Abstract — In this paper we present for the first time electrospraying from fountain pen probes. By using electrospray contactless deposition in an AFM setup becomes possible. Experiments on a dedicated setup were carried out as first step towards this goal. Spraying from 8 and 2 µm apertures was observed. For the 2 µm apertures the onset voltage as function of the gap height was studied.

Keywords: AFM, Fountain Pen, Electrospray, Deposition, COMSOL

I – Introduction

Atomic Force Microscopy (AFM) is an advanced technique developed for the characterization of surfaces with a nanoscale resolution. AFM is a form of Scanning Probe Microscopy (SPM) and was first introduced by Binning et al. [1]. A very sharp tip on a flexible cantilever is scanned over a surface. Due to tip-surface interaction forces, the cantilever is deflected, which is optically detected. Originally AFM was intended for imaging and measurements. With the development of the dip-pen by Piner et al. [2], deposition on nanoscale became possible and opened a whole new field of possibilities. The first working fountain pen was demonstrated by Deladi et al. [3]. The concept of the fountain pen is schematically depicted in Figure 1.

A liquid reservoir is connected to an aperture at the probe tip by means of a fluidic channel. By making contact between tip and surface, liquid is deposited by a liquid meniscus. Due to capillary forces the channel is self-filling and supplies the liquid to the tip-aperture during writing. Another application is the transfer of living cells [4]. FluidFM technology (Cytosurge, Switzerland) was used in that case to apply over- and under-pressure to tip less probes.

In this paper electrospray is investigated as new option for liquid deposition on nano-scale. In electrospray a high electric field is used to disperse a liquid into droplets. Different spray modes exists depending on liquid parameters. The most common mode is called cone-jet mode and was studied by Taylor [5] and others. Electrospray has many applications in the field of nanotechnology, for example nano particle/film production, direct deposition and mass spectrometry [6]. Traditionally electrospray deposition is performed using pulled glass capillaries. Large patterns were written, for example, by Park et al. [7].

Using electrospray as deposition technique offers several advantages:

- Contactless deposition.
- Deposition becomes less dependent on the relative humidity.
- Deposition is no longer dependent on tip/liquid/substrate interaction.
- Advanced applications become possible e.g. electro encapsulation.

Electrospray in an AFM setup has been demonstrated before by Kaisei et al. [8]. However, in their experiments they used traditional AFM probes which were modified by Focused Ion Beam (FIB) milling. In this paper batch fabricated fountain pen probes with minimal aperture size of 2 µm were used. In order to visualize the electrospray process, the AFM setup was replaced by a dedicated setup on top of an inverted microscope. In this paper we demonstrate that it is possible to use electrospray as liquid deposition technique from fountain pen probes. Onset voltage as function of gap height is investigated.

In the next section the expected onset voltage is discussed. The experimental setup is presented is described in Section III. In Section IV experimental results are presented. Conclusions are drawn in the last section.

II – Theory

For electrospray to occur, the electrostatic pressure acting on the meniscus must overcome the Laplace pressure (which is the pressure difference over the liquid meniscus due to the curvature of the meniscus). The minimal voltage where electrospray starts is called the onset voltage. If a spherical meniscus shape is assumed with the radius of curvature equal to the aperture radius ($r_{\text{aperture}}$), the Laplace pressure can be found using

$$P_{\text{laplace}} = \frac{2\gamma}{r_{\text{aperture}}},$$  \hspace{0.5cm} (1)

where $\gamma$ is the surface tension in J/m$^2$. The electrostatic pressure acting on a conducting surface is given by the Maxwell stress.
Figure 2: COMSOL simulation model to estimate the electric field acting on a 1 µm radius meniscus.

Table 1: Dimensions of the fountain pen probes.

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<thead>
<tr>
<th></th>
<th>Cantilever</th>
<th>Channel</th>
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<tbody>
<tr>
<td>Length</td>
<td>150 µm</td>
<td>1300 µm</td>
</tr>
<tr>
<td>Width</td>
<td>30 µm</td>
<td>20 µm</td>
</tr>
<tr>
<td>Height</td>
<td>3.9 µm</td>
<td>3 µm</td>
</tr>
<tr>
<td>Thickness</td>
<td>470 nm</td>
<td></td>
</tr>
</tbody>
</table>

\[ P_{\text{maxwell}} = \frac{1}{2} \varepsilon_0 E_s^2. \]  

In this equation \( E_s \) is the electric field in V/m perpendicular the surface and \( \varepsilon_0 \) the permittivity of vacuum. By equating Equation 1 and 2 the following estimation for the onset electric field can be found:

\[ E_{\text{onset}} = \sqrt{\frac{4\gamma}{\varepsilon_0 \text{aperture}}}. \]

For a 2 µm aperture and the surface tension of water, this would require an electric field of \( 1.8 \times 10^8 \) V/m. With use of COMSOL the required potential to obtain this electric field on the meniscus was estimated. The simplified model, shown in Figure 2, consists of a nitride cantilever with uniform electrode on top and a droplet at the same potential.

In Figure 8 the obtained expected onset voltages are plotted.

III – Experimental Details

A. Fountain pen probe

The (FluidFM) fountain pen probes that were used for the experiments had a flat cantilever (no tip as shown in Figure 1) and a higher stiffness than the standard fountain pen probes. A microscope image of the silicon nitride probe is given in Figure 3. Dimensions are given in Table 1. Aperture size was either 8 or 2 µm. Pillars inside the micro channel provided mechanical stability and improved filling characteristics.

B. Experimental setup

For the experiments a dedicated setup was build, shown in Figure 4 (similar to the FluidFM system).

The setup was build on top of an inverted microscope (Leica DMI 5000 M). A 100 µm thick glass plate coated with Indium Tin Oxide (ITO) was used as conductive (transparent) substrate. The probes were glued to a polycarbonate block which is connected to a fluidic Lee tube. By means of this connector pressure could be applied to the liquid inside the probe. Holder block with probe were connected to a linear translation motor, which could vary the height of the probe (with respect to the substrate) with a resolution of 1 µm. Angle between cantilever and substrate was approximately 10 degrees. An positioning meter (with a resolution of 1 µm) was connected to the objective stage of the microscope. Height difference between probe and substrate was measured by focussing successively on the topside of the ITO and the aperture of the probe. Electric contact to the liquid was made by a platinum wire inserted into the channel in the polycarbonate block. A Keithley 237 high voltage Source Measurement Unit (SMU) was used for the experiments. A triax cable connects the SMU to the setup. The resistance between ITO substrate and the SMU ground wire was 8.7-11.1 Ω. A photo of the experimental setup is shown in Figure 5.

Initial experiments indicated a strong dependence of the leakage current on the relative humidity. For example, at 10 V, a relative humidity of 44% resulted in a leakage current of 0.03 nA while a relative humidity
Figure 5: Photograph of a fountain pen probe attached to a polycarbonate block with fluidic and electric connections. Through the ITO electrode the microscope objective can be seen.

Table 2: Properties of the liquids used (DI = deionized water, IPA = isopropyl alcohol, AA = acetic acid).

<table>
<thead>
<tr>
<th></th>
<th>DI water</th>
<th>DI/IPA/AA</th>
</tr>
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<tbody>
<tr>
<td>Composition</td>
<td>100%</td>
<td>(50%/50%/)+5m%</td>
</tr>
<tr>
<td>Resistivity $\rho$</td>
<td>88.5 $\Omega$ cm</td>
<td>819 $\Omega$ cm</td>
</tr>
<tr>
<td>Surface tension $\gamma$</td>
<td>72 mJ/m$^2$</td>
<td>25 mJ/m$^2$</td>
</tr>
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of 61% resulted in a leakage current of 2 nA. To reduce the influence of the relative humidity, a N$_2$-fumehood was installed over the setup (not shown in Figure 5). This caused the leakage current to drop below 1 pA (up to at least 600 V). Properties of the liquids that were used for the experiments are given in Table 2. All liquids were filtered with a 0.2 µm PTFE syringe filter before use.

IV – Results and Discussion

A. 8 micron apertures

A probe with 8 µm aperture, filled with DI/IPA/AA was used for the first experiments. At a gap (height difference between aperture and substrate) of 22 µm, spraying occurred around 400 V. During spraying, it was clearly visible that liquid was deposited on the substrate. However, during ramping of the voltage the end of the cantilever was wetted. The wetted cantilever is shown in Figure 6a and c (Figure 3 shows a cantilever that is not wetted). This wetted area caused spraying from the edges of the cantilever which shown in Figure 6b. This effect is unwanted because the deposition process becomes uncontrollable. It is likely that the low surface tension of the liquid (which should lead to a low onset voltage) was the reason for the wetting of the cantilever. Furthermore, it appeared that the IPA left stains on the substrate. To minimize wetting of the cantilever and staining on the substrate, DI water was used for the subsequent experiments.

During the experiments no deflection of the cantilever could be observed. This indicates that the stiffness of the cantilever was sufficiently high.

B. 2 micron apertures

After successful spraying from a fountain pen with 8 µm aperture, experiments with 2 µm apertures were conducted. With smaller apertures, smaller gap distances become possible, which lead to smaller deposition spot sizes. When the probe was not filled with liquid, the leakage current was lower than 1 pA. The voltage was increased from 0 V to 600 V with steps of 5 V. After each voltage step, a delay of ten seconds was introduced to allow the system to settle before the current was measured. After filling the probes with DI water, a strong increase in current was observed above the onset voltage.

A typical current/voltage plot is shown in Figure 7. Around 400 V the current begins to fluctuate over time with each voltage step. When the voltage is increased to 550 V the current rapidly increases until the compliance set on the SMU is reached. Liquid on the substrate could be observed. However, instead of a continuous spray, droplets hitting the substrate were observed. It is
expected that by reaching the compliance, the voltage is significantly lowered leading to a pulsating effect in the electrospray current. When a 100 GΩ series resistance was inserted between SMU and probe, a continuous flow could be obtained. However, the effect is not yet well understood.

### C. Measured onset voltage versus gap

From the current plots (e.g. Figure 7) it is difficult to determine the exact onset voltage. However, the voltage at which the current continuously reaches the compliance (and liquid deposition can be observed on the substrate), is clearly defined. Therefore, this point is considered as the onset voltage. For different gaps the onset voltage was determined, results are shown in Figure 8. Channel resistance was not taken into account. Error margin in the gap measurement was at least 1-2 µm and the voltage was measured with a step size of 5 V. The last measurement set (2012-06-04) contains measurements conducted with the 100 GΩ series resistance. Voltage step size was 20 V in that case. The compliance was set to 1.0 nA for the last set and 0.5 nA for the others.

For gap spacings up to 20 µm the model (described in Section II) is in agreement with the experimentally obtained onset voltages. However, for larger gaps the model predicts a significant higher onset voltage. It should be noted that the experimentally obtained onset voltages are higher than the electric breakdown voltages of air that are known for metal electrodes. Therefore, especially for larger gaps, electric breakdown of air can not be ruled out. In addition, the model assumes that the liquid surface is equipotential and has a spherical shape, which is only a coarse approximation.

An alternative option to prevent wetting of the cantilever is to apply a hydrophobic coating on the cantilever or use fountain pen probes with tip (like depicted in Figure 1). The electric field enhancement at the pyramidal tip might also reduce the onset voltage. By using liquids with lower surface tension, the onset voltage can be further reduced. In the current setup only z-actuation is possible. Application in a commercial AFM setup is pursued. This gives the possibility to more accurately determine the gap height and with x-y translation, writing would become possible. However, based on the high onset voltages, electric breakdown is a critical aspect that requires further investigation.

### V – Conclusions

A new technique for liquid deposition from fountain pen probes has been presented. By using electrospray, contactless deposition can be achieved. Spraying from the edge of the cantilever was observed with probes filled with water/isopropanol/acetic acid (8 µm aperture). Wetting of the end of the cantilever is the most likely explanation. With 2 µm aperture probes filled with water, spraying from the nozzle was possible. A pulsating effect was observed, probably due to the electronic oscillations in the measurement setup. Onset voltage as function of the gap spacing was studied. A simple model could predict the onset voltage up to 20 µm gap height.

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### References