

Patterning Polymeric Structures with 2 nm Resolution at 3 nm Half Pitch in Ambient Conditions

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ABSTRACT

The miniaturization limits of electronic and mechanical devices depend on the minimum pattern periodicity that is stable in ambient conditions. Here we demonstrate an atomic force microscopy lithography that enables the patterning of 2 nm organic structures with 6 nm periodicities in air. We also demonstrate that the lithography can be up-scaled for parallel patterning. The method is based on the formation of a nanoscale octane meniscus between a sharp conductive protrusion and a silicon (100) surface. The application of a high electrical field (~ 10 V/nm) produces the polymerization and cross-linking of the octane molecules within the meniscus followed by their deposition. The resulting pattern periodicities are very close to the ultimate theoretical limits achievable in air (~ 3 nm). The chemical composition of the patterns has been characterized by photoemission spectroscopy.

The miniaturization trend in the fabrication of electronic, mechanical, and optical devices has prompted the emergence of nonconventional patterning methods^{1–6} as well as the optimization of established lithographies.^{7–9} Several alternative lithographies such as microcontact printing,^{2,3} nanoimprint,¹⁰ or scanning-probe-based lithographies^{11,12} have demonstrated their suitability to pattern a variety of materials and structures such as semiconductors and metals as well as organic^{13,14} and biological¹⁵ molecules. One common and so often required feature to handle a large variety of soft, organic, and biomolecules is that those methods should be compatible with operating under air or liquid interfaces. Although scanning probe microscopes have demonstrated atomic and/or molecular manipulation in ultrahigh vacuum and/or low temperatures,^{16,17} either the reactive character of clean surfaces or the existence of thermally activated diffusion processes have prevented to turn atomic-scale manipulation into a nanolithography. In the above experiments, a single manipulation or modification mark involved 0.4–1 nm.

Presently, atomic-force-based nanolithographies have produced the smallest reproducible feature size at room temperature and atmospheric pressure. Alternating nanostructures of octadecanethiol and decanethiol monolayers with 14 nm lattice periodicities and 8 nm of full width at half-maximum (FWHM) have been produced by nanografting.¹⁸ High-

density data storage on ferroelectric materials by AFM has demonstrated bit sizes and periodicities of 5 and 13 nm, respectively.¹⁹ Scanning probe nano-oxidation has patterned silicon oxide lines with 13 nm lattice periodicities.²⁰ Although some sub-1 nm modifications by scanning tunneling microscopy were reported in air,²¹ those experiments lacked the reproducibility to enable a lithographic process.

On the other hand, nanoimprint lithography has demonstrated the ability to pattern arrays of lines with a 12 nm periodicity and a half pitch of 6 nm.²² Conventional lithographies such as photolithography⁷ or electron beam lithography⁸ have recently reported periodic structures with 29.9 and 27 nm pitch, respectively. Theoretically, the minimum lattice periodicity that would lead to a stable pattern in ambient conditions is about 2–3 nm. This figure comes from the van der Waals size of an unreactive nanoparticle (1–1.5 nm) and a minimum edge-to-edge separation between two features identical to the feature size. Consequently, there is a factor 4–6 between the above patterns and the theoretical limit.

Here we develop a method for patterning silicon surfaces with organic structures that leads to modifications of 2 nm and lattice periodicities of 6 nm, i.e., an improvement of a factor of 2 from previous results. We have used an atomic force microscope (AFM) to induce the deposition of organic structures derived from octane into a silicon (100) surface. The silicon surface was covered by a native oxide of about 0.6 nm in thickness. The nanostructures were generated after

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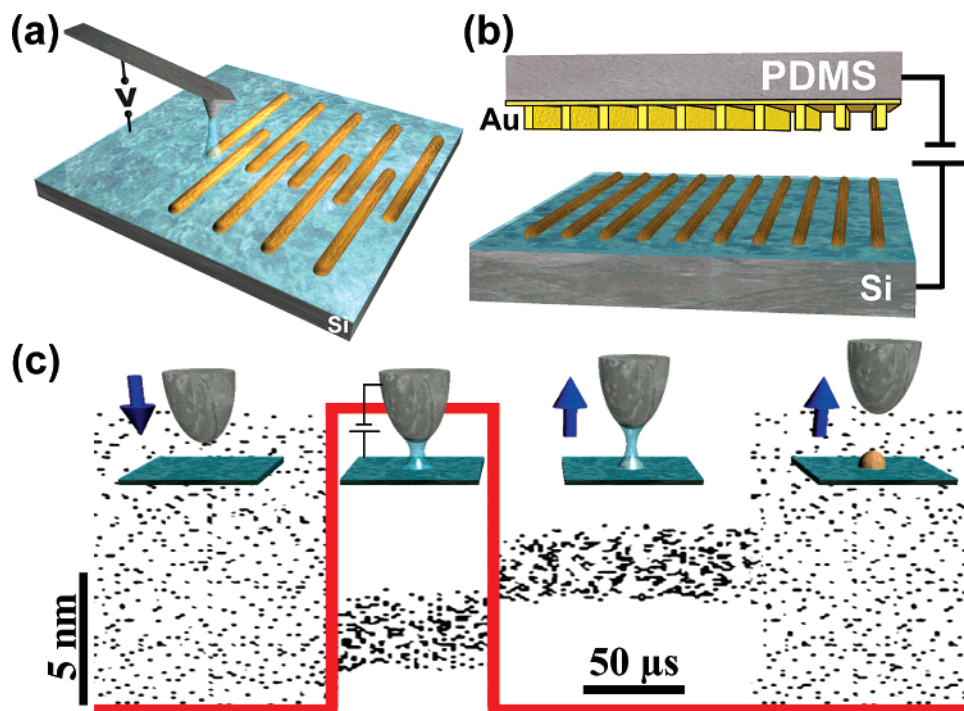


Figure 1. (A) Schematics of the patterning process by using an AFM operated in the noncontact mode. The modification process is mediated by the formation of a nanoscale octane meniscus. (B) Schematics of the setup for performing the lithography in parallel. For clarity purposes, the liquid menisci bridging the stamp protrusions and the Si surface are not shown. (C) Individual steps of the meniscus and pattern formation under the application of an external voltage in AFM nanolithography. The real-time dependence of the AFM cantilever deflection before, during, and after the application of a voltage pulse (thick red) is also shown. Each dot represents the instantaneous tip amplitude. Peak-to-peak amplitude is 11 nm. The trace of the voltage pulse is plotted in thick red (pulse width 80 μ s).

applying voltage pulses between the silicon probe and the silicon surface in a chamber that was saturated with octane vapor. The voltage pulse induced the formation of a liquid meniscus. Within this meniscus, we hypothesized that the electric field breaks some carbon–hydrogen bonds and produces the polymerization and cross-linking of the carbon chains. In our experiment, the surfaces were separated by 2–5 nm. Typical voltage pulses were about 35 V and 50 μ s. The sample was biased positively with respect to the tip. The nanostructures are chemically and mechanically stable in ambient conditions.

The experiments were performed with a dynamic atomic force microscope operated in the low-amplitude solution (noncontact) and with additional circuits to apply voltage pulses.²³ The microscope was placed into an inner box with inlets for dry nitrogen and organic vapors. The inner box was enclosed in an outer box with an output to extract leaked organic vapors. First, the AFM chamber was purged of water vapor by flushing dry N₂ for about 30 min. This reduced the relative humidity below 2%. Then the chamber was filled with either octane (octane, anhydrous, 99+%, Sigma-Aldrich). The octane vapor kept the relative humidity below 2%. Noncontact AFM nanolithography was performed with doped n⁺-type silicon cantilevers (Nanosensors, Germany). The force constant k and resonance frequency f_0 were about 35 N/m and 320 kHz, respectively. The cantilever was excited at its resonance frequency. The semiconductor samples were p-type Si(100) with a resistivity of 0.1–1.4 Ω cm.

The organic solvent menisci bridging tip and sample were field-induced by applying an external voltage between tip

and sample. The voltage is referred to the tip, so positive (negative) polarity means the sample is biased positively (negatively) with respect to the tip. To fabricate the lines with the AFM, we apply a sequence of voltage pulses. The continuity of the line is obtained when the size of the individual structure is larger than the lateral distance between pulses.

The chemical composition of a reference sample (Si(100) wafer) and of the patterned sample were studied by X-ray photoemission spectroscopy (XPS). The XPS spectra have been recorded in a separated ultrahigh vacuum chamber with a base pressure in the low 10^{−9} mbar. For in-depth profiling XPS experiments, the samples have been etched using Ar⁺ ions with energy ranging from 0.5 to 1.4 keV; the incidence angle of the Ar⁺ beam was 42° with respect to the normal of the sample. XPS spectra were recorded at different depths, i.e., after removing overlayers of different thickness. The removed thickness during ion etching has been estimated to be 0.18 Å/ μ A min as explained elsewhere.²⁴ The angle θ between the hemispherical analyzer (Specs,PHOI BOS 100) and the plane of the surface was kept at 60°, and the X-ray radiation was the Mg K α line ($h\nu = 1253.6$ eV). The analysis was performed by following the evolution of the photoemission peaks of Si 2p, C 1s, and O 1s core levels for both the reference and the nanostructured samples. In all cases, the Shirley background and the X-ray satellites were removed and the quantitative XPS analysis was performed with the CasaXPS software.

We also demonstrate that the same physical process is amenable for parallel patterning by using a print-based local

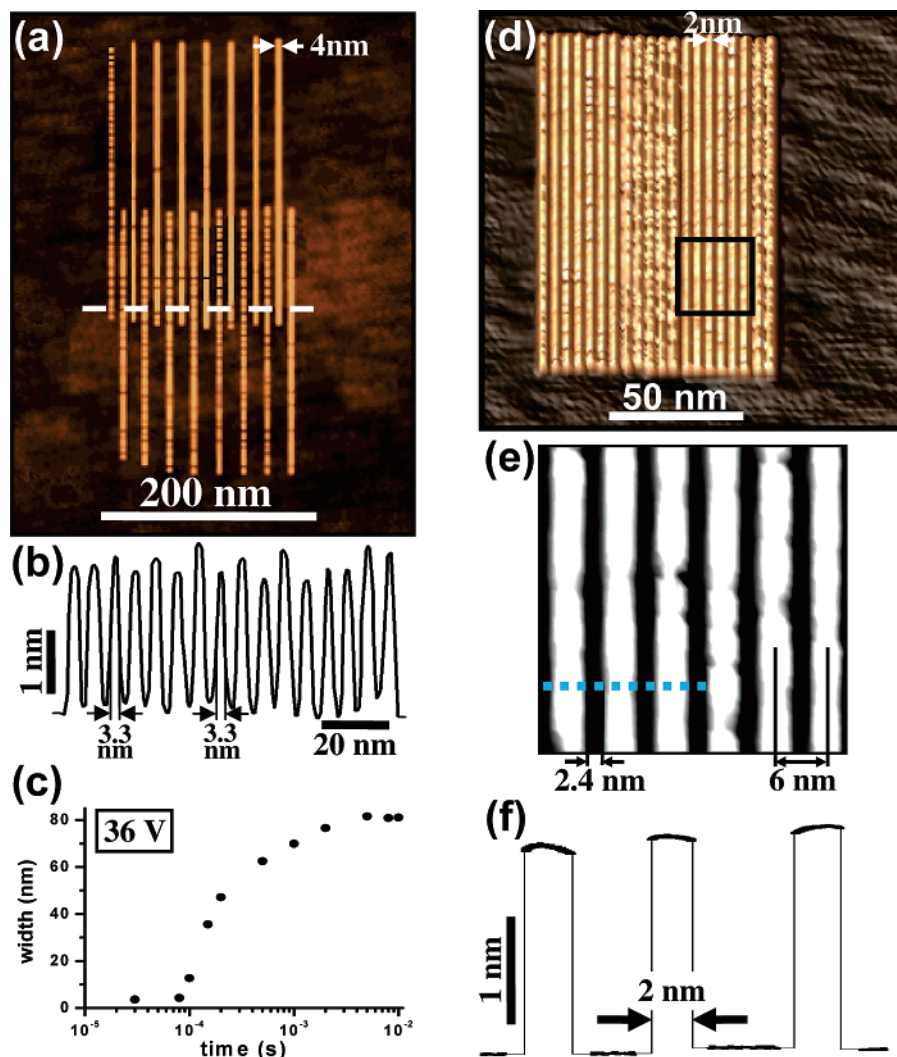


Figure 2. (A) Amplitude modulation AFM image of a set of 16 interdigitated lines of 275 nm in length with a separation between nearest-neighbor lines of 10 nm. To generate the lines, a sequence of voltage pulses of 36 V for 80 μ s was applied. (B) Cross-section along the line marked in (A). The lines protrude 2.5 nm from the substrate and have an average width of 4.3 nm. Lines that have widths of 3.3 nm are marked. (C) Line-width (fwhm) dependence on pulse duration. (D) AFM image of a pattern made of 20 continuous lines where the periodicity is 6.2 nm. A sequence of voltages pulses of 36 V for 30 μ s was applied. (E) AFM high-resolution image in the marked area shown in (D). (F) Deconvoluted profile of a selected set of three lines (dashed line in (E)).

nanolithography instrument.²⁵ This instrument enables replication of cm² stamps on silicon surfaces in a few seconds. This result has a twofold value in that it demonstrates that ultrahigh resolution patterning in ambient conditions is compatible with parallel patterning. Second, it enables performing of chemical compositional analysis with conventional instrumentation. The schematics of both sequential and parallel patterning are illustrated in parts a and b of Figure 1, respectively. Figure 1c shows the steps of the field-induced formation of an octane meniscus as well as the nanostructure generation. The schematic of the meniscus formation and the fabrication process is accompanied by a real-time AFM tip deflection recorded during a single fabrication event.

Figure 2 shows two different arrays of parallel lines. A set of 16 interdigitated lines of 275 nm in length with a separation between nearest-neighbor lines of 10 nm is shown in Figure 2a. To fabricate the lines, we have applied a sequence of voltage pulses of 36 V for 80 μ s. The time to

pattern any of the above lines is $\sim$ 30 s, i.e., several orders of magnitude larger than the pulse time. The patterning time is limited by the conventional software and electronics used to perform the experiments.

The cross-section (Figure 2b) shows the lines protruding 2.5 nm from the Si substrate. Some individual lines show widths of 3.3 nm while the average fwhm is 4.3 nm. Kinetics studies enable definition of the conditions to generate ultranarrow lines. The dependence of the line width with the pulse time shows three regions (Figure 2c), a flat region below 10⁻⁴ s with widths in the 2–5 nm range. For pulses above 10⁻³ s, the size saturates about 80 nm. In the middle, there is a continuous transition between sub-10–80 nm structures. Figure 2d shows a pattern made of 20 continuous lines, where the periodicity is 6.2 nm. In this case, a sequence of voltages pulses of 36 V for 30 μ s was applied. A zoom into the marked region allows us to establish the accuracy of the patterning process. The lines are very homogeneous with a fluctuation in the line width below 1 nm.

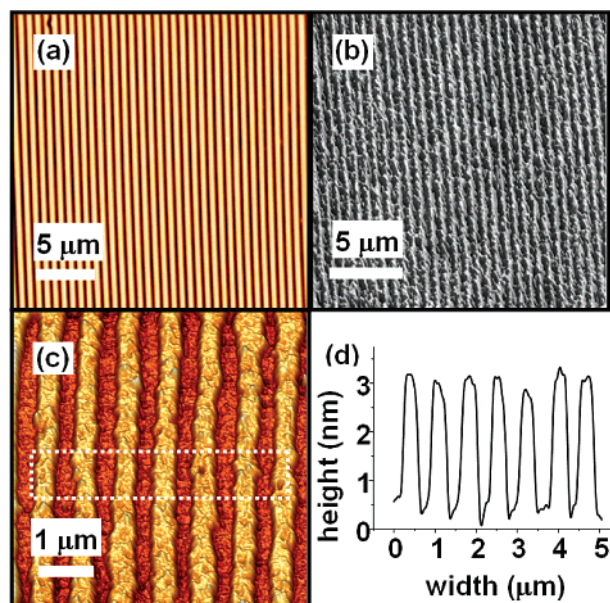


Figure 3. (A) AFM image of a region of the gold-coated DVD stamp used for parallel patterning. (B) AFM image of an array of polymer lines fabricated in parallel by using a gold-coated DVD stamp. (C) Higher resolution AFM image of the replica. The pattern periodicity is 740 nm, which coincides with the stamp periodicity. (D) Cross-section along the line marked in (B). The lines show an average height value of 3 nm.

The above line widths, albeit small, are 1.5–2 higher than the *true* widths. The ultrasharp silicon tip's size (~ 2 nm) is comparable to vertical height of the lines (~ 2.5 nm), consequently, the AFM images are highly convoluted.²⁶ For example, the image of a Dirac's delta function of 2 nm in height generated by a spherical tip of radius 2 nm would have a fwhm of 0.8 nm. In our case, the reconstructed image can be obtained from the imaged surface and by assuming a tip size given by the sharpest profile obtained in the cross-section. The reconstructed image shows a cross-section of ~ 2 nm at the base (Figure 2f). We also remark that the aspect ratio of the lines is about 0.5 for the unreconstructed lines and 1 for the reconstructed image.

The physical process that enables the patterning of 2 nm structures in ambient conditions is also amenable for parallel processing under the same conditions. To this purpose, we have used a local nanolithography instrument, where the AFM probe has been replaced by a stamp with billions of reliefs. Parts a and b of Figure 3 show, respectively, AFM images of the stamp and its replica. In particular, the replica shows a region of $20.8 \times 20.8 \mu\text{m}^2$ that contains 29 stripes with a periodicity of 740 nm. The lines were generated by pressing the stamp on the silicon substrate in an atmosphere saturated with octane vapor and by applying a voltage pulse of 36 V for 1 min. Figure 3c shows a higher resolution image of the same pattern. In this case, the pattern periodicity was established by the stamp periodicity, a gold-coated DVD sample with a periodicity of 740 nm (Figure 3a). A cross-section along the line marked in Figure 3c shows the lines protruding 3 nm from the bare Si substrate (Figure 3d).

We have also studied the physical process responsible of the patterning process as well as the chemical composition

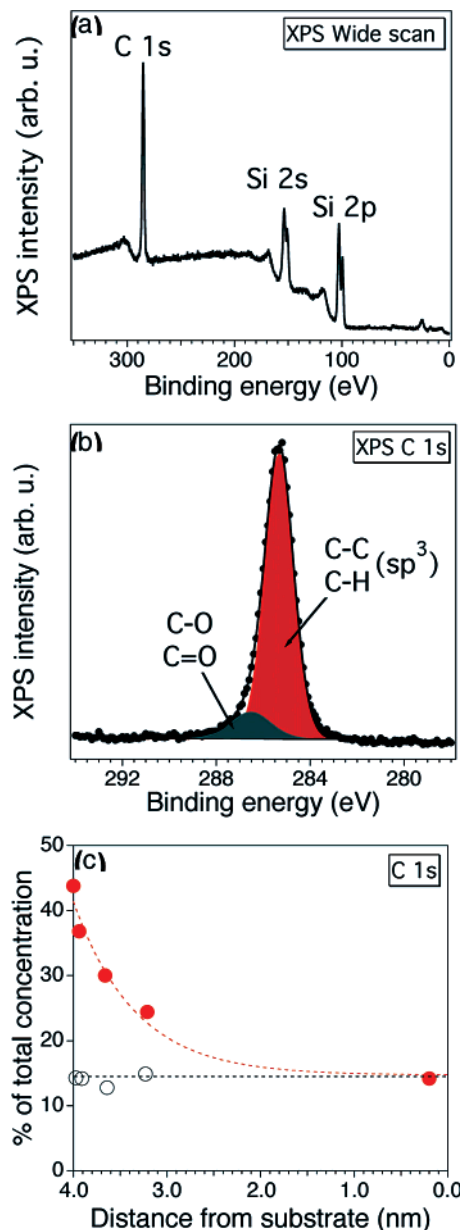


Figure 4. (A) Wide X-ray photoemission spectrum (XPS) of a sample patterned by local chemical nanolithography with a parallel instrument. (B) XPS C 1s core-level spectrum of a patterned sample. The two deconvolutions are plotted. The filled dots joined by a continuous line represent the experimental data, while the deconvolution are plotted in gray for the carbon–oxygen bonds and in red for the C–C and C–H bonds. (C) Evolution of the C concentration from the Si baseline for the patterned sample (filled circles). The reference sample is plotted by open circles.

of the fabricated structures. Suez et al. performed AFM patterning by immersing the tip in a liquid cell filled with *n*-octane.²⁷ They showed that the fabricated structures were etch-resistant in $\text{NH}_4\text{F}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$; as a consequence, they suggested that structures were carbon-based material produced by the field-induced decomposition of the solvent. We have also verified the structures fabricated here were etch-resistant in HF. This result points out to a likely organic composition.

The chemical composition of the fabricated structures has been characterized by photoemission spectroscopy experi-

ments (XPS) on the structures such as the one shown in Figure 3b. The wide XPS spectrum reveals three different peaks (Figure 4a). The highest signal is centered at the C 1s core-level binding energy. The smaller peaks correspond to the emission from the Si 2s and 2p core levels. A higher energy resolution spectrum on the C 1s core level is shown in Figure 4b. The deconvolution of the peak reveals two components at 285.2 and 286.7 eV. The binding energy at 285.2 eV corresponds to either C–C or to C–H bonds in the sp^3 configuration,^{28,29} whereas the component located at 286.7 eV corresponds carbon–oxygen bonds.²⁸ Figure 4c shows the variation of the C concentration as a function of the distance from the surface as extracted from the XPS depth profiles. The overall carbon amount of the patterns has increased 300% relative to the reference sample. In-depth spectroscopy analysis shows that the carbon amount decreases to the reference sample surface levels (unpatterned silicon (100)) at approximately 3 nm below the surface. This is fully consistent with the thickness of the fabricated pattern (~ 3 nm, see cross-section in Figure 4c). A detailed XPS profile (not shown) shows that the increase of the carbon concentration on the patterned sample is mostly due to either C–C or C–H bonds. The presence of C on the reference sample is due to unavoidable contamination during sample transfer.

The spectroscopy studies enable a proposition that the organic deposits are made by the polymerization and cross-linking of the $CH_3-(CH_2)_6-CH_3$ molecules. This process is field-induced by the extremely high electrical fields present at the interface, which has a mean value of about 10 V/nm with peaks up to 25 V/nm. The electric field could supply up to 2 eV over the length of either C–H or C–C bonds. Those values are very close to the carbon–hydrogen covalent bond energy. Cross-linking of poly(*N*-vinyl carbazole) has been achieved by nanoscale discharge with AFM.³⁰

We report the fabrication of the smallest periodic patterns (6.2 nm) made in ambient conditions. The achieved pattern periodicity is very close to the ultimate theoretical limits for periodic patterning in ambient conditions (~ 2 – 3 nm) and also close to the smallest periodic pattern made in any condition (~ 1 nm). The process is based on the field-induced deposition of organic structures formed on octane nanoscale liquid meniscus. We also demonstrate the physical process can be up-scaled by patterning cm^2 regions in 1 min.

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