Micromachined fountain pen for atomic force microscope-based nanopatterning

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We present a tool that can be used in standard atomic force microscope and that enables chemical, chemical/mechanical, or physical surface modification using continuous liquid supply. The device consists of a reservoir micromachined into the probe support that is connected to fluidic channels embedded in a V-shaped cantilever. Via the fluidic channels, the liquid reaches the tip. The fluid transport to the sample surface is demonstrated and fountain pen lithography applications are presented. © 2004 American Institute of Physics. [DOI: 10.1063/1.1823040]

Atomic force microscopy (AFM) is extensively used in material science. The technique developed for surface characterization was adopted in other application fields like determination of materials properties, and surface modification. Here we present a modified AFM probe with integrated fluidic channels running over the cantilever beams, which can replace the pulled glass capillaries used in the localized chemical and electro-chemical experiments, and enables the use of standard AFM equipment for these experiments. The probe may extend the dip-pen lithography and the nanoscale dispensing as the amount of ink available for writing is significantly increased, the supply of ink can be more controlled, and the mass of the probe is only slightly and reproducibly changed as is important for resonant operations.

The concept of the micromachined fountain pen (MFP) was proposed by Kim et al., but no fully functional devices have been reported. We developed a different fabrication route for the fluidic channels and the connection to the tip. The fluidic channels transport the fluid from the reservoir, embedded in the support of the AFM cantilever, to the tip [Fig. 1(a)]. The device is combined with a previously developed tool for in situ characterization of surface modification, consisting of two cantilevers carrying tips (Fig. 2).

The fabrication process of the device is based on standard AFM probe fabrication combined with additional techniques for the fluidic functionality. The reservoir is powder blasted into the Pyrex™ support of the cantilevers. The channels are fabricated by sacrificial etching of polycrystalline-Si lines encapsulated between two SiN layers, patterned to compose the cantilever beams [Fig. 1(a)]. The outlet of the fluidic channel is photolithographically defined at the base of the pyramidal tip, thus the sharpness of the tip (tip radius ~30–40 nm) is not altered relative to the standard fabrication.

Fluid transport from the reservoir to the tip of the MFP was tested by measuring the resonance frequency shift of the cantilever with water-filled channels relative to the initially empty tool. Prior to testing the devices were annealed in an oven heated to 280 °C for functionalizing the fluidic channels by burning out possible organic contaminants deposited onto the channel walls. We observed with optical microscope that the water flowed almost instantaneously in treated channels, which is in correspondence with Poiseuille flow driven by a capillary pressure of several bars. We also observed that the filling speed decreased over time, thus the heat treatment had to be repeated after storing the samples for days or more. An MMAFM-2, manufactured by Digital Instruments, was used for all experiments. Exciting the cantilevers with dry channels by the piezo-stack of the AFM for a certain frequency range (0–500 kHz) in tapping mode, we found two resonance modes (dashed line in Fig. 3). After filling the reservoir with a water droplet by a syringe, a shift in resonance frequency was observed for both modes (continuous line in Fig. 3). The frequency shift for both modes is in accordance with calculations incorporating the additional fluid mass. Considering the cross-sectional areas of the cantilever and the densities of water and SiNx, a 3.2% increase of the mass of the cantilever was expected, which is in correspondence with the observed 1.6% shift in the resonance frequencies.

The change of tip–substrate adhesion strength was measured to demonstrate that the fluid reaches the sample surface and facilitate the wetting of the sample surface. The observation of resonance frequency shifts of the cantilever in tapping mode (Fig. 3) clearly shows that the cantilever was covered by liquids up to 20 nm from the sample surface.

FIG. 1. Micromachined fountain pen for AFM-based nanopatterning. (a) Cross section of MFP through the outer cantilever; (b) fabricated MFP with one inlet (reservoir) for the channels in the V-shaped cantilever; (c) MFP with separate inlets for the channels in the cantilever.

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face. Significant increase in adhesion strength was observed when the channels were filled with water compared to dry contact conditions. Figure 4 shows the measured pull-off force for a Si$_3$N$_4$ tip, located on the outer cantilever (as shown in Fig. 2), in contact with a polished single-crystal Si sample, which due to the presence of native oxide was hydrophilic in nature. The calculated spring constant of the cantilever was 0.055 N/m. The pull-off force increased four times when water was inserted into the reservoir, which convincingly shows that the water reached the sample–tip interface. For a spherical tip of radius $R$ the contact force is given by $4\pi R\cos \theta$. Good correspondence with the measured pull-off force was found assuming a contact angle of $20^\circ$, a tip radius of 30 nm, and taking the surface tension of water.

Two different writing experiments were performed to test the MFP functionality. In the first experiment 1-octadecanethiol (ODT) dissolved at 0.1 mM in CH$_2$Cl$_2$ was used as ink on a 20-nm-thick sputtered gold surface for a proof of concept. The ink forms a self-assembled monolayer (SAM) when brought in contact with a gold surface. Each line in Fig. 5(a) was generated by five scan cycles with a contact force of 1 nN at a speed of 4 $\mu$m/s. The friction image was obtained by frame scanning at 80 $\mu$m/s using the same tip as for SAM writing. The thinnest lines generated by adsorption of SAM on gold surface were 0.5 $\mu$m. We estimate that the limitation of the width of the lines is determined by the diffusion due to continuous ink flow, beside the well-known effect of the sharpness of the tip and the roughness of the sample surface. Optimization of the tip geometry, ink flow-rate (through size of outlet holes, viscosity and wetting properties of the ink), and smoothness of sample surface could further decrease the critical width.

The second MFP experiment was localized chemical-mechanical etching of a chromium (Cr) surface. Previously reported Cr etching by means of a quartz nanopipette emphasized the importance of using the technique for mask repair. Two lines were etched using Cr etchant Selectipur® (MERCK 111547, ammonium cerium(IV) nitrate—main active component) into a 25-nm-thick Cr sputtered onto a single-crystal Si wafer [Fig. 5(b)]. A line at 90° orientation to the longitudinal axis of the cantilever was etched by three scan cycles with 5 $\mu$m/s speed at 5 nN contact force, and another at 45° orientation by one scan cycle under the same conditions. The created features were analyzed by frame scanning with the same tip after the channels dried. The first line was 25 nm deep and 0.8 $\mu$m wide (the tip reached the Si), while the second was 14 nm deep and 0.35 $\mu$m wide. The width of the trenches was measured at the horizontal plane defined by the unmodified topography. The tapering of the trench is similar to the shape of the tip, which indicates that with sharpened tips better resolution could be achieved.
This letter demonstrated the fabrication and operation of the MFP, and presented evidence of fluid transport from the reservoir to the tip with resonance frequency shift and pull-off force measurements. The proof of principle in fountain pen lithography applications by writing a SAM pattern and localized etching of a chromium surface was demonstrated.

The MFP is suitable for standard AFM equipment. The tool was fabricated in batch process, enabling an economically viable fabrication which may have a big impact in AFM based lithography.

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