An approach to control of droplet size in nanoscale dispensing

Aiping Fang, Erik Dujardin and Thierry Ondarçuhu
Nanosciences group, CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, Cedex 4, France

e-mail: ondar@cemes.fr

Abstract. Nanoscale dispensing (NADIS) has been recently developed for liquid deposition and manipulation. In NADIS, atomic force microscope probe milled by a focused ion beam was used for nanoscale dispensing of liquid. We present an approach to control the size of dispensed droplets by several parameters such as the aperture size on the probe, the surface energy of both tip outer wall and sample surface. A fine control of the droplet size down to the nanometric scale may provide potentials for surface nanopatterning of molecule deposition.

1. Introduction
Better liquid deposition and manipulation techniques at sub-micron levels could have impact on biological assays or functional devices technologies [1-4]. The newly developed nanoscale dispensing system [5-6] consists in a hollow atomic force microscope probe modified by focus ion beam (FIB) lithography for opening a small aperture at its apex for on-demand deposition of single sub-micrometer size droplets in ambient environment. On the one hand, as a versatile technique for manipulation of liquid, NADIS is able to deposit a wide range of soluble molecules. On the other hand, as a nanopatterning technique based on atomic force microscope (AFM), NADIS could offer a deposition resolution down to the nanometric scale. In this work, we explore the possibility to pattern liquids on various surfaces and show an approach to a fine control of the deposited volumes from femtoliter down to attoliter. The potential ability of dispensing liquids down to sub-100nm level on chemically reactive surface suggests its potential applications in miniaturized biological assays and nanodevice fabrications [7].

2. Experimental
In a continued effort to reduce the size of liquid deposits, we have developed an improved protocol to drill small apertures at the apex of NADIS tip by FIB lithography. A two-step approach enables to (i) thin the wall of commercial AFM tip into a funnel-shaped membrane and (ii) to mill a sub-200 nm aperture precisely located at the apex (figure 1).

In order to obtain substrates with controlled but varying surface energies, the SiO₂ samples were first cleaned in a freshly prepared Piranha solution (a 3:1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide, v/v) for 15 min, followed by copious rinsing with deionized water and dried under a stream of pure argon. The samples were immediately transferred into a vacuum chamber, where an atmosphere of either 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (Lancaster Synthesis) or aminopropyltriethoxysilane (Aldrich) was maintained under vacuum for 2 and 20 min, respectively. Advancing \( \theta_{\text{adv}} \) and receding \( \theta_{\text{rec}} \) contact angles of glycerol on fluorinated surface are 95° and 85°,
respectively. $\theta_{\text{adv}}$ and $\theta_{\text{rec}}$ of glycerol on amine-modified surface are 53° and 27°, respectively. The cleaning and surface treatment procedures were similar for the gold-coated NADIS tips but using dodecanethiol for 30 min.

Figure 1. FIB milling process for sub-200 nm aperture in NADIS tips. (a) the two-step milling process consist in (1) thinning the tip wall and (2) drilling the aperture at the apex. This process results in precisely positioned 150 nm (b, side view) and 80 nm (c, axial view) apertures.

A Multimode PicoForce AFM (Veeco) was operated in force curve mode to transfer the liquid by contacting the loaded tip with the substrate. All experiments were performed with glycerol-based liquids because of its very low volatility, which makes it possible to utilize an open reservoir under ambient atmosphere. In order to observe the trace of the deposited droplets on the substrate, we used solutions of a ruthenium polypyridine complex [8] with a concentration of 16 mM in 9:1 mixture of glycerol (Aldrich) with deionized water. This solution was loaded on the modified tip with the help of a microinjection (Narishige) connected to a micromanipulator (The Micromanipulator Inc.). Images of the resulting spots by tapping-mode AFM with a silicon probe provide information on the size of the deposited droplets on the surface.

3. Results and Discussion
In order to study the role of sample surface energy in the deposition process, we used one NADIS tip for the liquid deposition on different surfaces with various properties. The NADIS tip has an aperture of 400 nm without any further treatment thus giving a hydrophilic outer wall. Dispensing of droplets with this tip on an amine surface yielded droplets with a uniform diameter of about 1 µm (Figure 2a). When a highly hydrophobic fluorinated sample was used, the deposited droplets turned out to be much smaller, with an average diameter of 60 nm (Figure 2b). This size is much smaller than the aperture size of the tip but, compared to the case on amine surface, the droplet size is not uniform even leading to missing droplets.

These results indicate that sample surface energy has a crucial influence on the amount of transferred liquid and offer a means to control the deposition down to nanometric sizes. However, the fluorinated surfaces required for small dimensions are chemically inert, which makes it impractical for applications. Consequently, we focused on dispensing nanodroplets on chemically active amine surface.

Figure 2. AFM images of deposited droplets on hydrophobic surface and a highly hydrophobic surface; tip aperture size: 400 nm. Scale bars are 1.0 µm.
In order to better control the droplet size on amine surface, we performed an alkanethiol treatment on the tip outer wall surface thus rendering it hydrophobic in an attempt to confine the liquid at tip apex. When such a tip with a 200 nm aperture was brought into contact with the surface, deposition of 430 nm droplets was obtained (Figure 3a) showing a confinement effect compared to non-treated tip (data not shown). In order to evidence whether the role of tip surface energy was preponderant over other parameters, we fabricated tips with more complex surface functionalization obtained by combining FIB machining and surface chemistry. The gold-coating was removed by FIB to expose a hydrophilic silicon nitride zone around the tip apex. As schematized in figure 3b, a hydrophilic zone of 800 nm was defined around an aperture of 80 nm. The defined zone remains hydrophilic after a dodecanethiol treatment of the tip. Uniform depositions of droplets with a diameter of about 730 nm were achieved with this tip on amine surface in spite of a much smaller aperture size. This dimension is comparable with that of the hydrophilic region and can be explained by the fact that liquid contact line pins on the boundary between hydrophilic and hydrophobic zones (Scheme in figure 3b). A comparison of results from figure 3a and b shows that the tip surface wetting properties plays a dominant role in deposition.

**Figure 3.** Deposition on amine surface by tips with controlled outer wall surface energy. Schematics of liquid spreading on tip and substrate surfaces, schematic axial view of tip outer wall and AFM images of deposited droplets are shown from right to left for (a) a 200-nm aperture on an unmodified tip apex and (b) a 80-nm aperture on a tip where the gold coating within a area of ~800 nm at the vicinity of apex was removed. Scale bars in AFM image: 1.0 µm.

In order to test ultimate resolution of the technique, we used tips with smaller aperture size as well as hydrophobic tip surfaces. When a hydrophobic tip with an aperture of 70x120 nm² was used, deposition of 250 nm droplets on amine surface was achieved (figure 4a). When the tip aperture decreases to 35 nm, ultrasmall droplets at 70 nm can be obtained on the same surface under the same conditions (Figure 4b). In this situation, we find that the size of the droplets on amine surface is about the double of the aperture. Based on the fine control of the deposition parameters, such as the surface energy, tip aperture size, reliable deposition at large area with manageable droplet size could be routinely achieved. As an example, Figure 4c shows a 15 × 15 array of droplets at 250 nm deposited on an amine surface.
Figure 4. Arraying ultrasmall droplets on amine surface. A 5 × 5 array of nanodroplets with a) a size of 250 nm by a tip with a 120 nm aperture; b) a size of 70 nm by a tip with a 35 nm aperture; c) a 15 × 15 array of nanodroplets with a size of 250 nm by the same tip used in a). All tips were treated to obtain highly hydrophobic outer wall. The arrays were achieved by the automatic protocol with Nanoscope Software (PicoForce™, v.6.12).

4. Conclusion
We have shown for the first time the fabrication by FIB of NADIS tips with aperture smaller than 100 nm. The optimized deposition protocol provided a fine control of droplet deposition down to 70 nm level on chemically reactive surface, which suggests the potential applications of NADIS in miniaturized biological assays and nanodevice fabrications. Further research dedicated to site-specific dispensing using a nano-positioning table [9] is currently in progress.

Acknowledgement We thank André Meister, Raphaël Pugin and Harry Heizelmann (CSEM, Neuchatel, Switzerland) for continued collaboration and many fruitful discussions and Gérard Benassayag (CEMES) for assistance on the FIB The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) is gratefully acknowledged.

References
[1] Huang Z Y, Wang P C, MacDiarmid A G, Xia Y N and Whitesides G M 1997 Langmuir 13 6480-6484
[2] Delamarche E, Bernard A, Schmid H, Michel B and Biebuyck H 1997 Science 276 779-781
[3] Hong S, Zhu J and Mirkin C A 1999 Science 286 523-525
[4] Bruckbauer A, Ying L, Rovery A M, Zhou D, Shevchuk A I, Abell C, Korchev Y E and Klenerman D 2002 J. Am. Chem. Soc. 124 8810-8811
[5] Meister A, Jeney S, Liley M, Akiyama T, Staufer U, de Rooij N F and Heizelmann H 2003 Microelectron. Eng. 67-68 644-650
[6] Meister A, Liley M, Brugger J, Pugin R and Heizelmann H 2004 Appl. Phys. Lett. 85, 6260-6262
[7] A. Fang, E. Dujardin, T. Ondarçuhu, in press.
[8] Viala C and Coudret C 2006 Inorg. Chim. Acta 359 984-989
[9] Ben Ali M, Ondarçuhu T, Brust M and Joachim C 2002 Langmuir 18 872-876