

Patterning Organic Semiconductors Using “Dry” Poly(dimethylsiloxane) Elastomeric Stamps for Thin Film Transistors

Alejandro L. Briseno,^{†,‡} Mark Roberts,[‡] Mang-Mang Ling,[‡] Hyunsik Moon,[§]
E. Joseph Nemanick,[‡] and Zhenan Bao^{*,‡}

Department of Chemistry and Biochemistry, University of California—Los Angeles, Los Angeles, California,
Department of Chemical Engineering, Stanford University, Stanford, California, the University of Michigan,
Ann Arbor, Michigan, and Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, California

Received December 4, 2005; E-mail: zbao@chemeng.stanford.edu

The field-effect mobilities of amorphous silicon devices have been recently surpassed by organic transistors.¹ Significant contributions arise from material-property tuning,^{2a} dielectric–semiconductor interfacial engineering,^{2b,c} and device optimization.^{2d–f} Patterning of organic semiconductors is crucial for the fabrication of large arrays of devices and complex circuits. A desirable patterning method should be simple, high throughput, functional over a large area, and cause minimal degradation to the organic semiconductor and/or the device performance. Several printing methods have emerged as suitable candidates with results demonstrating adequate device performance (e.g., soft lithography,^{3a,b} ink-jet printing,^{3c,d} thermal laser transfer printing,^{3e} selective dewetting,^{3f,g} etc.). In this communication, we demonstrate a method of transferring unreacted low molecular weight (LMW) siloxane oligomers from freshly prepared “dry” PDMS stamps for patterning organic semiconductors and conducting polymers into functional devices via selective wetting. The semiconductors were patterned onto the modified surfaces via dip-coating with well-resolved feature sizes as small as 1 μm . Functional transistor arrays exhibited field-effect mobilities as high as 0.07 cm^2/Vs . The proposed printing method eliminates the need to ink SAMs for fabricating patterns and results in a simple, fast, and highly reproducible method of patterning organic semiconductors from solution. The method herein also produced a flexible transistor composed of patterned PEDOT source–drain electrodes.

Conventional photolithography involves elaborate, time-consuming, and expensive systems. Moreover, photolithographic patterning of organic semiconductors tends to degrade device performance due to material degradation or delamination from the wet chemical processing required in the subtractive methods. These limitations have encouraged the development of alternative techniques that are low-cost, simple, and capable of patterning over large areas onto a variety of substrates. For instance, microcontact printing (μCP) has recently demonstrated high-resolution, large-area patterning onto flexible surfaces.⁴ In a typical μCP process, the PDMS stamp is first inked with a solution (i.e., an ink). Defects are frequently introduced during printing due to ink smearing and diffusion on the substrate⁵ or elastomer deformation. It is also known that the PDMS elastomer stamps release LMW oligomers during contact printing,^{6a,7a–e} which are transferred to the substrate forming a hydrophobic surface. This surface residue has shown to affect the purity and quality of the “inked” SAMs^{7b} and has interrupted conductivity in metal films produced via nanotransfer printing.^{6a} It has also been shown that oligomer residues adsorbed onto substrates from PDMS render poor wettability and delamination of organic semiconductor and metal films.⁸ Inganäs and co-workers patterned substrates with PDMS oligomers to fabricate high quality films of

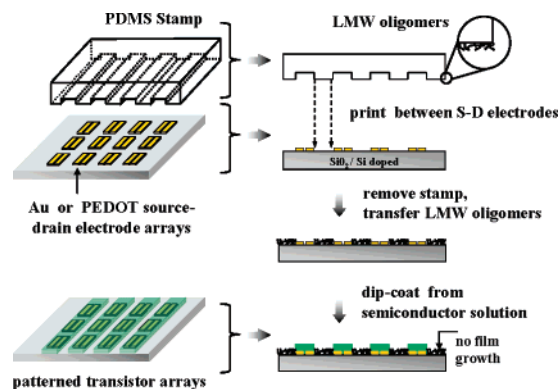


Figure 1. Schematic procedures for patterning PDMS oligomers onto substrates.⁹ Organic semiconductors are deposited via selective wetting only on hydrophilic regions that do not make contact with the PDMS stamp.

conductive and fluorescent polymers with feature sizes of 10–100 μm in range.^{7d} That study, however, did not show the fabrication of a functional device. We show in this communication that μCP can be used to print high resolution, hydrophobic patterns onto a hydrophilic surface with a dry PDMS stamp. The patterned surface can subsequently be used for selective wetting of organic semiconductors with the capability of producing large arrays of functional transistor devices.

Patterning of substrates (SiO_2 , Si, ITO, flexible polyimide, and polyester) begins by preparing a hydrophilic surface.⁹ The substrates were immediately contacted with a patterned PDMS stamp to transfer oligomers onto the substrates producing hydrophobic regions. During contact, LMW oligomers from the PDMS stamps are transferred to a hydroxyl-terminated surface. Figure 1 illustrates the schematic printing process utilized to pattern organic thin film transistors (OTFTs). Source and drain electrodes prepared using conventional photolithography were used to examine the performance of a transistor device constructed with a deposited regio-regular poly(3-hexylthiophene) (P3HT) active layer on a PDMS-patterned substrate. As illustrated in Figure 1, the channel regions between S–D electrodes do not come in contact with the protruded features from the PDMS stamps. This is accomplished by aligning markers on both the substrate and stamp in order to ensure proper registration.

A variety of organic semiconductors are deposited by dip-coating⁹ only in the regions which did not make contact with PDMS, that is, the channel regions (Figure 2). The devices were measured under ambient conditions in the absence of light. Arrays of 5-chlorotetracene (5-CT)^{2a,6c} semiconductor wires yielded mobilities on the order of $10^{-4} \text{ cm}^2/\text{Vs}$ (Figure 2c), consistent with reported literature values.^{2a} Figure 3a shows output characteristics of a regio-regular P3HT patterned device, while Figure 3b shows that of a flexible transistor with patterned PEDOT electrodes and a thin P3HT active

[†] University of California—Los Angeles.[‡] Stanford University.[§] University of Michigan.^{*} California Institute of Technology.

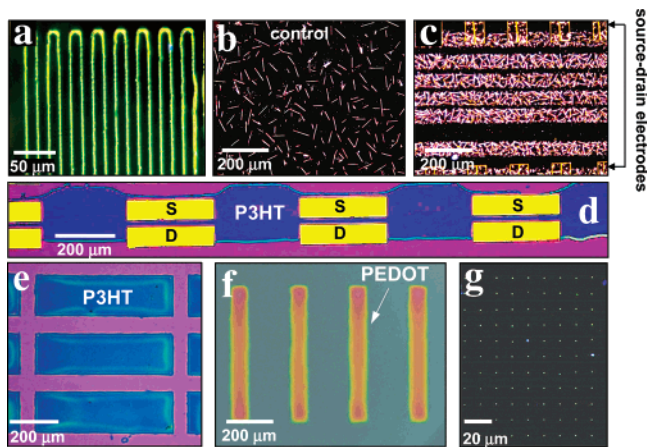


Figure 2. Optical micrographs of (a) patterned P3HT lines on SiO₂, (b) 5-CT wires randomly deposited on a SiO₂ surface stamped with "hexanes-extracted" PDMS,⁹ and (c) source-drain device arrays patterned with 5-CT semiconductor wires from pristine PDMS stamps containing transferable oligomers. (d) Arrays of transistor devices patterned with P3HT, (e) P3HT patterned arrays on SiO₂, (f) PEDOT source-drain electrodes patterned on SiO₂, and (g) 1 μm dots of P3HT patterned on SiO₂. It should be noted that the organic materials do not deposit in regions that are printed with patterned PDMS oligomers, but instead in the contact-free regions only. Average P3HT film thickness = 10–15 nm.

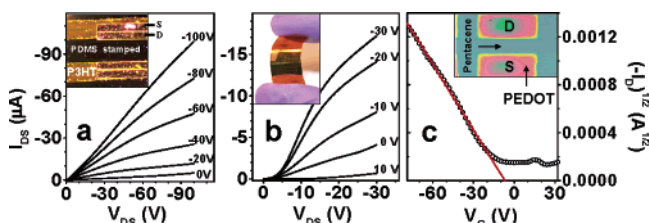


Figure 3. Output characteristics of (a) devices patterned with P3HT, (b) a flexible P3HT device with patterned PEDOT electrodes (inset: flexible transistor on a Kapton substrate),⁹ and (c) a linear plot ($I_d^{1/2}$ vs V_g) from a patterned PEDOT source-drain device with a thin pentacene film.

layer.⁹ Patterned P3HT devices (inset in 3a) showed mobilities ranging from 0.01 to 0.03 cm²/Vs, while flexible PEDOT–P3HT devices in Figure 3b showed mobilities on the order of 10^{−4} cm²/Vs. Arrays of PEDOT electrodes with a thin vacuum-deposited pentacene film were also fabricated by this method with mobilities ranging from 0.01 to 0.07 cm²/Vs (Figure 3c).⁹ PEDOT patterns of 2 cm × 3 cm were fabricated with no visible defects. At least six device arrays were tested for each device and material. The good mobility in these devices demonstrates that this printing method has potential use in large-area, flexible organic electronic applications.

Using ellipsometry, quartz crystal microbalance (QCM), FTIR, X-ray photoelectron spectroscopy (XPS), contact angle measurements, and mass spectrometry, we confirmed that PDMS stamps unquestionably "leach" oligomers.⁹ We determined that the presence of oligomers is directly related to the degree of cross-linking in the stamp.⁹ It was found that a very thin PDMS film (typically 1.3 nm) can be printed onto a hydrophilic substrate with freshly prepared PDMS stamps.⁹ The static water contact angle of bare SiO₂ changed from 7.6 ± 3.9 to 93 ± 2° on PDMS-stamped substrates as a result of the transition from a hydrophilic, high-energy surface to a hydrophobic, low-energy surface. We believe LMW oligomers stamped onto hydroxylated substrates were strongly bound if not covalently attached¹⁰ since the printed oligomer patterns could not be rinsed away with solvents, including toluene, chloroform, hexanes, 2-propanol, dichloromethane, tetrahydrofuran, or chlorobenzene.⁹ The oligomers in PDMS stamps were extracted by a 3 day soaking in hexane or acetone, resulting in a measured weight loss of ~3.0 ± 0.2%, consistent with literature

reports.¹¹ Oligomer extraction was further verified by conducting a control experiment: when SiO₂ surfaces are printed with "oligomer-extracted" PDMS stamps (Figure 2b), no semiconductor patterning was observed due to insufficient surface energy contrast. However, when pristine stamps are employed for printing substrates, well-resolved patterned devices can be produced (Figure 2c).

In conclusion, we report a simple method of patterning organic semiconductors from solution with resolutions as small as 1 μm. Solution-patterned organic thin film transistors were fabricated and tested using this method, and several patterns were attainable. This dry printing method is simple and does not require any ink. It can be easily scaled to a very large area on various substrates with potential in applications where large-area printing is required for fabricating organic electronic devices.

Acknowledgment. This paper is dedicated to Professor Fred Wudl's (UCLA) 65th birthday. A.L.B. acknowledges the Bell Labs Graduate Research Fellowship. Z.B. acknowledges partial financial support from the Finmeccanica Faculty Scholar Award, the 3M Faculty Award, the Center for Polymeric Interfaces and Macromolecular Assemblies (NSF-Center MRSEC under Award Number DMR-0213618), and the Stanford Center for Integrated Systems.

Supporting Information Available: Experimental conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, *303*, 1644–1646.
- (2) (a) Moon, H.; Zeis, R.; Borkent, E.-J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, Ch.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322–15323. (b) Kelley, T. W.; Boardman, L. D.; Dunbar, T. D.; Muires, D. V.; Pellerite, M. J.; Smith, T. P. *J. Phys. Chem. B* **2003**, *107*, 5877–5881. (c) Kobayashi, S.; Nishikawa, T.; Takenobu, T.; Mori, S.; Shimoda, T.; Mitani, T.; Shimotani, H.; Yoshimoto, N.; Ogawa, S.; Iwasa, Y. *Nat. Mater.* **2004**, *3*, 317–322. (d) Ling, M. M.; Bao, Z. *Chem. Mater.* **2004**, *16*, 4824–4840. (e) Shen, Y.; Hosseini, A. R.; Wong, M. H.; Malliaras, G. G. *ChemPhysChem* **2004**, *5*, 16–25. (f) Roichman, Y.; Tessler, N. *Appl. Phys. Lett.* **2002**, *80*, 151–153.
- (3) (a) Bao, Z.; Rogers, J. A.; Katz, H. E. *J. Mater. Chem.* **1999**, *9*, 1895. (b) Chabinyc, M. L.; Salleo, A.; Wu, Y.; Liu, P.; Ong, B. S.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2004**, *126*, 13928–13929. (c) Arias, A. C.; Ready, S. E.; Lujan, R.; Wong, W. S.; Paul, K. E.; Salleo, A.; Chabinyc, M. L.; Apte, R.; Street, R. A.; Wu, Y.; Liu, P.; Ong, B. *Appl. Phys. Lett.* **2004**, *85*, 3304–3306. (d) Kawase, T.; Sirringhaus, H.; Friend, R. H.; Shimoda, T. *Adv. Mater.* **2001**, *13*, 1601–1605. (e) Lefenfeld, M.; Blanchet, G.; Rogers, J. *Adv. Mater.* **2003**, *15*, 1188–1191. (f) Chabinyc, M. L.; Wong, W. S.; Salleo, A.; Kateri, E. P.; Street, R. A. *Appl. Phys. Lett.* **2002**, *81*, 4260–4262. (g) Lee, K. S.; Blanchet, G. B.; Gao, F.; Loo, Y.-L. *Appl. Phys. Lett.* **2005**, *86*, 74102–74104.
- (4) (a) Rogers, J. A.; Bao, Z.; Baldwin, K. W.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H. E.; Amundson, K.; Ewing, J.; Drzaic, P. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835. (b) Loo, Y.-L.; Willet, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* **2002**, *81*, 562–564.
- (5) Balmer, T. E.; Schmid, H.; Stutz, R.; Delamarche, E.; Michel, B.; Spencer, N. D.; Wolf, H. *Langmuir* **2005**, *21*, 622–632.
- (6) (a) Felmet, K.; Loo, Y.-L.; Sun, Y. *Appl. Phys. Lett.* **2004**, *85*, 3316–3318. (b) Loo, Y.-L.; Willet, R. L.; Baldwin, K. W.; Rogers, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 7654–7655. (c) Briseno, A. L.; Aizenberg, J.; Han, Y.-J.; Penkala, R. A.; Moon, H.; Lovinger, A. J.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2005**, *127*, 12164–12165. (d) Loo, Y.-L.; Lang, D. V.; Rogers, J. A.; Hsu, J. W. P. *Nano Lett.* **2003**, *3*, 913–917. (e) Zaumseil, J.; Meitl, M. A.; Hsu, J. W. P.; Acharya, B. R.; Baldwin, K. W.; Loo, Y.-L.; Rogers, J. A. *Nano Lett.* **2003**, *3*, 1223–1227.
- (7) (a) Glasamstar, K.; Gold, J.; Andersson, A.; Sutherland, D. S.; Kasemo, B. *Langmuir* **2003**, *19*, 5475–5483. (b) Graham, D. J.; Price, D. D.; Ratner, B. D. *Langmuir* **2002**, *18*, 1518–1527. (c) Choi, G.-Y.; Kim, S.; Ulman, A. *Langmuir* **1997**, *13*, 6333–6342. (d) Wang, X.; Ostblom, M.; Johansson, T.; Inganäs, O. *Thin Solid Films* **2004**, *449*, 125–132. (e) Li, X.-M.; Peter, M.; Huskens, J.; Reinhoudt, D. N. *Nano Lett.* **2003**, *3*, 1449–1453.
- (8) Ames, D.; Chelli, S. *J. Surf. Coat. Technol.* **2004**, *187*, 199–207.
- (9) See Supporting Information for experimental details and additional data.
- (10) It is possible that the PDMS residue may become covalently bound to Si–OH surfaces by close contact with the surface similar to a previously reported reaction: Sullivan, T. P.; van Poll, M. L.; Dankers, P. Y. W.; Huck, W. T. S.; *Angew. Chem., Int. Ed.* **2004**, *43*, 4190–4193.
- (11) Change, J. W.; Gorur, R. S. *IEEE Trans. Dielect. Electron. Insul.* **1994**, *1*, 1039–1046.

JA058226V