Direct Patterning of Organic-Thin-Film-Transistor Arrays via a “Dry-Taping” Approach

By Shuhong Liu, Héctor A. Becerril, Melbourne C. LeMieux, Wechung Maria Wang, Joon Hak Oh, and Zhenan Bao*

Organic thin-film transistors (OTFTs) have attracted a great deal of interest because of their potential for use in electronic devices, such as electronic paper,[1–3] sensors,[4–6] and radio-frequency (rf) identification cards.[7,8] One important issue in fabricating OTFTs is the patterning of the organic-semiconductor layer. Patterning organic semiconductors is beneficial because it reduces or eliminates parasitic current paths (crosstalk) between neighboring devices, and results in a significant decrease in the “off” current.[9–16] Thin films of polymeric materials are usually prepared from solution, and can be patterned using various techniques such as screen printing, inkjet printing, molding, etc.[17–22] Small-molecule semiconducting materials have good thermal and chemical stability and typically exhibit better performance than polymers.[10] However, it is technically challenging to pattern these small-molecule semiconductors because they are often insoluble in many solvents and are commonly vapor-deposited. While photolithography can be used for patterning such films, it is generally avoided because the solvents involved in the subsequent steps can cause degradation and delamination of the organic semiconductors.[3] In commercial applications, therefore, shadow masks are usually used. Unfortunately, the resolution of this method is limited, largely due to the existence of an air gap between the mask and the semiconductor thin film.[9,10,23] To overcome this problem, several techniques based on printing or stamping have been recently developed, allowing the patterning of semiconductor thin films in the sub-micrometer range.[9,10,24] However, in these methods, shadow masks are still used to define source/drain contacts after the semiconductor has been independently patterned, which again prohibits the fabrication of devices with small features.

Recently, Scotch tape, which is commercially available, was used in the patterning of OTFTs.[25,26] In this communication, a simple yet efficient method for patterning small-molecule OTFT arrays through a “dry-taping” approach using Scotch tape is presented. In this method, Scotch tape is gently pressed onto the surface of an organic thin film that has been previously deposited on a substrate bearing a patterned Au film. When the tape is peeled off, the semiconductor material directly above the Au pattern and the Au film itself are selectively removed, while those portions of semiconductor material sitting directly on the substrate remain, resulting in patterned organic semiconductors on substrates. Based on this approach, the patterning of a variety of solution- and vapor-deposited organic small-molecule semiconductors on different surfaces has been demonstrated. One interesting feature of this patterning process is that if Au films containing both connected and disconnected patterns are designed, only the continuous portions of the Au films are selectively lifted off during the taping process, while discrete Au domains (with feature sizes below ~100 μm) as well as organic films on top of these remain on the substrates. Therefore, by designing appropriate Au patterns, patterned semiconductor films covering source–drain electrodes can be directly prepared after the taping process. To demonstrate the concept, large arrays of bottom-contact pentacene field-effect transistors (FETs) have been fabricated. Since the pentacene films were not exposed to any solvent during the patterning process so that no damage was incurred, the patterned devices exhibited excellent performance, with mobilities as high as 0.65 cm² V⁻¹ s⁻¹ and on/off ratios of 10⁶–10⁷. Compared to unpatterned devices, the off current is reduced by approximately four orders of magnitude in the patterned devices. Additionally, the parasitic leakage currents that are evident in the unpatterned devices are eliminated in the patterned transistors.

Figure 1a is a schematic of the patterning process. First, an organic-semiconductor thin film is deposited uniformly onto a substrate patterned with a Au film. Second, Scotch tape is gently pressed onto the surface of the organic thin film and then peeled off. The organic film on top of the continuous Au film is in contact with the tape and is selectively removed along with the Au pattern, leaving behind patterned semiconductor thin-films on the lower SiO₂ surface. The optical microscopy images in Figure 1b–g show patterned thin films of a variety of different p- and n-channel organic semiconductors, including 5,5’-bis(4-tert-butylphenyl)-2,2’-bithiophene (dtb-P2TP, Fig. 1b), trimethylsilily-substituted quarterthiophene (TMS-4T, Fig. 1c), pentacene (Fig. 1d), hexathiopentacene (HTP, Fig. 1e), copper phthalocyanine (CuPc, Fig. 1f), and copper hexadecafluoro phthalocyanine (F₁₆CuPc, Fig. 1g). From these images, it can be seen that ordered arrays of semiconductor features with different sizes and shapes, such as squares, rectangles, hexagons, stars, etc., can be obtained over relatively large areas. The magnified images in the insets show that the patterned films have well-defined edges and are located on a clean background (no Au residue exists in the background regions), indicating the cleanliness and high selectivity of this patterning approach.

[1–3] Prof. Z. Bao, S. Liu, Dr. H. A. Becerril, Dr. M. C. LeMieux, W. M. Wang, Dr. J. H. Oh
Department of Chemical Engineering
Stanford University
Stanford, CA 94305 (USA)
E-mail: zbao@stanford.edu

DOI: 10.1002/adma.200802201
This patterning method allows deposition of organic-semiconductor thin films via both solution- and vapor-processing techniques. Figure 1b shows the optical microscopy image of patterned dtb-P2TP thin films deposited via a dip-coating process. When the sample was observed between cross polarizers (inset of Fig. 1b), the films exhibited strong birefringence, indicating a high degree of crystallinity. Deposition techniques that offer control over the orientation of the organic semiconductor can also be used to prepare the organic thin films. As a demonstration of this concept, aligned TMS-4T films prepared through a solution-shearing technique, are depicted in Figure 1c. Figure 1d–g shows optical microscopy images of various organic semiconductors prepared via vacuum deposition. It is noted that, in this patterning process, the organic semiconductor can be patterned onto surfaces with different properties, ranging from the extremely hydrophilic SiO2 surface (static water contact angle ≈0°) to the hydrophobic n-octadecyl triethoxysilane (OTS)-treated SiO2 surface (static water contact angle ≈98°). It is known that the performance of organic FETs is strongly dependent on the properties of the dielectric surface,[28] thus it is advantageous that this patterning process can be applied to different surfaces. This method is reproducible with high yield. For each pattern presented in Figure 1, at least three samples were prepared and no noticeable difference was observed for different runs. The size of each sample was at least 1 cm × 1 cm, with a patterning yield close to 100%; the patterns shown in Figure 1 represent random regions on the samples.

One interesting property of this patterning process is that only continuous Au films are lifted off during the taping process, while disconnected Au domains (feature sizes below ~100 µm) remain on the substrate. Therefore, if Au patterns containing both connected regions and individual squares are designed, as illustrated in Figure 2a, patterned semiconductor films covering the exposed SiO2 surface as well as isolated Au squares can be obtained after taping. The corresponding optical microscopy images of the pentacene films on patterned substrates before and after tape are shown in Figure 2b and c, respectively. To further evaluate the results of the patterning process, atomic force microscopy (AFM) characterization was carried out on the surface enclosed in the square in Figure 2c. From the AFM amplitude image (Fig. 2d), uniform pentacene films can be seen on both individual Au domains (region 1) and the exposed SiO2 surface (region 2), indicating that the pentacene films on these two surfaces were not damaged by the tape. The observation that the pentacene grains exhibit different morphologies on the Au (region 1) and SiO2 (region 2) surfaces is in agreement with results reported in previous studies.[29,30] In contrast, no pentacene or Au residue was observed on
the surface from which the continuous Au films were lifted off (region 3 in Fig. 2d). The latter surface is clean and smooth, with an average roughness of ~0.17 nm.

Insight into the dry-taping process will now be given. First, the metal mask was designed to have poor adhesion to the SiO₂ surface, so that it did not pass the “Scotch-tape test”, which is a widely used empirical method to evaluate the adhesion of a coating to a substrate. The Au mask had a thin Ti layer (<1 nm) so as to provide sufficient adhesion and allow patterning via photolithography and lift-off, but not sufficient adhesion to pass the Scotch-tape test. Second, the Scotch tape was only gently pressed onto the organic thin film, so that the tape first contacted the surface of the organic film deposited on the Au, and was only in partial contact with the surface of the organic film that was located directly on the SiO₂. This selective taping resulting from differences in the height of the film worked well for exposed SiO₂ regions less than 100 μm in size, while films with larger lateral dimensions had a higher probability of being contacted with Scotch tape, and partial removal of the organic film on the SiO₂ surface was observed. However, this limitation does not seem to be a problem, because for features larger than ~100 μm shadow-masking has been proven to be an effective method to pattern materials. Third, the strong Au–Au interactions are believed to play an important role in the patterning process. Since only a small portion of the organic-semiconductor/Au film is initially in contact with the Scotch tape, most of the film that is not contacted by the tape is most probably lifted off by neighboring Au atoms that are already on the tape, as a result of the strong Au–Au bond. To support this hypothesis, Au films transferred to the tape were imaged using an optical microscope; no noticeable cracks were observed. Furthermore, it was also observed that, without Au films as templates, continuous organic films with similar patterns could not be completely lifted off by Scotch tape, probably as a result of the weak interaction between organic molecules compared to that between Au atoms. Finally, this taping approach works less effectively for patterning polymers than for patterning small molecules. It was observed that when a polymer film on Au was lifted off, the neighboring polymer film on SiO₂ was also partially peeled off as a result of the strong interactions between the polymer chains, resulting in patterned films with poorly defined edges.

This dry-taping process allows the direct fabrication of large arrays of patterned bottom-contact FETs. The Au template used for device fabrication, which is very similar to the template used in Figure 2, is shown in inset 1 of Figure 3a. The main difference is that, instead of having one individual Au pad in the center of each exposed domain (Fig. 2b), two separate Au pads that will later serve as source and drain electrodes were fabricated in this case (Fig. 3a, inset 1). Based on the observations previously discussed, it is not difficult to predict that patterned pentacene films covering exposed regions and two disconnected Au pads will be obtained after the taping process. Using this approach, the direct fabrication of large arrays of patterned bottom-contact pentacene FETs is achieved. The pentacene films were deposited on the Au templates before the taping process. The transfer and output characteristics of patterned and unpatterned pentacene FETs at different drain-source voltages, V_DS, were measured. Transfer characteristics were measured at a fixed drain-source voltage, V_DS = -100 V, I_DS: drain-source current, V_G: gate voltage.

Figure 3. a) Bright-field optical microscopy images of patterned bottom-contact pentacene FETs. Inset 1): Bright-field optical microscopy image of pentacene films on Au templates before the taping process. Insets 2,3): Magnified bright-field (2) and cross-polarized (3) optical microscopy images of the patterned devices. The SiO₂ surfaces were treated with HMDS before pentacene deposition. Transfer and output characteristics of b) patterned and c) unpatterned pentacene FETs. Transfer characteristics were measured at a fixed drain-source voltage, V_DS = -100 V, I_DS: drain-source current, V_G: gate voltage.
approach, large arrays of patterned pentacene FETs were fabricated, as shown in Figure 3a. As can be seen from the magnified images in Figure 3a (insets 2 and 3), the pentacene film on one device is separated from those on neighboring devices. Organic transistors with densities of up to ~50 transistors mm\(^{-2}\) were fabricated, and no partial ripping of the organic-semiconductor/Au areas was observed. For the nontransistor patterns, a feature density as high as ~2500 features mm\(^{-2}\) was fabricated, and no partial ripping was observed. Here, it should be noted that the electrodes do not have to be isolated pads if the electrodes and the template are not patterned in one step. Two levels of lithography can also be performed, one defining the Au electrodes and lines between them with a strong Ti adhesion layer, and the other defining the Au template that is weakly bonded to the substrate. Figure 3b shows the well-defined transfer and output characteristics of a typical patterned pentacene transistor. The average mobility (from five randomly selected devices) calculated in the saturated regime was 0.48 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (the highest mobility measured was 0.65 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), and the typical on/off ratio was ~10\(^{-9}\)–10\(^{-10}\). The output characteristics exhibited excellent gate-modulated current at low source-drain voltages. For comparison, devices with unpatterned pentacene layers were also fabricated (all the other parameters for patterned and unpatterned devices were kept the same). For unpatterned devices, an average mobility (from five randomly selected devices) of 0.48 ± 0.03 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was obtained, which was in the same order as that of patterned devices. However, the off current for unpatterned devices (~10\(^{-7}\) A) was much higher than that of patterned devices (<10\(^{-11}\) A), and the typical on/off ratio for unpatterned devices was only ~10\(^{-5}\)–10\(^{-6}\) (Fig. 3c). In the output characteristics of the unpatterned devices, the presence of a parasitic leakage current at low source–drain voltages is obvious. This result indicates that patterning of organic-semiconductor layers is essential for fabricating devices with high on/off ratios and low parasitic leakage currents.

In conclusion, a simple method for patterning small-molecule organic semiconductor thin-films by a dry-taping approach is reported. No solvent is involved in the patterning process and no damage to the organic-semiconductor layer is incurred. Patterning of a variety of solution- and vapor-deposited organic semiconductors on different self-assembled-monolayer-treated surfaces has been demonstrated. By combining this patterning process with alignment techniques such as solution shearing,\(^{[13]}\) patterning of organic crystalline thin films with aligned orientations has also been achieved. This patterning technique allows the direct fabrication of large arrays of bottom-contact pentacene FETs with high performance. Patterned devices exhibited mobilities as high as 0.65 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and on/off ratios of 10\(^{6}\)–10\(^{7}\). The on/off ratios of the patterned devices were approximately four orders of magnitude larger than those of unpatterned ones. The parasitic leakage currents that are evident in the unpatterned devices were also eliminated in patterned transistors. Preliminary results indicate that this patterning strategy is also applicable to patterning other nanoscale materials, such as carbon nanotubes. Future research will involve the replacement of the Au used in the low-adhesion films with other cheaper materials.

**Experimental**

A highly doped Si wafer with a thermally grown dry oxide (300 nm) was used as the substrate. Various Au patterns were fabricated by conventional photolithography (metal thickness: Ti = 0–1 nm and Au = 45 nm). For patterning the semiconductor thin films, the SiO\(_2\) surfaces were either treated with OTS (C\(_{16}\)H\(_{33}\)Si(OH)\(_{3}\)) \(^{[28]}\) or left untreated before deposition of the organic thin film. For device fabrication, SiO\(_2\) dielectric surfaces were treated with hexamethyldisilazane (HMDS) using a standard industrial Yield Enhancement System (YES-100). 45 nm pentacene, HTP, CuPc, and F\(_{16}\)CuPc films were vacuum-deposited onto the above-prepared substrates at room temperature at a deposition rate of ~0.2–0.3 Å s\(^{-1}\) and at 10\(^{-4}\) Torr (I Torr = 133.32 Pa). dtb-P2TP films were prepared by dip-coating a substrate from a 1.2-dichlorobenzene solution of concentration ~2.5 mg mL\(^{-1}\). TMS-4T films (20–30 nm) were prepared via a solution-shearing process \(^{[27]}\). Au templates were removed by gently placing 3M Scotch tape on the above-prepared substrates and manually peeling off the tape from the edge of the substrate. Electrical characterization of the transistor devices was performed under ambient conditions using a Keithley 4200SCS semiconductor parameter analyzer.

**Acknowledgements**

The authors thank A. L. Briseno for providing hexathiopentacene.

Received: July 29, 2008
Revised: September 17, 2008
Published online: February 19, 2009


