NANO LETTERS

2001
Vol. 1, No. 4
193−195

Patterning a Conjugated Molecular Thin Film at Submicron Scale by Modified Microtransfer Molding

Massimiliano Cavallini,* Mauro Murgia, and Fabio Biscarini

Istituto di Spettroscopia Molecolare-CNR, Via P. Gobetti 101, I-40129 Bologna, Italy

Received January 29, 2001

ABSTRACT

We propose the fabrication at submicron resolution of a patterned thin film of tris(8-hydroxyquinolinato)aluminum(III) (AlQ_3) on a SiO/Si surface by modified microtransfer molding. The film is formed during the printing process. In this manner, it is possible to obtain a patterned homogeneous film with nanometer-size features by a single step, with no change to its adhesion and mechanical properties.

The development of all-plastic electronics that are disposable and low-cost and have a low environmental impact is based on conjugated materials where the desirable charge and energy transport properties merge with light weight, flexibility, and elasticity typical of polymer and molecular systems. The impact of plastic electronic devices relies on the development of large area, fast, and few-step processes. Currently, there is a need for downscaling the lateral size of the active layer,[1] with a view to enhancing the material response. The relevant transport phenomena in conjugated materials occur at the nanometer level, and thin film growth techniques, such as vacuum sublimation or spin casting, are not capable of lateral control at the nanometer scale. Nanostructured conjugated films can be obtained either by means of the self-organization processes[2] or by conformal growth onto a suitable nanostructured template that can be fabricated by different techniques such as scanning probe lithography[3] or photolithography.[4]

Photolithography, which is the most successful technology in microfabrication, cannot be applied directly to molecular thin films at the nanometer scale because of the limitations due to diffraction, according to the Rayleigh equation.

In recent years, several fabrication techniques as alternatives to photolithography have been developed. Among these there are the so-called soft lithographies that use a soft mold or stamp[5,6] and an ink made of self-assembly molecules, such as alkanethiols.[7] These techniques are reliable at the micro- and submicrometer scale, and resolution down to 30 nm for replica molding has been demonstrated.[8] It would be desirable to adapt them in such a way that the conjugated material can be directly printed onto the substrate, without need for masks and intermediate steps. In this respect, the only reported attempt was nanoimprint lithography (embossing) of AlQ_3 films in a vacuum down to 200 nm resolution.[9] Embossing[10] requires a high pressure or high temperature (hot embossing)[11] that could change the mechanical properties and compromise the flexibility.

In this Letter, we show the direct molding of a patterned thin film of tris(8−hydroxyquinolinato)aluminum(III) (AlQ_3) onto a Si/SiO surface by modified microtransfer molding. AlQ_3 is one of the most widely used materials for its high luminescence efficiency in organic light-emitting devices.[12,13] We demonstrate that we are able to reproducibly transfer submicron features of the mold. The process is made in one step and takes a few minutes. The film is formed during the transfer process, is continuous, and does not exhibit signs of stress or rupture. Since there is not any specificity between the mold and AlQ_3, we suggest that our procedure may be of general use for molecular materials.

To pattern an array of AlQ_3, we used soft lithography with solvent to mold a thin film of AlQ_3 by modified microtransfer molding (μTM) on a submicron scale.[14] The μTM of systems with solvents is a soft lithographic method where a drop of liquid “ink” containing a precursor of a polymer, is applied to the patterned surface of the mold and the excess “ink” is removed. The mold is then placed in contact with a substrate and either heated or irradiated. After the liquid has cured to solid, the mold is peeled away, leaving a polymeric replica on the substrate. In our experiment, the ink is a CH_2Cl_2 solution of a molecule (not polymer) highly viscous in the solid-state AlQ_3[2] and we modified the μTM in the last steps. After applying a drop of ink to the surface of the mold, we placed it on the surface of the sample without removing the excess ink and without heating the sample. Therefore, the last step is the same as the last one in solvent assisted micro molding (SAMIM).[15] SAMIM is another soft lithographic

* Corresponding author. E-mail: M.Cavallini@ism.bo.cnr.it.

10.1021/nl0155072 CCC: $20.00
Published on Web 03/16/2001

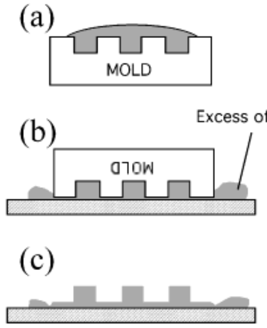

Figure 1. Schematic illustration of the procedure for modified microtransfer molding. (a) A drop of liquid "ink" is applied to the patterned surface of mold and without removing the excess of AlQ_3 solution. (b) After that the mold is placed in contact with a substrate. (c) After liquid has evaporated (about 2 min) the mold is peeled away, leaving a continuous patterned film of AlQ_3.

method similar to embossing. In SAMIM the mold is wetted by a solvent and is brought into contact with the surface of the material, while the embossing does not use the solvent. The solvent swells a thin layer and it transfers the mold motif. The resolution of SAMIM can be under 60 nm.[15] A schematic illustration of our procedure for modified μTM is shown in Figure 1.

The mold was a piece of Au-coated recordable compact disk (RCD). Before Au coating we recorded a periodic sequence of "1 0 0" in binary language on the whole RCD. A blank CD consists of a sequence of grooves; the typical distance between grooves is 1.4 μm, their depth is 230 $\pm$ 15 nm, and width is 400 nm. The writing of "1 0 0" sequences on the RCD yields a regular sequence of holes 20 $\pm$ 2 nm deep and with a pitch of 750 nm along a groove. The RCD mold was then coated with 500 nm of Au by evaporation in a high vacuum. An atomic force microscopy (AFM) image of the mold is shown in Figure 2a, and its negative (obtained by inverting the gray scale in the topography image) in Figure 2b and the line profile in Figure 2d clearly shows the finer structure recorded within the grooves.

Our "ink" was a 2 mg/mL solution of AlQ_3 in CH_2Cl_2 (Aldrich, spectroscopy grade). AlQ_3 was previously purified by sublimation in a vacuum. The substrate was a SiO/Si wafer (with native oxide) cleaned by sonication; 2 min in acetone (chromatography grade) and then 2 min in 2-propanol (spectroscopic grade). We put 10 μL of the solution on the patterned mold, and then the mold was placed on the surface (during this process we spend about 2 s, it is empirically assessed on the basis of trial–error). The solution to be transferred has to become more viscous, but not completely. The pressure of imprinting was low (50 g/cm^2). This extra pressure was applied in order to prevent the stamp from floating over the mold, resulting in inhomogeneous height of the printed features. The value reported yields reliable features over areas of several micron squares. After 2 min the film had become solid; then we carefully removed the mold from the sample. When the solvent evaporates, AlQ_3 forms a solid phase, so the morphology of the molecular thin film is molded by the morphology of the stamp. The films were then imaged by scanning probe microscopy operated in contact mode: the morphology was investigated by AFM and the local mechanical properties, viz. compliance and friction, were mapped by force modulation microscopy (FMM) and lateral force microscopy (LFM), respectively.

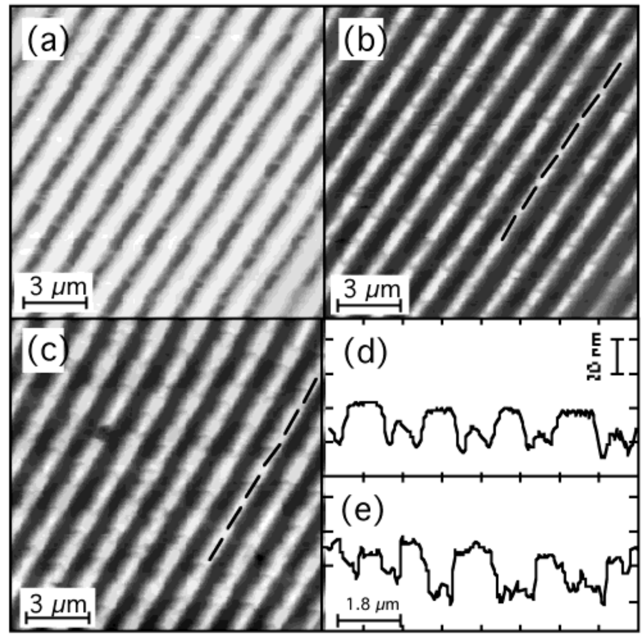

Figure 2. (a) AFM image of mold. (b) Image obtained by inverting the contrast in Figure 2a. (c) Printed AlQ_3 thin film. Line profiles of (d) the mold and (e) the printed film, along the dashed lines in Figure 2b,c, respectively. The grayscale in (a)–(c) is $\Delta z = 350$ nm.

Figure 2c and the line profile in Figure 2e show the printed AlQ_3 pattern: the motifs in the groove are perfectly reproduced along the molecular lines (compare with Figure 2b and the line profile in Figure 2d). From the comparison between the profiles of the inverted mold and the molded AlQ_3 film, it should be noted how both the pitch and the aspect ratio of the structures along the grooves are retained in the molding and transfer process, with an accuracy of only 1–2 nm along the vertical direction. In other words, the information recorded on the RCD was effectively transferred to an electroactive material. The latter could be read at a different frequency, in the optical range for instance. Alternatively, replicas of prepatterned molds may serve for production of arrays of an electroluminescent material.

In Figure 3 we show the maps of the mechanical response by FMM (Figure 3a) and LFM (Figure 3b). LFM does not exhibit any compositional contrast, the only variations in contrast can be associated with changes of slope at the protruding walls. Similarly, the FMM contrast only changes at the slopes of the walls, which suggests that the molding and transfer process has not changed the elasticity of AlQ_3. Thus, we infer that our molding process yields a continuous AlQ_3 film spread over the SiO/Si substrate, but modulated by the pattern of the mold. This allows our structures to be compared with the one obtained by direct nanoimprinting in a vacuum,[9] but with a considerably simpler and accessible method.

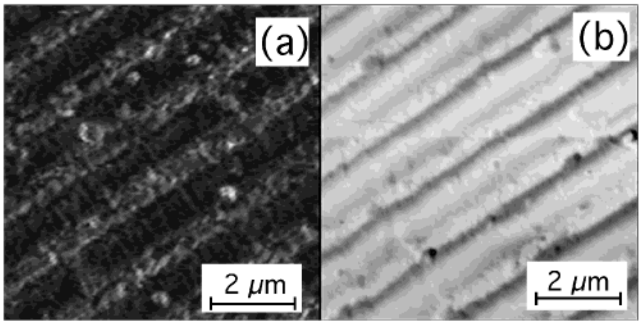

Figure 3. FMM image (a) and LFM image (b) of printed film. (a) was acquired with a vertical modulation of $\delta z = 2$ nm superimposed to the topography with the sample-and-hold technique, (b) was acquired with a scan direction of 45° with respect to the symmetry axis of the cantilever.

In conclusion, we propose a modified μTM applied directly to a conjugated molecular material to yield a patterned conjugated thin film with submicron periodic features, and a vertical resolution at the nanometer level. The pitch reported in our work is substantially due to the stamp used (a RCD). The resolution limit of the method has not been fully explored, but we are confident that at the moment we are limited just by the dimension of the stamps available to us. Our procedure is single step, cheap, versatile, and reproducible, and allows transfer of motifs at submicrometric scale from a mold to molecular thin film without compromising the mechanical properties of thin films.

Here we used AlQ_3 because it is one of the most important conjugated materials, but in principle we can easily extend this process to many other soluble molecular materials.

Acknowledgment. We thank Carlo Taliani for stimulating discussions, we acknowledge partial support from CNR-PFMSTA II-DEMO (postdoctoral fellowship M.C.) and Programma Coordinato Nanotecnologie-Progetto SCRIBA.

References

(1) Rogers, J. A.; Dodalabapur, A.; Bao, Z.; Katz, H. *Appl. Phys. Lett.* **1999**, *75*, 1010.
(2) Brinkmann, M.; Biscarini, F.; Taliani, C.; Aiello, I.; Ghedini, M. *Phys. Rev. B Rapid Commun.* **2000**, *61*, R16339.
(3) Calleja, M.; Anguita, J.; Garcìa, R.; Birkelund, K.; Pérez-Murano, F.; Dagata, J. A. *Nanotechnology* **1999**, *10*, 34.
(4) Okazaki, S. *J. Vac. Sci. Technol. B* **1991**, *9*, 2829.
(5) Xia Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550.
(6) Quake, S. R.; Scherer, A. *Science* **2000**, *290*, 1536.
(7) Kumar, A.; Whitesides G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002.
(8) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J. A.; Prentiss, M.; Whitesides, G. M. *Science* **1996**, *273*, 347.
(9) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85.
(10) Scheer, H.-C.; Schulz, H.; Hoffmann, T.; Sotomayor Torres, C. M. *J. Vac. Technol. B* **1998**, *16*, 3917.
(11) Mönkkönen, K.; Lautanen, J.; Kettunen, V. Leppänen, V.-P.; Pakkanen, T. T.; Jääskeläinen, T. *J. Mater. Chem.* **2000**, *10*, 2634.
(12) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.
(13) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck W. R. *Nature* **1999**, *397*, 121.
(14) Zhao, X.-M.; Xia, Y.; Whitesides, G. M. *Adv. Matter.* **1996**, *8*, 873.
(15) Kim E.; Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Adv. Matter.* **1997**, *9*, 651.

NL0155072