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Floating Tip Nanolithography

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ABSTRACT

We demonstrate noncontact, high quality surface modification of soft and hard materials with spatial resolution of ∼20 nm. The nanowriting is based on the interaction between the surface and the tip of a standard atomic force microscope illuminated by a focused femtosecond laser beam and hovering (at ambient conditions) 1−4 nanometers above the surface without touching it. Field enhancement at the tip−sample gap or high tip temperature are identified as the causes of material ablation.

Optical lithography has been the key enabling technology for microelectronics in the last few decades, but its spatial resolution is restricted by the optical diffraction limit to dimensions typical to the optical wavelength. Even the shortest UV wavelength currently in use (157 nm) does not provide the resolution required by the ever decreasing feature sizes of the "NANO" revolution. Reliable methods for subdiffraction lithography are constantly being sought, and surface modifications by different interactions with the sharp tip of an atomic force microscope (AFM) are prominent among them. In order of increasing complexity, the simplest of the three main methods used in this context is the direct mechanical scratching of a surface by a sharp tip, and the related technique of mechanically scratching of a thin over coating polymer layer followed by etching of the surface to be modified.[1] Next, the tip may be heated, resistively or by a focused laser beam[2,3] for a more pronounced effect on the surface. The use of hot tips was reported for thermal writing,[4–6] for nanoindentation by resistively heated nanosize probes,[7,8] or for the initialization of chemical transformations.[9] The third possibility in this hierarchy is based on the well-known electromagnetic enhancement of a laser field in the vicinity of a sharp tip.[10] A different approach to surface modification is the high spatial resolution writing with foreign molecules (ink) on surfaces, as is done very well with the DPN (dip pen nanolithography) method.[11] Note, however, that in DPN the surface itself is not modified, but rather material is added to it.

The successful implementation of all these methods, as well as any other approach that will be based on a sharp AFM tip being in close proximity to the surface to be modified, require accurate control, and knowledge of the tip−sample gap (TSG). The introduction of apertureless scanning near-field optical microscopy (ASNOM) with its obvious advantages of high spatial resolution based on the tip sharpness, and tolerance to high-density electromagnetic power channeled much of the current work toward commercial AFMs where tip−sample gap is controlled by monitoring the reflection of a laser beam from the back of the cantilever into a position sensitive photo detector.[12–14] While in principle such instruments should have provided a high degree of control over the tip position,[15] in practice, the accurate determination of the TSG, especially in real time, is rather difficult. Furthermore, the task of harmlessly approaching a sharp tip to a solid surface and holding it at a constant distance of only a few nanometers is still quite impossible on standard AFMs. The conventional scheme consists of an approach to the surface till "hard contact", followed by nominally raising the tip to the desired TSG. This approach does not work: with stiff cantilevers (∼40 N/m) sharp tips are known not to survive the hard contact, and with soft tips (∼2 N/m and less) the tip remains "stuck" to the surface by capillary, electrostatic and other surface forces, and when released, it "bounces" much farther than the desired few nanometers, typically to tens of nanometers above the surface (for further elaboration of this point, see the Supporting Information, Part A). As significant is the fact that the susceptibility of AFM piezo-ceramic scanners to temperature and humidity variations makes it practically impossible to maintain fixed TSG for a reasonable time without the constant verification by means of an active feedback loop. The noncontact operational mode of an AFM is rather useless for proximity tip surface interactions as it is based on a feedback loop that involves large amplitude oscillations at the mechanical resonance frequency of the cantilever, with a large mean distance between the tip and sample surface (typically 20−40 nm).

In this paper, we demonstrate floating tip nanolithography (FTN), a high quality noncontact surface modification with high spatial resolution within a commercial AFM. Using the hot-tip effect, we write on a soft polymer (reliably, reproducibly, and without physical contact between the tip and

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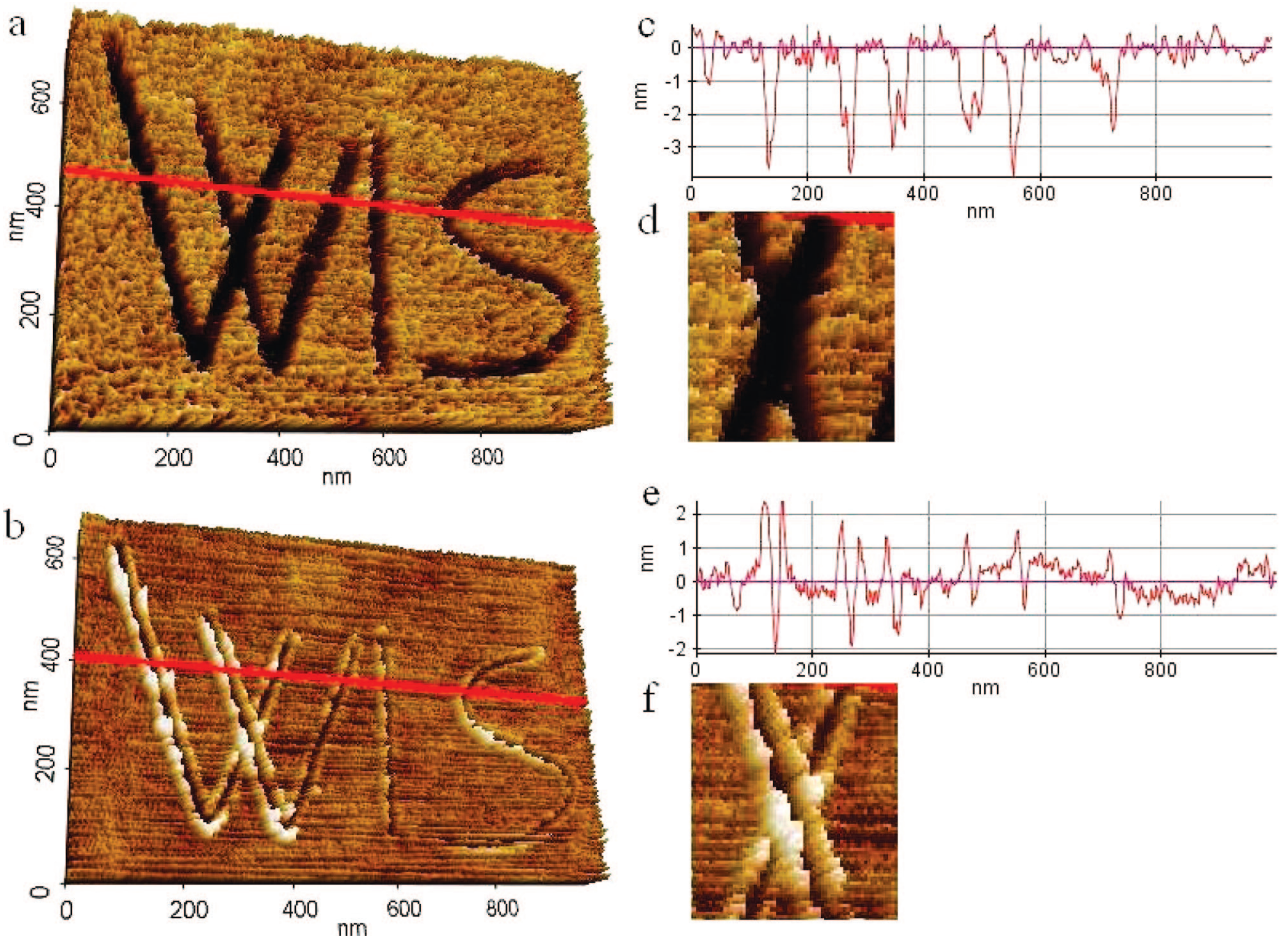

Figure 1. (a) Hot floating tip writing WIS (for the Weizmann Institute of Science) on AZ4620 photoresist film. The writing speed was 50 nm/sec at tip−sample gap 3 ± 2 nm and the average laser power was $\sim 3 \times 10^5$ W/cm^2. (b) Direct mechanical scratching of the same polymer with an identical cold tip. Profiles c and e correspond to the red cross-section lines in panels a and b; images d and f are the magnified line intersections in panels a and b, respectively.

the surface) lines of ∼20 nm width and 2−4 nm depth. When compared to mechanical scratching by either cold or hot tips, our results clearly demonstrate the advantages of the newly introduced noncontact FTN methodology. We further use the same approach for noncontact writing on a gold film, where the physical effect leading to the material ablation is the electromagnetic enhancement of the femtosecond laser field under the sharp tip. In what follows, we show and discuss the advantages of the noncontact nanowriting, both by the hot tip and the electromagnetic enhancement effects. In both these sections, for the clarity of the presentation, we assume that we are able to control the TSG at will, and to position the tip at the desired gap above the surface. We postpone to the Experimental Methods the discussion of the newly introduced method enabling us to keep the tip hovering above the surface at a constant TSG of only a few nanometers for long durations of time and without ever touching the surface. The technical details of the method, as well as the calibration procedures we had to develop, may be found in the Part A of Supporting Information.

Hot Tip Lithography. To realize FTN with a hot tip, we illuminated the tip with a beam of an external femtosecond laser. The laser light was focused in an ASNOM configuration by a 15 mm lens at an incident angle 70° to a small spot (diameter of 3−5 μm) a few microns above the tip apex so as to prevent any possibility of surface modification by direct interaction with the laser beam. The surface consisted of a silicon wafer over which a thin layer (a few microns) of a standard photoresist (AZ4620) was spin-coated. This polymer is known[16] to survive baking at 200 °C, and we had to heat the tip well above this temperature to see any effect (see Supporting Information, Part B). Experiments with a higher temperature compound, AP2210A (thermal decomposition temperature 518 °C), under identical conditions showed similar results, but required much higher tip temperatures.

Figure 1a depicts a typical result of the floating tip nanolithography by a hot tip. Lines of ∼20 nm widths and ∼3 nm depth are shown, the writing is very clean, the material is clearly removed (ablated) away, and at the resolution afforded by these measurements there is no visible heat affected zone (HAZ) around the ablated lines.

Figure 1b depicts the equivalent situation for lithography by mechanical scratching by a cold tip of the same surface. On the basis of our methodology, we can control the actual pressure applied by the tip on the surface (see below), and in order to make a valid comparison, we used the following procedure: the experiments were run several times at different (increasing) pressures, and the results examined. For low pressures, the scratching was barely visible, becoming progressively deeper, till at some point, the tip breaks. The results shown in figure 1b are the best "cold tip scratch" that can be compared in terms of line width and depth to the ones in figure 1a. Under these conditions, after several repetitions of the experiment, the tip was worn out or damaged as was verified either by direct SEM observations of the tip or by the deterioration in resolution of the scanned images. The differences between the noncontact nanowriting and the best mechanical scratching are clearly seen in the line profiles (Figure 1c,e): in the case of the mechanical scratching, the material removed from the line is piled up on the side. When the entire written area is profiled and digitally processed carefully, we find that under conditions of mechanical contact the material volume was preserved, as distinct from the FTN case where material is removed. This effect is demonstrated clearly at the intersection of two lines shown at larger magnification: whereas in the FTN writing (Figure 1d), the two lines cross without disturbing each other, and from looking at the picture one cannot tell which line was written first; in the case of the mechanical scratching, (Figure 1f), the second line overwrites the first and the "removed" material covers the "trench" dug by the first, displaying a clear advantage for the hot tip noncontact nanolithography. Experiments (not shown) performed with a hot tip in contact with the surface (under different pressures and at different temperatures) led to similar conclusions. While it might be possible to find optimal conditions for specific experimental conditions, the FTN approach provides a general, robust tool for surface modification under ambient conditions.

The letters written in Figure 1 are hundreds of nanometers in dimension, and it is therefore difficult to appreciate the advantages of the noncontact FTN in terms of accurate lithography. In a second set of experiments, we opted to write much smaller shapes, in an attempt to check the limits of resolution for the method. In figure 2 we present the results of such experiments: a square, a circle, and a pound sign were written, by FTN of a hot tip, and by direct mechanical scratching. The differences are even more pronounced than before. Whereas the FTN writing (Figure 2a) maintains the desired shape, the shapes in Figure 2b are distorted. Careful volume integration reveals again that no material was removed by the mechanical method, it was "pushed" according to the direction of motion of the tip, whereas significant amount of material was removed by the hot, floating tip.

Moreover, while the shapes on the left are symmetrical, the shapes on the right show the effects of cantilever torsion and flexure which vary for different directions of relative movement.

The schematic drawing in Figure 3 provides an explanation for the operation of FTN with a hot tip. A sharp tip with a radius of curvature of 10 nm (as per its specifications) is maintained at a sample gap of a few nm (i.e., 3 nm in the figure). The tip is heated by a laser beam focused to a spot a few microns above the apex and the heat is efficiently transferred from the tip apex to the surface, causing the local surface temperature to rise well above the melting point of the polymer. Several works have shown that under ambient conditions, at a separation of a few nanometers the heat flow from the hot tip to the surface is substantial.[17–19] Moreover, McCarthy et al.[20] measured the temperature of a tip illuminated by a focused laser beam, and have shown that even under very mild tip irradiation, the temperature rise may reach hundreds of degrees. Our own numerical simulations verify that for the actual conditions of our laser irradiation, the tip indeed reaches a temperature of a few hundred degrees, enough to affect the polymer surface (see Supporting Information, Part B for details).

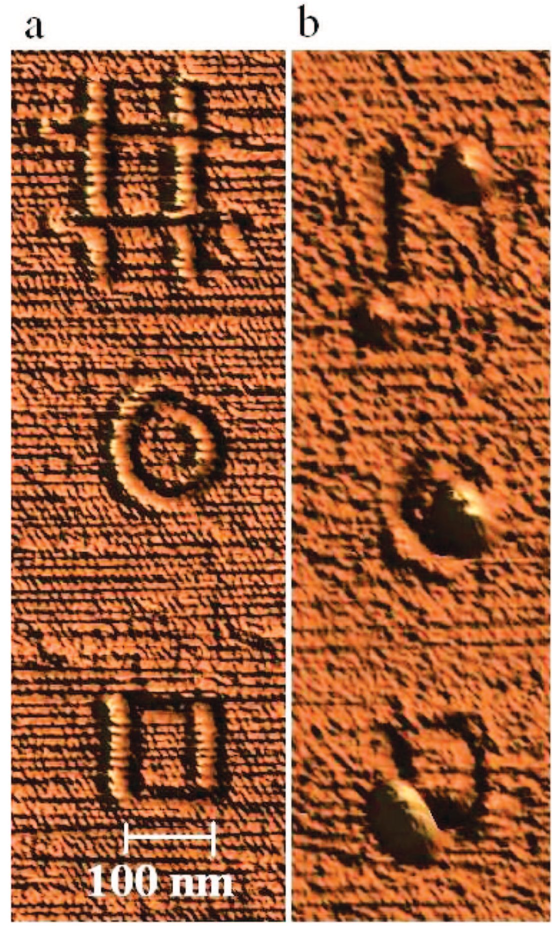

Figure 2. AFM performed writing of small forms on the polymer surface: (a) by means of laser-heated tip in the FTN regime and (b) by direct mechanical cold tip scratching.

The ability to use hot tips for surface nanostructuring was recognized a long time ago, and even considered for commercial applications in data storage in the IBM Millipede system.[21] The unique design of the very thin cantilevers and short tips of the Millipede system[8] was optimized for the special purpose of fast writing and reading of digital data (typically point indentations). For the general purpose of surface structuring (continuous lines and shapes) with traditional AFMs, direct mechanical contact between standard tips and the surface often leads to undesirable results, such as tip contamination, tip breakage, unintended indentation, and scrubbing of soft material surfaces. These difficulties

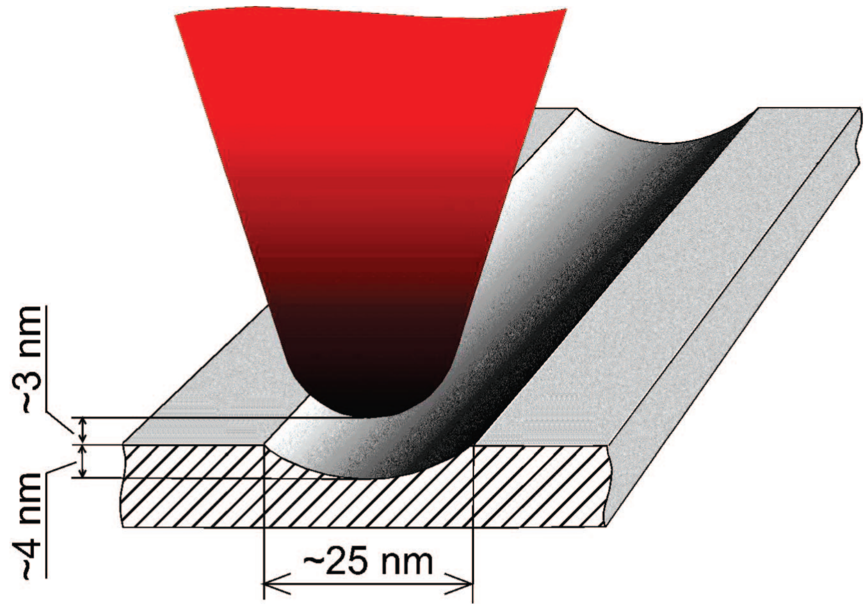

Figure 3. Idealized shape of the hot-floating-tip-produced trench with the parameters extracted from the experimental data presented in Figure 1a.

clearly justify the need for a truly noncontact mode of operation.

Field Enhanced Lithography. The next example we wish to consider is surface modification by the enhanced electric field under the sharp tip. Metallic surface structuring by an AFM tip illuminated by an ultrashort laser has been previously reported, and the literature contains two conflicting explanations for its mechanism. The first relies on material ablation due to plasmonic electromagnetic field enhancement under the tip,[10] and the alternative explanation is based on rise in tip temperature due to laser absorption, and the ensuing tip elongation which causes the hot tip to mechanically hit the surface[2] and chisel away material. Both mechanisms are operative under most "standard" conditions of irradiation of an ASNOM tip by a strong laser beam, and for the first time we can separate them by being absolutely sure the tip is never in mechanical contact with the surface.

The result for the modification of a gold surface is presented in Figure 4. The tip was floating approximately 3 nm above the surface, laser light, polarized along the tip axis, was focused on the tip apex, and it was independently verified that the laser alone (without the tip) does not affect the surface. The tip temperature was much lower than the melting temperature of gold (see Supporting Information, Part B), so that the "hot-tip effect" can be safely disregarded. The observed written lines are ∼20 nm wide and ∼1 nm deep, material is actually removed and does not accumulate near the trench as can be clearly seen from the picture, and the cross-section provided on the right panel of figure 4.

Experimental Method and Floating Tip Basics. Our setup is based on a commercial AFM XE-120 (Park Systems Corp.), custom designed for optical access and ASNOM applications. In the Z (vertical) direction, the height of the tip above the sample is controlled by a stacked piezoelectric actuator, physically separated from the $X-Y$ (horizontal) scanner on which the sample is mounted. The system provides external remote access to practically all operational parameters. To monitor and control the TSG, we introduced very low amplitude (<1 nm) oscillations to the cantilever at a frequency far from its mechanical resonance, and used the measured response of the sensor for our feedback system. Figure 5 depicts the typical behavior of an Olympus AC160TS cantilever (spring constant 42 N/m, resonance frequency 342 kHz) near the surface. The black curve is the familiar dependence of the cantilever deflection on the distance, while the blue and red curves give the response (phase and amplitude respectively) of the cantilever to the oscillatory voltage (at frequency 75 KHz) driving the small oscillations as measured by the reflection of a probe beam from the back of cantilever into the quadrant position sensitive photo detector (QPSPD). The cantilever mean deflection is measured by the dc component of the QPSPD response, whereas the amplitude and phase of the oscillations are extracted from the ac term. While lowering the tip toward the sample, at a TSG of about 5−7 nm, the tip begins to feel the surface forces. As the tip approaches closer, the amplitude of the oscillations drops and a phase shift gradually builds up to 180 degrees which we interpret as a "hard contact". Intuitively, this change of phase is quite understandable: as the tip sets closer and closer to the surface, the pivot of cantilever motion shifts from one of its end to the other, providing a reversal of the phase. The curves in Figure 5 are quite typical, even though the exact shape may depend slightly on the specific experimental conditions, such as humidity, sample material, position of the laser spot on the cantilever, etc. As can be seen in Figure 5, the phase of the oscillations presents a single-valued function which is very suitable for TSG control in the range of 1 to 4 nm. To realize this control, we built a feedback circuit comprising of the lock-in detected signal from the QPSPD and the voltage fed to the Z-scanner.

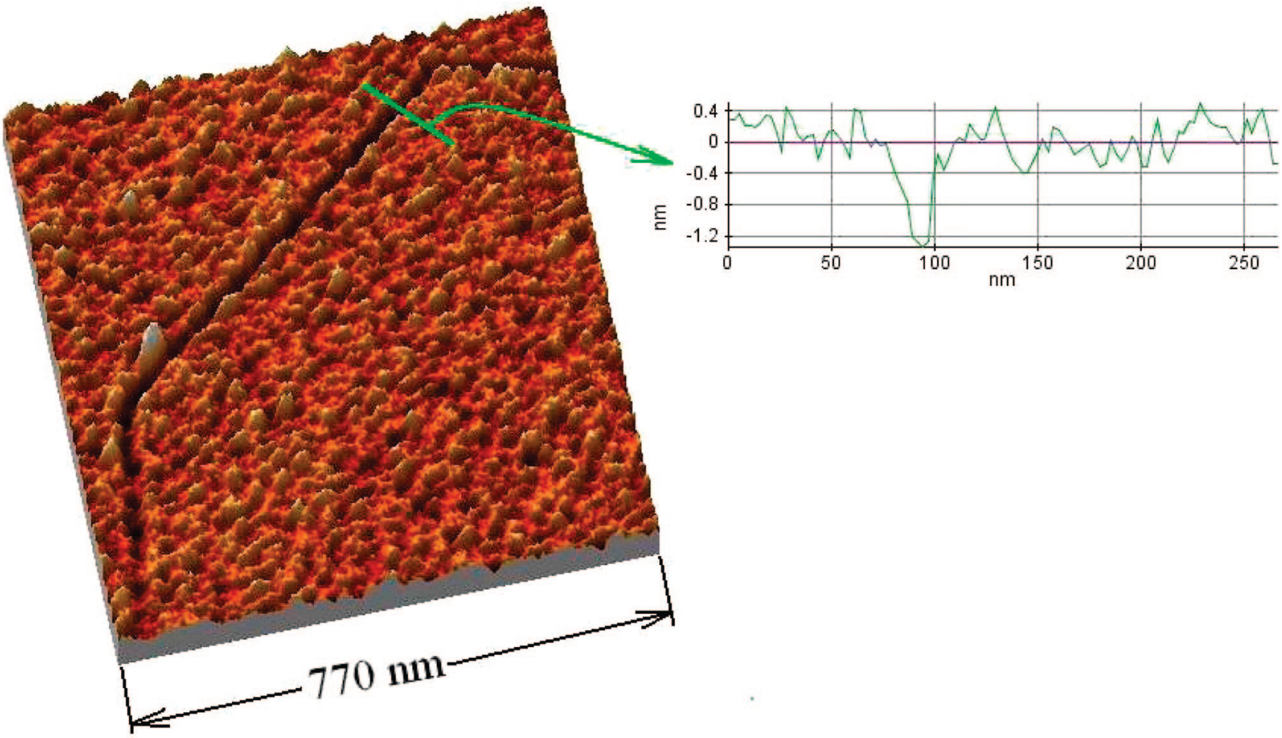

Figure 4. Floating tip nanolithography on a gold film (15 nm of Au on a Si wafer with 2 nm of Cr buffer layer). Writing speed, laser power, and TSG are the same as those of Figure 1.

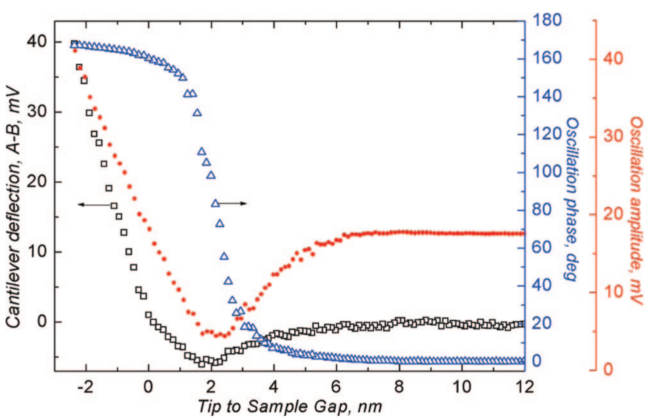

Figure 5. QPSPD measure of the cantilever deflection (black), phase (blue), and amplitude (red) response to small oscillation driving (<1 nm at 75 kHz) as a function of the TSG for a stiff cantilever (42 N/m).

The independent calibration of the relative displacement of the Z-scanner is straightforward, but the determination of the absolute TSG value, and in particular of the TSG = 0 point, cannot be done based on this figure alone. This task, however, is made possible by means of a procedure which is based on the scattering of the evanescent field at the interface of two media. The reader is referred to Part A of the Supporting Information for the details of the experimental system, as well as for a full description and analysis of the calibration procedure.

We use an ultrafast femtosecond laser (Micra, Coherent Inc.) providing pulses of 800 nm central wavelength, ~20 fs duration at average power of up to 500 mW at a repetition rate of 80 MHz. Whereas for the hot tip effects we could have used a CW laser, the choice of the femtosecond laser stems from the wish to have high peak intensities so that we can observe nonlinear effects and electromagnetic field enhancement by the sharp tip. Finite element analysis of the tip temperature rise under irradiation, performed with parameters similar to our experimental conditions, provided information about the temperature rise, as well as the approach to thermal equilibrium. It was directly confirmed that the "quasi-continuous" operation at a high repetition rate of laser pulses allows the tip to reach a thermal equilibrium, enabling us to calibrate out any miscellaneous effects such as cantilever bending and tip elongation, that may have caused ambiguity in earlier works (see Supporting Information, Part B for details). Last technical point: because the cantilever oscillates at a frequency that is very far from mechanical resonances, the heating does not affect the working curve "phase versus TSG" of the AFM.

In conclusion, the unique properties of noncontact floating tip nanolithography were demonstrated and discussed. We showed nanowriting and surface modification on polymer and metal films with spatial resolution of about 20 nm width and a few nm depth without direct contact with the sample surface. The new method enables reproducible, continuous tip surface interactions at a gap of a few nanometers, and can be used for contactless material processing. The FTN method is applicable for any commercially available AFM operating under ambient conditions with standard tips, it does not require a special design of the cantilever. For the purpose of this controlled noncontact processing, we had to develop a new mode of operation for atomic force microscopes which enables scanning a tip at a predetermined low height above the sample without touching the surface. Our novel approach to the control of the tip−sample gap is based on very small amplitude (<1 nm) forced oscillations of the cantilever at a frequency far from its main mechanical resonance. When the AFM tip is illuminated by a femtosecond laser, surface modification occurs based on either one of two mechanisms: a hot tip interaction with a surface, leading to the melting/evaporation of the material, or electromagnetic field enhancement under the tip triggering the material ablation. Future applications to other metallic surfaces, as well as to the initiation of surface chemical molecular modifications will be discussed in forthcoming publications.

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Supporting Information Available: The details of the experimental system, the tip−sample gap calibration technique, and the estimation of the tip temperature under laser illumination are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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