Patterning of α-Sexithiophene Single Crystals with Precisely Controlled Sizes and Shapes

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Organic single-crystal field-effect transistors (FETs) are ideal device structures for studying fundamental science associated with charge transport in organic semiconductors and have demonstrated superior performance and outstanding electrical characteristics.[1–6] However, it remains a technical challenge to integrate single-crystal devices into practical electronic applications. A major difficulty is that organic single-crystal devices are usually fabricated through the hand selection and placement of individual crystals on a device structure, which prohibits the mass production of devices at high density and with reasonable throughput.[7,8] We recently reported a novel patterning approach which employs physical vapor transport to fabricate large arrays of patterned organic single crystals.[7,9,10] In this technique, rough thin-film domains of octadecyltriethoxysilane (OTS) or carbon nanotube (CNT) bundles were microcontact-printed onto a clean Si/SiO₂ surface, and the nucleation of vapor-grown organic single crystals was restricted to the printed OTS or CNT domains.[7,9,10] Using this technique, a variety of high-mobility organic semiconductors including pentacene, tetracene, α-sexithiophene (α-6T), and so forth were successfully patterned, and large arrays of organic single crystal FETs with mobilities as high as 2.4 cm² V⁻¹ s⁻¹ were reported. However, two main issues still remain to be addressed. First, with either OTS or CNTs as templates, the size and shape of organic crystals are not well controlled. The nonuniformity in size and shape of patterned organic crystals will result in differences in "effective" channel width and thus variation in device performance. Second, it was observed that the crystals of

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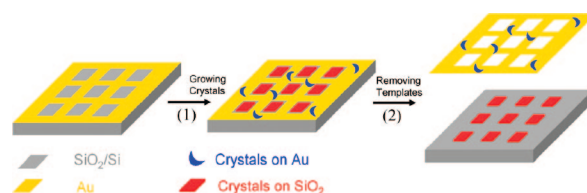

Figure 1. Schematic of the crystal patterning process. (1) Crystals are grown onto a substrate with patterned Au films. (2) Au films and α-6T crystals on top of Au surface are removed.

some molecules such as α-6T do not grow conformably to the substrate surface when CNTs are used as nucleation sites. These nonflat crystals have poor contact with substrates and are difficult to integrate into FET applications. Therefore, it is highly necessary to develop another template which not only allows the deposition of organic single crystals on designed locations but also flat geometry and well-defined sizes and shapes.

In this communication, we demonstrate that an SiO₂ surface with patterned Au films can act as an effective template for the aforementioned purpose. α-6T, which is a well-known organic semiconductor and has been widely used in FET applications,[11–13] was selected as a model system for this study. On Au/SiO₂ films with patterned holes in the Au film, it was observed that α-6T crystals either nucleate on the top of the Au film or from the edges of the Au film, in which case they then continue to grow two dimensionally on the SiO₂ surface. Crystal growth on SiO₂ terminates only when approaching the side walls of patterned Au films. Thereby, the sizes and shapes of α-6T crystals are precisely determined by that of the Au patterns. After the gold film is stripped off, large arrays of α-6T crystals with controlled sizes and various shapes such as stripes, squares, hexagons, and so forth are obtained. Top-contact FETs fabricated with ribbon-like α-6T crystals exhibited mobilities as high as 0.1 cm²/(V s).

Figure 1 shows a schematic of this patterning process. In the first step, α-6T single crystals are grown onto a substrate with patterned Au films using procedures similar to one described previously.[9] We know through previous experience that α-6T grows into large and flat crystals on SiO₂ and small and curved crystals on Au. Second, after crystal growth, the Au film is removed and with it the crystals that grew on top of the Au. This leaves behind a patterned array of α-6T crystals on a SiO₂ surface.

Figure 2a,b shows α-6T single crystals grown on a SiO₂ surface with patterned Au regions. In the bottom part of Figure 2a, it can be seen that α-6T crystals grown on Au and SiO₂ show very different morphologies. On Au, α-6T forms three-dimentional (3-D) crystals of smaller size (<10 μm in length and width), while on SiO₂, flat and large two-

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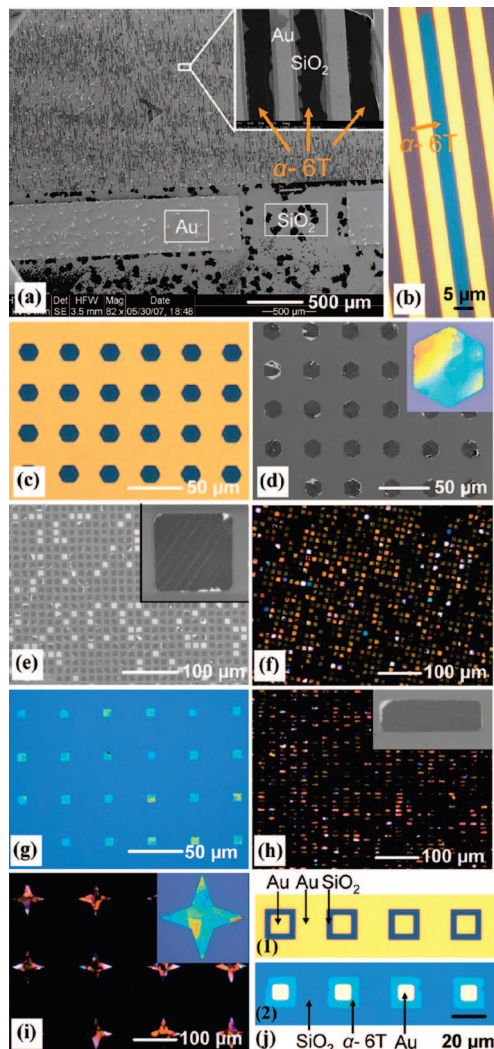
Figure 2. (a, b) SEM image (a) and optical micrograph (OM) (b) of α-6T crystals grown on surface with patterned Au stripes. (a) The inset SEM image shows the close-up of the regions marked with solid lines. (b) Brighter regions show the Au stripes, and dark regions show the SiO₂ surface. The arrows point to α-6T crystals. (c) OM of a substrate with patterned Au films. Brighter regions show Au films, and darker regions show SiO₂. (d–i) OM and SEM images of α-6T crystals with different sizes and shapes on SiO₂ surfaces. (d) SEM image; inset: OM. (e) SEM image. Darker squares show α-6T crystals, and brighter squares show the regions missing crystals. (f) Cross-polarized (CP) OM. (g) OM. (h) CPOM; inset: SEM image. (i) CPOM; inset: OM. (j) OMs of a substrate with patterned Au films (1) and patterned crystals on the same substrate (2).

dimensional (2-D) crystals (∼50 μm in length and width) are formed. It has been widely reported that organic semiconductors deposited on Au and SiO₂ surfaces usually show different morphologies.[14–17] More interestingly, it was observed that when the size of the voids in the Au film are smaller than the typical size of crystals grown on unpatterned SiO₂ surface (∼50 μm), the α-6T crystals fill the SiO₂ voids in the Au film entirely. Therefore, their shape and size can be easily controlled. As shown in the upper part of Figure

2a,b, α-6T crystals have an elongated shape on patterned SiO₂ stripes, with the width of crystals (∼5 μm) equal to that of the SiO₂ stripes (∼5 μm). It seems that the α-6T crystals stop growing when they approach the side walls of the Au film.

In order for patterned α-6T crystals to be integrated into device structures, it is very important to remove Au templates after crystal growth. A "dry" taping process which we developed previously to pattern organic semiconductor thin films[18] was applied to remove Au templates. In this method, scotch tape is placed gently on a substrate with α-6T crystals and then manually peeled off. It was observed that continuous Au films and 3-D crystals on top of the Au films are selectively removed, leaving behind patterned 2-D crystals on the substrate. The advantage of this method for removing the Au film is that the α-6T crystals are not exposed to any solvent or etchant, avoiding potential degradation of the α-6T crystals.

Through designing substrate patterns with different sizes and shapes, α-6T crystals of various sizes and shapes can be fabricated as shown in Figure 2c–j. Figure 2c shows the substrates patterned with Au films containing hexagonal voids that expose the SiO₂ surface. After the crystal growth and the "taping" process that removes the gold, arrays of α-6T crystals with exactly the same size and shape as designed SiO₂ regions were obtained (Figure 2d). Similarly, patterned α-6T crystals with square (Figure 2e–g), rectangular (Figure 2h), and star shapes (Figure 2i) can also be grown with yield higher than ∼80%. In cross-polarized optical micrographs (Figure 2f,h,i), these crystals show strong birefringence, indicating a high degree of crystallinity. Furthermore, from the inset of Figure 2e, we can see arrays of parallel cracks on a α-6T crystal, indicating its single-crystalline nature.[19] One interesting property of this "taping" process is that only continuous Au films are removed, while individual Au domains remain on the substrates. Then by designing surface patterns as shown in the upper part of Figure 2j, α-6T crystals with complex shapes surrounding patterned Au squares were also achieved.

The nucleation of α-6T crystals was studied using substrates with different Au patterns. It was observed that when only a small amount of the total surface area is covered by gold, most crystals nucleate from the side wall of Au patterns (Figure 3a). In this case most α-6T are deposited on the SiO₂ surface and reach the edges of Au pattern by surface diffusion. The edges of the Au film are energetically favorable locations of adsorption owing to the increased coordination that is offered to the molecules there. The side walls of the Au film may also be rougher than the top surface of Au films, further enhancing this effect. An increased probability for nucleation at surface discontinuities is supported by theoretical and experimental evidence.[7,10,20,21] In the inverse case, that is, when the Au film covers a large

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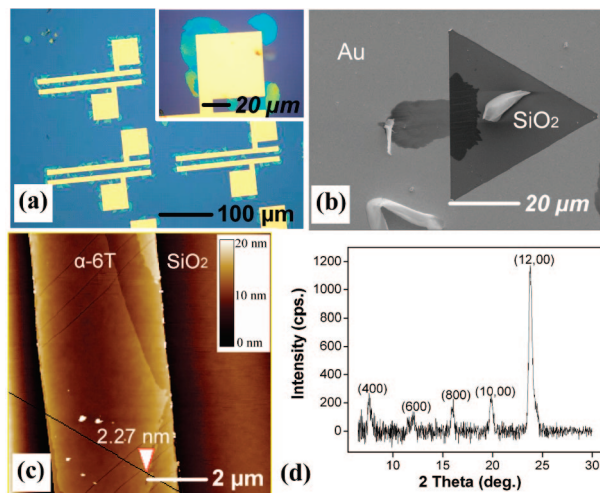(21) Granasy, L.; Borzsonyi, T.; Pusztai, T. *Phys. Rev. Lett.* **2002**, *88*, 206105.

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Figure 3. (a, b) OM (a) and SEM (b) images of α-6T crystals nucleated on surfaces with patterned Au films. (c) AFM height image of a ribbon-like α-6T crystal. The triangles indicate the step edge of one layer. (d) XRD analysis of α-6T crystals.

portion of the substrate surface, crystals nucleate randomly on top of the Au surface and then grow out into the SiO_2 voids as shown in Figure 3b.

Atomic force microscopy (AFM) was used to study the morphology of obtained α-6T crystals. From Figure 3c, it can be seen that the obtained crystals are composed of several layers, with the thickness of each layer (indicated by the triangles) being ∼2.3 nm, corresponding to a single layer of α-6T molecules. The average thickness of the obtained crystals is ∼10−20 nm, which is smaller than that of the Au patterns (∼45 nm). This may explain why the Au film can act as a barrier for crystal growth. Furthermore, similar to the result shown in Figure 2e, a series of parallel cracks on different layers were observed on inspection by AFM (Figure 3c). In order to support that the orientation of the cracks is related to the crystal orientation instead of the strain on the substrate, 10 neighboring crystals were randomly selected and inspected. It was found that cracks on the same crystal show the same orientation, while cracks on different crystals show different orientations without a noticeable trend. This result suggests that the crack orientation is associated with the crystal orientation, and crystals with aligned cracks are most probably single crystalline. The crystals were also characterized by X-ray diffraction (XRD), which indicates that the molecules crystallized on substrates with an edge-on orientation, that is, the long axis of the α-6T molecule being nearly perpendicular to the substrate surface.[12]

To evaluate the electrical properties of obtained crystals, top-contact FETs were fabricated by depositing source and drain electrodes through a shadow mask on α-6T ribbons. The optical micrograph of obtained devices is shown in Figure 4a. Figure 4b displays the well-defined transfer and output characteristics of a typical α-6T transistor. The output characteristics exhibit excellent gate-modulated current in the saturation region. Average mobilities (from 10 randomly selected devices) calculated in the saturated regime were
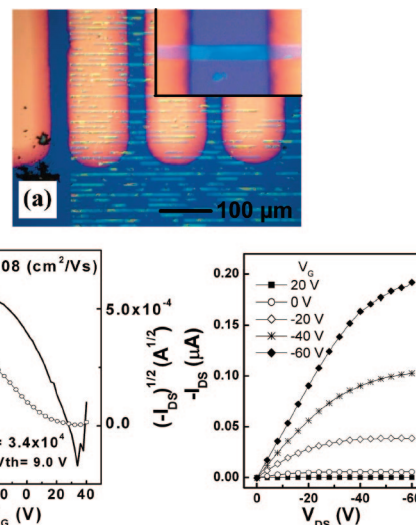

Figure 4. (a) OM of top contact FETs with α-6T ribbons. (b) Transfer and output characteristics of typical α-6T single crystal field-effect transistors. Transfer characteristics were measured at a fixed source-drain voltage, V_{DS} = −60 V. I_{DS}: source-drain current, V_G: gate voltage.

0.040 ± 0.008 cm^2/(V s) (the highest mobility measured was 0.10 cm^2/(V s)), and typical on/off ratios were ∼$10^3−10^4$. As discussed previously, there are aligned cracks on some of the crystals, and we believe that these cracks may affect the measured mobility. The mobility of these α-6T ribbons was higher than the α-6T thin films prepared through thermal evaporation. For α-6T thin films, top-contact FETs with similar channel lengths showed the best mobility of 0.02 cm^2/(V s) with films deposited at 120 °C.[22] The improvement in field-effect mobility might be attributed to the larger grain size and fewer grain boundaries in α-6T ribbons.[23,24]

In summary, we have demonstrated that an SiO_2 surface with patterned Au films can act as an effective template to pattern α-6T single crystals with flat geometries. It was observed that α-6T crystals nucleate from the edge or the top surface of Au films and then grow two dimensionally on the SiO_2 surface. The sizes and shapes of α-6T crystals are precisely determined by that of the Au patterns. Large arrays of α-6T crystals with controlled sizes and various shapes such as stripes, squares, hexagons, and so forth were achieved. Top-contact FETs fabricated with ribbon-like α-6T crystals exhibited good performance, with mobilities as high as 0.1 cm^2/(V s). So far this patterning approach has been only applied to grow α-6T crystals.

Supporting Information Available: Detailed experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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