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Sequential and parallel patterning by local chemical nanolithography

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Abstract

Nanometre-size menisci of various liquids such as water, ethanol, 2-propanol, octane, and 1-octene have been formed and used to confine chemical reactions by using an atomic force microscope. The application of a bias voltage between a conductive scanning probe tip separated a few nanometres from a sample surface enables the field-induced formation of a nanometre-size liquid meniscus. Those menisci are subsequently used to fabricate nanometre-size structures on different materials. The growth kinetics of the fabricated nanostructures depends on the chemical nature of the liquid. Higher growth rates are obtained with octane. The differences in growth rates underline differences in the chemical composition of the fabricated motifs. We report the fabrication of different nanostructures such as arrays of dots, wires and stripes. The fabricated motifs can be used as templates for the growth of conjugated molecular materials. We also show that the local chemical processes can be scaled up for parallel patterning. Patterning arrays of parallel lines 100 nm apart has been demonstrated over mm^2 regions.

1. Introduction

The last decade has seen the emergence of a fascinating variety of nanoscale manipulation and modification approaches based on the use of scanning probe microscopes [1–7]. Some of the most successful approaches are those based on the spatial confinement of a chemical reaction within a nanometre-size region [5]. In many cases of interest a nanometre-size liquid meniscus is used to either confine the lateral extension of a chemical reaction or to control the lateral diffusion of organic molecules. In particular, water menisci have been extensively used to fabricate nanoscale oxides of different materials (local oxidation). The present knowledge enables us to establish some similarities between local and conventional anodic oxidation. An atomic force microscope (AFM) tip is used as a cathode and the water meniscus formed between the tip and the surface is the source of the oxyanion species [8–10]. The strong localization of the electrical field lines near the tip apex and the lateral confinement of the oxyanion species within the liquid meniscus give rise to a nanometre-size oxide dot.

A large variety of materials has been patterned by local oxidation such as metals [10], semiconductors [11–13], dielectrics [14], perovskite oxides [10, 15] and self-assembled monolayers [16].

Recently, it has been shown that nanostructures could also be fabricated by using an atmosphere saturated with organic solvents such as ethyl alcohol, hexadecane, 1-octene and octane [17–20]. In the former case, the fabricated structures on a silicon surface were no longer oxides but showed the formation of silicon carbide and carbon sp^2 compounds [21]. In the latter case, it was shown that the nanostructures could be used as etch-resistant resists [18].

Here, we perform local chemical modifications by using and manipulating nanoscale menisci of water, ethanol, 2-propanol, octane, and 1-octene. Those menisci are used to fabricate nanometre-size structures on different materials. The growth kinetics is highly dependent on the chemical nature of the liquid meniscus. Higher growth rates are obtained with octane. The observed differences in growth rates underline differences in the chemical composition of the fabricated

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motifs. We report the fabrication of different nanostructures such as arrays of dots, wires, and stripes. The patterns fabricated by using water menisci on silicon surfaces can be used as templates for the growth of conjugated molecular materials. We also show that the local chemical processes can be scaled up for parallel patterning by replacing the AFM tip with a stamp with multiple protrusions.

2. Experimental set-up

The local chemical nanolithography was performed with an amplitude modulation atomic force microscope (figure 1(a)) operated in the low amplitude solution (noncontact or attractive regime) and with additional circuits to apply voltage pulses. The microscope was placed in an inner box with inlets for dry nitrogen and water or organic vapours. The inner box was enclosed in an outer box with an output to extract leaked organic vapours. First, the AFM chamber was purged of water vapour by flushing with dry N_2 for about 30 min. This reduced the relative humidity below 1%. Then, the chamber was filled with one of the following solvents, ethanol, 2-propanol, octane or 1-octane vapours (Sigma-Aldrich). Those vapours keep the relative humidity below 1%. The local oxidation experiments (water meniscus) were performed with the AFM exposed to the laboratory relative humidity (30–40%).

Noncontact nanolithography was performed with an AFM operated in the amplitude modulation AFM mode [22]. We have used doped n+-type silicon cantilevers (Nanosensors, Germany). The force constant k and resonance frequency f_0 were about 42 $\mathrm{N\,m^{-1}}$ and 320 kHz, respectively. The cantilever was excited at its resonance frequency. The silicon samples were p-type Si(100) with a resistivity of $\rho \sim$ 10–12 Ω cm, the InP was of n-type ($\rho \sim 7 \times 10^{-4}\ \Omega$ cm), and the GaAs was n-type with $5 \times 10^{-3}\ \Omega$ cm. The Nb sample consisted of 10 nm of Nb deposited by sputtering on a Si(100) substrate.

The parallel patterning was performed by using a specially built instrument that consists of an isolated chamber where the sample and a stamp are placed face to face. The chamber has inlets for controlling the relative humidity inside. The stamp and the sample approach are controlled by using micrometric screws. The stamp is made by e-beam lithography with multiple parallel motifs that are silicon stripes of 20 μm length, 100 nm tall and 200 nm wide. Each line is separated from the next by a gap of 100 nm.

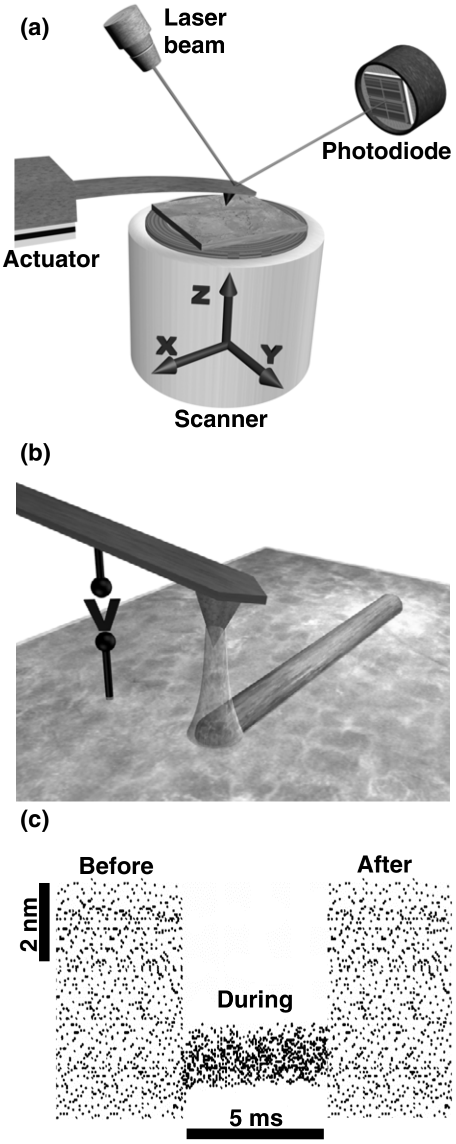

Figure 1. Schematic description of the AFM used to perform local chemical nanolithography. (a) Overall view of the AFM system. (b) A liquid meniscus bridging the tip and the sample mediates the nanofabrication process. (c) Experimental cantilever–tip oscillation as a function of time before, during, and after the application of a voltage pulse of 36 V for 100 μs. Each point indicates the instantaneous tip deflection. The dotted aspect of the tip's oscillations is because the oscillation period is about five orders of magnitude smaller than the pulse time width.

3. Local chemical nanolithography

Local chemical nanolithography is a new lithographic method based on the spatial confinement of chemical reactions within a liquid meniscus formed between an AFM tip and the sample surface. The chemical composition of the fabricated structures depends on the chemical nature of the liquid meniscus.

3.1. Local oxidation nanolithography

In scanning probe-based oxidation a water meniscus provides both the chemical species (oxyanions) and the spatial confinement for the anodic oxidation of a nanometre-size region of the sample surface [8–10]. The application of a voltage pulse between the tip and the sample polarizes the water molecules in the gas phase and those absorbed on the sample surface. When the voltage is above a certain threshold value, a field-induced liquid meniscus is formed between tip and sample surface. The AFM tip is used as a cathode and the water meniscus provides the electrolyte (figure 1(b)).

Figure 1(c) shows the tip oscillation as a function of time before and after the application of the voltage pulse. When the pulse is on the electric field deflects the mean position of the tip and reduces its oscillation amplitude. After turning the pulse off, the amplitude remains reduced and the tip mean position is slightly deflected towards the surface because the field-induced

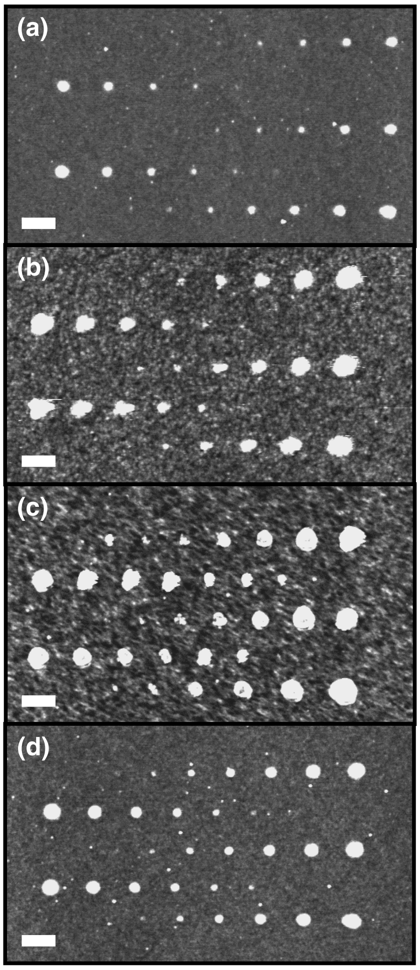

Figure 2. Oxide dots produced on different materials: (a) Si, (b) GaAs, (c) InP, (d) Nb. For each line, the dots have been done at constant voltage and with nine different oxidation times (0.0003, 0.001, 0.003, 0.001, 0.03, 0.1, 0.3, 1, 3 s). The white bar is 200 nm.

liquid meniscus exerts an attractive force between the tip and the surface.

Figure 2 shows several oxide dots fabricated by the above methods in different semiconductor and metallic surfaces such as silicon, gallium arsenide, indium phosphide, and niobium. The dots have been generated by applying pulses with a fixed voltage (12 V, sample positive) at different pulse times (0.0003, 0.001, 0.003, 0.001, 0.03, 0.1, 0.3, 1, 3 s). There is a clear dependence of the dot size with the pulse duration and sample chemical composition. This dependence will be discussed below.

3.2. Local chemical modifications by using organic menisci

Local chemical nanolithography has also been performed by liquid menisci made of organic solvents such as ethanol, 2-propanol, octane or 1-octene. The formation of a liquid meniscus from organic solvents is similar to the process to form a water meniscus.

In figure 3(a) we show an array of 49 dots formed in an octane atmosphere. Each dot has been formed by the application of a voltage pulse of 36 V for 100 μs. The dots' apparent width and height are 8 and 2.8 nm respectively. Figure 3(b) shows an array of dots fabricated in an ethanol atmosphere. Each dot has been formed by the application of a voltage pulse of 20 V for 100 μs. The nanostructures fabricated with octane have a much better aspect ratio (height/width) than those obtained in ethanol (0.1 versus 0.016). However, for the same conditions, the nanostructures fabricated in ethanol are larger.

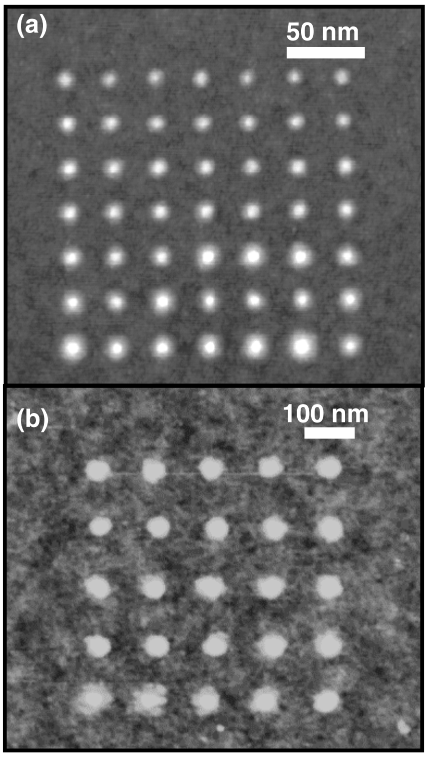

Figure 3. Arrays of dots fabricated by using octane (a) and ethanol (b) liquid menisci. Voltage pulses of 36 and 20 V were applied for (a) and (b) respectively. In both cases the pulse duration was 100 μs.

3.3. Kinetics and chemical analysis

The size of the nanostructure formed depends on the duration and strength of the voltage pulse as well as on the nature of the liquid meniscus. We start with the growth kinetic studies involved in local oxidation because they have been thoroughly studied [23–25]. The general trend is as follows. The local oxidation process in aqueous environments is characterized by a high initial growth rate that decays rapidly and finally saturates. The dependence of the height and width of the oxides with the oxidation time shows a logarithmic dependence for Si, GaAs, InP and Nb. These results are also in agreement with the results reported by other authors. The general behaviour observed for the oxidation of different surfaces under a water environment is not preserved when changing the nature of the liquid meniscus.

Figure 4 shows two plots of the vertical growth of the structures produced under different liquid environments with time. Figure 4(a) illustrates the semilogarithmic dot height dependence on pulse duration and liquid menisci composition

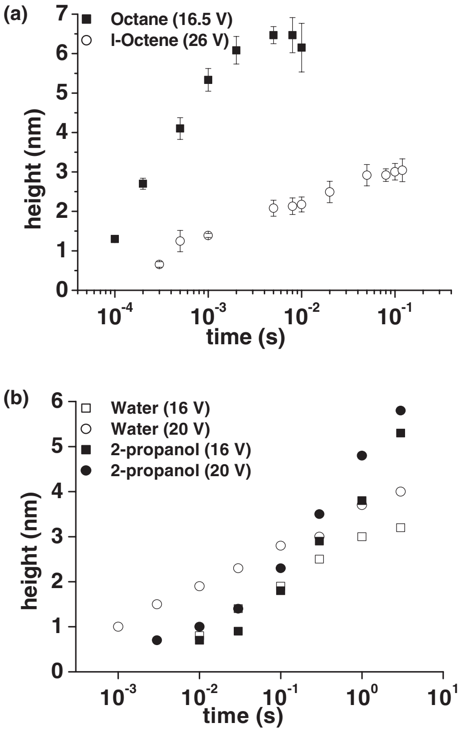

Figure 4. Height dependence of the dots with pulse duration for different solvents: (a) octane and 1-octene, (b) water and 2-propanol.

for applied voltage pulses of 16.5 and 26 V for octane and 1-octene, respectively.

In figure 4(b) the expected linear logarithmic dependence is obtained for water, while in the case of the structures produced in 2-propanol the curve shows a more quadratic trend, in agreement with the results reported for the case of ethanol [17].

We have compared the nanomotive growth kinetics by using different solvents such as water, ethanol, 2-propanol, octane, and 1-octene. For that purpose we have used a power-law parameterization,

$$h(t, V) = bt^{\gamma} \tag{1}$$

where h is the nanostructure height above the substrate baseline, t is the duration of the pulse and $\gamma = 1/(\delta + 1)$. The parameters (b, γ) characterize the growth process: b depends on the voltage and liquid nature while γ depends on the chemical nature of the fluid. Equation (1) has been deduced by considering space-charge accumulation during growth and a charge trapping–detrapping mechanism [24, 25].

For octane we obtain (32 nm, 0.28) while for 1-octene we obtain (4.63 nm, 0.17) (figure 4(a)). Those values should be compared with the ones obtained in water, 2-propanol and ethanol environments (for similar voltages). Values of (9.3 nm, 0.32), (4 nm, 0.3) and (3.48 nm, 0.12) have been obtained for ethyl alcohol, 2-propanol, and water, respectively. The kinetic parameters (b, γ) deduced for octane are the highest ones measured by scanning probe methods, while for 1-octene they are comparable, albeit slightly higher, to those of water.

The fabricated nanostructures show remarkably different parameters depending on the liquid that forms the meniscus; this can be considered as an indication of the different chemical composition of the fabricated motifs. For example, the modifications produced in water are etched in HF, while the ones produced in alcohol still remain after the HF etching. It is well known that the application of a pulse under a water environment yield oxides as reaction products. Several spectroscopy techniques on different materials have confirmed the nature of the structures [12, 21]. However, the modification of the surfaces in an alcohol environment produces carbon-rich structures, as was confirmed for the case of silicon on ethanol [21].

Table 1. Summary of the behaviour of the different nanostructures with respect to etching in HF.

	Etch resistant in HF	
	Yes	No
Water		X
Ethanol	X	
Octane	X	
1-octene		X

The different chemical structure could also explain the results obtained for octane and 1-octene. Figure 4(a) shows that 1-octene presents a linear logarithmic dependence and height values similar to those of water. Furthermore, the fabricated structures are etched by exposing them to HF. On the other hand, octane yields higher structures that saturate very quickly and are etch-resistant to HF. While octane is a nonpolar molecule, the double bond in the 1-octene makes it polar. The fact that the structures obtained in 1-octene present a similar behaviour to those obtained in water could be due to the formation of a water instead of an 1-octene meniscus. As a polar molecule, 1-octene is also very hydrophilic, and thus could be easily contaminated by water. The presence of water should be then avoided when working with polar molecules, such as 1-octene or alcohols, to avoid the formation of a water meniscus. The etch-resistant properties of the fabricated structures with respect to HF are summarized in table 1.

4. Template growth of conjugated molecular materials

One of the most promising applications of local oxidation nanolithography is its use as templates for the growth of organic, biological molecules or semiconductor nanostructures [29, 30]. Here we study the template growth of sexithienyl molecules (T6) onto arrays of parallel lines fabricated by local oxidation. The T6 molecules were deposited onto the nanofabricated substrates by sublimation in ultrahigh vacuum. Figure 5 shows that the morphology of the T6 changes when the nucleation occurs in the vicinity of the array. The initial isotropic island growth changes sharply when the growing island touches the array of parallel lines. There, the T6 molecules penetrate the patterned area, forming long fingers parallel to the silicon lines. Template growth of T6 arises from the interplay between kinetics of growth and the preferential interactions with the patterned structures. The kinetic parameters allow the molecules to follow the contours of the growing island until they reach the silicon oxide line. The trapped charges within the local oxide generate a weakly screened long-range electrostatic potential, which becomes

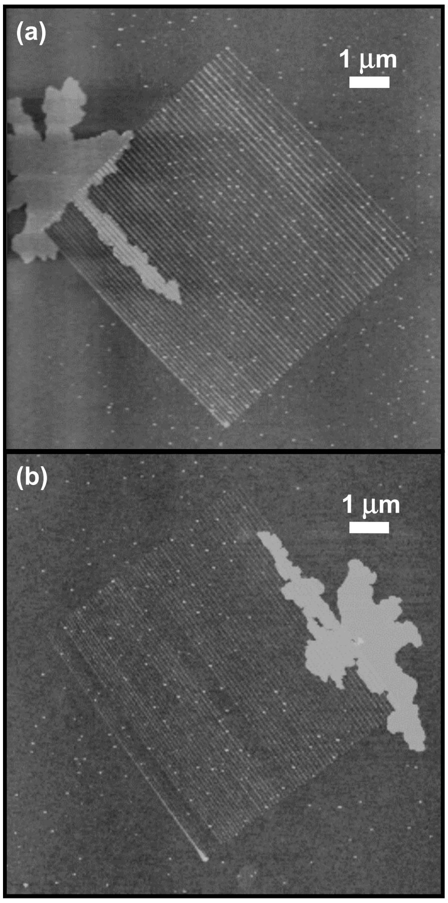

Figure 5. Template growth of T6 molecules onto a local oxide patterns. The array of stripes of the local oxide pattern defines the preferential direction for the molecule's growth. The remarkable morphological differences between the T6 nanostructure on the stripes and the T6 grown on the bare silicon substrate illustrate the template growth process.

especially relevant in the case of T6 because of its large anisotropic polarizability together with the inhomogeneous charge density distribution along the thiophene chain.

5. Parallel nanopatterning by local oxidation

Local oxidation nanolithography by AFM is amenable to parallel processing by replacing the AFM tip by a stamp with millions of reliefs (figure 6) [26–28]. We have designed a master stamp of 1 cm^2 with multiple parallel reliefs to perform local oxidation processes in parallel by using e-beam lithography. The reliefs are silicon stripes of 20 μm length, 100 nm height and 200 nm width. Each line is separated from the next by a gap of 100 nm. The stamp is inserted inside a soft press machine specifically built in our laboratory for making experiments of parallel local oxidation. The stamp is electrically connected to a DC power supply for negative polarization and positioned above a clean silicon sample (p-doped Si(100), resistivity 10 Ω cm). The sample is placed on a base that has three flexible elements. Those elements enable movement in the three orthogonal directions. The stamp and the sample are contained in a sealed chamber with two inlets that permit the introduction of different gases such as water, ethanol or other vapours. Figure 5 illustrates the individual steps required for a parallel local oxidation process. In the first step the stamp and the sample are separated and covered with a thin layer of adsorbed water molecules. The mechanical contact together with the application of a bias produces the formation of a water meniscus. At this point the flexible elements of the base allow a uniform distribution of the pressure on the sample. Finally, applying a 30 V voltage pulse for 1 min causes the oxidation process to occur, and one can also in a posterior step remove the nano-motifs created by etching with HF. Figure 7(a) shows an AFM image of a representative region of the stamp. Figure 7(b) shows an AFM image of the parallel oxidation replica. The cross-section of the stamp (c) and the replica (d) show that the oxidation process reproduces the stamp reliefs but with a height of 5 nm.

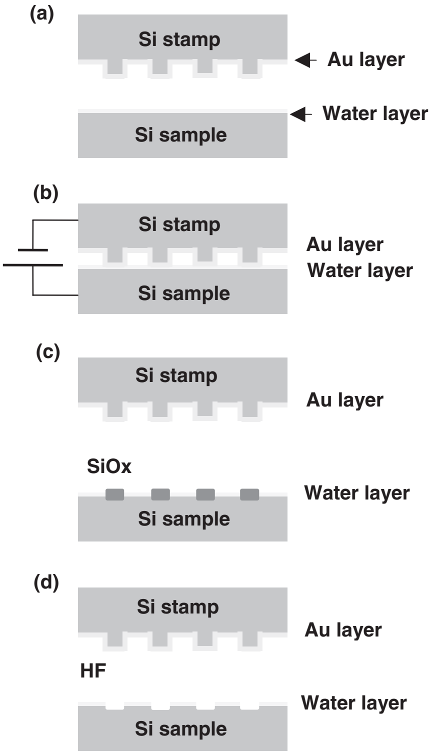

Figure 6. Schematic diagrams of the parallel oxidation process. (a) A thin layer of water covers both the stamp and the sample surfaces. (b) Mechanical pressure is exerted between the stamp and the sample while a bias voltage is applied. The water meniscus provides the oxyanions for the oxidation process. (c) Nano-reliefs created on the sample.

6. Summary

Local chemical nanolithography is performed by confining chemical reactions within the limits of nanoscale liquid menisci such as water, ethanol, 2-propanol, octane, and 1-octene have been formed and used to confine chemical reactions by using an atomic force microscope. The application of a bias voltage between a conductive scanning probe tip separated a few nanometres from the sample surface enables the field-induced formation of nanometre-size liquid menisci. Those menisci are subsequently used to fabricate

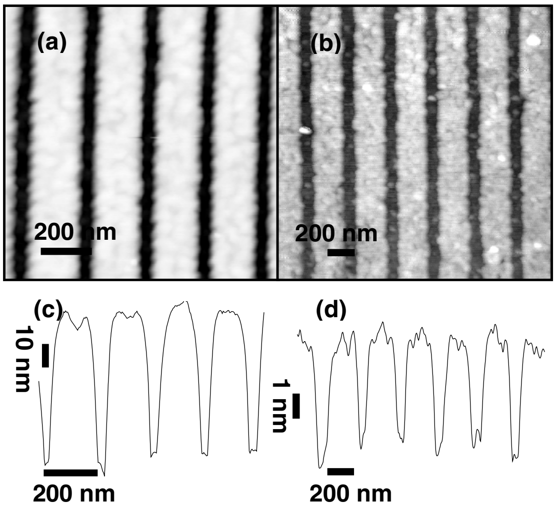

Figure 7. (a) Amplitude modulation AFM image of gold-coated silicon stamp. The stamp consists of 20 × 20 μm^2 rectangular patches. In each patch there is an array of parallel lines with a 300 nm pitch. (b) AFM image of the parallel oxidation replica. Cross-sections of the stamp (c) and the replica (d).

nanometre-size structures on different materials. The growth kinetics of the fabricated nanostructures on silicon surfaces depends on the chemical nature of the liquid. Higher growth rates are obtained with octane. The differences in growth rates underline differences in the chemical composition of the fabricated motifs. We report the fabrication of different nanostructures such as arrays of dots, wires, and stripes. The fabricated motifs can be used as templates for the growth of conjugated molecular materials. We also show that the local chemical processes can be scaled up for parallel patterning. Patterning arrays of parallel lines 100 nm apart has been demonstrated over mm^2 regions.

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