

# Photolithographic patterning of organic electronic materials

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## Abstract

The realization of organic electronic technologies requires the availability of patterning techniques that are compatible with chemically sensitive materials. We demonstrate an approach that allows the photolithographic patterning of organic films without their exposure to harmful solvents, and achieves micrometer resolution. Examples of additive and subtractive patterning of polymers as well as small molecules show this approach to be quite generic. The fabrication of a pentacene transistor with a 2  $\mu\text{m}$  channel length and conducting polymer electrodes is demonstrated.

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## 1. Introduction

The past two decades were characterized by tremendous progress in the performance of organic electronic devices such as light emitting diodes, thin film transistors, and photovoltaic cells [1–3]. The progress has been so remarkable, that the term “organic electronics” is now being used to describe the vision of an electronic technology using semiconductors, conductors and dielectrics based on organic materials [4]. A critical step for the realiza-

tion of organic electronics is the availability of patterning techniques that are compatible with these materials. Although great strides have been achieved in our ability to pattern organics, the techniques used in the mature and entrenched industry of silicon processing have made little impact in this field. This is primarily due to incompatibilities between chemicals used in photolithography and the vast majority of organics. Overcoming these incompatibilities promises a breakthrough in the manufacturing of organic electronics since it would provide for massively parallel output along with process knowledge and equipment already available from a very successful industry. As a first step towards this goal, we report on a generic approach for the photolithographic patterning of organic

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materials with micrometer resolution. We demonstrate the applicability of this approach to the additive and subtractive patterning of conducting polymers, as well as semiconducting small molecules. A pentacene transistor with 2  $\mu\text{m}$  channel length and conducting polymer electrodes is fabricated as a proof-of-concept.

The particular challenge of patterning chemically-sensitive organic materials has stimulated much invention, and numerous approaches have been developed for making patterned structures with small features [5]. Particular attention has been paid in the patterning of semiconductors, used in organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs). Shadow masking has been the canonical technique for patterning low molecular weight materials, which are usually processed into films using vacuum deposition [6]. A stencil is placed either in contact with, or in close proximity to the substrate, and defines the areas that are coated with a film. Inkjet printing, on the other hand, is the technique of choice for polymeric materials, which are processed into films from solution [7]. It involves a modified inkjet or bubblejet printer that delivers small droplets of polymer solution to selected places on the substrate. Both of these techniques leave a lot to be desired. Large area stencils are hard to fabricate and need to be rigorously maintained to remove material that has been deposited on them. Inkjet printing, on the other hand, requires specially formulated inks and non-standard equipment, and it is a serial (hence low throughput) process. Certain recently developed techniques such as imprint lithography [8,9], micro-contact printing [10], and organic vapor jet deposition [11] seem to overcome some of these limitations. Photolithography, however, which is the technique of choice for the patterning of inorganic electronic materials, remains the single most attractive thin film patterning technique to date. This is due to the host of advantages photolithography offers, which include straightforward scaling to large area substrates, availability of a broad basis of equipment and expertise, and the high throughput fabrication associated with its inherently parallel nature.

## 2. Subtractive patterning approach

In photolithography, the film to be patterned is coated with a polymeric photoresist, which is deposited by spin coating. The photoresist is then exposed

to light through a photomask which carries the pattern to be transferred to the film. A developer (typically an alkaline solution) is used to remove the exposed parts in positive photoresists, or the unexposed parts in negative photoresists, replicating the mask pattern (or its reverse) on the photoresist film. Using the remaining photoresist as a contact mask, an etching step is then used to transfer the pattern to the underlying film. The etching can be dry (i.e. reactive ion etching), or wet (i.e. use of suitable solvent), depending on the nature of the film to be etched and the substrate. Finally, the photoresist is stripped off by an appropriate solvent. The incompatibility of organics with conventional lithography arises primarily due to the solvents used for the deposition, the development and the removal of the photoresist. The solvents used in these three steps have, with a few exceptions [12], detrimental

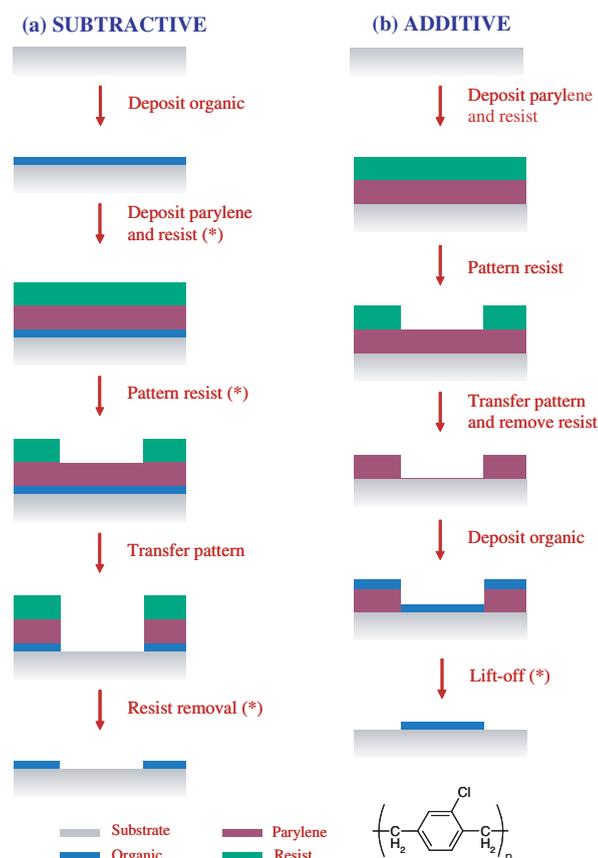


Fig. 1. Subtractive (a) and additive (b) photolithographic patterning approaches for organic films. The asterisks indicate the steps where the organics film would be damaged during conventional photolithography. The chemical structure of parylene-C is shown on the bottom.

effects on organic films, including dissolution, cracking, swelling, and delamination. Although chemical modification of conjugated polymers to include a photoactive element that allows their direct (without using a photoresist) patterning has been recently demonstrated [13], such a solution requires custom chemistry for each material used.

In Fig. 1a, an approach for carrying out the above photolithographic process on organic films is shown (experimental details are given at the end of this section, after the concept is described). The key to this approach is the use of parylene-C [poly (*para*-xylylene), Fig. 1, from now on referred to as parylene], to protect the organic film during the deposition and development of the photoresist, as well as to strip the photoresist in a dry (solvent-free) manner. Parylene is a chemical vapor deposited (CVD) polymer with a number of useful properties that endow it with applications as a barrier layer in electronic circuits and medical devices [14]. It is deposited near room temperature and gives rise to conformal coatings that can be applied on chemically sensitive materials (such as organics) without damaging them. The coatings are pinhole-free for films of sufficient thickness (typically >500 nm thick). Once deposited, parylene films are nearly inert; they resist solvents, strong acids and bases. As a result, conventional photolithography can be

carried out on top of these films, as shown in Fig. 1a. Once developed, the photoresist (which is positive tone as indicated in Fig. 1a), serves as a mask for a dry etch step that is used to transfer the pattern to the parylene and the organic film below. In fact, Kymissis et al. have used photolithography to patterned a parylene layer, and selectively etch an underlying pentacene film [15].

In addition, and most importantly, parylene films show relatively weak adhesion to a number of organic films. Their adhesion is good enough for the parylene films to remain securely in place throughout all processing steps indicated in Fig. 1a, including deposition and development of the photoresist, plasma etching, and handling of the sample. Parylene films can, however, be peeled off from a variety of organic films, a process that can be assisted with adhesive tape. Peeling the parylene strips off the photoresist in a solvent free manner and leaves the patterned organic material on the substrate.

The patterning approach shown in Fig. 1a is subtractive and leads to organic films that are the reverse of the photomask when positive tone photoresist is used. Examples of organic films patterned using this approach are shown in Fig. 2. Fig. 2a shows 1  $\mu\text{m}$  wide trenches, etched in the conducting polymer poly(3,4-ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS), (b) spiral shaped trenches in PEDOT:PSS. The width of the trenches is 4  $\mu\text{m}$ , (c) 1  $\mu\text{m}$  wide lines of PEDOT:PSS on a 10  $\mu\text{m}$  pitch, and (d) spiral lines with a 4  $\mu\text{m}$  width made from ruthenium tris-bipyridine,  $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ .

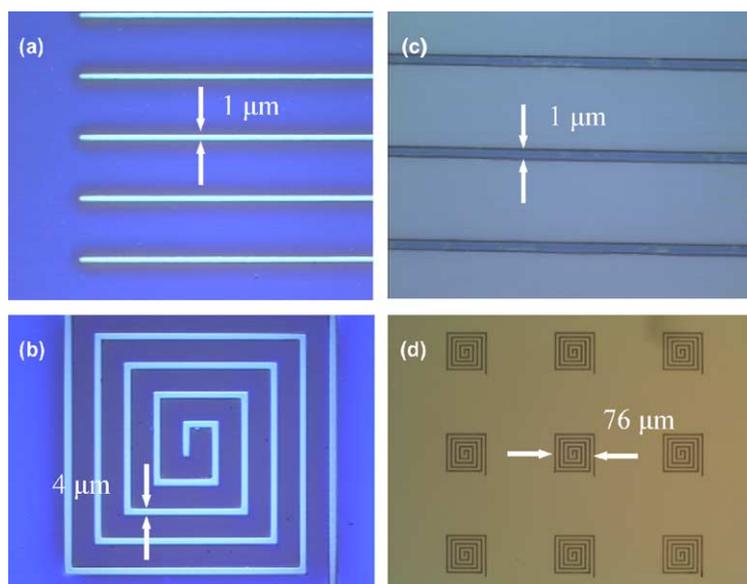


Fig. 2. Optical micrographs showing examples of organic electronic films patterned using the subtractive (a–b) and the additive (c–d) approaches: (a) 1  $\mu\text{m}$  wide trenches etched in the conducting polymer poly(3,4-ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS), (b) spiral shaped trenches in PEDOT:PSS. The width of the trenches is 4  $\mu\text{m}$ , (c) 1  $\mu\text{m}$  wide lines of PEDOT:PSS on a 10  $\mu\text{m}$  pitch, and (d) spiral lines with a 4  $\mu\text{m}$  width made from ruthenium tris-bipyridine,  $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ .

(PEDOT:PSS). Such trenches can be used, for example, to define the channel in OTFTs [2]. Fig. 2b shows spiral shaped trenches in PEDOT:PSS. The width of the trenches is 4  $\mu\text{m}$ , and the picture shows how well the parylene layer peels, even around tight corners.

The structures in Fig. 2 were fabricated as follows: The organic films were deposited on oxidized silicon wafers by spin coating. The parylene deposition took place in a PDS 2010 chamber from Specialty Coating Systems, in which the substrate was held at room temperature. The parylene layers were 1.5  $\mu\text{m}$  thick. Shipley SPR220 3.0 positive photoresist was spun on the substrate and was baked in a convection oven (at sub-100  $^{\circ}\text{C}$ ) to prevent damaging thermally sensitive organic layers. The patterns were exposed on a GCA 5X I-line stepper and developed with MIF300 developer. The process was optimized beforehand to yield near vertical sidewalls. The pattern formed in the photoresist during the photolithographic step was transferred to the parylene layer and the underlying organic film through an anisotropic oxygen plasma etch on a Plasma-Therm PT72. The etch rate was in the range of 120–160 nm/min. Peeling the parylene films was accomplished mechanically, and removal was sometimes assisted by attaching Scotch tape to the surface of the parylene before lift-off.

### 3. Additive patterning approach

A second popular way for patterning films using photolithography involves lift-off. In the lift-off process, the photoresist is used as a contact mask. It is deposited directly on the substrate, and it is exposed and developed to leave parts of the substrate bare. The film to be patterned is subsequently deposited and coats the bare parts of the substrate and the surface of the photoresist. An appropriate solvent is used to dissolve the remaining photoresist, removing the part of the film that was deposited on it. The problem with this process arises due to the incompatibility of organics with the solvent used for the removal of the photoresist.

Fig. 1b shows an approach for carrying out the above photolithographic process on organic films. Parylene is used here in the place of the photoresist to enable the dry lift-off of the organic. This approach, which relies on the limited adhesion of parylene to the substrate, was originally developed by Ilic and Craighead for patterning of biological materials such as proteins and cells [16]. The actual peeling

process used a combination of Scotch tape and tweezers to peel the entire film from the substrate, starting from an edge. Once the edge is lifted, the film separates easily. The force required to peel parylene from various substrates has been investigated by Takeuchi et al. [17]. Examples of organic films patterned using this approach are shown in Fig. 2. These films are the direct image of the photomask when positive tone photoresist is used, and the overall process is additive. Fig. 2d shows 1  $\mu\text{m}$  wide lines of PEDOT:PSS on a 10  $\mu\text{m}$  pitch, and Fig. 2e shows spiral lines with a 4  $\mu\text{m}$  width made from ruthenium tris-bipyridine,  $[\text{Ru}(\text{bpy}_3)]^{2+}(\text{PF}_6^-)_2$ , a material used in OLEDs [18]. Finally, Fig. 3a shows an array of square pixels with a 4  $\mu\text{m}$  edge made from pentacene, an organic semiconductor used in OTFTs [2]. Such structures can be used, for example, to define pixels in OLED displays, or to define the p- and n-type regions in TFT circuits [2]. An AFM micrograph shown in

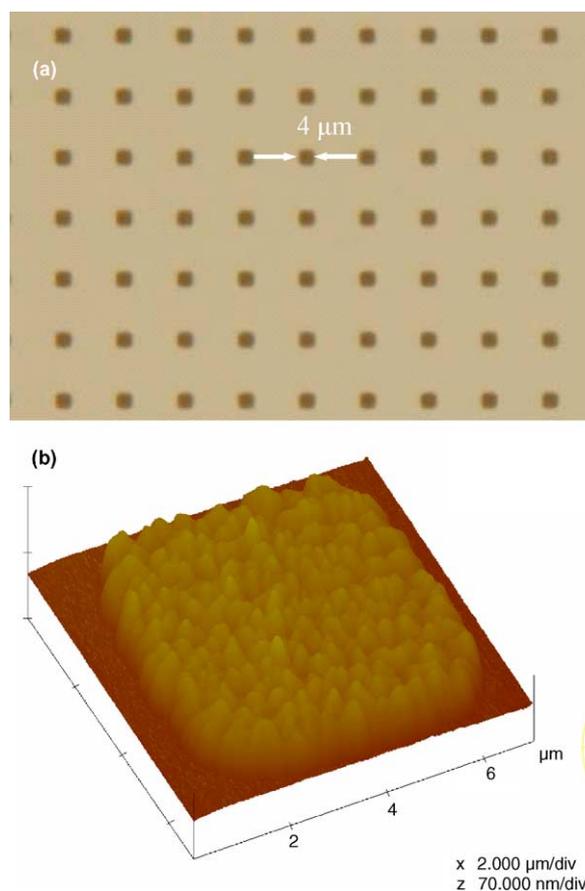


Fig. 3. Pentacene patterned using the additive approach: (a) optical micrograph of an array of square pixels with a 4  $\mu\text{m}$  edge and (b) atomic force micrograph of a 4  $\times$  4  $\mu\text{m}^2$  pentacene pixel.

Fig. 3b reveals well-defined edges and uniform pentacene thickness.

The structures in Fig. 3 were fabricated as follows: Parylene was deposited on oxidized silicon wafers as described previously. Its patterning was also conducted in the same way as in the subtractive approach, but the photoresist was hard baked prior to exposure (it was found that heating at temperatures as high as 130 °C did not appear to affect the integrity of the parylene layer). After the parylene patterning, the residual photoresist was stripped off with an acetone/isopropanol bath before the deposition of the organic film and the wafer was treated in a UV/ozone cleaner. The organic material was subsequently deposited by spin coating (PEDOT:PSS and  $[\text{Ru}(\text{bpy}_3)]^{2+}(\text{PF}_6^-)_2$ ), or vacuum sublimation (pentacene). The parylene layer was peeled off mechanically, as in the subtractive approach.

#### 4. Discussion

The two approaches discussed here have some similarities as well as some differences. Both avoid exposure of the organic film to solvents used in photolithography, enabling a wide range of organics to be patterned without the need for custom synthesis. Both rely on the poor adhesion of parylene on a variety of substances. We found parylene films to peel easily from a variety of substrates used commonly in organic electronics, including freshly cleaned Au, indium tin oxide, and silicon oxide. Peeling of parylene films from glass substrates has also been reported in literature, as a way to fabricate dielectrics for OTFTs [19]. This makes the additive approach suitable to a variety of structures needed in organic electronics. Moreover, since the surface of the organic is left pristine, this approach is well-suited for applications where the quality of that organic surface is critical.

In the subtractive approach, the surface of the organic film comes in physical contact with parylene and runs the risk of getting damaged during the deposition and removal of the parylene film. In addition, successful peeling of the parylene requires stronger adhesion at the bottom (substrate/organic) than at the top (organic/parylene) interface. We found the success of this approach to be material dependent. Parylene peels easily from PEDOT:PSS and  $[\text{Ru}(\text{bpy}_3)]^{2+}(\text{PF}_6^-)_2$  films deposited on a variety of substrates. Moreover, the conductivity of a 100 nm thick PEDOT:PSS film did not change upon deposition and removal of parylene, indicating that the pro-

cess was benign. On the other hand, peeling parylene from pentacene and  $\text{C}_{60}$  films was not reproducible, and in certain cases the films would not peel at all. More detailed studies are necessary to understand the limitations of this technique. It should be stressed, however, that there is considerable latitude for tuning the properties of the organic/parylene interface, so that this patterning method becomes widely applicable. First, other derivatives of parylene, as well as other CVD films such as fluorocarbons [20] can be used to tune the properties of the top interface and strike the right balance between good adhesion and ease of delamination. Second, the peeling of the parylene films, which was carried out manually in this work, can be achieved, with better control, by a commercial delaminator. Third, CVD films that are soluble in supercritical  $\text{CO}_2$  (which does not dissolve most organic films), offer an alternative to mechanical removal [21].

#### 5. Demonstration of multi-level patterning

The photolithographic approaches described here can be used for the fabrication of organic electronic circuits, which require the patterning of more than one layers. This is demonstrated in Fig. 4, which shows a pentacene transistor with a 2  $\mu\text{m}$  channel length and PEDOT:PSS electrodes. The transistor was fabricated by first applying the additive approach to pattern 1-mm long, 50- $\mu\text{m}$  wide stripes of PEDOT:PSS (the PEDOT:PSS film was deposited on an oxidized p-type silicon wafer, which served as the gate electrode, with a 300 nm thick thermal oxide serving as the gate dielectric). A second additive step was then used to deposit a  $2 \times 75 \mu\text{m}^2$  island of pentacene, which was done by vacuum sublimation. The etching step that preceded the deposition of the pentacene partitioned the PEDOT:PSS stripe in the middle, defining the source and drain electrodes, separated by a 2  $\mu\text{m}$ -long channel. This channel length was chosen for experimental convenience, and does not represent the limit of this technique (e-beam lithography can be used to define smaller channels).

The electrical characteristics of the transistor, which were measured under high vacuum in a probe station using Keithley 2400 source-meters, are shown in Fig. 4c. The transistor had a field effect mobility of  $6.1 \times 10^{-3} \text{ cm}^2/\text{V s}$ . This is considerably lower than the mobility measured in pentacene transistors with polyaniline electrodes [22], indicating that further optimization of the patterning process

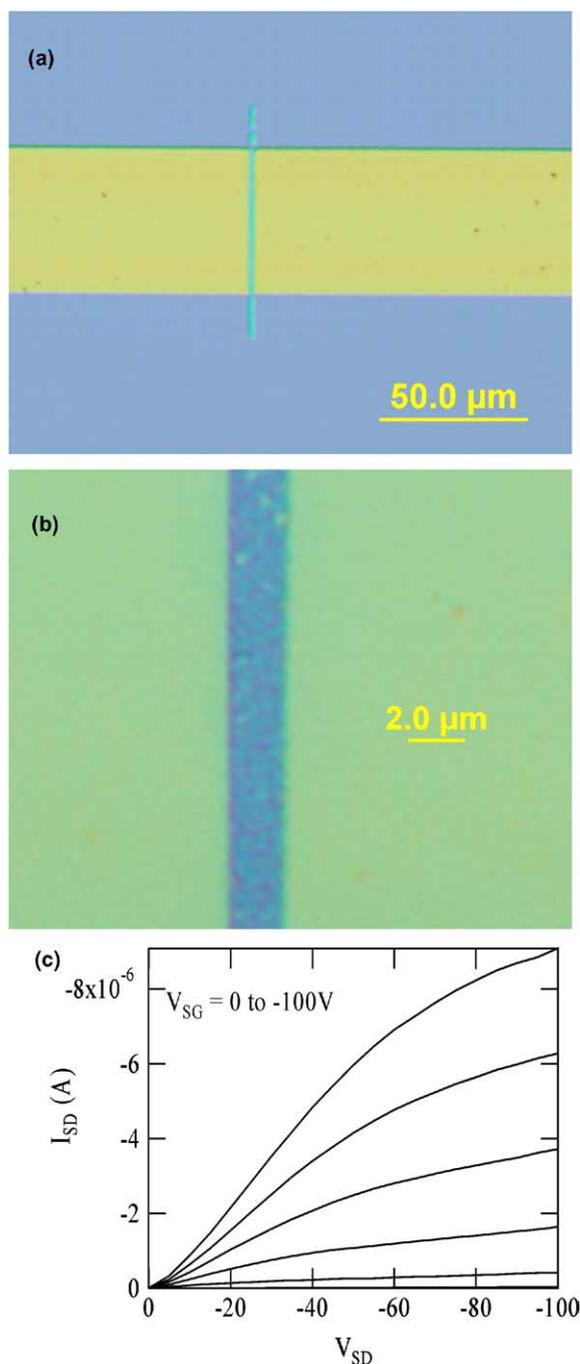


Fig. 4. Optical micrograph of a pentacene transistor with a 2 μm channel length and PEDOT:PSS electrodes fabricated by combining the subtractive and the additive approach (a). The channel region is shown in more detail in (b). Transistor characteristics are shown in (c).

is needed. Lefenfeld et al. [23] discussed contact issues for bottom electrode polymer transistors and demonstrate polymer transistors that perform

well, showing the possibility for improvement with this process. The contact issues may be residual from the etch step creating a thin damaged region on the sidewalls of PEDOT:PSS. Since the parylene layer is more than a micron thick, and with  $\sim 1$  μm or residual resist, shadowing of the pentacene may be a factor. Additionally, physical sputtering from the oxygen plasma step may cause roughening of the oxide layer, decreasing the mobility somewhat, but this has not yet been determined. It should be noted that devices with channel lengths of 25 μm exhibited less pronounced contact limited behavior and mobilities in the  $10^{-2}$  cm<sup>2</sup>/V s range.

The OTFT of Fig. 4 shows the applicability of this patterning approach to the fabrication of organic circuits. In addition to OTFTs, other devices can also be fabricated. For example, in systems where the parylene film can be peeled from the organic, the additive approach can be repeated to pattern different materials side-by-side. This way, red, green and blue pixels for full-color OLED displays can be sequentially patterned by repeating the additive approach three times. Similarly, sequential patterning of p-type and n-type organic semiconductor islands can be used for the fabrication of complementary OTFT circuits. The fabrication of such devices is currently underway.

## 6. Conclusions

In conclusion, we have demonstrated the photolithographic patterning of chemically sensitive organic electronic materials using parylene as an intermediary. With two complimentary patterning approaches available, a wide variety of structures with small dimensions may be fabricated out of low molecular weight as well as polymeric electronic materials. As a result, photolithography may yet play a role in future organic electronics manufacturing efforts.

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