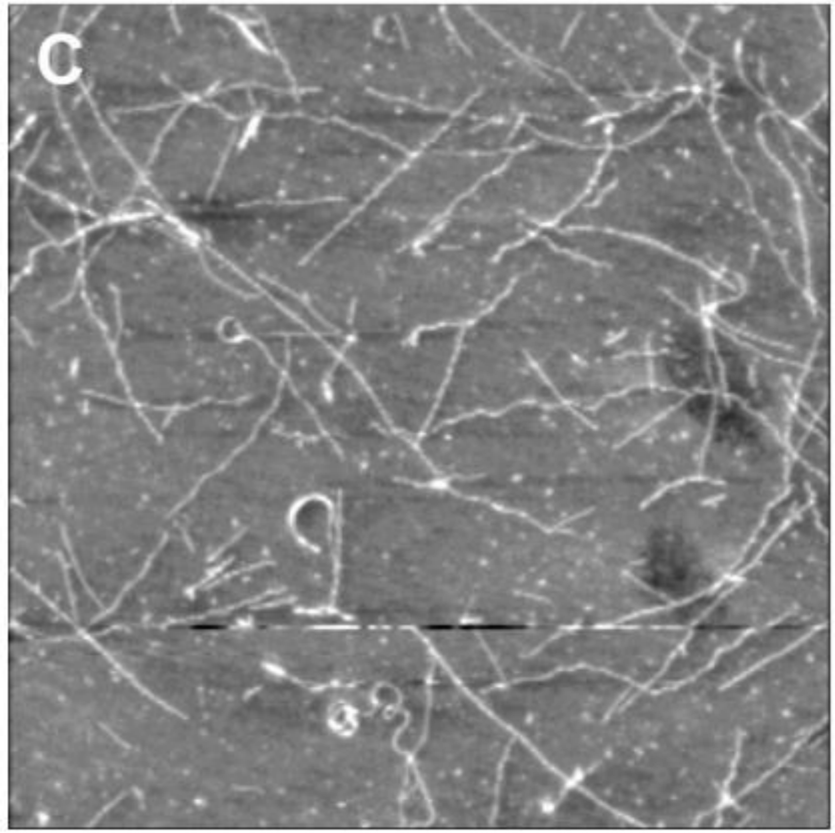
AFM in liquid environment

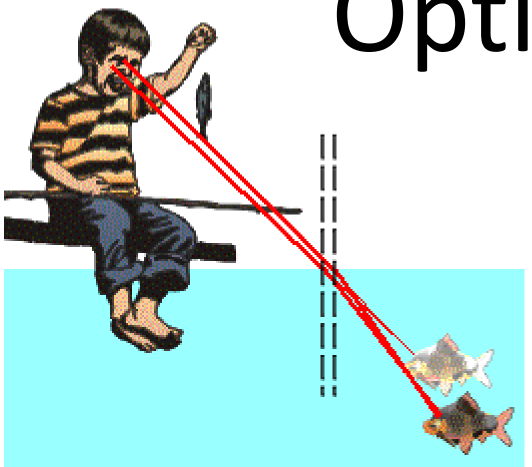


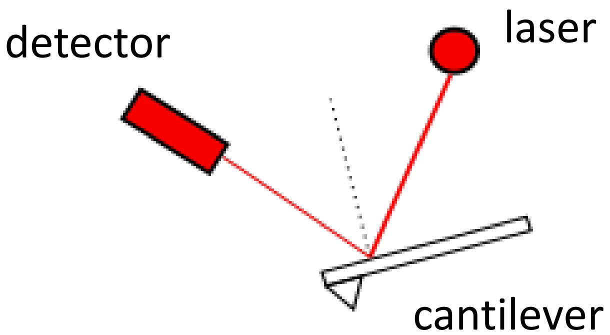
Wawer J., Krakowiak J., Szociński M., Lustig Z., Olszewski M., Szostak K., INTERNATIONAL JOURNAL OF BIOLOGICAL MACROMOLECULES, **70** (2014) 214

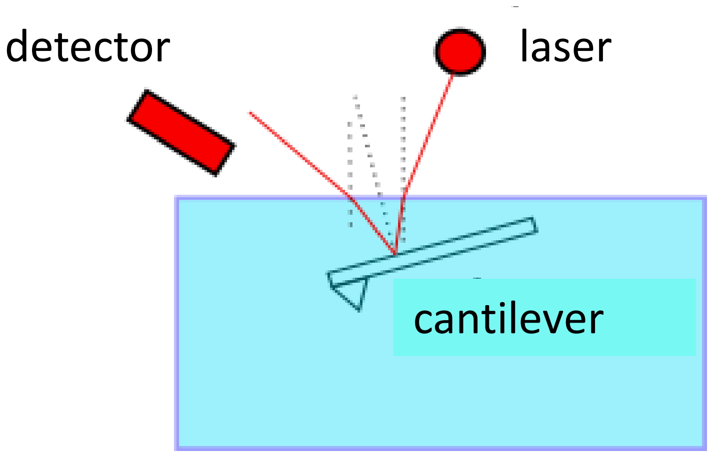
Introduction

- Important advantage of atomic force microscopy (also tunneling microscopy) is the ability to work in different environments (vacuum, controlled atmosphere, liquid environment).
- AFM enables imaging of delicate biological materials in their natural state.
- The use of electrochemical mode allows for the modification of surface properties in situ by changing the electrode potential.
- Measurement using AFM in a liquid environment involves several problems specific to the working environment.

Optical pathway







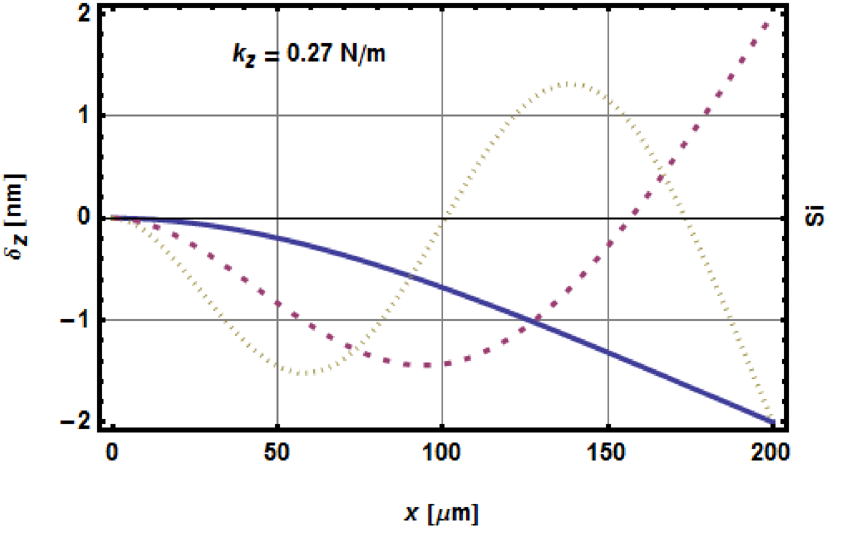
- The presence of an additional liquid / air surface significantly changes the path of the laser beam. This introduces the need to calibrate the position of the laser spot **after immersing the probe in the solution**.

Cantilever oscillations

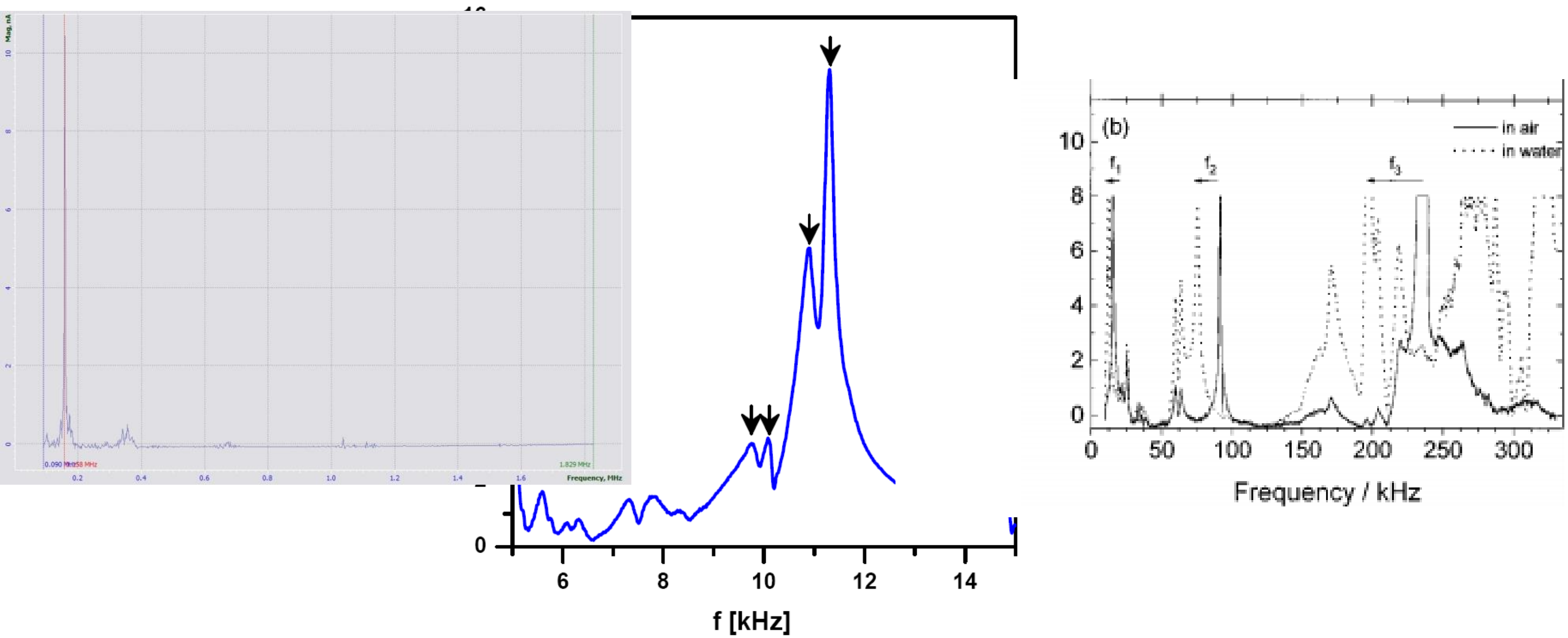
- The resonant frequency of the lever is important even in the case of contact measurements (without vibrating the lever). At an appropriate scanning frequency, the lever can be excited to oscillate (unfavorable phenomenon). The solution of the lever movement equation suggests the existence of several "modes" of oscillations and different frequencies.
- General equation of cantilever deformation:

$$\rho A \frac{\partial^2}{\partial t^2}\delta_z(x,t) + EI_z \frac{\partial^4}{\partial x^4}\delta_z(x,t) = 0$$

Dror Sarid, „Scanning force microscopy with applications to electric , magnetic and atomic forces”, Oxford University Press, 1994, str. 9

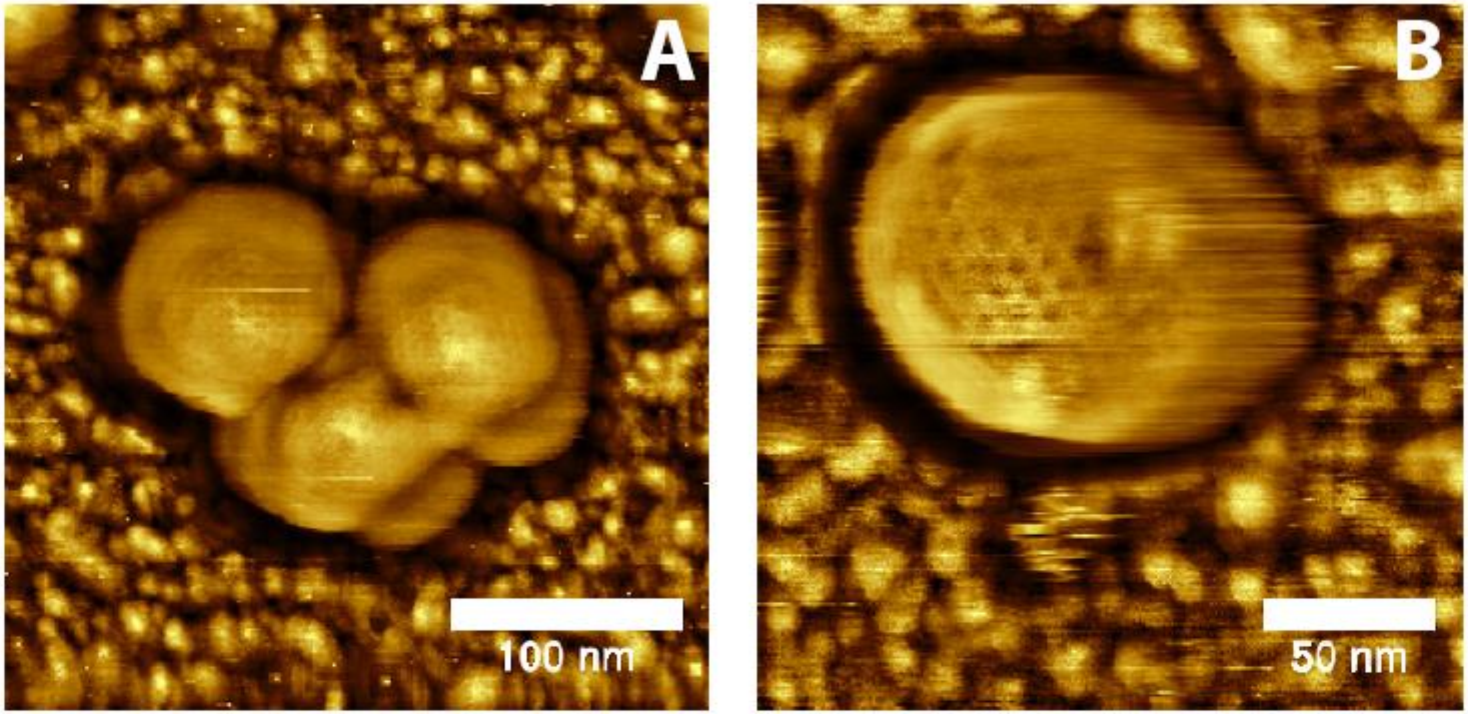


Resonance curve



In the case of oscillations in liquids, their amplitude is smaller, additionally the frequencies are shifted. The worst, however, is the fact that there are a lot of new resonance peaks, resulting for example from the excitation of acoustic waves by the vibrating lever. **The peaks on the frequency response do not have to correspond to the lever oscillations.**

Example: microbiology



AFM images of virus-like particles scanned in a liquid. These self-assembled retrovirus structural proteins in vitro form particles with a length of approximately 80 nm. The grid visible in Figure B is not an artifact, its presence has been verified by means of electron microscopy.

Example: microbiology

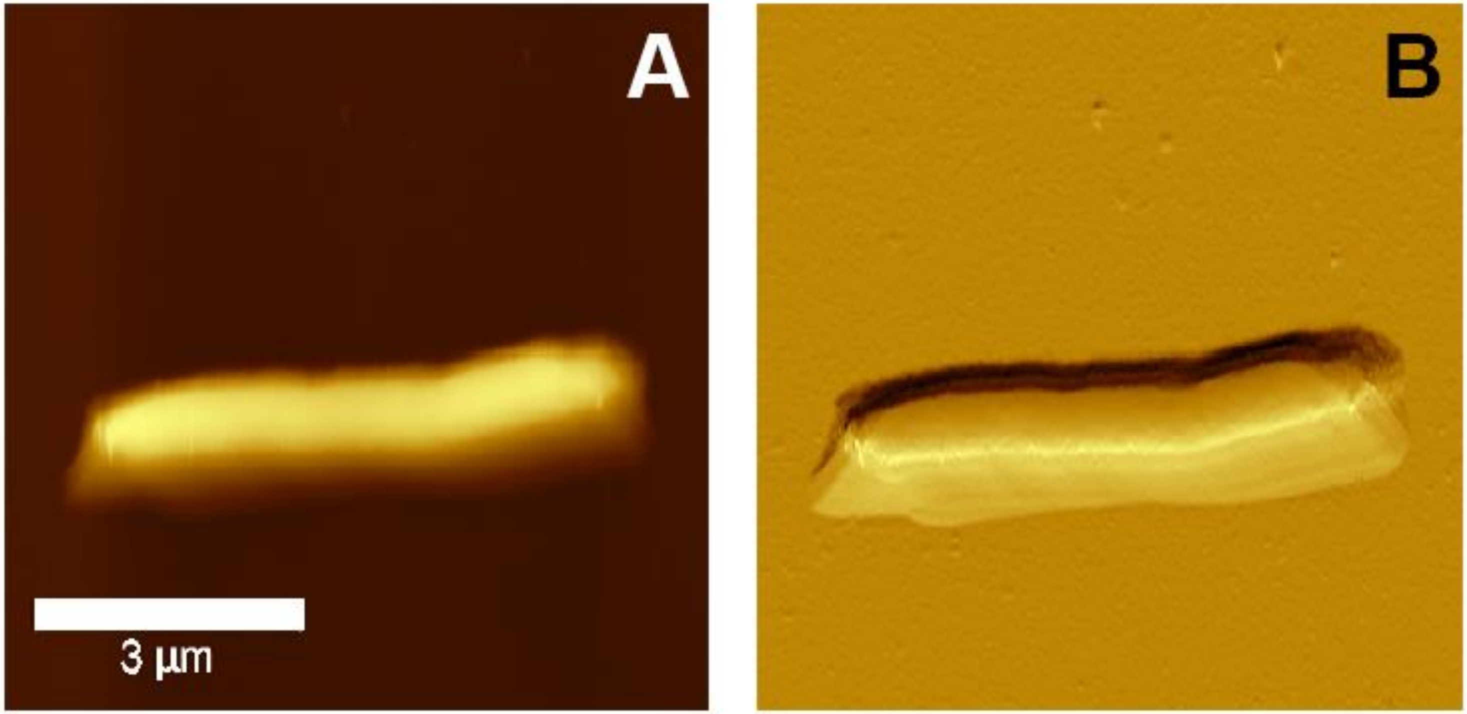
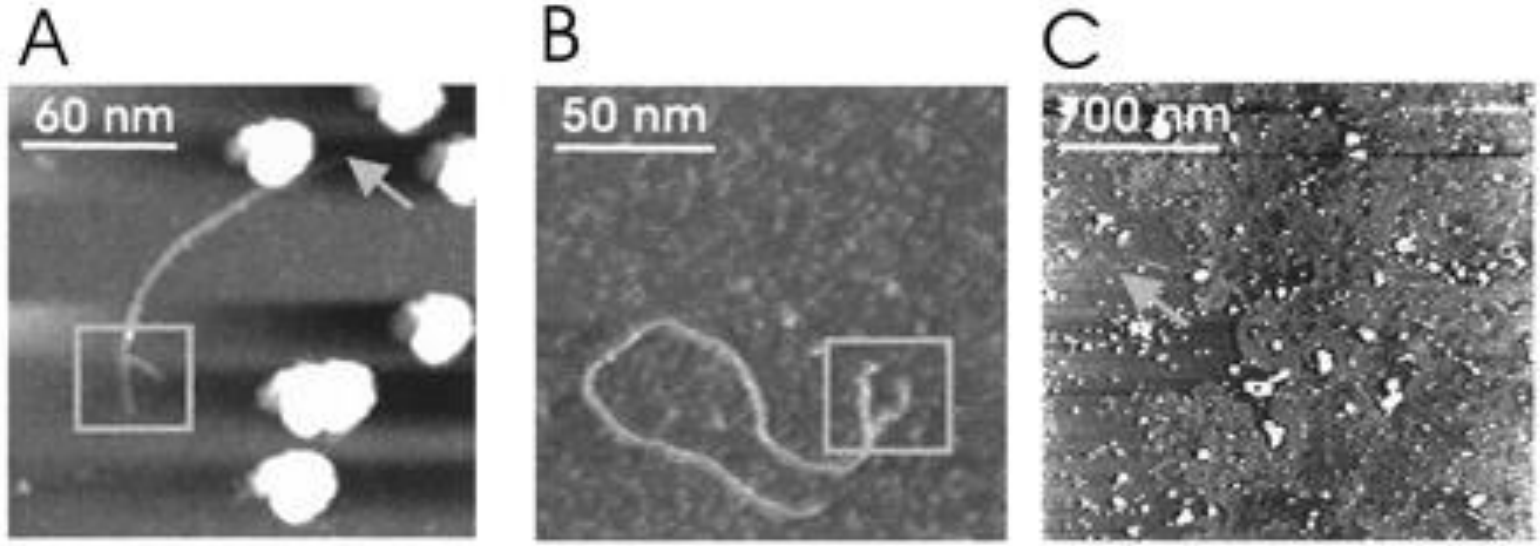


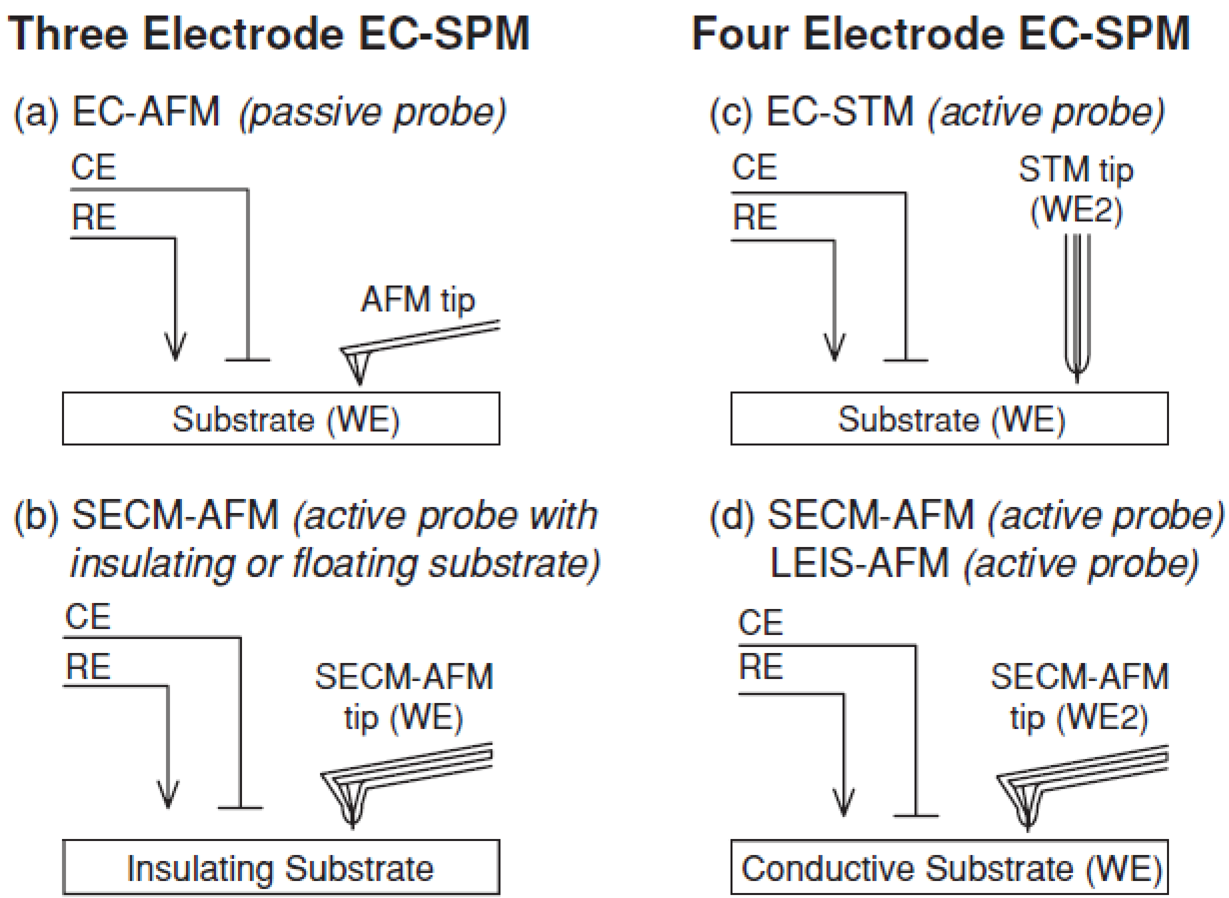
Image of AFM Escherichia coli obtained in a liquid medium. E. coli was immobilized on a polylysine-coated environment using half-contact mode with a silicon nitride probe. Structure details are visible either on topography (A) or on derivative (B). The bottom artifact is caused by the irregular shape of AFM tip.

Example: microbiology



(A) RNA molecules released from virus capsids. At the end of the chains, fork lengths of approx. 30 nm are visible. The size of the scan is around 200 nm.
(B) Individual RNA molecules separated from the virus, also containing a forked structure. The size of the scan is around 150 nm.
(C) Tightly packed RNA molecules on mice obtained after virus exposure to low pH. Several virus particles can be seen as bright white spots, and RNA molecules are packed tightly to form a 1.5 nm layer. Isolated RNA particles with a length of about 1 µm (arrow) were observed sporadically. Scan size 2 µm.

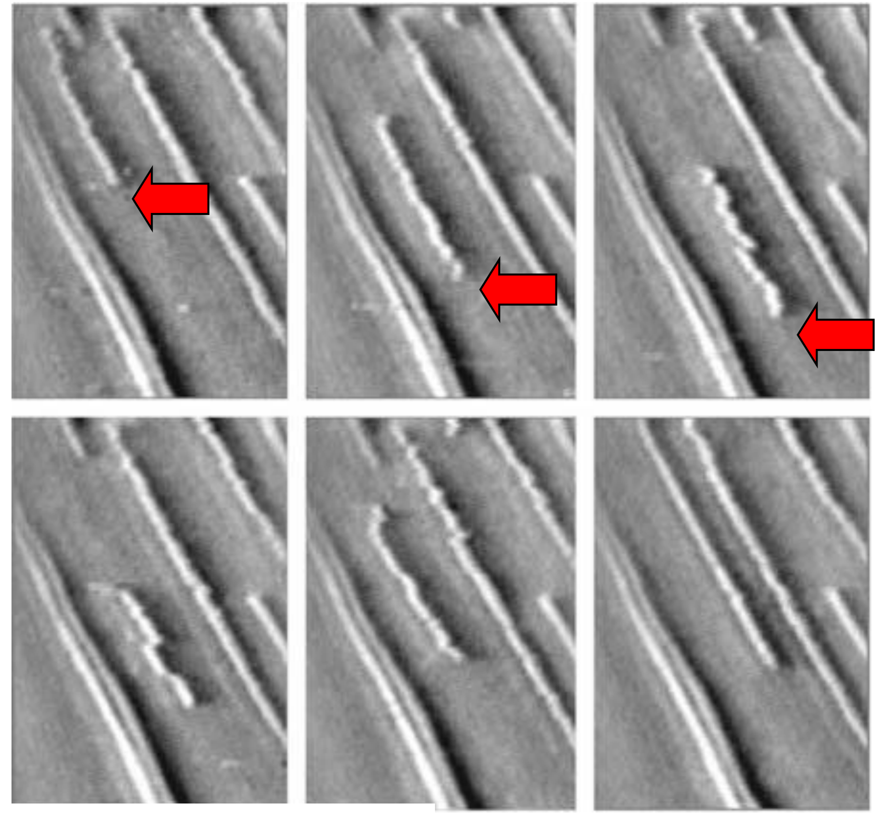
Electrochemical probe microscopy



- Different variants of probe microscopy in electrochemical conditions require different hardware configurations.

STM in liquid environment

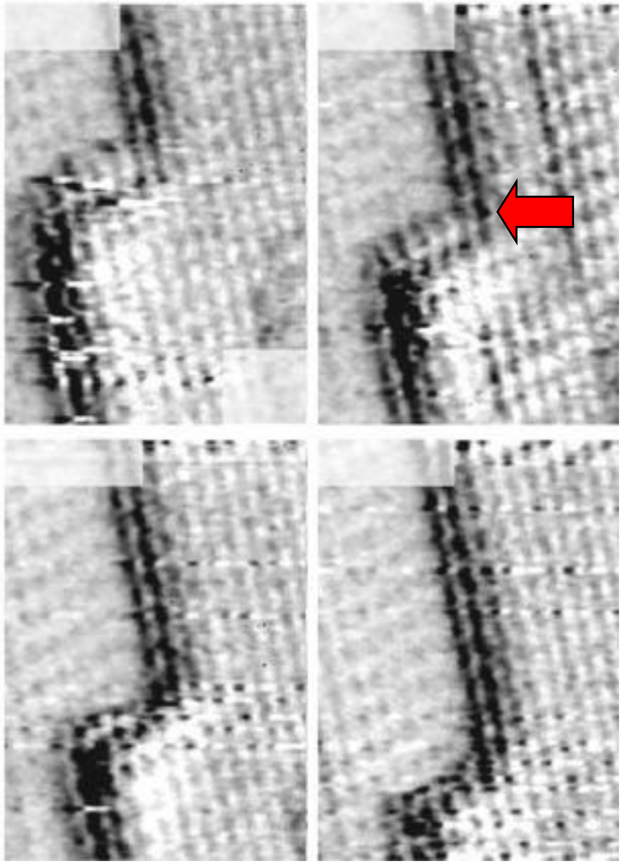
Thanks to the STM technique, it is possible to directly observe the surface features of a material with nanometric dimensions, including particles and atoms. It was also possible to use probe microscopy to study dynamic systems such as surface diffusion or dissolution and redeposition of the substance in electrochemical conditions.



Diffusion of chains of gold atoms on the Au surface (100). A solution of 0.01 M Na_2SO_4 with chloride content.

M. Labayen, C. Ramirez, W. Schattke, O. M. Magnussen, Nat. Mater., **2** (2003) 783.

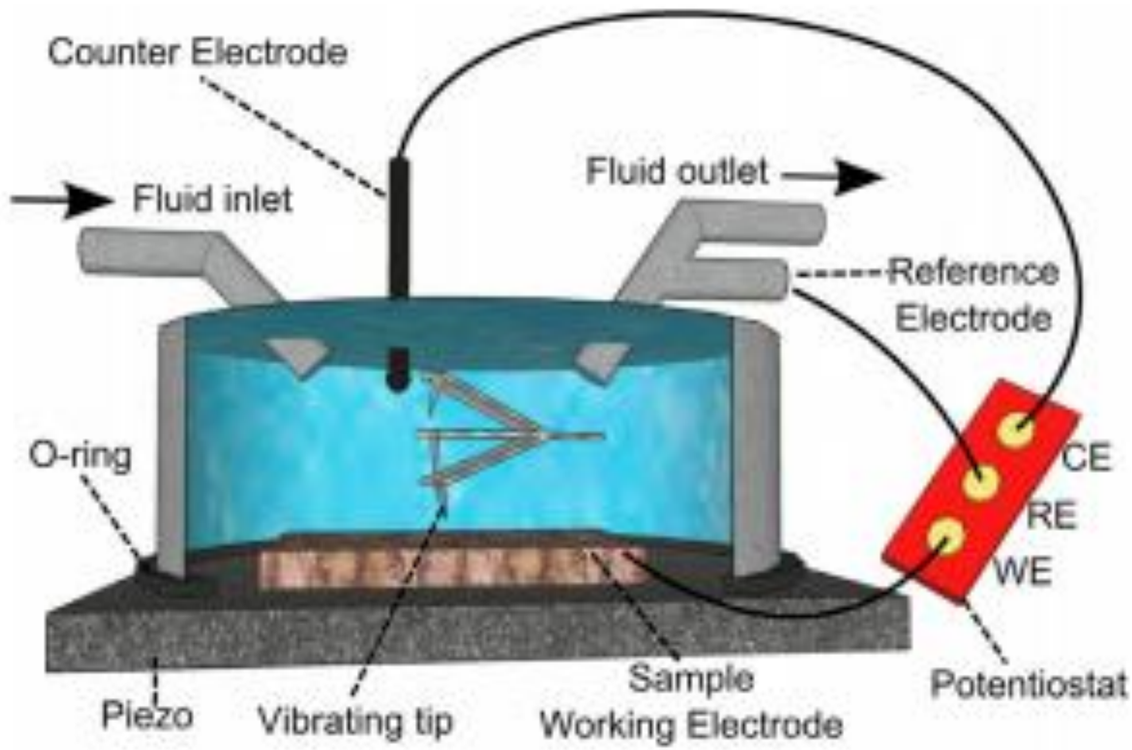
Exemplary applications of STM



Sequence showing the dissolution of the terrace on the surface of Cu (100) in 0.01 M HCl. The frames are recorded every 100 ms.

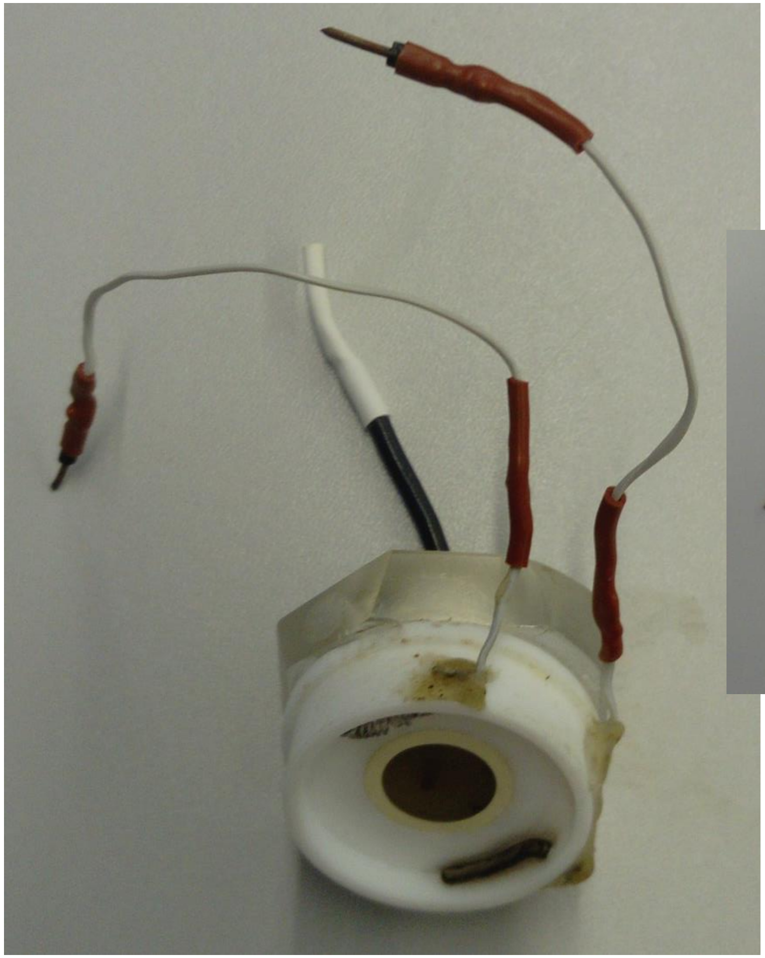
O. M. Magnussen, L. Zitzler, B. Gleich, M. R. Vogt, R. J. Behm, Electrochm. Acta, **46** (2001) 3725.

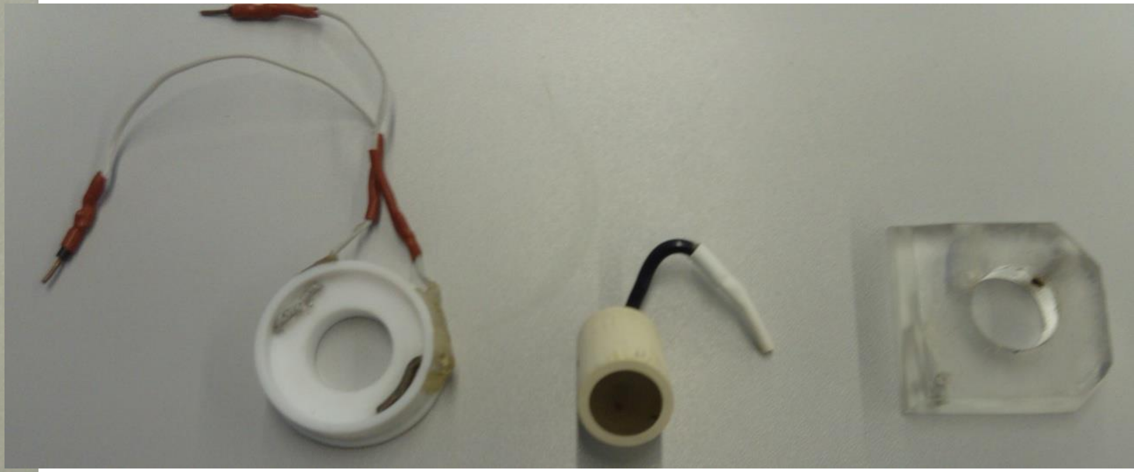
AFM liquid cell



Liquid cell used in electrochemical measurements

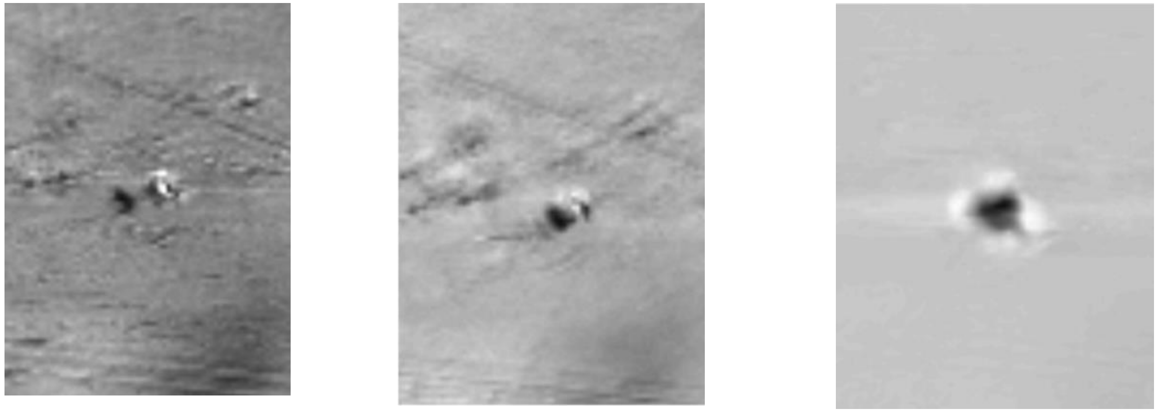
Cell construction



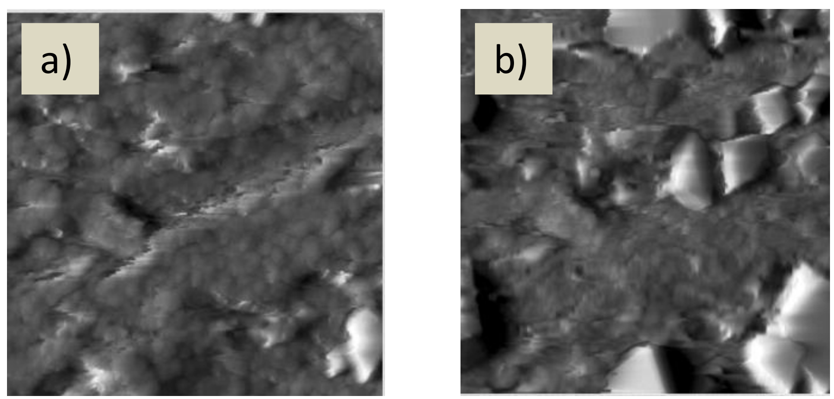


Practical implementation of the measuring cell used in the electrochemical AFM.

Electrochemical AFM



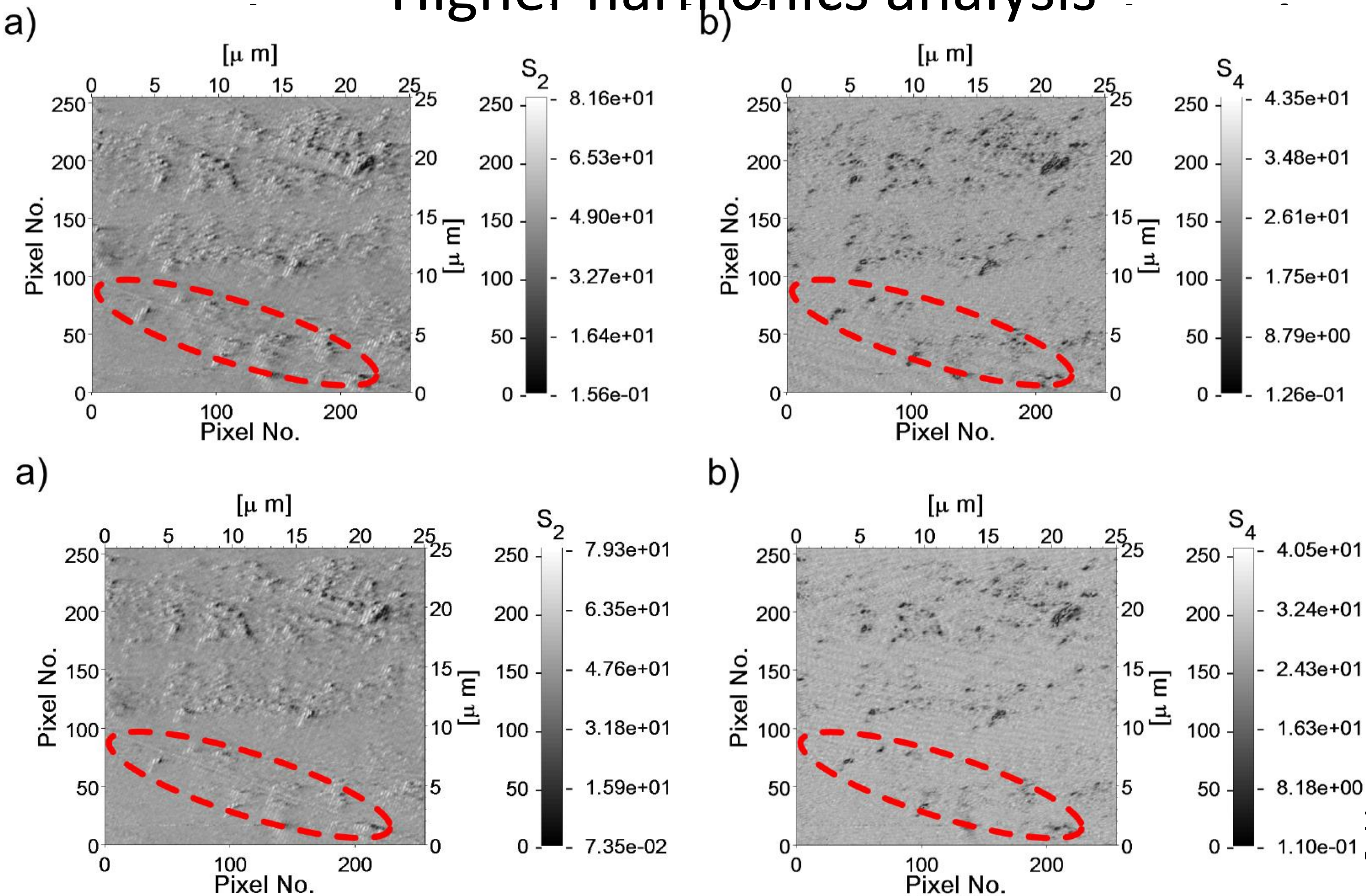
Development of pitting on the surface of AISI 304 steel after exposure to anodic polarization in 3% NaCl solution.



Topography of the anode layer formed on lead in 0.5 M H2SO4 after 15 minutes polarization at E = 1.27 V or Pt (a) and after 15 minutes polarization at E = 1.17 V or Pt (b)

K. Darowicki, K. Andrearczyk, J. Power Sources 189 (2009) 988.

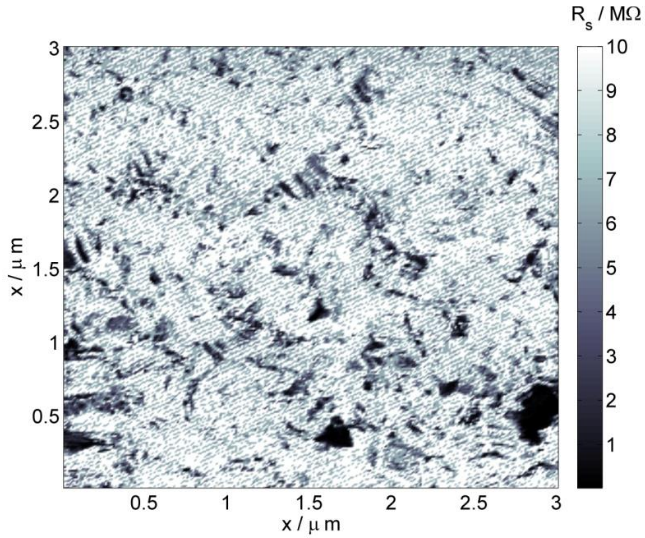
Higher harmonics analysis



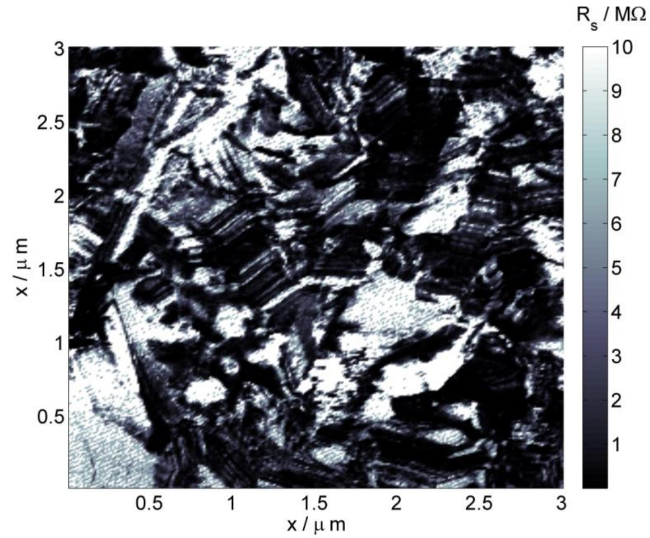
Darowicki, S. B. and A. Z. and J. S. and K. (2017). Corrosion process monitoring by AFM higher harmonic imaging. *Measurement Science and Technology*, *28*(11), 114001.

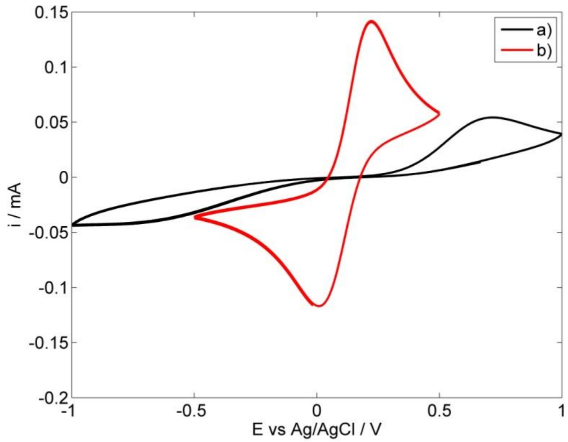
Correlation of AFM and electrochemistry

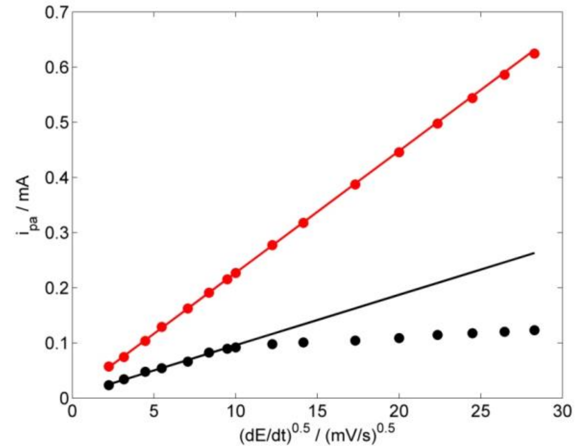
a)



b)

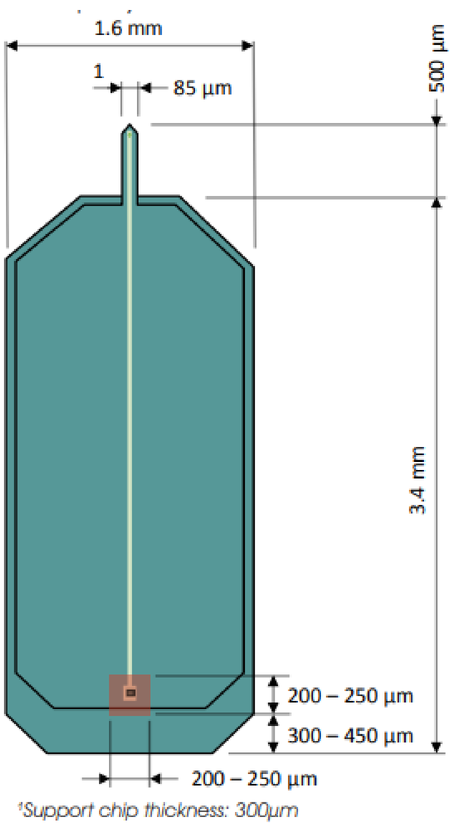


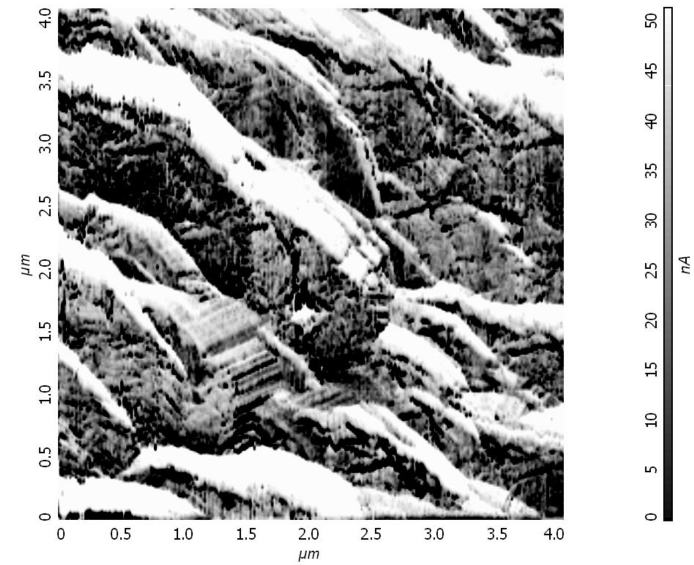




Diamond doped with boron is a very promising material in the technique of electrochemical sensors. Unfortunately, there are a number of factors affecting the heterogeneity of its surface and thus the complications of interpretation of the electrochemical response of sensors based on this material.

Obstacles





„Very little work has been done in this area, as it is difficult to combine these two techniques and still collect data fast enough for experimentally significant processes to be studied with a scanning probe technique"

Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale, Tom 1, Sergei V. Kalinin, Alexei Gruverman, Springer Science & Business Media, New York 2007, str 285.