FIB Based Micro Fabrication Technique for a Novel Type of Scanning Electrochemical Microscopy Probes

A. Lugstein[1], C. Kranz[2], E. Bertagnolli[1]

[1] Institute for Solid State Electronics, TU Wien, Floragasse 7, 1040 Vienna, Austria

[2] Institute for Analytical Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

Scanning Electrochemical Microscopy is a powerful technique to obtain *in situ* information of a wide range of processes occurring at interfaces. However, one major drawback of this technique is the lack of high spatial resolution compared with AFM or STM, due to the interference of the currents originated by the topographical and the electrochemical effects, respectively. Hence, a simultaneous but independent sensing of both, the topographical and the electrochemical information with high spatial resolution is a major issue in the field of scanning electrochemical microscopy (SECM). In this paper, we present a Focused Ion Beam (FIB) based technology, which, for the first time, enables the realization of an independent, simultaneous sensing of both the topography and the electrochemically active interface [1]. By remodeling an AFM-cantilever, an isolated ring-shaped electroactive metallic surface was integrated in the probe, whereas the residual AFM-tip was applied to gain the topographic information.

1. Introduction

Miniaturization of electrodes and electrochemical transducers by microfabrication processes is one of the fundamentals in modern electroanalytical chemistry [2]. Laterally resolved information on a sub-micrometer scale was added to electroanalytical chemistry with the invention of Scanning Electrochemical Microscopy (SECM) [3], [4]. This analytical method provides spatially resolved information on interface processes, which can be obtained by the possibility to use all common electrochemical methods, such as amperometry, potentiometry or cyclic voltammetry. The changes of the diffusion limited Faraday current at the microelectrode due to hemispherical diffusion of a redox mediator is recorded while scanning in constant height in the x,y-plane within a distance of a few electrode radii above the sample surface. The current response as a function of the microelectrode position is mainly influenced by the morphology and the reactivity of the investigated surface and the distance between microelectrode and sample. One major drawback of this technique is the lack of sufficient spatial resolution compared to AFM or STM, as long as a current dependent mode for positioning of the micro-electrode is used. Any further progress in information quantification and qualification has to address (i) sub-micrometer to nanometer-sized electrodes (nanoelectrodes) for improved lateral resolution, (ii) the integration of current independent height information and (iii) the precise knowledge of the distance between the electrode tip and the sample surface. Consequently, the combination of SECM with other scanning probe techniques such as

Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), Scanning Nearfield Optical Microscopy (SNOM), etc. is of particular interest in order to overcome the current limitations and to obtain complementary surface information. Several approaches have been reported so far to overcome the "fixed height problem in conventional SECM experiments". A constant current mode combined with a vertical tip position modulation was already described in 1992 [5], [6]. A second approach based on electrochemical signaling uses convective effects when the microelectrode is moved with high speed perpendicular to the sample surface [7]. However, both methods do not provide current independent information on the tip-to-sample distance. Though, this approach is restricted to a few practical applications. An innovative possibility to circumvent this drawback is to integrate an electroactive area within a defined distance to the sample surface in a conventional AFM tip. In the present paper we discuss this novel approach applying a Focused Ion Beam (FIB) technique to produce a microelectrode integrated in a standard AFM tip. Thus, for the first time a precisely defined and constant held distance between the microelectrode and the sample surface can be obtained, thus allowing a simultaneous independent recording of the topographic and electrochemical information.

2. Experimental

The formation of the SECM electrode comprises coating of the AFM cantilever with thin conductive and insulating layers by RF sputtering respectively plasma enhanced chemical vapor deposition (PECVD) and the modeling of the integrated ultramicroelectrode by FIB cutting.

Conventional silicon nitride cantilevers were initially subjected to a RF-sputter coat forming a 5 nm chromium layer to ensure good adhesion of the subsequently deposited metal layer. The electrode material in form of a thin gold layer (100 nm to 400 nm) was then sputtered onto the cantilever. Finally a thin insulating and chemically inert SiO_2/Si_3N_4 sandwich layer was deposited (PECVD) onto the metal coated cantilever (Fig. 1). In order to produce homogeneous, dense films without pinholes the cantilever had to be annealed at 300 °C.

The well-defined microelectrode integrated in an AFM tip at a certain distance above the apex of the tip was generated by a FIB pattern process as shown in Fig. 1. The electrode formation includes several diametrically opposed cuttings, which are repeated several times in order obtain the demonstrated tip geometry. A major prerequisite for a simultaneous electrochemical and high resolution topographical imaging is the quality and stability of the re-modeled AFM tip. In order to ensure high resolution imaging, the original tip is re-established by FIB. Even smaller curvatures than usual for conventional Si_3N_4 tips are achieved and thereby the quality of the AFM image after the entire modification procedure could be improved. As a final step, re-deposited material was removed from the electrically active part of the tip.

The electrical contact was provided by an insulated copper wire (diameter: 0.2 mm) glued with a conducting silver epoxy resin to a small exposed area of gold layer at the end of the cantilever mount.

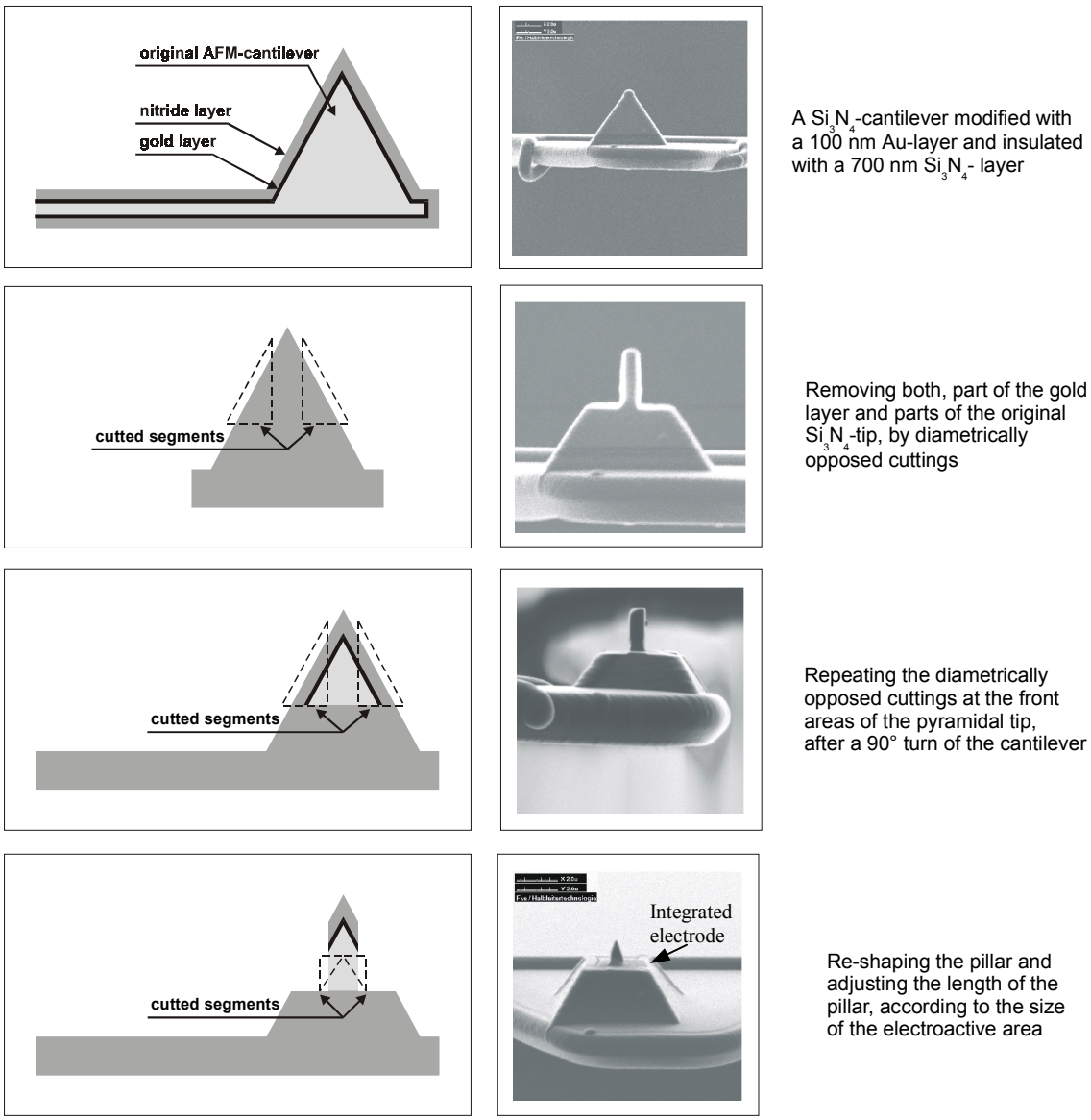


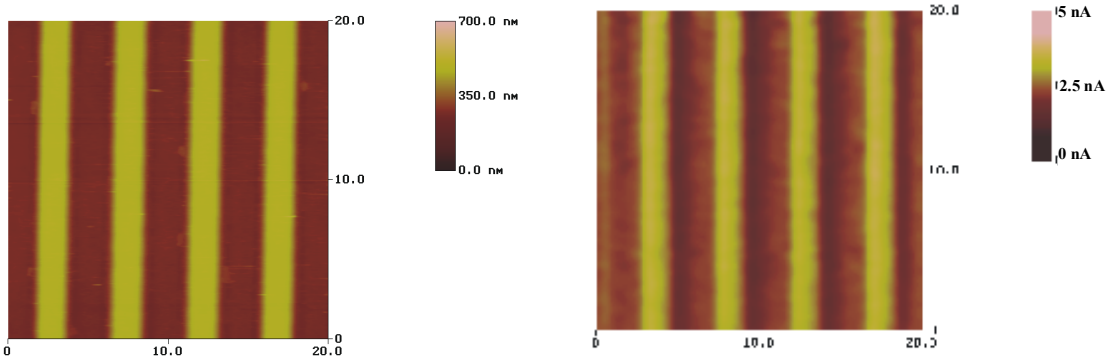
Fig. 1: Ion beam assisted modification of the AFM-tip. Schematic view of the processing steps (left) and the corresponding FIB-images (right).

AFM imaging was performed using a Nanoscope III atomic force microscope. The electrochemical investigations were performed in a fluid cell using an NPI VA10 potentiostat. All images were obtained in contact mode operation. The electrochemical setup was located in a Faraday cage. First results of simultaneous topographical and electrochemical measurement are shown in Fig. 2. A micromachined gold grating on gallium arsenide with a periodicity of 4.2 µm and a height of 0.45 µm was used as a model surface.

3. Conclusion

We present a novel technique which enables for the first time the integration of a microelectrode into an conventional AFM tip using an ion beam assisted approach, allowing simultaneous mapping of topographical and laterally resolved electrochemical informa-

tion. This development allows to position the electroactive area in a precisely defined and deliberately chosen distance to the very end of a scanning probe tip. Based on the opportunity to exactly adjust the distance of the electroactive area to the sample surface by adapting the length of the topographical probe with a micromachining technique like FIB, an optimized and defined working distance is ensured without theoretical fitting of current/distance approach curves. This procedure ensures high resolution topographical imaging and a precisely defined and constant distance between the integrated electrode and the sample surface within the working distance for electrochemical mapping. The demonstrated design is not limited to amperometric electrodes but can be extended to potentiometric electrodes or integrated electrochemical sensors, which are particularly difficult to position in a defined distance above a sample surface.



(a) (b)

Fig. 2: Imaging of a gold grating (periodicity 4,2 µm). Simultaneously recorded AFM image (a) and corresponding SECM signal (b).

Acknowledgements

The authors thank Gernot Friedbacher (Institute of Analytical Chemistry, Vienna University of Technology) for the possibility to use the AFM-SECM facilities.

References

[1] Patents pending, A 1011/2000 G01N, June 09, 2000; A 1012/2000 G01N, Jun. 09, 2000.

[2] M.I. Montenegro, A.A. Queiros, J.D. Daschbach, Microelctrodes: Theory and Applications, Kluwer: Dordrecht, NL, 1990.

[3] H.Y. Liu, F.-R.F Fan, C.W. Lin, A.J. Bard, J. Am. Chem. Soc. 1986, 108, 3838.

[4] R.C. Engstrom, M. Webber, D.J. Wunder, R. Burgess, S. Winquist, Anal. Chem. 1986, 58, 844.

[5] D.O. Wipf, A.J. Bard, Anal. Chem. 1992, 64, 1362.

[6] D.O. Wipf, A.J. Bard, D.E. Thallman, Anal. Chem. 1993, 65, 1373.

[7] K. Borgwarth, D.G. Ebling, J. Heinze, Ber. Bunsen-Ges. Phys. Chem. 1994, 98, 1317.