NANOSTRUCTURING OF POLYMERS IN LIQUID BY THE USE OF POLYMER CRAZING

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Abstract. The development of nanostructures is usually based on UV- or DUV-lithography. Using these techniques, a new set of lithographic masks has to be generated for each step in development. Other methods to create nanostructures are the direct writing techniques like e-beam, but this techniques suffer from very high installation and operation costs.

To overcome these cost and time intensive procedures we have developed an *in-situ* technique which allows to write lateral structures with a resolution of 80 nm over an area of up to 100 µm in square with simultaneous characterization. This method is based on a conventional scanning force microscope modified for the use in a development liquid onto a commercial available PMMA/MA e-beam resist and is independent of the substrate material. Specific variations of the tip force which define the depth of structuring allow even structures with oblique faces. Furthermore it has to be emphasized that negative structures can be processed on the in fact positive resist. The created patterns could act as templates for the deposition of e.g. metals or alloys. This can be followed by further lithographic processes of the presented method.

For the structuring a completely new mechanism is used. The polymer chains are not cracked as in e-beam lithography, but the crazing of the polymer is used. With new experiments we can prove the fundamentals of the presented technique.

In this presentation we will illustrate the feasibilities of this method with respect to electrochemical applications on several examples.

1. INTRODUCTION

For the fabrication of sub-micrometer electrochemical structures by lithography techniques several approaches are available. The techniques can be separated in lithography by beam techniques, imprint or print techniques, and lithography by probe techniques.

The beam technologies suffer especially from the financially expenditure. The technologies are available of creating structures down to several nanometers [1] but the invests only for the lithography tools are much too high for small research facilities. Additionally for mask based techniques for each further research step a new set of masks has to be created which is very cost intensive.

Microimprint or print technologies seem to be very promising for the future of lithography while it is a parallel technology feasible of creating structures below 100 nm [2]. With the microcontact printing this is possible directly on electrodes by deposition of a self assembled monolayer on top of a gold electrode [3] or by the use of a conductive stamp and the oxidation of the electrode [4]. But like in optical lithography for changes in the design or structures new masks for the stamp production must be created.

For these purposes, fast and low cost changes of an electrode design, probe based lithography techniques are useable as the changes are only be made in software and the writing speed is not of the same importance in the research environment as in the industry.

For nearly each probe technique like scanning tunneling microscopy (STM), scanning near field optical microscopy (SNOM) or scanning force microscopy (SFM) approaches for lithography have been made.

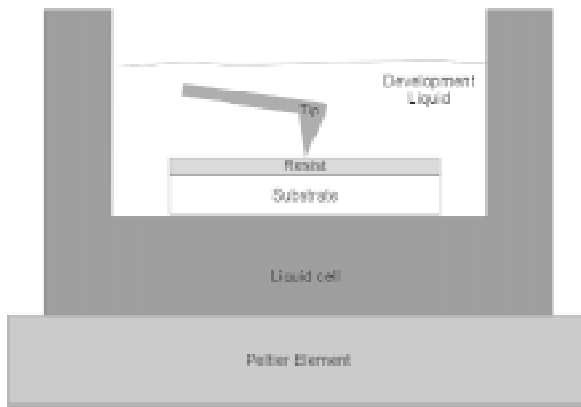Corresponding author: L.J. Balk, e-mail: balk@uni-wuppertal.de

Fig. 1. Schematic diagram of the experimental configuration.

By the use of STM, structures can be written by direct oxidation of the conducting surface, e.g. Silicon or Titanium, with a minimum line width of 20 nm [5]. For this technique the surface usually has to build up stable oxides to get reproducible structures. Thick oxide films are not possible to be produced because the STM tip will be enclosed in the built oxide and destroyed while scanning. It is also possible to modify oxide films with the STM [6, 7]. The STM is also suitable of structuring low thickness resists by exposing then with the tunneling current [8] and of the deposition of metal directly on the surface [9].

Scanning near field optical microscopy (SNOM) has been applied to several types of photoresist like amorphous silicon [10] or gelatin [11]. The resist is exposed by the emitted light of the SNOM tip. Lithography with the SNOM usually has the problem of too large tip apertures, the difficulty of the reproducibility of the aperture shape, and the wide angle in which the light is leaving the tip. This leads to non regular structures down to 80 nm and to the limitation to thin resist below 100 nm thickness.

With the Scanning Force Microscope (SFM), different approaches have been carried out. It can be used in a similar way like STM to oxidize the surface by a conducting SFM-tip [12]. This technique covers less problems in comparison to STM while the grown oxide does not enclose the scanning tip, fixate, and destroy it. Lithography by SFM in conventional photo resist is feasible, too. This technique is also able to create complex structures like lines and areas with structure sizes down to 35 nm in a process called microploughing or nanoindentation [13, 14, 15]. Both techniques relying on direct structuring of the resist are only suitable for thin resists with thicknesses up to 50 nm.

The technique presented here is feasible to create structures down to 80 nm as well as big structures up to 100 μm even on thick e-beam resists which has been described before. But at that time several mechanisms for structuring had to be discussed [16]. On the one hand a mechanism like in beam technologies, where the polymer molecules are broken by the applied energy, in our case the pressure of the tip, and on the other hand a structural mechanism where the internal organization of the polymer molecules is changed by polymer crazing, which would lead to a totally different mechanical behavior of the resist [17].

2. EXPERIMENT

The experiments were carried out with a scanning force microscope (Explorer, TopoMetrix). It was equipped with a *z*-scanner suitable for liquids and high force tips that give the ability to apply forces of more than 30 μN to the sample. Below the scan device a *x/y*-table has been mounted to allow a movement of the sample without lifting the SFM. For fixation of the samples a cell made of brass and suitable for liquids is used in which the samples are mounted with small screws. The liquid cell is equipped with a peltier element for chilling or heating of samples and liquid in a temperature range between 0 and 50 °C (Fig.1).

Sample preparation consists of cleaning the substrate which usually has been Silicon because of its flatness in Aceton, p.A., in a supersonic bath. The resist (ARP-610-08, Allresist) was spun onto the substrate at 3000 rpm leading to a film thickness of 400 nm. Then the samples were pre-baked in an oven at 190 °C for 60 min.

For the experiments the liquid cell was filled either with a mixture 1:3 of Methylisobutylketone, p.A., and Isopropanol, p.A., or pure Isopropanol, and the sample pieces were fixed in it. The SFM tip was lowered on the surface and with the known spring constant of the tip cantilever the correlation between tip deflection and applied force could be measured. With this a force, for structuring usually between 10 and 20 μN, could be chosen. For the writing of structures the tip had to be moved over the desired pattern with a maximum speed of 100 μm/s.

For a controlled movement of the tip even on complex patterns a program has been written which permits to convert sketches or drawings into the wanted movement of the tip. In the program colors can be related to forces to be applied.

After the structuring procedure the surface has been scanned in the imaging mode with a force of
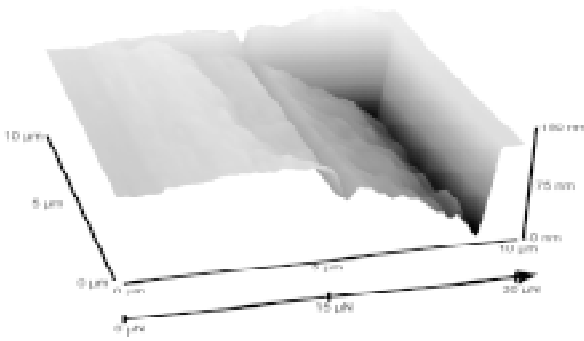
Fig. 2. SFM image of the resist structure written under force variation.

Fig. 3. a) Structure written with MIBK; b) Structure written without MIBK under same conditions (18 repetitions, 20 µm/s scan speed, 10 µm line length, scan forces: 1: 21 µN; 2: 18 µN, 3: 15 µN, 4: 12 µN, 5: 9 µN, 6: 6 µN, 7: 30 µN).

only 0.25-0.75 µN. To lower the effects e.g. of the scan controlling while the structuring, the image were scanned in an angle of 90° to the structuring movements.

3. RESULTS AND DISCUSSION

What could be seen during structuring was the building of two different types of structures dependent on the applied force. For the usual forces of 10 – 20 µN the resulting structures have a positive shape which means that resist has been removed. In a region of low forces up to 5 µN the structures show a totally different negative form. It is possible to create positive and negative structures in the same structuring scan by changing the applied force during the scan. This can be seen in the SFM image in Fig. 2. The force of the SFM tip has been risen from 1 to 30 µN. The resulting structure shows a negative shape in a force region from 4 to 17 µN and a positive structure with a nearly linear slope dependent of the applied force. Forces higher than 30 µN were not applied because this would have lead to a scratching into the resist.
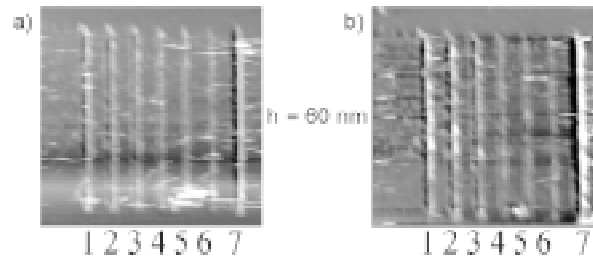
For the explanation of the mechanism we focussed on the variation of force, constitution of the development liquid, and the number of scan repeats for structuring.

The most important effects additional to the depth of the structuring were found for the variation of the liquid and the scan repeats.

The Methylisobutylketone (MIBK) is the active component of the developer for e-beam resists. The experiments with our technique were always carried out with MIBK as it seemed to be necessary for structuring. But as its amount was lowered in the development liquid successively it could be found that the structuring was not dependent of the MIBK quantity and took place without any MIBK as well (Fig.3). Using a theory of molecular bond braking in the resist polymer like in beam technologies this result could not be explained.

In Fig. 4 an image is shown where the tip has been moved between two lines that were structured and the force was not lowered. This resulted into a short line with a negative structure. The difference between the positive and negative structures in this image could only be found in the number of repeats
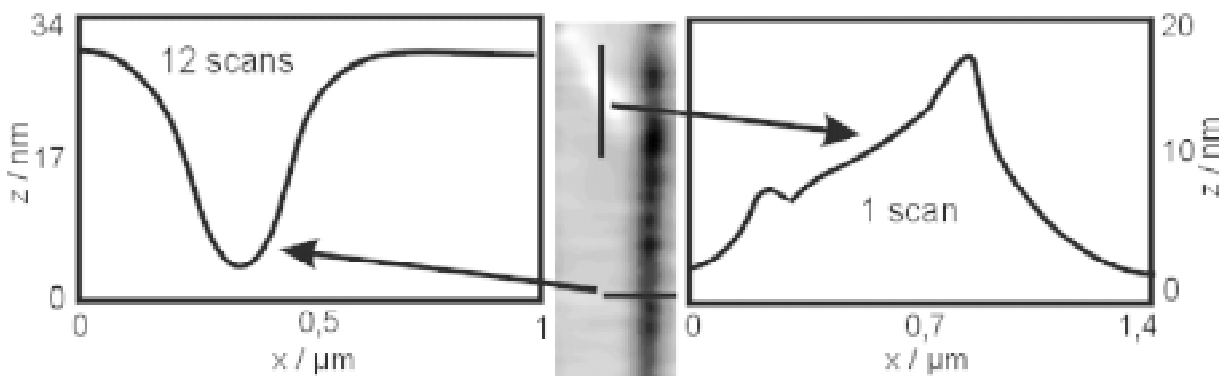

Fig. 4. Positive structure after 12 scans on the same line, polymer is removed by the SFM tip; negative structure after 1 scan on the same line, polymer is not removed but swollen.

Exhibit polymer to tip-force and movement | Crazes already built up in front region, back region only impressed | Begin of the mechanical removing of the crazes | Tip removes the polymer into the surr. liquid | Resulting structure

Fig. 5. Model for structuring by usage of polymer crazing. The removed material is left behind in the surrounding liquid.

that had been carried out. Considering the different directions of the structured lines lead into experiments that showed no dependency of the scan direction. This means that the decision if a positive or a negative structure is formed is not only dependent on the applied force but also on the number of repeats that are carried on the surface. Further experiments showed no sharp boundary between positive and negative structuring dependent on the number of scans. For 20 µN it lies between 3 and 5 repeats.

With these results we could conclude that the structuring could not take place with a mechanism of bond braking. Therefore the mechanism that is responsible for the structuring must be the crazing, where the polymer modification is changed in the first scans from amorphous to more ordered structure in form of fibrils and in the subsequent scans these fibrils can be broken by the tip (Fig. 5).

The knowledge of the mechanism has been necessary to make a prediction for example to the minimum structure size that could be reached by the technique. The limitations of the technique are for small structures in the region of 80 nm that had already been reached. The maximum structure size is not limited while the writing speed seems mostly been restricted by the scan controllers which are responsible for a matching force. The maximum

speed has been 300 µm/s which leads to a time for 100x100 µm of about 3 min.

For production of electrochemical structures like for example microelectrodes we used our lithography program. It can convert plotter files into a movement of the scan system independent how complex the structures are. In Fig. 6 a result of the feasibility of the program is shown. It transforms the picture of one of the authors into a resist structure of less than 10 µm width and height.

We were able to deposit copper into a 5x5 µm resist pad on a 20 µm circular electrode. But we were not able to control the deposition possibly due to leak currents and capacitive currents on the whole contact area of resist and electrolyte. The resulting 20 µm copper cluster is shown in Fig. 7.

Further on we created arrays in the resist (Fig. 8) which could be used as templates for electrochemical reactions. An idea for additional experiments could be found in Fig.9: A subsequent structuring and deposition process leads to microstructures that could not be created with conventional lithography in such an easy way. Between the single steps only the liquids have to be exchanged. Furthermore the technique would be able to image the structures between the step and in case of errors to remove these.
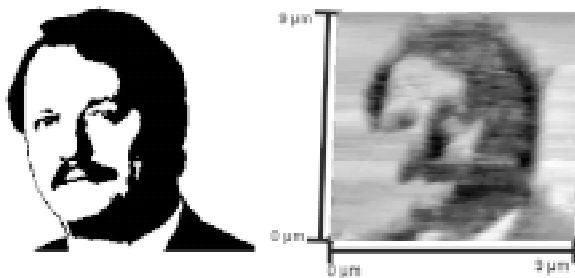

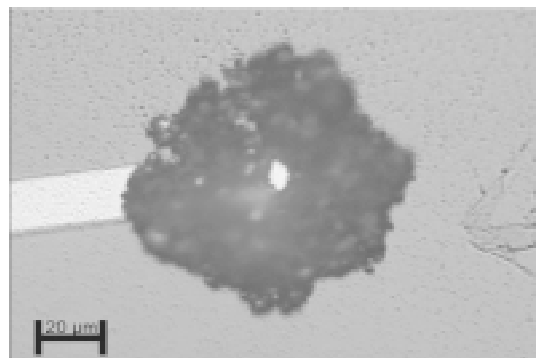**Fig. 6** Transference of a picture in the resist with the help of the lithography program.

Fig. 7. Light microscopic picture of the copper cluster deposited into a 5x5 µm electrode written into the resist on a 20 µm gold electrode.
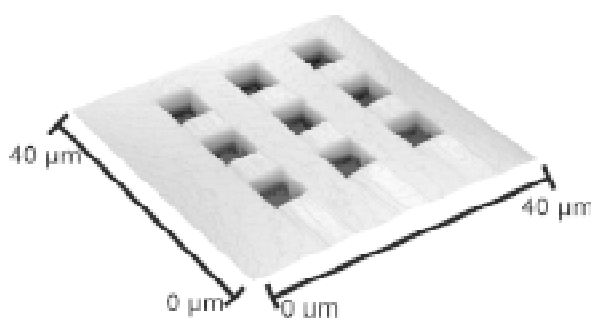
Fig. 8. Array of nine 5 µm squares written in resist; possible usage as template for electrochemical applications.

Fig. 9. Possible application of the lithography for successively structuring and deposition in an electrochemical environment.

4. CONCLUSIONS

In conclusion, we have demonstrated a reliable mechanism for the structuring of e-beam resist using the scanning force microscope. The used mechanism can not be found in any other lithography technique and is based on the structural modification of the resist provided by polymer crazing followed by the mechanical removal of the built fibrils in a further step. Moreover we could show that it is possible with our technique in combination with our lithography program to create even complex structures in commercially available resist. Because of the, compared to other probe based lithography technique, thick resist it should be able to transfer the created patterns by etch technique into the substrate as well as deposit metal subsequently into the structures electrochemically.

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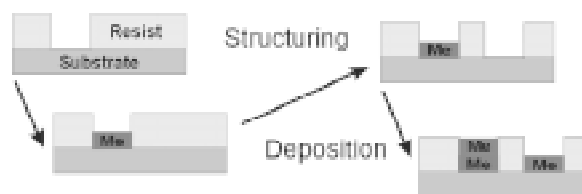[3] H.X.He, Q.G.Li, Z.Y. Zhou, H. Zhang, S.F.Y. Li and Z.F. Liu // *Langmuir* **16** (2000) 9683.

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