Probe-Based 3-D Nanolithography Using Self-Amplified Depolymerization Polymers

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Scanning probes are capable of addressing and modifying surface structures on the atomic scale,[1] a capability that has been exploited to create molecular logic devices.[2] However, in real-world applications, the production of nanoscale patterns and devices requires substantial throughput capabilities in combination with sufficient tip endurance to address areas on the order of 0.1–1 mm^2 at high resolution. At a typical pixel pitch of 10 nm, this translates to 10^8–10^{10} pixels being written with a single tip. Therefore a highly sensitive patterning approach that is gentle on the tip would be indispensable. Besides the well-established method of local anodic oxidation,[3–5] recent developments in this direction are the field-induced deposition of materials[6,7] and the tip-induced modification or removal of thermomechanically responsive organic materials.[8–12] In addition, it has been shown that on polymeric substrates the wear on a sliding silicon tip can be virtually eliminated,[13] which is a prerequisite for high-resolution patterning on technologically viable scales. Other stimuli have been used to structure polymers locally using atomic force microscopy (AFM) tips, e.g., mechanical forces in plowing[14] and ultrasonic patterning[15] or electron irradiation using field emission from the tip.[16]

In this paper, we describe the fabrication of two- and three-dimensional structures based on the local removal of a resist polymer using heated tips. Previous experiments have shown that sufficient energy is provided by heated tips to break the chemical bonds of a Diels–Alder material,[11] which subsequently decomposes into volatile monomer units. However, the overall patterning efficiency is low. The efficiency can be dramatically enhanced by using self-amplified depolymerization (SAD) polymers. Here, the breaking of a single bond induces the spontaneous depolymerization of the entire polymer chain,[17,18] a concept that was first demonstrated in the early 80's as a dry lithography approach. Recently it was discovered that using phthalaldehyde SAD polymers two-dimensional nanoscale patterns can be written with high efficiency.[19] Here we demonstrate that the material also serves as an excellent etch mask and that the decomposition reaction is fast in comparison with the mechanical motion of the tip. Hence, structures can be written at <2 μs exposure time per pixel, and the patterning capability can be extended to the third dimension in one writing step. Furthermore, the high efficiency allows the removal of large volumes of material without affecting the writing properties of the tip.

Virtually any arbitrarily shaped structure can be engraved into the SAD polymer using a hot tip. **Figure 1A** shows the patterning principle. The cantilever style probe sensor is made from silicon and comprises a capacitive platform for exerting a loading force by electrostatic means and a resistive heater for heating the tip, which is integrated on top of the heater. In a stand-by position, the tip rests 300 nm above the polymer surface. For writing, the tip is heated by applying an appropriate voltage U_H across the resistive heater element. An electrostatic force pulse is provided by applying a voltage U_F between the substrate and the cantilever for a duration of 2–14 μs. The pulse brings the tip into contact with the polymer surface, and the hot tip locally heats the polymer, thereby triggering the unzipping reaction of the SAD material as shown schematically in Figure 1B. We observed that the reaction is efficiently activated within a time frame of several μs when using a heater temperature of 700 °C. The temperature of the polymer in contact with the tip is lower, however, and depends on the tip geometry, the resistance of the thermal interface between tip and polymer, and the spreading resistance in the polymer. Experiments and theoretical models show that the actual increase relative to room temperature in the polymer below the tip apex is approximately 0.4 – 0.6 times the heater temperature, that is, 300 to 400 °C (for details see Reference [20]). The writing of a pixel terminates when the capacitive loading force is switched off, causing the cantilever to snap back to its rest position above the surface. Empirically we found that below a heater temperature of 500 °C the thermal stimulus is not sufficient to induce the depolymerization reaction. However, a remnant material response is still observed with the typical characteristics of thermomechanical embossing, viz., the formation of rims as a result of volume conservation, high writing forces on the order of several 100 nN, limited patterning depth on the order of nanometers, and strong interference between closely spaced pixels.[21]

The depth of a written pixel at a heater temperature of 700 °C and a force pulse duration of 14 μs is shown in Figure 1C as a function of the applied force, where the force is normalized to zero at the patterning threshold. The patterning depth is a linear function of the applied load, and a mere increase in the

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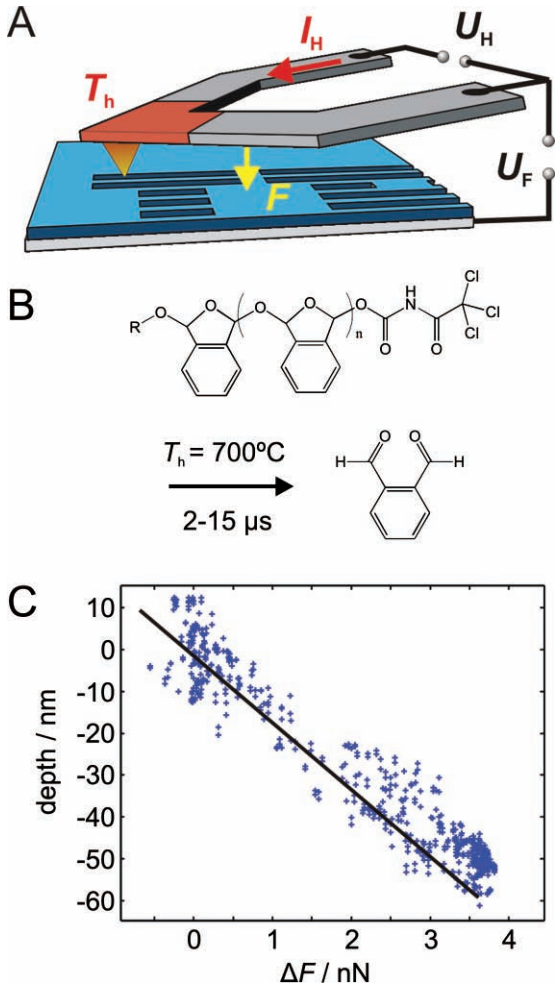

Figure 1. A) Schematic of the patterning method. The AFM-style cantilever comprises integrated heaters for heating the tip and for sensing the topography (not shown). The tip rests ~300 nm above the surface if no voltages are applied. To pattern a pixel, short voltage pulses U_H and U_F are applied to heat the tip and to pull the tip into contact by electrostatic means, respectively. B) Structure of the polyphthalaldehyde polymer used in this study. At typical patterning parameters, heater temperature of T_H = 700 °C and pulse durations of 2–14 µs, the polymer is converted into its monomer constituents by self-amplified depolymerization. C) Plot of the patterning depth as a function of the applied force for a force pulse duration of 14 µs. The black line indicates the force required to bend the tip to the respective depth as calculated from the spring constant of the cantilever of 0.065 N/m.

force of 3.5 nN leads to an increase in the patterning depth from 0 to 50 nm. For comparison, the force required to lower the tip against the restoring force of the cantilever structure is shown as black line in Figure 1C (the slope of the line corresponds to the spring constant of 0.065 N/m of the bending mode of the force sensor). Within experimental errors, the line coincides with the data points. Hence we conclude that the penetration depth during writing is not restricted by reaction forces from the polymeric material. Such a behavior can only be rationalized if the timescale to decompose the polymer chains and subsequently remove the monomer units from the apex region is fast in comparison to the mechanical interaction time.

In **Figure 2** we exemplify the application of the patterning process for creating the replica of a fractal carpet pattern. The pattern has been chosen to demonstrate patterning uniformity, covering length scales from micrometers to nanometers. The bitmap representing the structure contains 441 × 441 pixels. It has been written using a pixel pitch of 20 nm, resulting in a 8.8 × 8.8 µm^2 patterned area. The depth of the recessed regions is 16 ± 1 nm, and pillars of 40 × 40 nm^2 size are correctly reproduced. No traces of material pile-up, which would typically be formed in a thermomechanical embossing process, can be discerned at the edges of the structures. Furthermore, the imaging resolution is not impaired by the writing process, indicating that the tip has not been abraded or contaminated by material pick-up.

For silicon processing, it is important that resist structures can be transferred into the substrate material. The result of a direct transfer of the pattern by a SF_6 reactive ion etch (RIE) is shown in Figures 2B and C. The material exhibits an excellent etch selectivity of a factor of 6 with respect to silicon. This is surprising considering the thermodynamic fragility of the polymer. As a result, structures with steep side walls could be fabricated. The smallest free-standing pillars in the Si replica

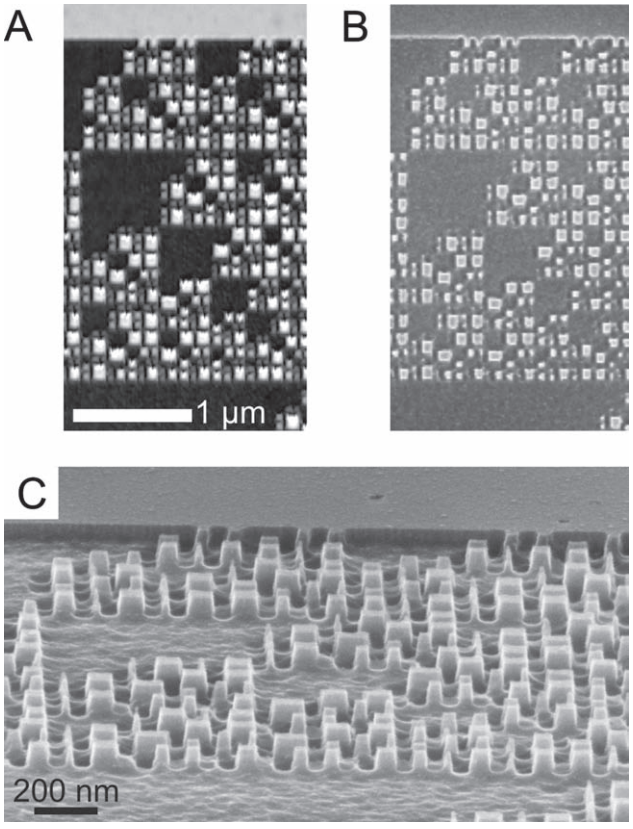

Figure 2. A) AFM topographical image of a pattern created using a heater temperature of 700 °C and a force pulse duration of 2 µs. The patterning depth amounts to 16 nm in a 50 nm thick polyphthalaldehyde film. B) Scanning electron microscopy image of the same area after reactive ion etching (RIE) into the silicon substrate. C) Tilted view (45°) of the same area. The height of the structures is ~90 nm, corresponding to a depth amplification by a factor of 6. The thin pillars are ~30 nm wide, whereas the grooves between the structures are ~50 nm wide.

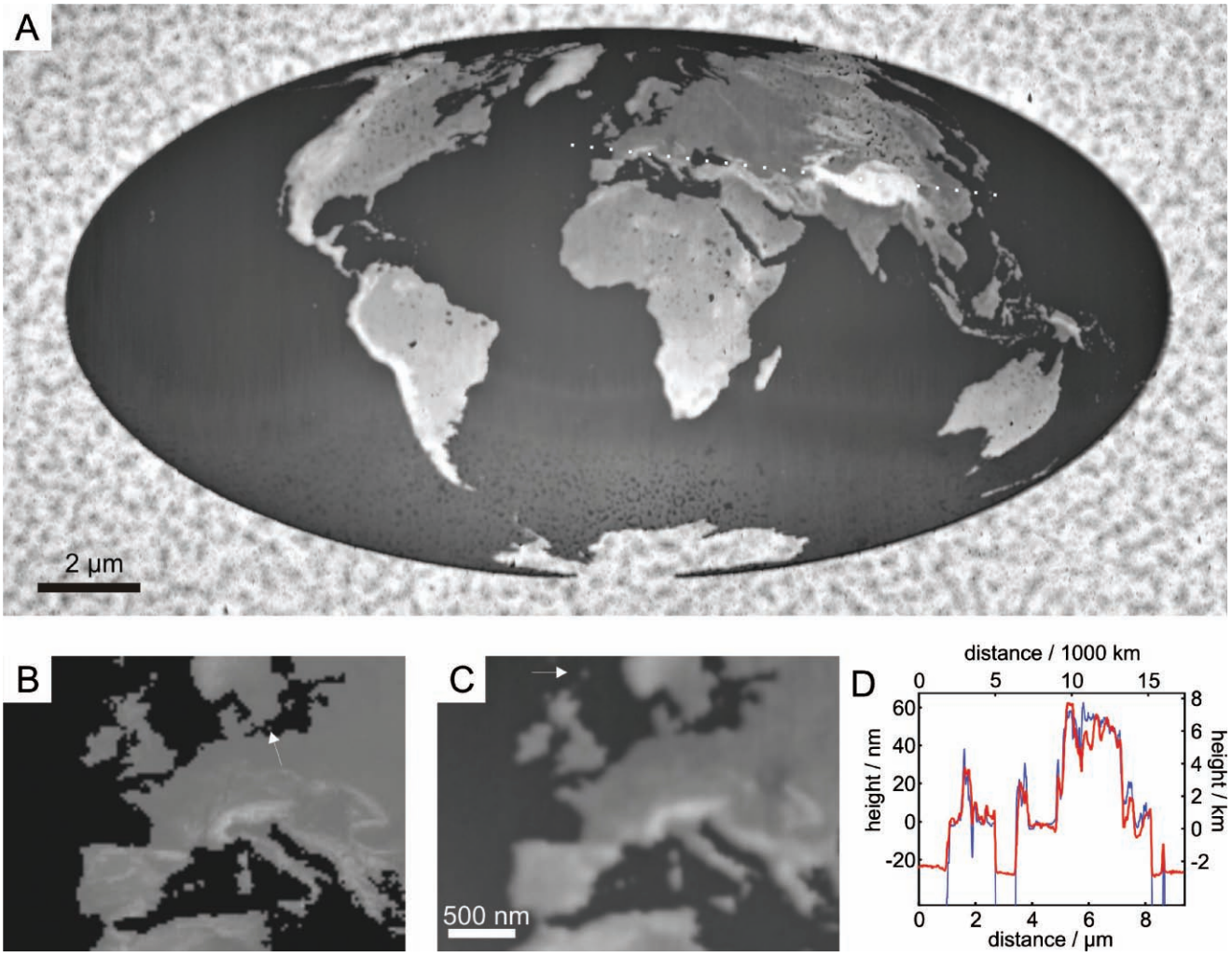

Figure 3. A) AFM topography (raw data) of a 3D world map (adapted from GTOPO30, U.S. Geological Survey, http://eros.usgs.gov) written into a 250 nm thick polyphthalaldehyde layer. The relief is composed of 5×10^5 pixels with a pitch of 20 nm. A tip heater temperature of 700 °C and a force pulse duration of 14 µs were used for reproduction. The height information of the original data was linearly transposed into a force range of 10 nN. The full pattern was written in one step at a pixel rate of 60 µs; the total patterning time amounted to 143 s. B) and C) Comparison of a sub-area in (B) the programmed bitmap and (C) the imaged relief. The white arrows indicate positions with features of 1 (in B) and 2 (in C) pixel width in the original bitmap. The 2 pixel wide features were correctly reproduced, corresponding to a resolution of ~40 nm for the patterning process. D) Cross-section profiles along the dotted line shown in (A), for the original data (blue line) and the relief reproduction (green line). The cross-section cuts, from left to right, through the Alps, the Black Sea, the Caucasian mountains, and the Himalayas.

have a diameter of ~30 nm, are 90 nm tall, and correspond to the 40×40 nm^2 pillars observed in the AFM scan of the patterned SAD polymer. The discrepancy in the silicon image can be explained in terms of a not fully anisotropic Si etch and tip convolution effects in the AFM image.

The linear force-depth relation in combination with the high writing efficiency make the material an ideal candidate for direct writing of three-dimensional structures. The world map shown in **Figure 3A** has been written in a single patterning step encoding the depth by a linear transformation of the world elevation data to a force map. In the reproduction, a height difference of 8 nm corresponds to 1 km of real-world elevation. The image comprises 5×10^5 pixels written at a pitch of 20 nm, and the writing of the pattern took 143 s. The nominal thickness of the SAD polymer film is 250 nm. The oceans appear to be recessed by 5 km in the reproduction to enhance the contrast to the continents. At the periphery of the map, the surface roughness of 11 nm_{RMS} of the pristine film can be seen. It is unusually high for a spin-cast film, which can be attributed to the high volatility of the solvent. Note that the roughness in the patterned areas amounts to only 0.4 nm_{RMS}, significantly less than that of the virgin surface. As discussed above, the timescale for the exposure reaction is fast in comparison to the mechanical motion of the indenter. As a consequence one expects the writing depth to be controlled by the mechanical swing of the cantilever only and not by the amount of material that needs to be consumed. This conjecture is corroborated by the force depth relation, shown in Figure 1C, determined from the topographic map. Also, the cantilever motion is reproducible on the nm scale for each

pixel, which leads to the flat recessed areas in particular and to an accurate reproduction of the entire image in general. Also note that the volume of the material removed in the writing of the world map corresponds to a cube of 3.4 μm edge length, yet no traces of tip contamination or deposition of fragments could be detected.

In conclusion, we have exploited the highly responsive nature of polyphthalaldehyde polymers to a heat stimulus provided by a hot silicon tip to create arbitrary three-dimensional patterns with ~40 nm lateral and 1 nm vertical resolution. At heater temperatures of 700 °C, the depolymerization reaction occurs fast on the timescale of the cantilever motion and allows the patterning of a thin film on a microsecond timescale. Moreover, there is no significant additional force required to penetrate the film, which enables the fabrication of three-dimensional structures in a single patterning step at the same throughput as achieved for two-dimensional structures. Interestingly, the material also exhibits good RIE etch resistance, enabling the direct pattern-transfer into silicon substrates with a vertical amplification of 6. The unique capability to create nanometer precise three-dimensional structures makes it a perfect technique for generating templates that can then be multiplied and printed by the technologies developed for nano-imprint lithography.[22,23] We see potential applications in printing optics on chips,[22] fabricating three-dimensional nanomedical particles,[24] or the creation of nanoscale three-dimensional templates for shape matching self-assembly of objects such as nanorods or –cubes.[25]

Experimental Section

Material and Sample Preparation: The phthalaldehyde polymer was synthesized in an anionic cyclopolymerization at –78 °C in tetrahydrofuran (THF) as described in detail in Ref. [19]. Polymerization was quenched with trichloroacetyl isocyanate (TCAI), which provides a protective end group preventing depolymerization as the reaction returns to room temperature. The polymer used in this study had a molecular weight Mn of 36080 g/mol and a polydispersity index of 1.14. The phthalaldehyde polymer was deposited by spin coating from THF solution onto 2" highly doped silicon wafers. Films of 50 and 250 nm thickness were prepared.

Thermomechanical Writing and Reading: The spring constant of the cantilevers is obtained by a finite-element simulation of the cantilever, for which the thickness of the levers is obtained by scanning electron microscopy. The cantilevers typically have a spring constant of 0.1 + 0.1/-0.05 N/m and a lowest resonance frequency of 50-60 kHz. The indenter tip is of conical shape with a cone aperture of ~45° and an apex radius of less than 10 nm. The heater temperature is determined from the measured electrical resistance, using the known temperature dependence of the resistivity of doped Si. The electrostatic load force is calibrated in an independent experiment by measuring the lever deflection as a function of the applied potential.

Scanning of the tip is accomplished using a linearized commercial piezo scanner (Physical Instruments P-733-2D). To write a pixel, electrostatic force pulses are applied for a duration of 2–14 μs. A heater voltage raising the heater temperature up to 700 °C is applied for a longer duration to ensure the thermal equilibration of the heater. To pull the tip into contact with the sample takes about 1 μs and the response time for force transduction between tip and sample is less than 1 μs as inferred from model calculations[26] and experimental results demonstrating mechanical embossing at a 500 kHz indentation rate.[27]

Imaging of the polymer surface is performed using the same cantilever tip as used for writing the pattern. The tip is pulled into contact at the beginning of each line by applying an electrostatic force, which also provides an additional load force of ~10nN. The tip is released at the end of the line and does not touch the surface during retrace. No feedback is used to control the height of the cantilever base over the surface. The soft cantilever spring compensates for the topographic modulation of the sample surface, and the vertical displacement of the tip is measured by thermo-resistive means.[28,29] An integrated resistive element, the thermal sensor made of low-doped Si, which is thermally decoupled from the tip, is heated to ≈200 C using a constant voltage excitation. The temperature depends on the size of the air gap between the sensor and the sample which acts a cooling path. The electrical resistance of the sensor is determined by the temperature and is sensed via the excitation current which is thus a measure for the tip-sample distance. The pixel time during reading of 15 μs is adjusted to the response time of the thermal read sensor of ≤20 μs.

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