

Size and Shape Controlled Growth of Molecular Nanostructures on Silicon Oxide Templates

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Abstract

A new process for nanoscale fabrication of ordered monolayer films of conjugated organic molecules is presented. The process makes possible to grow sexithiophene monolayers (T6) at precise locations on a silicon substrate with a high degree of order while preserving the orientation of growth. The process is based on the integration of local oxidation nanolithography of the substrate and template growth of the molecular thin film. The former is used to fabricate silicon oxide arrays of parallel lines of 30-50 nm in width and several microns in length. Template growth arises from the interplay between kinetic growth parameters and preferential interactions with the patterned surface. The result is a monolayer film of organic molecules that conformally mimicks the features of the fabricated motives. This approach could be used to connect molecular domains of well defined size between metallic electrodes.

New approaches for the fabrication of planar devices based on materials by design are critical for the development of organic electronics^[1-6]. Assembling devices by self-organisation of functional elements that take the proper position and shape and establish connections with the other components, is a major aim of nanotechnologies. The advantage of this approach is twofold. On one hand, the possibility to implement additive manufacturing^[1], viz. the usage of the optimum amount of material needed for the performance of the device; and on the other hand, the capability of tailoring the relevant properties of those devices such as charge mobility, spin coherence length, charge separation or radiative relaxation by controlling the lateral size of the active material to a few tens of nanometers^[7-9]. Since the length scales of transport phenomena in conjugated materials are in the nanometer range, optimising the organisation at the nanometer scale would lead to an enhancement of the transport properties.

Currently there is not an established fabrication approach for conjugated materials that allows to preset the position, size and shape of domains. Consolidated thin film growth techniques in organic electronics, such as spin casting and organic molecular beam deposition (OMBD) lack the control of lateral size of the domains, due to random nucleation on one hand, and coalescence of uncorrelated domains on the other hand^[10].

In this letter we report a new process for the fabrication of molecularly ordered nanostructures made of sexithienyl (T6) on a silicon oxide template. The method yields monolayer stripes or wires, whose width ranges from few tens up to a few hundred nanometers. These low-dimensional structures are grown at pre-determined positions on the substrate, their shape and size being controlled by a template fabricated on the substrate.

The molecules on the template maintain their orientation with their long axis normal to the substrate, viz. the same orientation as those forming islands outside the template.

The process is based on the integration of local oxidation nanolithography of the substrate and template growth of the molecular thin film by high-vacuum sublimation on the fabricated pattern. Local oxidation is used to fabricate silicon oxide arrays made of either parallel lines or stripes. Their width is 30-50 nm and 400 nm respectively, their length is up to several micrometers. Template growth of T6 arises from the interplay between kinetics of growth and the preferential interactions with the patterned structures. The result is a monolayer film of organic molecules that conformally mimicks the features of the fabricated motives.

Local oxidation nanolithography is a new lithographic method based on the spatial confinement of the oxidation reaction within a liquid meniscus formed between a nanometer-size protrusion, usually, although not exclusively, the tip of an atomic force microscope (AFM), and the sample surface^[11-14]. The parallel upscaling of the local oxidation method makes this nanolithography suitable for large scale patterning of surfaces^[15-16].

An image of one of the patterns fabricated by local oxidation on a silicon wafer is shown in Figure 1. The pattern is made of 52 parallel lines that are 107 nm apart. Each line is about 6.5 μm in length, 50 nm in width and protrudes 2.6 nm from the substrate baseline (Fig. 1(c)). Each oxide line is fabricated by the sequential application of a series of voltage

pulses. A voltage pulse (24 V, 10 ms) generates an oxide dot of about 2-3 nm and 30-50 nm in height and diameter respectively. Between pulses the tip is displaced laterally 5 nm.

Sexithienyl molecules were deposited onto the nanofabricated substrates by sublimation in ultra high vacuum of the polycrystalline material from a Knudsen cell in an Organic Molecular Beam Deposition apparatus. In order to obtain the formation of two-dimensional ordered T6 layers, high substrate temperature during deposition, and low deposition rate and film thickness were chosen on the basis of the T6 film “kinetic” phase diagram^[17].

Figure 2(a) shows a representative monolayer island of T6 grown on the bare silicon substrate. The island consists of several gulf regions bound by a stepwise border. The coastline fractal dimension is found equal to 1.5, i.e, a value that is midway between fractal dimensions of DLA and compact islands, 1.7 and 1.3 respectively. The two-dimensional growth process could be explained by an extension of the deposition, diffusion and aggregation model that considers molecular diffusion along the island edges as a function of the energy of the bond formed by the incoming molecule with the nearest neighbours^[18].

The height of the island is about 2.5 nm (Fig. 2b), i.e., close to the van der Waals length of the T6 long axis, 2.7 nm. It matches half of the a-axis periodicity in the crystal structure (2.4 nm)^[19-20]. This indicates that the monolayers are growing with the molecules oriented almost normal to the surface which is consistent with other studies of thiophene oligomer thin film on glass, mica and silicon oxide^[21-23].

Figure 2(c) shows the angular distribution of the longest straight line across the island with respect to the pattern direction. The data have been taken from an statistical analysis of more than 100 islands grown far from patterned regions. The histogram shows a

rectangular distribution which underlines the absence of preferential growth directions on the bare (unpatterned) substrate.

The morphology of the island changes dramatically when nucleation occurs in the vicinity of the patterned area (Figs. 3a-c). The initial isotropic island growth, with features very similar to the ones observed far from patterned areas is abruptly stopped when the growing island touches the local oxide patterned area. There, the molecules penetrate the patterned area forming long fingers parallel to the silicon oxide lines. This gives rise to the formation of T6 wires or tracks of several microns in length and a few hundreds nm in width. The length of the molecular film is mostly determined by the length of silicon oxide lines (Fig. 3 (a)) while the width is controlled by the lateral size of the stripes or the separation of the oxide lines.

The mass gradient observed between the upper and lower parts of Fig. 3a suggests a net transport of the molecules from one side to the other of the patterned area. In the process a continuous track of T6 molecules was formed. In the narrowest region the track is about 100 nm in width (Fig. 3c). Inside the patterned region, the film shows a periodic modulation (brighter lines) as the result of the growth of the molecules on the silicon oxide motives.

The upper part of Fig. 3a shows that during the earlier stages of growth the island is in contact with several oxide lines, however, anisotropic growth is only observed across a few of them. This selection indicates that the interactions of the molecules as well as the surface diffusional barriers along the lines may vary from line to line (see discussion below). To make the effect of the lines more homogeneous, and to enhance the influence of the pattern onto the anisotropic growth of the T6 monolayer, we have reduced the pitch between oxide lines to 50 nm which, effectively, generates a set of oxide stripes (Fig. 4a).

Outside the patterned area the islands exhibit a morphology characterized by the presence of branches and fingers with no preferential orientation. However, the morphology changes dramatically within the patterned area. There, the molecules grow preferentially on top of the stripes and parallel to them. The coverage (the areal fraction covered by molecules) on top of the stripes is about 88% while outside the patterned area is about 50%.

The height difference between the topography of a silicon oxide motif with and without molecules on top corresponds to the height of the monolayer islands grown on the bare substrate (Fig. 4d). The local oxide does not perturb either the monolayer character or the orientation of the molecules with respect to the substrate, it only affects the direction of growth parallel to the silicon oxide nanostructures. This is a clear evidence of the possibility to fabricate low-dimensional structures and wires with molecules standing up with respect to the surface by template growth. It is important to notice that this method yields the optimum orientation for in-plane charge transport in field-effect transistors. Other rodlike thiophene oligomers and polymers can self-organise on surfaces to form fibrils and stripes, but the thiophene chains are oriented edge-on with respect to the substrate and with their long axis normal to the director of the fibril^[24].

Our results indicate that the formation of T6 wires is an interplay between kinetics effects controlled by the deposition parameters and preferential interactions with silicon oxide patterns. The kinetic parameters allow the molecules to follow the contours of the growing island until they reach the silicon oxide line (Fig. 3b). However, a reduction of the substrate temperature from 150° to 120° reduces the diffusivity of the molecules on the substrate, yielding smaller islands, and at the same time quenches the preferential growth of T6 on the patterns.

The morphological transition observed in Figures 3a and 4c from isotropic to anisotropic growth and the ensuing highly anisotropic growth of T6 fingers and stripes reveals a reduced activation barrier for diffusion within the patterned area. Such a high anisotropy strongly suggests that molecular order is coherently preserved within the growing island, and that the fingers are possibly made of a single ordered domain.

Local oxides protrude from the bare substrate and this introduces a corrugation across the lines. However, topographic changes of the substrate do not seem to play a significant role in the template growth observed. For example, when T6 was grown on a pattern consisting of a parallel array of trenches (about 1 nm deep) no evidence of template growth was found.

Compositional differences between native and fabricated oxides arise from the non-stoichiometric character of the local oxide as well as its defective nature, due to the presence of trapped ionic species during the growth of oxide at the Si/SiO₂ interface, e.g., $\equiv\text{Si}-\text{H}+\text{h}^++\text{H}_2\text{O}\rightarrow\equiv\text{Si}+\text{H}_3\text{O}^{+[25]}$. Small fluctuations in the tip-sample distance during the local oxidation process, would make the density of trapped charges inhomogeneous from line to line and from different segments along the same line. Thus explaining the variable width of the T6 track shown in Fig. 3. However, this effect is corrected by reducing the line pitch, i.e, by increasing the surface density of local oxides (Fig. 4).

Those charges, either buried or at the surface generate a weakly screened long range electrostatic potential, that becomes especially relevant in the case of T6 because of its large anisotropic polarizability together with the inhomogeneous charge density distribution

along the thiophene chain. Thus, the trapped charge in the oxide line is most likely the source of preferential, albeit not specific, interactions between the fabricated oxide lines and the molecules.

In conclusion, we have demonstrated a process for the fabrication of ordered low-dimensional structures of sexithienyl molecules. The process is based on the integration of local oxidation lithography of the substrate and template growth of the molecular thin film. The main result is the control of the shape anisotropy, the domain size and regularity of the edges, preserving at the same time the spatial correlation in the growing layer. The accuracy of the fabricated molecular domains is dictated by the quality of the lithography process that fabricates the template. The size of the domains is comparable to the extension of the fabricated motif while does not depend on the characteristic domain size of the material grown on the bare substrate. The present process is suitable for the fabrication of parallel arrays of nanometer-size T6 stripes and wires. The molecules in these low-dimensional domains stand with their long axis almost normal to the substrate which favours the conditions for in-plane charge transport in organic transistors. Those wires, due to their precise geometries, would allow systematic studies of charge transport in nanometer-size conjugated organic molecular wires placed between planar electrodes.

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Figure Captions

Figure 1. Dynamic AFM images of a parallel array of silicon oxide lines fabricated by local oxidation nanolithography. The lines are 106 nm apart with an average width of 50 nm. (b) High resolution image of the region marked in (a). (c) Cross-section along the line shown in (b). The lines protrude 2.6 nm from the substrate baseline.

Figure 2. Dynamic AFM image of a sexithiophene monolayer island in a region of the bare substrate far from the patterned areas. (b) Height profile of the T6 island. (c) Histogram of the angles between the longest straight line across T6 islands grown on the bare substrate and the oxide lines.

Figure 3. Dynamic AFM images of several T6 islands grown in the vicinity of a local oxide pattern. (b) High resolution image of the upper section and (c) High resolution image of the lower section. The narrowest section of the T6 track is about 100 nm. The anisotropic growth gives rise to the formation of a T6 wire of 6 μm and 400 nm in length and width (mean value) respectively.

Figure 4. Dynamic AFM images of T6 molecules grown on a parallel set of local oxide stripes. (a) Template growth of T6 on local oxide patterns. (b) Cross-section along the line marked in (a). (c) Anisotropic T6 growth on an array of local oxide stripes. (d) High resolution AFM image of the region marked in (c). The remarkable morphological differences between the T6 nanostructures on the stripes and those T6 islands grown on the bare silicon substrate illustrate the template growth process

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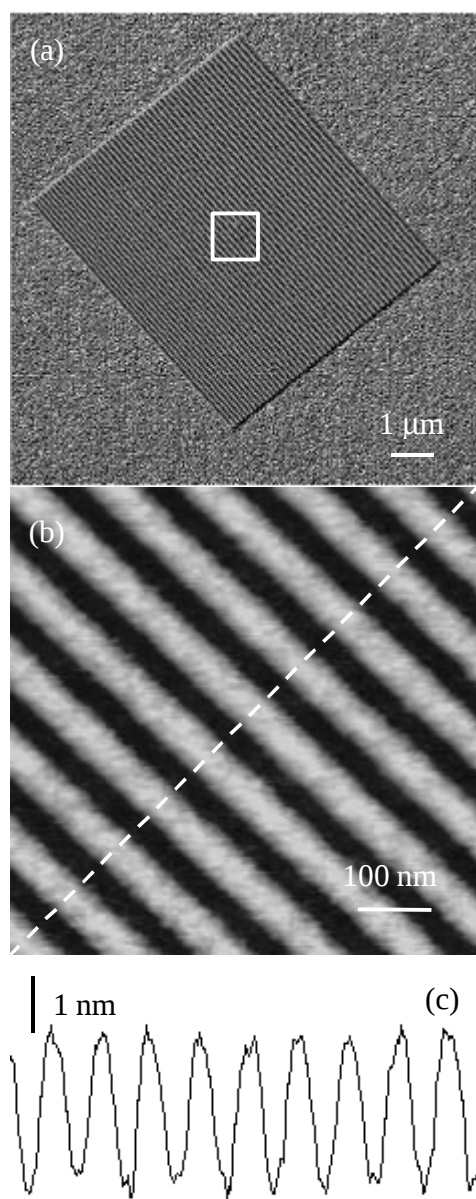


Figure 1

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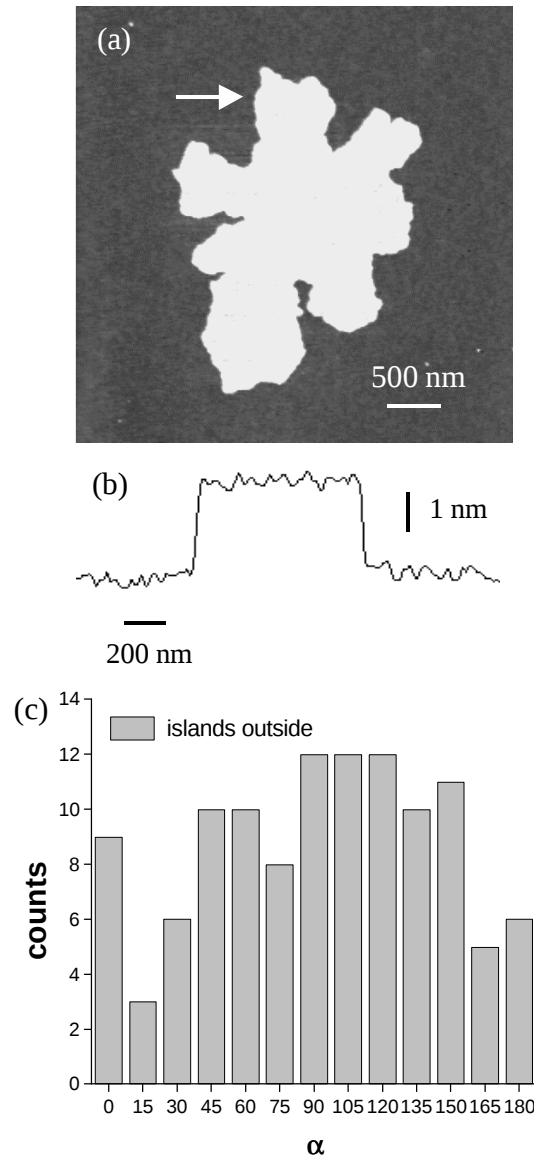


Figure 2

R. García, M. Tello, J.F. Moulin and F. Biscarini

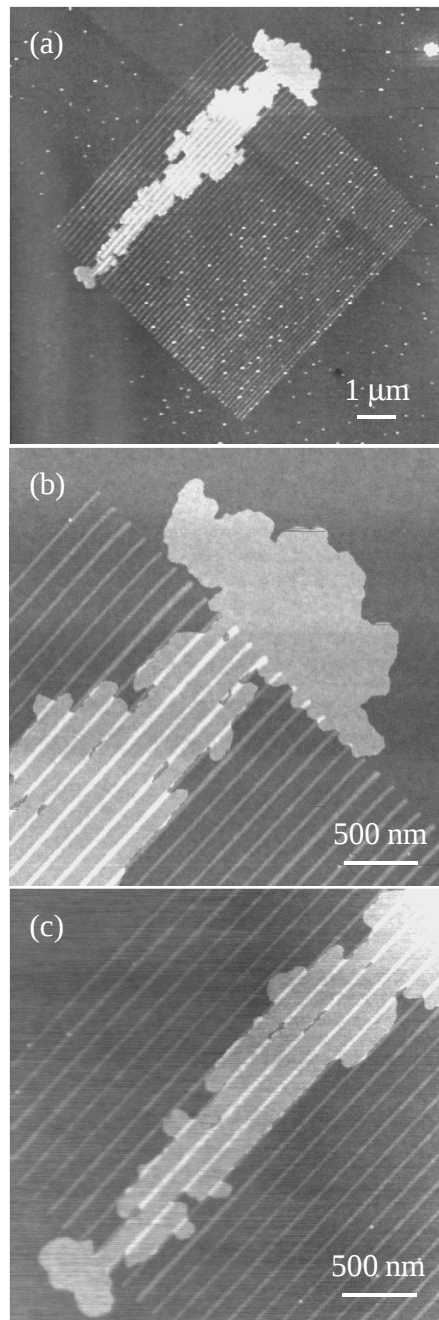


Figure 3

R. García, M. Tello, J.F. Moulin and F. Biscarini

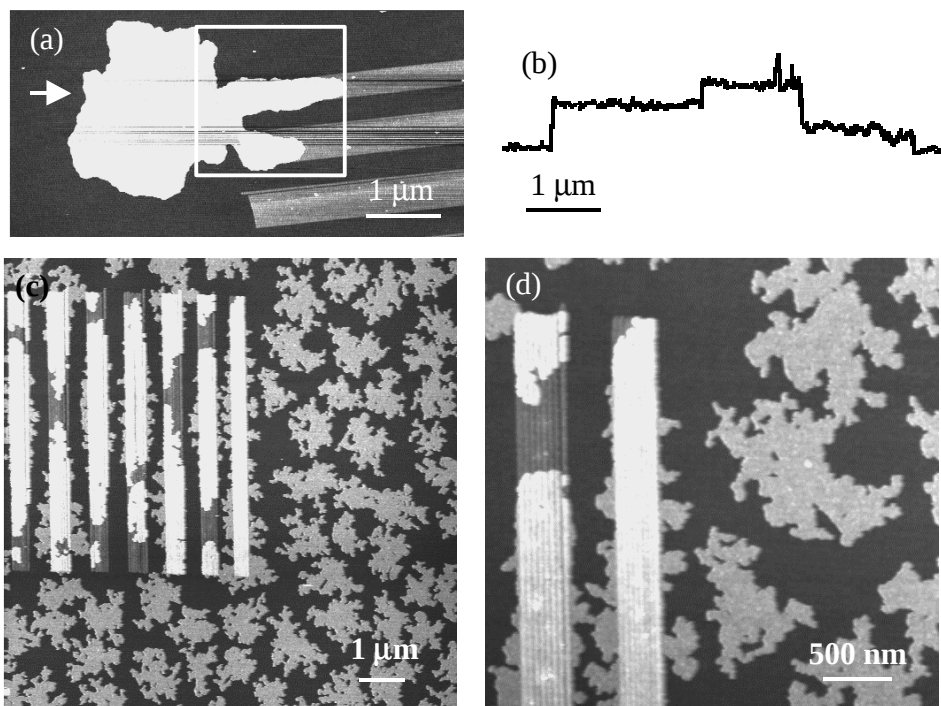


Figure 4

R. García, M. Tello, J.F. Moulin and F. Biscarini