

Electrochemical pattern formation in a scanning near-field optical microscope

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Abstract. Combining a scanning ion conductance microscope (SICM) probe with a scanning near-field optical microscope, we have obtained a new scanning probe microscope, which allows electrochemical surface modification and simultaneous near-field optical observation of the lithographic process. In this paper, the operation is demonstrated in principle using a CuSO_4 solution and a sample which is electrically conductive and transparent in the visible region (ITO coated glass). We also present some details such as shear force distance control in liquids and light guiding in pulled and filled micropipettes. Macroscopic experiments demonstrate localized deposition and allow to estimate parameters for microscopic deposition. Diameters of first deposited dots are smaller than $1 \mu\text{m}$.

In recent years, a variety of new scanning probe techniques has been developed to obtain more details, especially highly localized physical or chemical information, about sample surfaces. Simultaneously, many efforts have been made to find and improve near-field techniques for controlled surface modification. Electrochemical methods have been of particular interest [1].

This work presents a particular combination of scanning ion conductance microscopy (SICM) [2] and scanning near-field optical microscopy (SNOM) [3, 4] with electrochemical techniques. The SNOM approach to near-field optical imaging using shear force distance control is combined with the special probe tip capabilities of SICM. Together with common techniques for controlled local electrochemical deposition [5], this makes available a new kind of microscope which allows the in situ imaging of electrochemically created structures and even the monitoring of the deposition process.

The final aim of our project is the deposition of Cu on Si surfaces. The use of an infrared (IR) laser is therefore necessary to reach a reasonable transmittance through the Si substrate. For the preliminary experiments presented in this work, no IR laser was available, so a substrate was chosen which is transparent in the visible region.

In the present paper we describe the experimental setup, a macroscale experiment which allows to study the deposition without any restrictions arising from size effects, and present first results obtained with micrometer-scale tip apertures. From these experiments, conclusions for the miniaturization of pattern sizes are drawn.

1 Experimental

The setup is equivalent to a SNOM (Aurora stage, TopoMetrix Inc.) with a SICM tip. The tips were pulled from $100 \mu\text{l}$ and $10 \mu\text{l}$ micropipettes in a micropipette puller (Sutter Instruments P2000) and filled with an electrolytic solution. The SNOM allows the three-dimensional positioning of tip, sample, and objective for detection of transmitted light to be already given. Additionally, the shear force distance control, consisting of a laser and a four-quadrant photodetector, is implemented. For the electrochemical part of the microscope, experience gained from the scanning electrochemical microscope [6, 7] (SECM) is helpful. In the final setup, a bipotentiostat is necessary to control the electrochemical deposition below the tip. For the preliminary experiments, a two-electrode system consisting of a working electrode (Cu wire) and a counter-electrode of indium tin oxide covered glass (ITO) was used.

Figure 1 shows the principle of the experimental setup. The sample is mounted in a small custom-made glass receptacle. The side-walls of the receptacle have to be tilted so that the shear force laser beam (638 nm) may pass them without shift. The electrical contact with the ITO substrate is realized by silver glue and finally insulated under a heated two-component glue or wax. The tip is positioned above the sample surface in such a way that the shear force laser beam is reflected at both the probe tip and the sample surface below the tip. A dither piezo excites a lateral vibration of the tip, which may be detected by the four-quadrant photodetector.

Probe tip and receptacle are filled with a 1 mol/l aqueous CuSO_4 solution. As working electrode, a Cu wire is introduced into the micropipette. The voltage between Cu and ITO was supplied by a Source Measurement Unit SMU 237

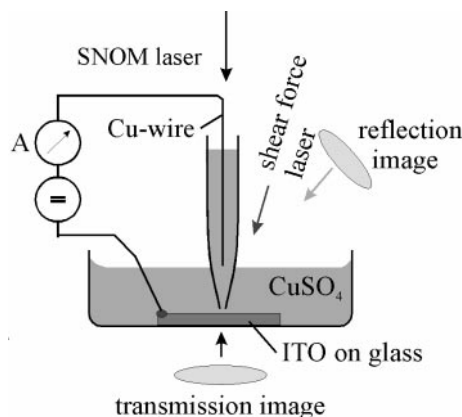


Fig. 1. Principle of scanning near-field optical microscope for electrochemical deposition

(Keithley Instruments), which allows the detection of electrical currents in the fA range.

The light for the transmission image is provided by a second laser working in the blue range (488 nm), which is part of the Aurora stage. It may be coupled into the micropipette by threading the fiber into the micropipette or by positioning the laser spot at the upper end of the micropipette. The first version results in a fully illuminated tip as shown in Fig. 2a, where the camera image of a water-filled micropipette is presented. In comparison to the light guiding of filled pipettes, the image of an unfilled pulled micropipette is shown in Fig. 2b at ambient light conditions and in Fig. 2c in darkness. It is noticeable that the light escapes at the fiber end and will be reflected at the inner micropipette surface, so that almost no light reaches the pipette end. In case of illumination from a distance, the light is guided only in the glass.

2 Macroscopic local deposition

Because the deposition behaviour of Cu on ITO was unknown, the deposition conditions were first investigated in a macroscopic experiment. To investigate localized deposition at the same time, original micropipettes with an inner diameters of 0.4 mm were used. The flat end of such a micro-

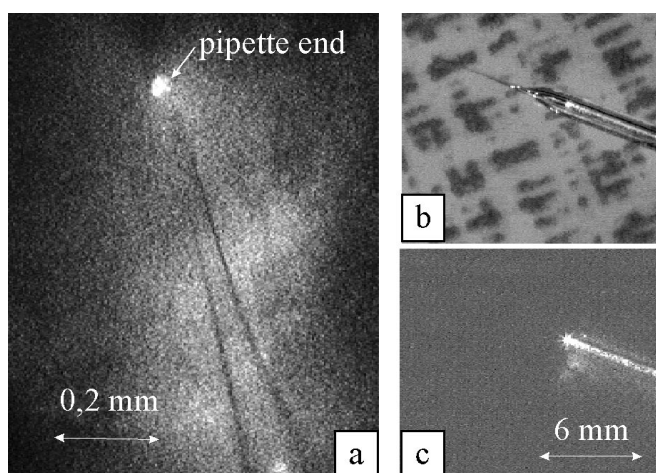


Fig. 2a–c. Optical images of pulled 10 µl micropipettes with illuminated optical fiber inside: **a** water filled; **b** unfilled at ambient light; **c** unfilled in darkness

pipette was positioned as close as possible above an ITO substrate surface.

At 1.5 V a visible Cu film is deposited in less than 1 min. Above 2 V, the electrolysis of water is initialized. In Fig. 3, a cyclic voltammogram taken with a speed of 50 mV/s is shown. It demonstrates that there is almost no voltage threshold for Cu deposition and a small threshold of 0.3 V for Cu dissolution. The cyclic voltammogram measurement results in a deposited Cu dot consisting of layers which result from single voltammogram cycles.

In Fig. 4a, the scanning electron microscope (SEM) images of three deposited Cu dots are shown. The left one is produced by maintaining the voltage (1.5 V) for 10 s. The higher resolution Fig. 4b shows that the initial states of Cu deposition on ITO are marked by the formation of single clusters. Most of them are situated along lines with undefined orientation (white arrows). Others are randomly distributed. It seems obvious that the deposition starts at structural defects of the ITO surface. The clusters in Fig. 4b have an average diameter of about 4 µm.

A cyclic voltammogram (Fig. 3) will result in the dot shown in Fig. 4c. The Cu film consisting of single particles is now closed in the central part. The average size of the single clusters is much larger than the average cluster size in Fig. 4b. Furthermore, the potential distribution within the electrolyte causes a decrease in film thickness from the center of the dot to the periphery. At the periphery, there are fewer clusters per unit area than in the center. Higher voltages will result in rougher particulate surfaces (right dot in Fig. 4a). The shape of the Cu particles does not suggest a single-crystalline nature, so a polycrystalline structure is assumed.

From these macroscopic experiments, the following predictions can be extracted:

- The electrochemical deposition of Cu on ITO under the conditions mentioned above results in patches of randomly distributed polycrystalline particles.
- The potential decrease within the electrolyte causes decreased deposition. In the worst case, the electrolysis of water starts before the Cu deposition is initialized.
- Owing to the small threshold, deposition without water electrolysis becomes possible.

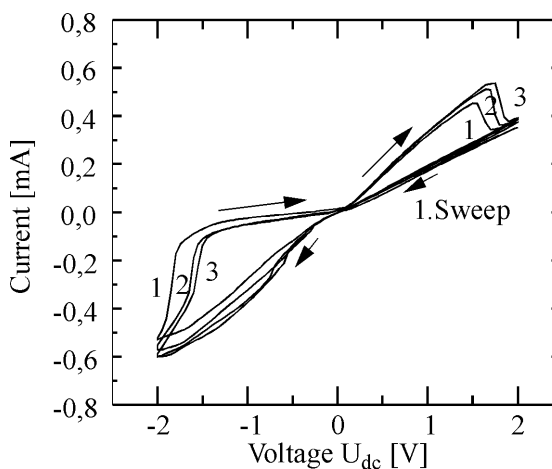


Fig. 3. Cyclic voltammogram of Cu wire in CuSO₄-filled micropipette with 0.4 mm diameter on ITO, speed: 50 mV/s

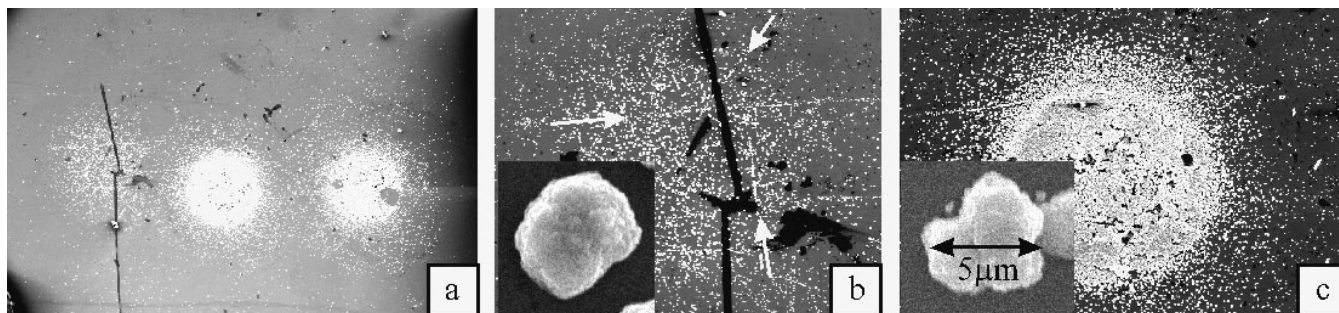


Fig. 4a–c. SEM images of electrochemically deposited Cu dots with 0.4 mm inner diameter: a complete sample; b enlarged left dot; c enlarged central dot from a

- The potential distribution around the tip apex causes a thickness profile of the deposited Cu structure.

3 Submicrometer deposition

Previous work has shown that shear force distance control in liquids is possible [8, 9]. Because the resonance frequency of pulled micropipettes depends on too many parameters, a conventional optical fiber was used for the preliminary experiments. Its resonance frequency of free vibration (air conditions, far from the surface) is about 60 kHz. In Fig. 5, the spectrum of the detected shear force signal in water is shown. The resonance frequency is shifted down to 12 kHz due to the strong damping in liquid. Additionally, the amplitude of oscillation is decreased. However, the signal is still an order of magnitude greater than the noise level, and it could be shown that the shear force feedback at 11.8 kHz is stable.

Knowing the parameters from the macroscopic Cu deposition, pulled micropipettes were mounted in the SNOM. In Fig. 6, images of the transmitted light through a micropipette with 30 μm inner diameter are shown. The light, which is coupled into the micropipette from a distance of several cm, propagates in the glass and not in the electrolyte (dark central part visible in the lower half of the images). Each of the images was taken at 1.5 V in different cycles of the cyclic voltammogram (50 mV/s, 1.5 V to -1.5 V). The transmitted light intensity decreases with each cycle, indicating the proceeding Cu deposition. The dissolution of Cu was also observed. The deposition profile due to the potential distribution at the tip is as visible as the formation of particles.

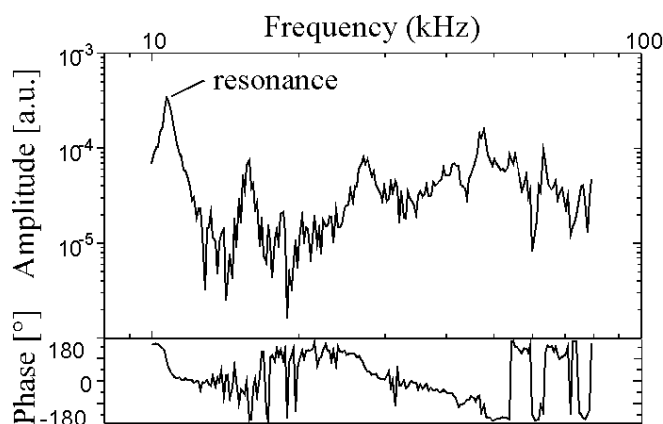


Fig. 5. Spectrum of the shear force signal from an optical fiber in water

Using smaller micropipette diameters, the transmitted light intensity decreases and the aperture of the pipette becomes invisible with the given objective and CCD camera. To observe the light transmission during deposition with a higher spatial resolution, the setup has to be improved by choosing an objective with a larger aperture and a more sensitive photodetector. Therefore, the approach between tip and sample is not observable with a camera.

Nevertheless, Cu deposition from smaller pipettes may be controlled without the optics by detecting the electrolytic current. In Fig. 7, a cyclic voltammogram of a micropipette with 10 μm inner diameter is shown. It demonstrates that Cu deposition takes place initially but stops suddenly after a short time. The remaining leak current corresponds to a resistance of about 1 G Ω , which may be the resistance of the solution. The breakdown of the deposition process is found earlier at depositing polarity (0.6 V) than at dissolving polarity (-1.2 V). This may be explained by the ion depletion of the CuSO_4 solution inside the tip. The effective concentration of the solution is lower inside the tip than outside the tip. Therefore, an earlier breakdown of the deposition was found. From this experiment, it may be deduced that continuous Cu deposition is possible only if a continuous electrolyte flow may be guaranteed to prevent the depletion of electrolytic solution. This flow may be realized by pushing the solution through the micropipette.

Because an in-situ observation of Cu deposition with small tip diameters was not possible with the given setup, we tried to deposit defined Cu structures with micrometer dimension by applying a constant voltage of 1.5 V and moving the tip in straight lines over the sample surface. Subsequently, the sample was investigated in the SEM. At the corresponding sample location, an assembly of Cu particles with less than 1 μm diameter was found. Most of them are positioned along straight lines (example inset in Fig. 8). This may be caused by the tip movement, but it is more probable that the straight lines are a result of the ITO surface structure, especially because the inner tip diameter was much larger than the structures found.

To check the chemical nature of the particles, energy dispersive X-ray analysis (EDX) was used. The spectrum shown in Fig. 8 contains high peak intensities for silicon (Si) arising from glass substrate, indium (In) from the ITO film and calcium (Ca) from contaminating water. Furthermore, a small peak of iron (Fe) originates from the vacuum chamber. The Cu-peak is obviously too large to be an artefact. The small intensity of the Cu-peak may be explained by the fact that the EDX signal results from the large excitation volume of X-rays

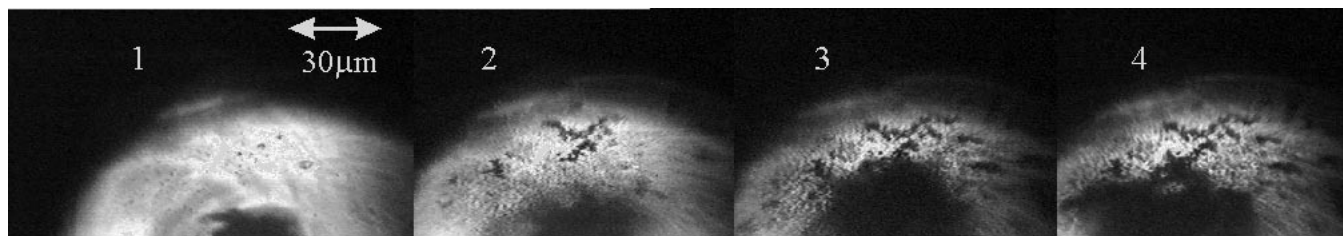


Fig. 6. Transmission images during a cyclic voltammogram from 1.5 V to -1.5 V at 1.5 V. Light is coupled into the micropipette from a distance of several cm (no light in electrolyte)

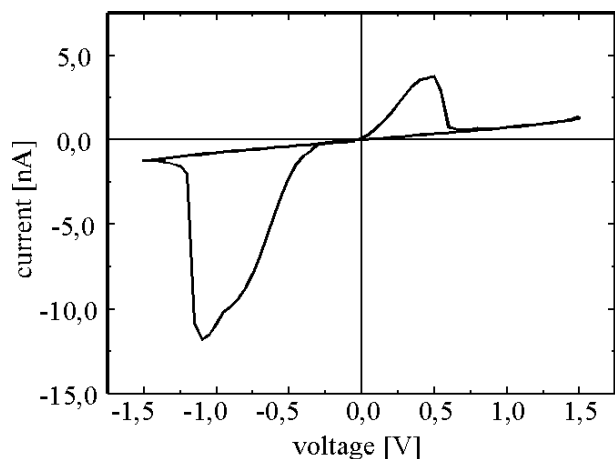


Fig. 7. Cyclic voltammogram of Cu wire in CuSO_4 -filled micropipette with $5 \mu\text{m}$ inner diameter on ITO, speed: 50 mV/s

in the sample, and the small Cu particles are situated only at the sample surface.

4 Summary and outlook

This work presents an idea of the possible operation of a scanning probe microscope, which allows the electrochemical deposition of structures with less than $1 \mu\text{m}$ dimensions in combination with the in-situ optical near-field observation using the same probe tip. The single experimental steps were studied separately at a testing system (Cu on ITO), which is too poorly defined to reach precise results but sufficient to check the experimental capabilities of the method. The macroscopic experiment has shown, that the deposition is concentrated below the tip, if tip and sample are close enough. Then, the structure size is comparable to the inner diameter of the tip, which can be decreased as far as 100 nm [8]. This small distance may be realized and controlled during scan using the shear force distance control in liquid. The optical observation was demonstrated in principle using micropipettes with $30 \mu\text{m}$ inner diameter.

These results show that some improvements in the setup are required:

- Circulation of the electrolyte is necessary to prevent a depletion of the electrolyte in the deposition region.
- For smaller tip diameters, an objective with a larger numerical aperture and a photodetector or photomultiplier will be useful.
- A four-electrode system controlled by a bipotentiostat will improve the electrochemical deposition conditions.

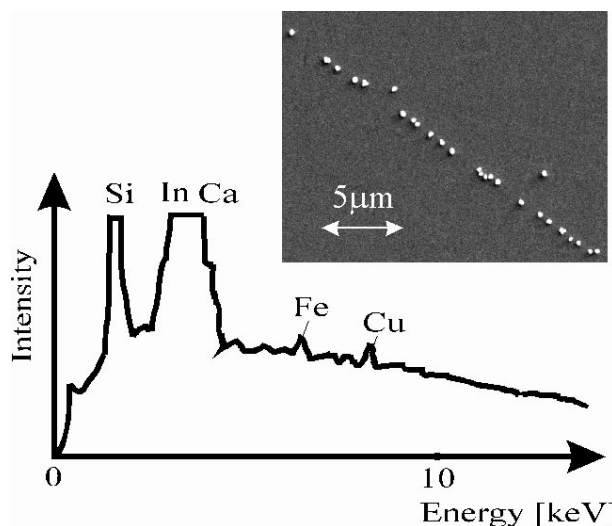


Fig. 8. EDX spectrum and SEM image of electrochemically deposited Cu structures

For applications, it would be more useful to use an Si wafer as substrate. To reach the transparent wavelength region of Si, the use of IR light is necessary. The final goal of those experiments may be the deposition and near-field optical imaging of defined structures with $0.25 \mu\text{m}$ dimensions.

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