini, *Mater. Sci. Eng., C* **2003**, *23*, 923.
- [25] S. Herminghaus, A. Fery, S. Schlagowski, K. Jacobs, R. Seemann, H. Gau, W. Mönch, T. Pompe, *J. Phys.: Condens. Matter* **2000**, *12*, A57.
- [26] O. Karthaus, C. Adachi, S. Kurimura, T. Oyamada, *Appl. Phys. Lett.* **2004**, *84*, 4697.
- [27] T. G. Stange, D. F. Evans, W. A. Hendrickson, *Langmuir* **1997**, *13*, 4459.
- [28] F. Brochard-Wyart, J. Daillant, *Can. J. Phys.* **1990**, *68*, 1084.
- [29] M. Maillard, L. Motte, M. P. Pileni, *Adv. Mater.* **2001**, *13*, 200.
- [30] O. Karthaus, L. Grasjo, N. Maruyama, M. Shimomura, *CHAOS* **1999**, *9*, 308.
- [31] O. Karthaus, T. Koito, M. Shimomura, *Mater. Sci. Eng., C* **1999**, *8*, 523.
- [32] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten, *Nature* **1997**, *389*, 827.
- [33] J. Zhao, S. Jiang, Q. Wang, X. Liu, X. Ji, B. Jiang, *Appl. Surf. Sci.* **2004**, *236*, 131.
- [34] L. M. Pismen, *Phys. Rev. E* **2004**, *70*, 021 601.
- [35] X. Wang, M. Östblom, T. Johansson, O. Inganäs, *Thin Solid Films* **2004**, *449*, 125.

DOI: 10.1002/adma.200500184

Laser Scanning Lithography for Surface Micropatterning on Hydrogels**

By Mariah S. Hahn, Jordan S. Miller, and Jennifer L. West*

Techniques that control the spatial presentation of moieties such as cell-adhesion peptides on surfaces are important for the advancement of tissue engineering, the elucidation of fundamental tissue structure–function relationships, and the for-

mation of immobilized cell and protein arrays for biotechnology.^[1] Cell and protein patterns have previously been created using a range of methods, including photolithography^[2,3] and soft-lithographic approaches such as microcontact printing,^[4] microfluidic patterning,^[5,6] and micromolding.^[7,8] The patterned substrates have generally been modified silicon or glass,^[9,10] whereas surface patterning of deformable, solvated substrates has not received a similar degree of attention. Many commonly used patterning techniques cannot be readily applied to high-fidelity patterning of deformable, solvated substrates. For example, microcontact printing is generally not applicable to such substrates due to lateral diffusion of the patterned molecule when the inked stamp comes into contact with the solvated substrate. Given the importance of deformable, solvated substrates, such as hydrogels, as scaffolds for soft tissue engineering applications, development of methods for direct, high-fidelity surface patterning of these substrates is desirable. This work develops confocal-based laser scanning lithography (LSL)^[11,12] for two-dimensional (2D) and three-dimensional (3D) surface patterning of hydrated, photoactive poly(ethylene glycol) (PEG)-based hydrogel substrates.

PEG-based hydrogels are biocompatible and intrinsically resistant to protein adsorption and cell adhesion, thus providing a biological “blank slate” upon which desired biofunctionality can be built.^[13] Acrylate-terminated PEG macromers undergo rapid polymerization upon exposure to UV or visible light when in the presence of appropriate photoinitiators.^[14,15] In this work, confocal-based LSL is used to surface pattern photoactive PEG-diacrylate (PEGDA) hydrogel substrates according to the methodology shown schematically in Figure 1. Briefly, a preswelled PEGDA hydrogel is positioned on the stage of a confocal laser scanning microscope (LSM), which is focused on the upper surface of the substrate. The user then creates a “virtual mask” by drawing “regions of interest” (ROIs), i.e., regions where laser irradiation is desired, using standard confocal LSM software. The LSM software converts these ROIs into instructions that dictate at which pixel locations the laser shutter is opened during an irradiation cycle. A thin layer of precursor solution containing fluorescently labeled acryloyl-PEG-peptide (ACRL-PEG-peptide) and a photoinitiator is then spread onto the substrate surface. Patterning is carried out using an irradiation cycle in which a laser line (selected to match the photoinitiator absorption band) is unidirectionally scanned across the ROIs at user-defined exposure times and intensity. Pattern arrays can be formed using a programmable motorized stage and sequential irradiation cycles. Unbound ACRL-PEG-peptide is rinsed away with phosphate-buffered saline (PBS), and the patterned regions can be observed via fluorescence microscopy.

Since the PEGDA hydrogels are swelled prior to surface patterning, feature distortion due to substrate swelling post-patterning is not an issue. Thus, a wide range of features, including free-form objects (Fig. 2a) and patterns down to at least 5 μm in size (Fig. 1), can be generated with high fidelity on the hydrated gel surfaces using this procedure. Since the

[*] Dr. J. L. West, Dr. M. S. Hahn, J. S. Miller
Department of Bioengineering
Rice University
MS 144, 6100 Main Street, Houston, TX 77005 (USA)
E-mail: jwest@rice.edu

[**] The authors acknowledge the NIH and the NSF for funding this work.