MICROMACHINED FOUNTAIN PEN AS A TOOL FOR ATOMIC FORCE MICROSCOPE-BASED NANOELECTROCHEMICAL METAL DEPOSITION

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ABSTRACT

We present a device that enables nanoelectrochemical deposition using Atomic Force Microscope. The micromachined fountain pen is a probe that consists of a fluidic reservoir, fluidic channels encapsulated in cantilevers and a pyramidal probe tip by which the fluid transfer to the sample surface takes place. Electrochemical metal deposition occurs on a sample surface when electrical current is driven through the electrical circuit, which is closed by the electrolyte solution. The smallest features that we succeeded depositing with this technique up till now are 3 nm high and 250 nm wide.

1. INTRODUCTION

Initially developed for surface characterization [1], the Atomic Force Microscope (AFM) was adopted in other application fields like mechanical surface modification [2], determination of various materials properties [3,4] and nanolithography [5,6].

The finite amount of liquid available for surface modification in dip-pen lithography applications [5] defined a trend to improve the technique by increasing the amount of ink. Adding inking wells to the chip [7] or dispensing liquid via hollow tips [6] are solutions that can extend the operation time, but do not enable applications that require continuous liquid flow. Efforts have been undertaken to overcome this deficiency by designing hollow cantilevers that can transport fluid for localized applications [8,9]. Successful operation of the Micromachined Fountain Pen (MFP) in AFM-based applications has been reported recently by writing Self-Assembled Monolayer (SAM) patterns on gold surface and by etching patterns in chromium layer using chemicals [9,10]. The possibility to use continuous fluid flow during operation is not only improving already known applications by it also extends the field of AFM-based surface modification. Since an electrical circuit can be closed by an electrical conductive fluid stream, the MFP should enable AFM-based electrochemical metal deposition from electrolyte solution.

State-of-the-art nanoelectrochemical depositions are carried out with pulled glass capillaries [11], requiring special instrumentation. Our goal was to create micro/nano structures by electrochemical deposition using standard instrumentation such as AFM equipment. The use of techniques such as dip-pen [5] and nanodispensing [6] is limited by the problems related to closing the electrical circuit via the electrolyte.

2. DESIGN AND FABRICATION

The MFP probe is designed in a way that a fluidic channel, which transports the fluid from the reservoir to the pyramidal tip located at the end of a cantilever, is encapsulated between two structural layers (Figure 1).

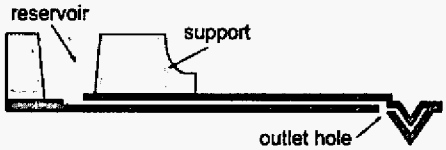

Figure 1. Fabricated Micromachined Fountain Pen. The fluidic reservoir is micromachined into the Pyrex probe-support.

A reservoir is micromachined into the Pyrex support, which allows fixing the MFP into AFM probe-holders (Figure 2).

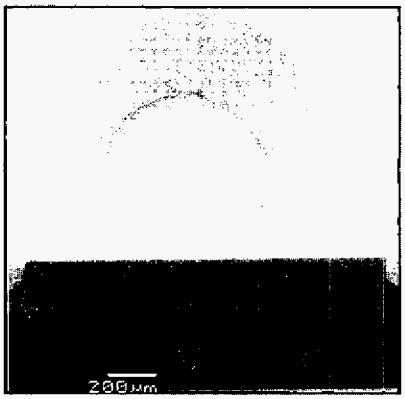

Figure 2. Fabricated Micromachined Fountain Pen. The fluidic reservoir is micromachined into the Pyrex probe-support.

The material chosen for the fabrication of the cantilevers was Si_xN_y due to its excellent mechanical properties and because it's hydrophilic nature facilitates fluid transport in capillaries and on the facets of the pyramidal tip. Due to good chemical resistance of the Si_xN_y to a large variety of chemicals, the application field of the MFP is hardly limited by the fluids that have to be transported via the channels. The thickness of the cantilevers is chosen in such a way that their elastic properties resemble to that of the commercial ones, in order to allow contact and tapping mode operations with AFM equipment. The MFP can be fabricated in batch process [10], enabling an economically viable fabrication,

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which may have a profound impact in AFM-based fluidic applications.

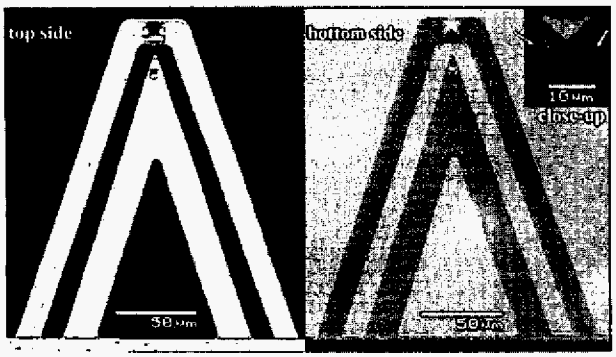

Figure 3. Top and bottom views of MFP cantilevers with photolithographically opened outlet holes. The close-up picture of the tip shows that the outlet holes are opened at the base of the pyramidal tip.

Figure 3 shows the close-up of the cantilevers. The fluidic channels embedded in the outer cantilever are 2 μm wide and 250 nm high. The outlet holes are opened photo-lithographically at the base of the pyramidal tip, thus the sharpness of the tip is not affected. The inner cantilever is used just for (in situ) detection purposes [12].

The fabrication process of the MFP is shown in figure 4 below. (a) deposition of Si_xN_y on <100> single-crystal Si wafer, (b) patterning of the Si_xN_y etching mask of the molds for the probe tips, (c) KOH etching of the molds for the tips, (d) removal of the Si_xN_y mask, (e) deposition of the first Si_xN_y layer for the MFP cantilevers, (f) patterning the outlet holes of the fluidic channels, (g) deposition of a polycrystalline-Si layer used as sacrificial material for the channels, (h) patterning the polycrystalline-Si for the channels, (i) deposition of the second Si_xN_y layer for the probe cantilevers, (j) patterning the MFP cantilevers, (k) patterning the inlet holes of the fluidic channels and patterning the backside Si_xN_y ring, (l) powder blasting of the fluidic reservoir into the Pyrex wafer, (m) dicing of the Pyrex wafer above the cantilevers to inhibit bonding, (n) anodic bonding of the Pyrex and Si wafers, (o) dicing of the Pyrex wafer to enhance breaking apart the probes after fabrication, and dicing of the Pyrex wafer to free the topside of the cantilevers, (p) removal of the sacrificial material from the channels and releasing the cantilevers in KOH bath.

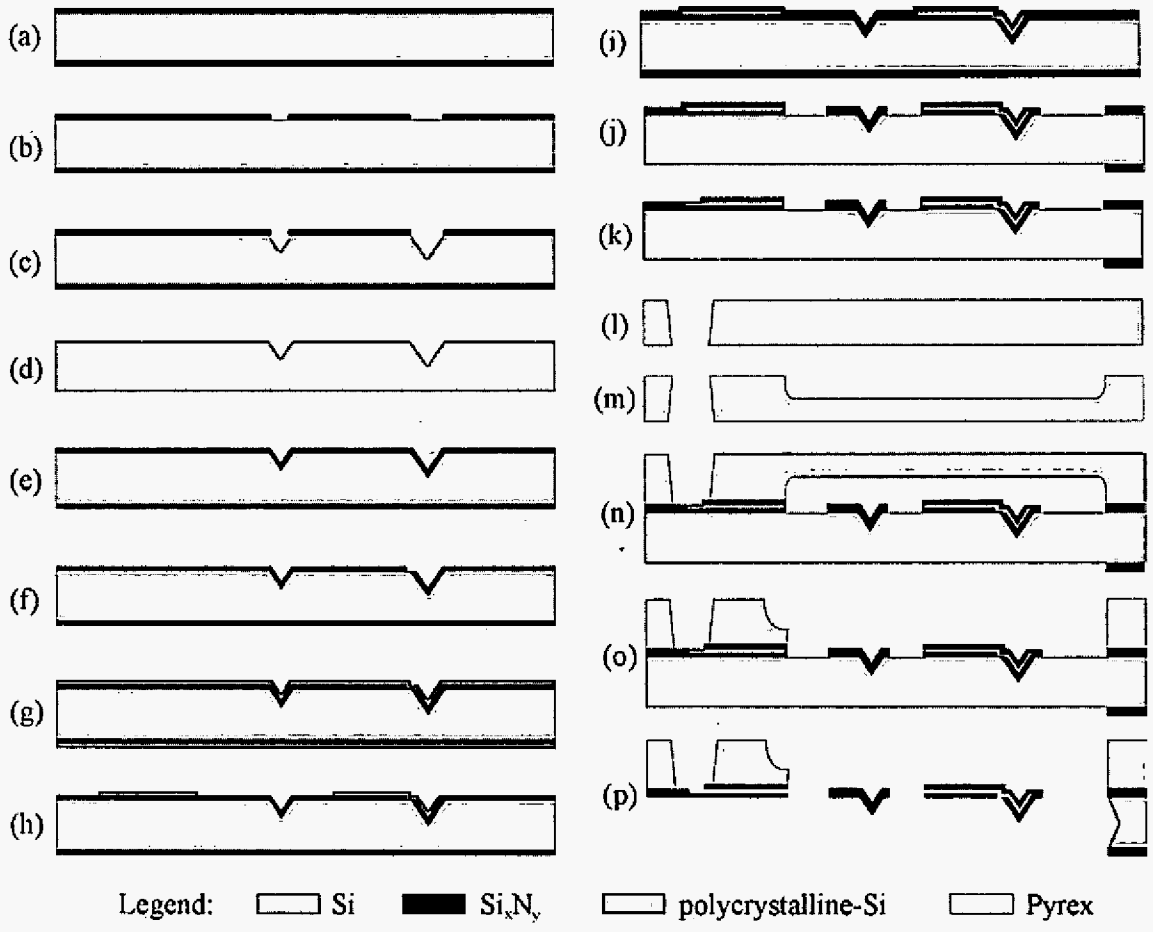

Figure 4: Fabrication process of the batch processed MFP.

3. Working Principle and Experimental Set-up

The fluidic transport in the channels embedded in MFP cantilevers has been reported previously [9], together with the proof of fluid transfer via the pyramidal tip to a substrate. It has also been shown that the MFP enables fountain pen lithography and localized chemical-mechanical surface modification [9,10].

This work focuses on a specific application that is important in constructing metallic nanostructures in a bottom-up approach. The working principle of the electrochemical AFM-based deposition is presented in Figure 5. The cathode, where material is deposited, has to be an electrical conductive material. The anode is a gold layer on the topside of the MFP probe, which also enhances the optical reflection of the laser beam onto the photodiodes. The wall of the truncated cone-shaped reservoir is also covered by gold due to the nature of the sputtering process, thus the electrical circuit is closed via the electrolyte as long as the reservoir is not completely empty. A DC source is used for the voltage driven experiments and the complementary electrical circuit was realized with platinum wires, which were glued to the substrate (cathode) and to the metallic support of the MFP probe (anode). Due to the small dimensions of the channel its electrical resistance is high (>> 10 MΩ for practical solutions). Therefore, for sufficient high driving voltages, the writing current is mainly determined by the channel resistance. More in detail, the channel resistance is given by:

$$R = \frac{l}{\kappa A} \qquad (1)$$

Where κ [S/m] is the conductivity of the electrolyte, l is the channel length, and A is the cross sectional area of the channel. In the experiments $CuSO_4$ dissolved at 1 mM in deionised water was used as electrolyte. For this solution, eq. (1) returns a channel resistance of approximately 110 GΩ. The electrochemical deposition was carried out at 10 V DC, which according to the channel resistance results in ~90 pA electrical current. Assuming a density of the deposited Cu of 9 x 10^3 kg·m^{-3} this corresponds with a deposition rate of 3 x 10^6 nm^3·s^{-1}.

The deposition procedure was the following:

i) insertion of electrolyte into the fluidic reservoir by means of a syringe;
ii) approaching the substrate with the pyramidal tip in contact AFM mode. The settings correspond to approximately 10-15 nN contact force for dry conditions.
iii) adjusting settings so that for dry contact condition the tip would snap off, but in reality the capillary forces present in the meniscus formed between the pyramidal tip and the substrate keep the tip in close proximity of the substrate;
iv) switching DC source on and starting pattern generation by scanning.

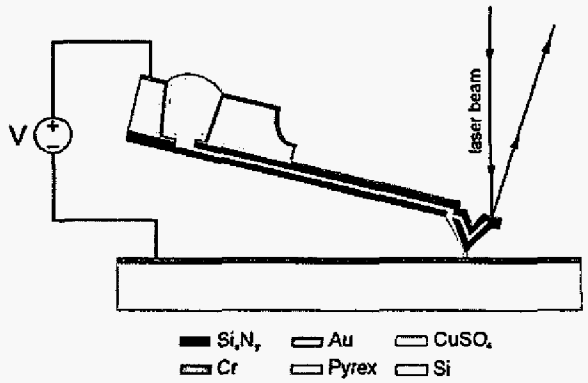

Figure 5. Principle of the electrochemical deposition with Micromachined Fountain Pen using Atomic Force Microscope. The cross section of the MFP illustrates the transport of the electrolyte from the reservoir to the substrate surface.

4. Results

Two experiments were performed to show the proof of principle of AFM-based nanoelectrochemical metal deposition. In both cases copper (Cu) structures were created from $CuSO_4$ electrolyte solution on two different substrates.

For the first experiment a 30 nm thick chromium (Cr) layer sputtered on <100> Si wafer was used as cathode, on which 20 μm long Cu lines were deposited (Figure 6). The electrochemical deposition was carried out in the scanning direction perpendicular to the longitudinal axis of the cantilevers at 0.4 μm/s scan speed. The obtained lines were examined by frame scanning at relatively low contact force due to the reduced hardness of the Cu compared to the Cr substrate. High scanning velocity and/or large contact force damaged the deposited Cu lines. The average height of the smallest lines that could be deposited with this technique was 3 nm, while the width was varying between 250-300 nm. The realized deposition rate of 3 x 10^5 nm^3·s^{-1} is one order of magnitude lower than expected. Possible causes for the difference are: i) we did not take into account the voltage drop at the electrodes, ii) in the calculation we did not include the electrical resistance of the surface film across the tip, from the channel exit holes to the contact region.

A second experiment was carried out to demonstrate that three-dimensional structures can be created by successive scanning on a particular region. A 100 nm thick gold layer sputtered on <100> Si wafer was used as substrate. Copper structures were created by two subsequent scan cycles on a 1x1 μm^2 frame at 0.4 μm/s scan speed. After the first time scanning the result was analyzed by frame scanning of a larger area. Deposition of Cu was observed as the section analysis in Figure 7 shows. The base of the structure is larger than the scanned area, which can be explained by the diffusion of the electrolyte solution on the substrate. The height of the structure is 28.1 nm. After the tip was repositioned on the initial 1x1 μm^2 frame, a second scanning was carried out, resulting in a hill with a height of 75.3 nm.

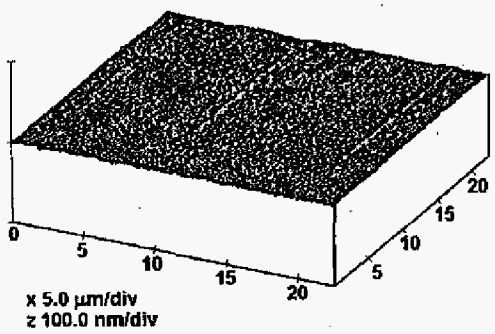

Figure 6. Three 20 µm long copper lines deposited onto a 30 nm thick sputtered chromium layer at 0.4 µm/s scan speed. The average height of the lines is 3 nm, while the width is between 250-300 nm.

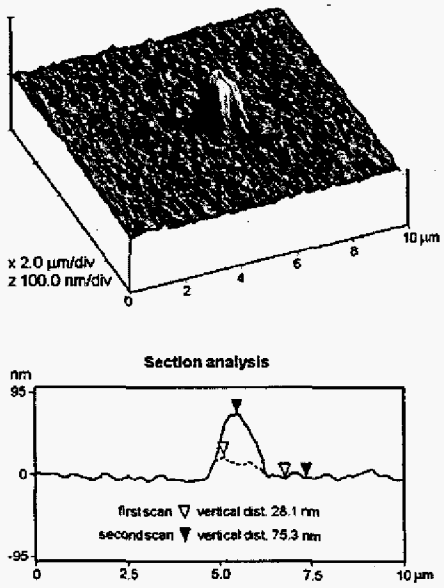

Figure 7. 3-D copper structure created by two complete scan cycles on a 1x1 µm² frame. The substrate was sputtered Au and the scan speed was 0.4 µm/s. The section analysis shows the height of the structure deposited by the first and second scan cycle. The width of the structure at the base is 1.25 µm and the maximum height was 28.1 nm after the first and 75.3 nm after the second scan cycle.

5. Conclusions and Discussions

We presented a device and a technique that enables deposition of micro/nanostructures electrochemically, by using standard AFM equipment.

The technique enlarges the application field of AFM in nanoscale surface modification, besides fountain pen lithography and localized chemical-mechanical surface modifycation.

Although preliminary results are promising, further optimization has to be carried out on fluid flow rate, electrolyte concentration and composition, electrical current density and choice of substrate material and characteristics.

Acknowledgments

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