

Micropatterning of Organic Semiconductor Microcrystalline Materials and OFET Fabrication by “Hot Lift Off”

Zhe Wang, Jian Zhang, Rubo Xing, Jianfeng Yuan, Donghang Yan, and Yanchun Han*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, The Chinese Academy of Sciences, P.R. China

Received June 9, 2003; E-mail: ychan@ciac.jl.cn

Patterning organic semiconducting materials over large areas with submicrometer spatial resolution is important for fabrication of integrated organic electronic devices. Thin films of polymeric materials are usually prepared from solution and patterned by printing techniques^{1–3} or techniques involving stamps or molds.⁴ Small-molecule semiconducting materials possess good thermal and chemical stabilities⁵ and typically exhibit better performance than polymers. However, small-molecule organic semiconductors are often insoluble in many solvents so that vacuum-deposition methods are commonly used to fabricate thin films of these materials. Conventional methods for micropatterning small-molecule films rely on rigid shadow mask technology. Unfortunately, this method is limited in resolution due largely to the existence of an air gap between the mask and the surface of the film. Several alternative patterning methods have also been developed: modified shadow mask technology using elastomeric membranes as masks⁶ and modified photolithography using double-layer photoresist.⁷ These methods have been successfully used for organic electronic device fabrication.

Here we demonstrate a method for simple and direct micropatterning of small-molecule microcrystalline films using an epoxy stamp. In this method a patterned, and partially cured, epoxy stamp is pressed onto the surface of a flat microcrystalline film that had been previously evaporated onto a substrate. The pressure and heat are carefully controlled to ensure intimate contact and adhesion between the epoxy stamp and the film. When the patterned epoxy stamp is lifted, the unwanted portions of the microcrystalline film are extracted, and a patterned film remains on the substrate. Since selective lift off of the microcrystalline film is achieved by pressing the patterned epoxy stamp on the microcrystalline film at elevated temperatures, we call this method “hot lift off”.

Further details of the materials and processes are now described. Thin films (~tens of nm thick) of small-molecule materials, such as copper phthalocyanine (CuPc), metal-free phthalocyanine (H₂Pc), *N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenylbenzidine (NPB), and tris(8-quinolinolato)aluminum (AlQ₃), were prepared on different substrates, including Si, ITO, using thermal evaporation procedures. A high-resolution patterned epoxy stamp was made with an elastic mold using the microtransfer molding (μ TM) procedure^{8,9} by curing the casting epoxy and its curing agent (4:1) (w/w) at room temperature for 24 h.

The procedure for the hot lift off process is outlined in Figure 1a. First, the prepatterned epoxy stamp is pressed onto the microcrystalline film with a pressure of approximately 10 kg cm⁻² for ~30 s. The pressure is then reduced to 2 kg cm⁻² and the sample heated to a temperature between 80~120 °C for approximately 20 min, resulting in further curing of the epoxy and the associated enhanced adhesion between the stamp and the film. After subsequent cooling to room temperature and removal of the load,

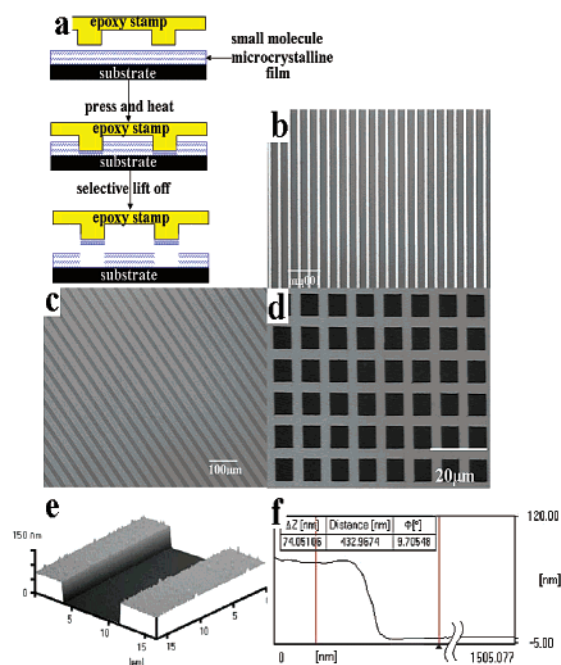


Figure 1. (a) Schematic illustration of the hot lift off process and optical micrographs of the microstructures of several organic semiconductor microcrystalline (b) CuPc/Si, (c) AlQ₃/NPB/ITO, (d) H₂Pc/Si. (e, f) cross sectional analysis of AFM image showing the morphology perpendicular to the edge of CuPc microcrystalline film pattern.

separation of the stamp from the film results in removal of unwanted regions of the film (in contact with the stamp), leaving a patterned substrate.

Three different structures obtained using the “hot lift off” method are presented in Figure 1, b–d. The striped pattern, Figure 1b, was created in a 70-nm-thick CuPc film (an active layer for organic field effect transistor (OFET)) on a Si substrate. The width of each dark stripe is ~20 μ m, and the spacing between stripes is 10 μ m. Figure 1c shows the pattern of the organic single heterostructure consisting of a 30-nm-thick hole transport layer NPB and a 40-nm-thick electron transport and light-emitting layer of AlQ₃ on ITO glass substrate. This structure would be used for organic light-emitting diode (LED) fabrication. The pattern shown in Figure 1d was created in a H₂Pc film on Si using a two-step hot lift off procedure. The first step is performed using the procedure outlined above, and in the second, the epoxy stamp was rotated by ~90° and the procedure repeated. The squares in the resulting pattern are each of area ~7 μ m by 7 μ m.

We now describe the mechanism by which the “hot lift off” method works. During the first step, the applied pressure (~10 kg cm⁻²) is sufficiently large to locally fracture the microcrystalline films along the pattern edges. This process is similar to other

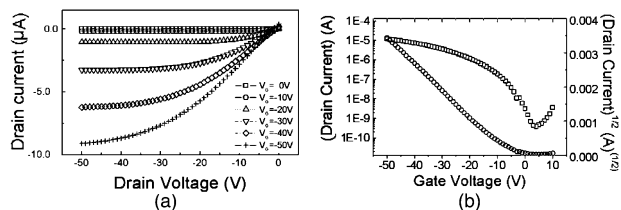


Figure 2. (a) Plots of I_D versus V_D at various V_G . (b) Plots of I_D versus V_G (right axis) and $I_D^{1/2}$ versus V_G (left axis) from a CuPc transistor that fabricated by hot lift off.

patterning techniques, such as cold welding,¹⁰ microcutting,¹¹ and lift up.¹² It is important to note that the morphology of each thermally evaporated films is characterized by a large number of grain boundaries with a distribution of dimensions, ranging from nanometers to micrometers. The intergranular spacing and distribution of microcrystallines depend on the deposition temperature and on the deposition rate.¹³ That the film fractures along the edges of the pattern is not unexpected because this film is brittle and the cohesive energy between the molecules is relatively weak. During the second stage, heating while applying a lower pressure, an intimate junction is formed between epoxy stamp and the microcrystalline film. Under these conditions the epoxy cures further, ensuring adhesion between the stamp and the film. The lift off process works because the adhesion between the epoxy and the microcrystalline film is stronger than the adhesion between the film and the substrate. We, in fact, estimated the work of adhesion between material i and material j ($W_{A,i,j}$), to illustrate this point.¹⁴ The work of adhesion between Alq3 and ITO is $W_{A,Alq3,ITO} = 41.0 \text{ mJ m}^{-2} < W_{A,Alq3,epoxy} = 64.5 \text{ mJ m}^{-2}$, $W_{A,Si,H_2Pc} = 43.1 \text{ mJ m}^{-2} < W_{A,epoxy,H_2Pc} = 65.4 \text{ mJ m}^{-2}$, $W_{A,Si,CuPc} = 44.7 \text{ mJ m}^{-2} < W_{A,epoxy,CuPc} = 65.7 \text{ mJ m}^{-2}$ (see Supporting Information). Clearly, selective lift off of regions of the film is to be expected. The sharpness of the features is limited by the size of grains (Figure S1) and by the pattern definition of the stamp. An atomic force microscope (AFM) scan across the CuPc microcrystalline thin film shows that the patterns obtained by the proposed technique have very smooth and vertical sidewalls and corners of nearly 90° (Figure 1e,f) with step-edge abruptness $< 200 \text{ nm}$.

Both stages are essential to create patterns in the film. If only the first, high pressure, stage is performed (not heating), adhesion is poor, and the pattern cannot be created. On the other hand, if only the second step is performed, the resolution of the pattern is unacceptable, with unwanted residual material remaining on the substrate, as illustrated in Figure S2. Only with both steps could appropriate regions of the microcrystalline film be selectively removed, with no residue remaining on the substrate (Figure S3).

To demonstrate the potential utility of the “hot lift off” procedure OFETs were fabricated and tested. A heavily n-doped Si substrate was selected as the gate electrode and the substrate; the Ta_2O_5 layer served as the gate insulator. A 70-nm-thick CuPc semiconducting film grown at temperature of 150°C was patterned by the “hot lift off” procedure, forming a $500\text{-}\mu\text{m}$ wide line on the Ta_2O_5 layer.

Subsequently, 30-nm-thick gold source and drain electrodes were deposited using a shadow mask defining a $50\text{-}\mu\text{m}$ channel length and a $1200\text{-}\mu\text{m}$ channel width. Plots a and b of Figure 2 show electronic characteristics for the device, which exhibits operation expected for a p-channel transistor. At a drain-source voltage of -40 V , this device has a carrier mobility of $\sim 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage (V_T) of -5 V , and the on/off ratio is $10^4\text{--}10^5$. These characteristics are comparable to the results obtained for CuPc OFET with simple test structure.¹³

In summary, in this paper we introduced a simple method, “hot lift off” procedure for creating micropatterns in organic semiconductor microcrystalline films used to fabricate organic OFETs. The method is a selective lift off process using “tailored” adhesion and pressure as the patterning-driven-force. Although we demonstrated the fabrication of organic, small-molecular microcrystalline patterns, we believe this technique is applicable to other microcrystalline materials, such as inorganic, organic–inorganic hybrid microcrystalline materials. The method is fast (printing process $\approx 20 \text{ min}$), can pattern large areas in one time, and can be carried out in open air. Our results indicate that “hot lift off” is an attractive alternative approach for conventional organic semiconductor microcrystalline patterning technique and offers great promise for organic integrated devices.

Acknowledgment. We are grateful to Professor Peter F. Green at University of Texas at Austin for stimulating discussions. This work is subsidized by the National Natural Science Foundation of China (50125311, 20274050, 20334010), the Ministry of Science and Technology of China (2002CCAD4000), and the Chinese Academy of Sciences (Distinguished Talents Program and Intellectual Innovations Project, KJCX2-SW-H07, KGCX2-205-03).

Supporting Information Available: Calculation of interfacial energy and work of adhesion (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Pardo, D. A.; Jabbour, G. E.; Peyghambarian, N. *Adv. Mater.* **2000**, *12*, 1249–1252.
- Bimstock, J. et al. *Appl. Phys. Lett.* **2001**, *78*, 3905–3907.
- Haskal, E. et al. *SID Dig. Technol. Pap.* **2002**, *33*, 776–779.
- Beh, W. S.; Kim, I. T.; Qin, D.; Xia, Y.; Whiteside, G. M. *Adv. Mater.* **1999**, *11*, 1038–1041.
- Simon, J.; Andre, J. J. *Molecular Semiconductors*; Springer-Verlag: Berlin, 1985.
- Duffy, D. C.; Jackman, R. J.; Vaeth, K. M.; Jensen, K. F.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 546–552.
- Kymissis, I.; Dimitrakopoulos, C.D.; Purushothaman S. *J. Vac. Sci. Technol., B.* **2002**, *20*, 956–959.
- Zhao, X. M.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 837–840.
- Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550–575.
- Kim, C.; Burrows, P. E.; Forrest S. R. *Science* **2000**, *288*, 831–833.
- Stutzmann, N.; Tervoort, T. A.; Bastiaansen, C. W. M.; Smith, P. *Nature* **2000**, *407*, 613–616.
- Granlund, T.; Nyberg, T.; Roman, L. S.; Svensson, M.; Ingan, O. *Adv. Mater.* **2000**, *12*, 269–273.
- Bao, Z.; Lovinger, A. J.; Dodabalapur, A. *Appl. Phys. Lett.* **1996**, *69*, 3066–3068.
- Wu, S. *J. Adhes.* **1973**, *5*, 39–55.

JA036581K