

Large area nanoscale patterning of silicon surfaces by parallel local oxidation

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Abstract

The homogeneity and the reproducibility of parallel local oxidation have been improved by introducing a thin film of polymethylmethacrylate (PMMA) between the stamp and the silicon surface. The flexibility of the polymer film enables a homogeneous contact of the stamp with the silicon surface to be achieved. The oxides obtained yield better aspect ratios compared with the ones created with no PMMA layer. The pattern is formed when a bias voltage is applied between the stamp and the silicon surface for 1 min. The patterning can be done by a step and repeat technique and is reproducible across a centimetre length scale. Once the oxide nanostructures have been created, the polymer is removed by etching in acetone. Finally, parallel local oxidation is applied to fabricate silicon nanostructures and templates for the growth of organic molecules.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Local oxidation nanolithography has emerged as a versatile nanofabrication and/or nanolithography method [1–3]. This method is based on the spatial confinement of the anodic oxidation between an atomic force microscopy (AFM) tip and the sample surface. A voltage applied between the tip and the surface induces the formation of a water meniscus. This meniscus acts as a nanoscale electrochemical cell. The polarity of the voltage is such that the tip acts as the cathode (negative) and the sample surface is the anode (positive). The electric field produces the oxidation of the surface inside the water meniscus. The technique provides ultra-small silicon oxide nanostructures with a lateral size of about 5 nm and a height in the 1–3 nm range. Local oxidation is a robust, reliable, and flexible lithographic method for the fabrication of nanoscale structures and devices [4–9]. However, the sequential character of the AFM limits the technological applications of the method. Furthermore, the patterning area is limited by the AFM scanner, which usually has a range of 10–50 μm .

To overcome the above limitation, several methods have been proposed for upscaling the local oxidation process by using a conductive stamp with multiple protrusions as a cathode. The original idea was proposed by Jacobs [10, 11]. The feasibility of the above proposal was demonstrated by Mühl *et al* [12] using a stamp with a few protrusions. Cavallini *et al* [13] used as a stamp a digital videodisc (DVD) sample and transferred its bits to a silicon surface. Martínez *et al* and Gwo

et al [14, 15] used silicon stamps to generate arrays of parallel lines separated by 100 nm over mm^2 regions and to organize the assembly of colloidal nanoparticle arrays onto charged self-assembled monolayers (SAMs). Sagiv *et al* used as the stamp an electron microscopy grid, in order to oxidize self-assembled monolayers [16–18].

The above experiments demonstrated the ability to pattern mm^2 regions with silicon oxide nanostructures. However, due to the misalignment between the stamp and sample surfaces, the patterning transfer was subject to several irregularities and inhomogeneities. In this contribution, we show that the parallel local oxidation process can be improved by introducing a sacrificial polymer layer between the stamp and sample surfaces. This layer deforms under the external load and adjusts the stamp–sample surface separation to keep a uniform pressure over the whole area. As a consequence the local oxidation process is uniform over a macroscopic surface. The overall process is stable, highly reproducible and allows the fabrication of different patterns with the same stamp. Finally, the parallel local oxidation is applied to fabricate templates for the growth of organic conjugated materials.

2. Experimental methods

2.1. Stamp and sample preparation

The stamps used for the experiments were obtained from a commercial digital versatile disc (DVD). This plastic recording

disc is made of polycarbonate. One side is patterned with an array of parallel lines with a periodicity of 760 nm. Each line has a full width at half-maximum (FWHM) of 350 nm and a height of 100 nm. The disc was cut into 1 cm² pieces and washed in pure ethanol to clean the surface. Then the polycarbonate stamps were coated with a double layer of metals by electron beam evaporation (5 nm Cr/50 nm Au).

Both p- and n-type silicon surfaces were used as substrates. To clean the substrates, the silicon surfaces were immersed and sonicated in an NH₄OH/H₂O₂/H₂O (1:1:10) solution for 15 min. After the cleaning, polymethylmethacrylate (PMMA; 1% in anisole) solution was deposited in a conventional spinner at 6000 rpm for 30 s. Then the sample was baked in an oven at 90 °C for 1 h. AFM measurements showed that the thickness of the PMMA layer was about 25 nm.

2.2. The effect of the PMMA layer on the pattern transfer

The stamp and the substrate were introduced into a home-made parallel oxidation instrument. In this instrument, the silicon substrate is fixed in a rigid sample holder and the polycarbonate stamp was located above the substrate on a mobile platform. The platform is moved downward by a micrometric screw until the stamp and the substrate reach mechanical contact. The stamp and the substrate are electrically connected to a voltage source. The different parts of the parallel oxidation machine are kept inside a sealed chamber with two gas inlets for controlling the relative humidity (RH).

The optimum oxidation results were obtained at a relative humidity of 70%. The control of the relative humidity was carried out by bubbling nitrogen air in pure water. After the thermal stabilization of the system, the platform was moved downward with the stamp until it was gently placed in contact with the silicon substrate. The force applied by the stamp to the substrate was measured by using a load cell [19].

Figure 1 shows a scheme of the process followed to fabricate silicon oxide patterns. The stamp/water/PMMA/silicon interface can be considered as an electrochemical cell where the stamp is the cathode, the silicon substrate is the anode and the water layer [20] adsorbed on the PMMA and the stamp generates the electrolyte. The oxide patterns are generated by applying a bias voltage of 36 V DC between the stamp and the substrate for 1 min [21].

The oxidation process also occurs without the PMMA layer as can be seen in figures 2(a) and (b). As one can observe from the images, the oxide lines are well defined and reproduce the features in the stamp. But if one makes an inspection of the entire sample one will find regions where the oxide stripes are linked together or they have different widths. Thus is due to the bending of the stamp when there is the first contact with the substrate. This creates a non-uniform distribution of the pressure along the sample surface.

Those defects disappear or are greatly reduced by introducing a PMMA layer. Figures 2(c) and (e) show the geometry of oxide lines under the PMMA layer. Once the oxide lines have been generated, the PMMA layer is eliminated by immersion in acetone. Figures 2(d) and (f) show the oxides lines after the removal of the PMMA. The cross-sections

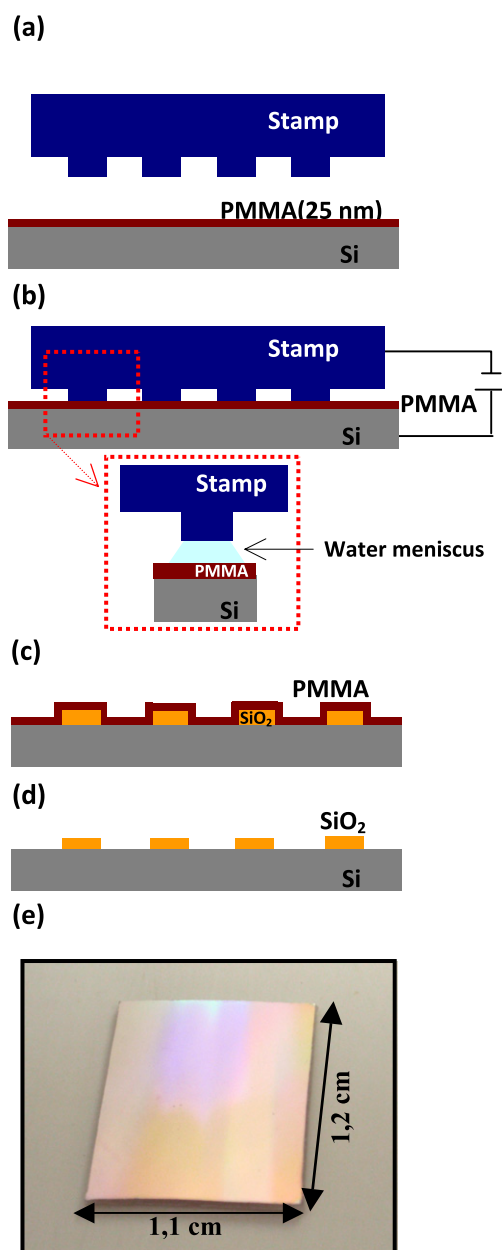


Figure 1. The parallel local oxidation process with a PMMA layer. (a) The deposition of a PMMA layer over the silicon surface. (b) The contact between the stamp and the substrate. The water meniscus supplies the oxyanions for the local oxidation process. (c) The pattern obtained over a thin layer of PMMA on silicon surface. (d) The oxide replica on the polycarbonate surface after acetone etching. (e) A photograph of the polycarbonate stamp used in the experiments.

taken along the marked lines of figures 2(e) and (f) reveal the differences in height and width between the bare silicon oxide lines and those covered with PMMA. We remark that the oxide lines keep the same geometry along the whole substrate. We have also observed that the oxides obtained with the PMMA layer provide better aspect ratios than the ones created in conventional parallel oxidation experiments.

The next step was to obtain the most suitable thickness of the PMMA layer for the parallel local oxidation. Apparently the use of thicker PMMA layers would improve the oxidation;

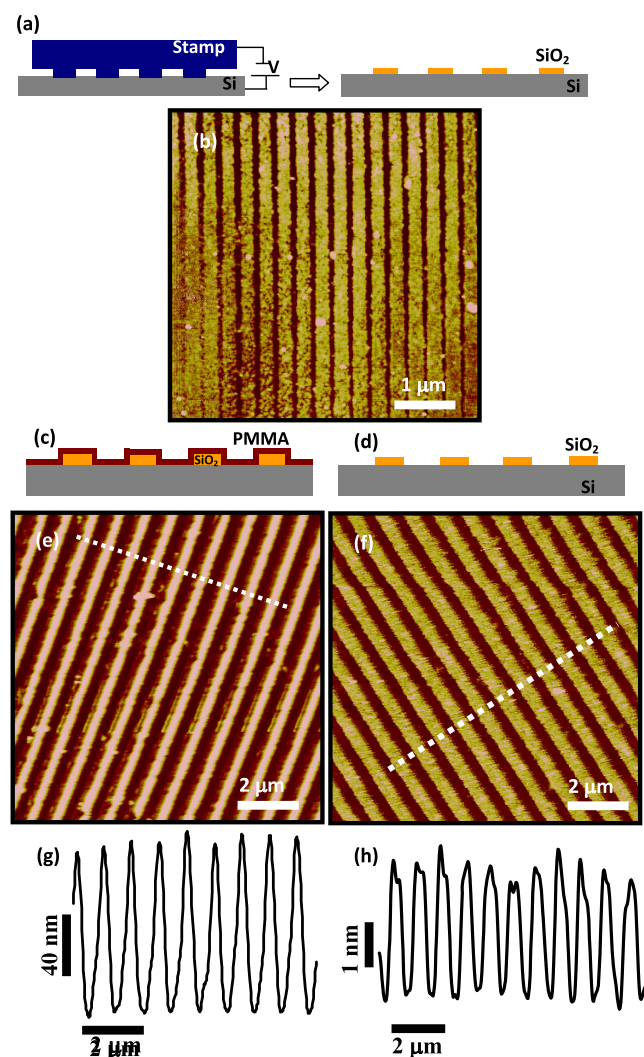


Figure 2. (a) Scheme of the parallel local oxidation process with no PMMA layer. (b) Amplitude modulation AFM image of stripes patterned on the silicon surface by parallel local oxidation. (c) Scheme of the cross-section of the patterned material before the removal of the 25 nm of PMMA layer. (d) Scheme of a SiO_2 pattern after the etching of the PMMA layer. (e) Amplitude modulation AFM image of a parallel oxidation replica. There is a 25 nm layer of PMMA on the top. The pattern was generated after the application of 36 V for 1 min. (f) Amplitude modulation AFM image of the oxide replica after the removal of the PMMA layer. (g) Height cross-section along the line marked in (e). (h) Height cross-section along the line marked in (f).

however thicker layers will prevent the diffusion of the oxyanions through the PMMA voids, and as a consequence, the ability to produce local oxides. The graph in figure 3(a) shows the oxide height dependence with respect to the PMMA thickness. The best result was achieved with a layer of 25 nm of PMMA that provides oxides with ~ 4 nm height. This value is decreased when thicker PMMA or no PMMA layer is used in the experiments. We have also studied the dependence of the patterned area with respect to the PMMA thickness (figure 3(b)). As one can observe from the histogram, the introduction of the PMMA layer in the oxidation process allows an increase of the contact area up to 70%, about twice more as compared with the case with no PMMA layer.

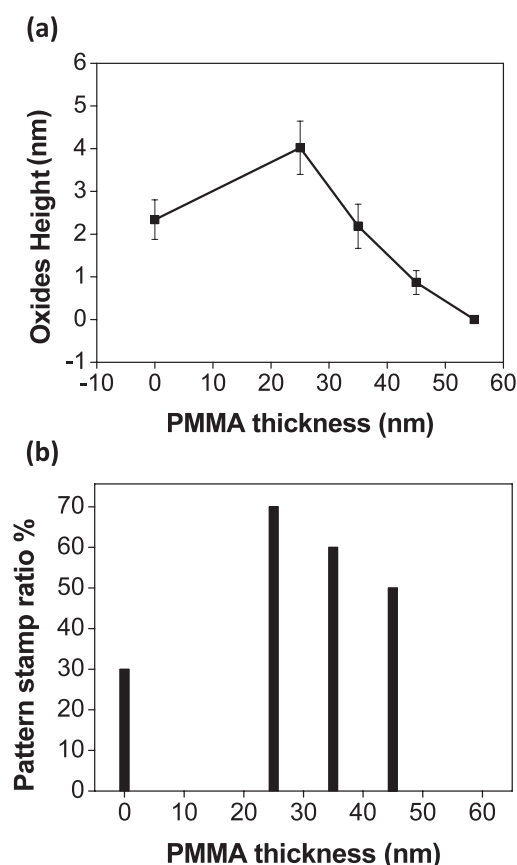


Figure 3. (a) Height of the oxides with respect to the thickness of PMMA. The error bars of the measurements have been estimated by measuring the root mean square value of the height distribution graphs. (b) Ratio between the total patterned area transferred to the silicon and the stamp surface as a function of the PMMA thickness.

To determine the properties of the oxide nanostructures for acting as either positive or negative masks we have exposed them to HF and plasma etching. On exposing the oxide patterns to HF vapours [22], the protruding oxide lines are converted into trenches that lie below the silicon surface baseline. This experiment confirms the silicon oxide nature of the fabricated lines because HF etches selectively silicon oxide versus silicon. In another experiment, the silicon oxide lines were used as a mask to create silicon lines. To fabricate silicon lines, the sample was introduced into a Plasma Reactive Ion Etching system (Plasma Lab 80, Oxford Instruments). The exposed silicon surface was etched with a plasma formed by SF_6 and O_2 in order to create silicon structures. The process is schematized in figure 4. The plasma etches the silicon with respect to the SiO_2 in a 20–1 ratio. Figure 4(b) shows how the oxide lines act as a mask for the silicon etching. The cross-section (figure 4(e)) along the line marked in figure 4(d) shows silicon structures with a height of about 50 nm, i.e., about 20 times higher than the original silicon oxide mask.

3. Investigating template growth of TTF molecules

One of the applications of AFM local oxidation is in the fabrication of templates to form molecular architectures [23].

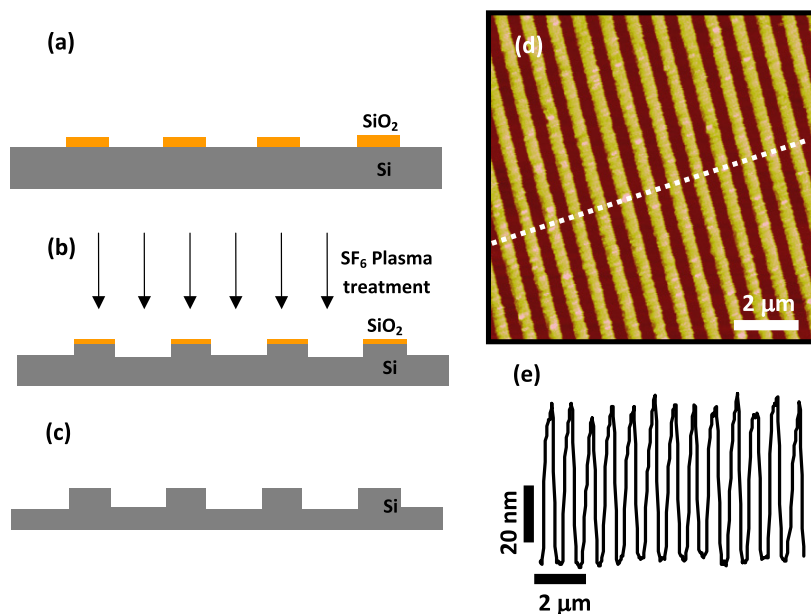


Figure 4. ((a)–(c)) Scheme for the fabrication of silicon nanostructures. (a) The oxide pattern on the silicon surface produced by the parallel oxidation process. (b) The plasma etching process. The silicon is etched with respect to the SiO₂ in a 20:1 ratio. (c) Silicon nanostructures fabricated by parallel local oxidation. (d) An amplitude modulation AFM image of silicon stripes with a 760 nm periodicity. (e) The height cross-section along the line marked in (d).

Here we show that silicon oxide patterns fabricated by parallel local oxidation can be used as templates for the growth of tetrathiafulvalene (TTF) derivatives [24, 25]. The experiment follows the scheme shown in figure 5(a). A drop of a solution of TTF nanoparticles is deposited over the silicon oxide pattern. The AFM phase image (figure 5(b)) reveals that the nanoparticles (black dots) are preferentially deposited on the silicon dioxide stripes due to electrostatic interactions. In that way one can perform a controlled patterning of the TTF molecules.

4. Discussion

We remark that the oxidation process also occurs without the presence of a PMMA layer. However, in those cases the patterns are prone to having more defects and irregularities. This happens because the polycarbonate stamp starts to bend once there is mechanical contact with the substrate. As a consequence, the pressure exerted by the stamp over the substrate is not homogeneous. This in turn gives rise to the presence of several defects in the local oxidation patterns. Those defects can be reduced by introducing a thin PMMA layer. The PMMA deforms upon contact with the stamp and it releases the stress of the stamp. So in this case there is not an appreciable stamp bending and the pressure over the stamp is homogeneous.

5. Conclusions

Parallel local oxidation has been improved by introducing a polymer layer of about 25 nm between the stamp and the silicon surface. The local deformation of this layer balances the pressure exerted by the stamp on the substrate. As

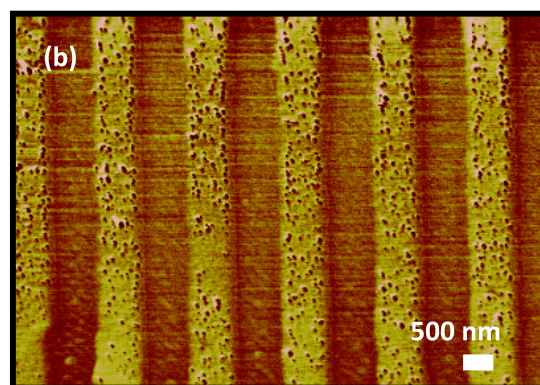
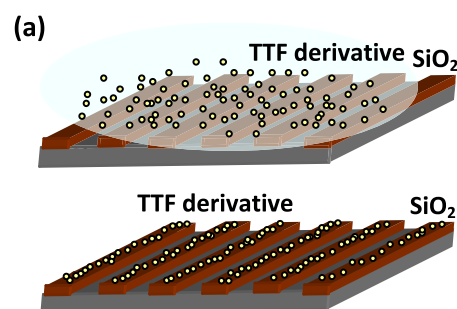


Figure 5. Template growth of TTF derivatives on top of silicon oxide lines. (a) The scheme of the process. A drop of a solution containing polycationic TTF derivative is deposited on the SiO₂ pattern produced by parallel local oxidation. The nanoparticles are driven by electrostatic interactions towards the SiO₂. (b) An AFM phase image of the same region after deposition of the TTF derivative.

a consequence the pattern transfer reproducibility has been greatly improved. Nanoscale silicon oxide lines have been patterned over a 1 cm² silicon surface with a very small number

of defects. The local oxide patterns have been used to generate masks for the fabrication of silicon features and templates for the growth of molecular architectures.

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