NTEGRA for EC PRESENTATION

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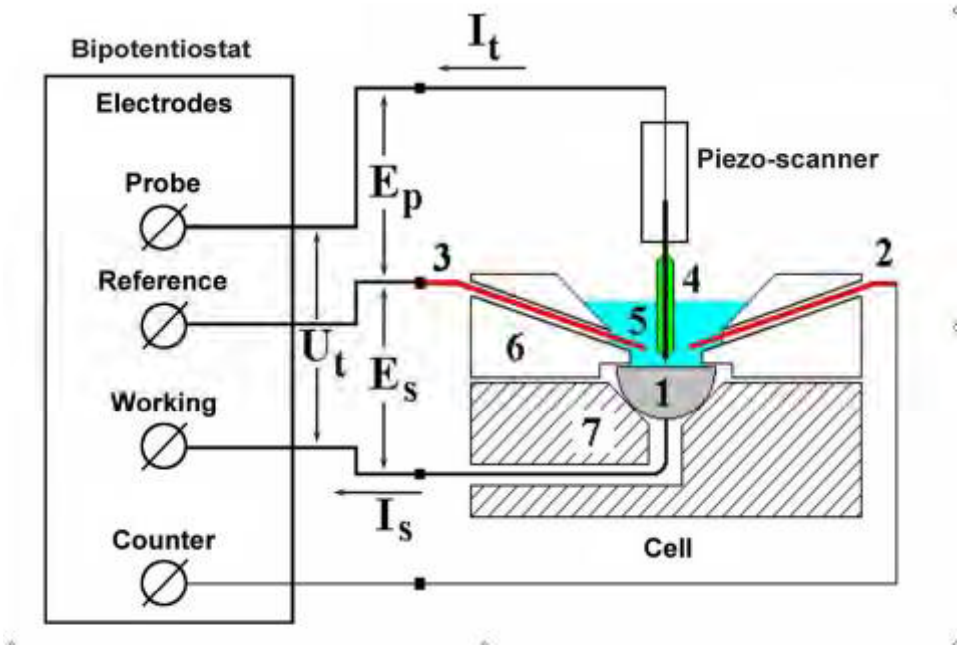
Application

Purpose:

In-situ control/modification of the surface morphology of single crystal and polycrystal electrodes (samples) during electrochemical process (in situ) in electrolyte solutions together with STM (max resolution – atomic) and AFM.

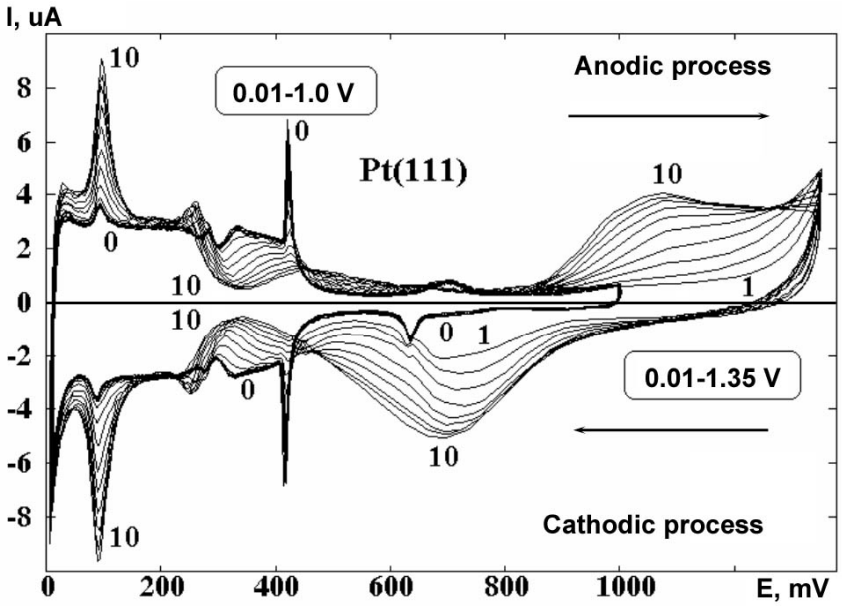
Basic Principles

Basic Working Scheme

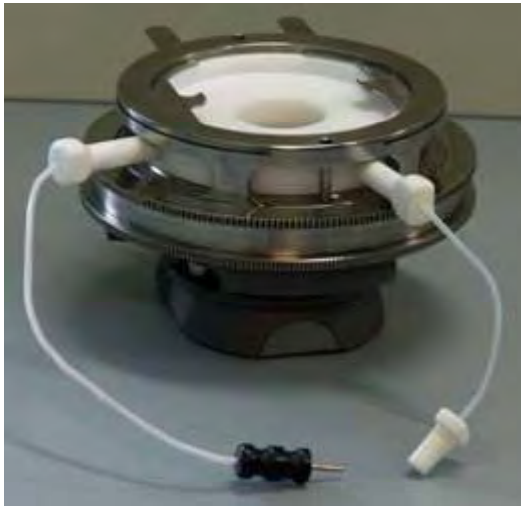


1. Sample
2. Counter Electrode
3. Reference Electrode
4. STM Probe
5. Electrolytic Solution
6. Cell
7. Cell Base

Cyclic voltammetry of Pt (111) in 0.05 M H_2SO_4 + 1 mM $CuSO_4$ solution



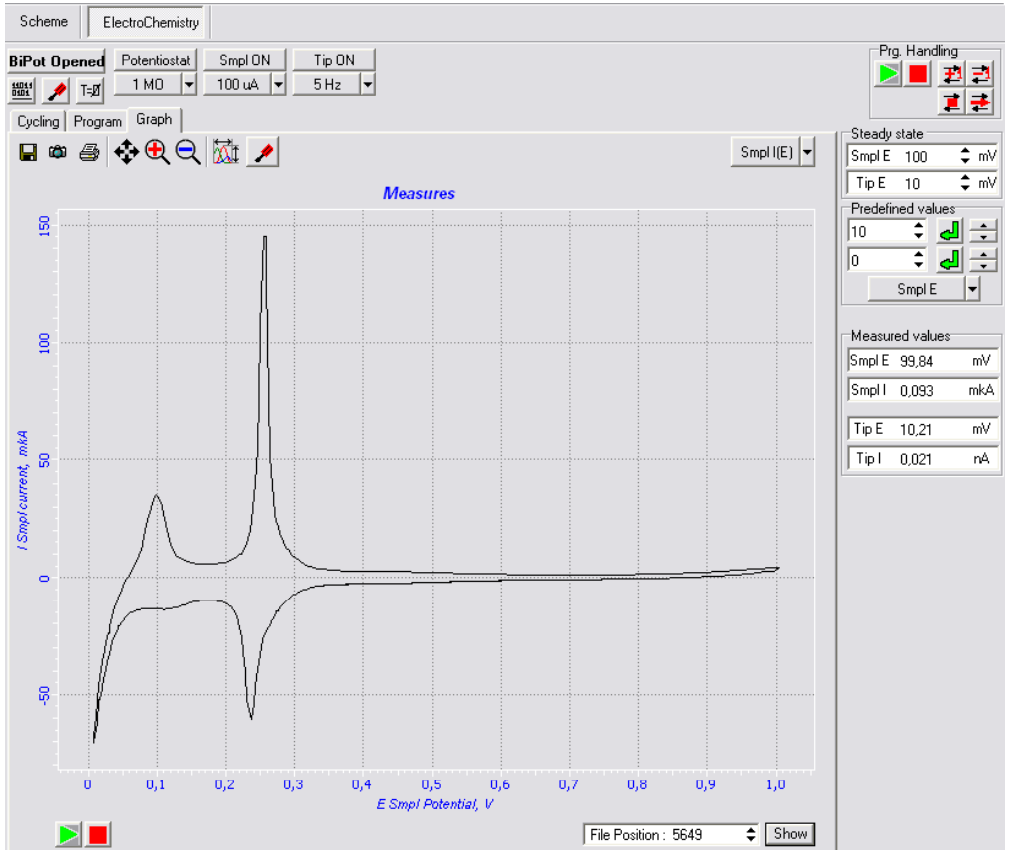
Electrochemical Cell



- Cell material: Teflon
- Platform: Standard orthogonal
- Max size: ∅35×10 mm
- Argon blow system

1. Working Electrode (sample)
2. Cell Base
3. Platform
4. Cell
5. Electrode Holder
6. Fixing Ring
7. Teflon Tube for Gas (Ar) Input
8. Heating/cooling unit

Bipotentiostat & Software



Bipotentiostat (possibility to use external)

- Output Compliance Voltage: ± 15 V
- Applied Voltage Range: ± 5 V (stability ± 1 mV)
- Current Ranges: ± 5mA; ± 100 μA; ± 2 μA (accuracy of measurement ±0.1 % of the range)
- Reference Input Impedance: > 10^{11} Ω

Software

- Modes: *manual*; *sweep* (1 mV/s to 100 mV/s), *pulse* (time resolution 10 ms); *potentiostatic current transients*; *cyclic and linear voltammetry*; *universal programmer*
- Computer: Pentium II or higher
- System: Windows 98/XP

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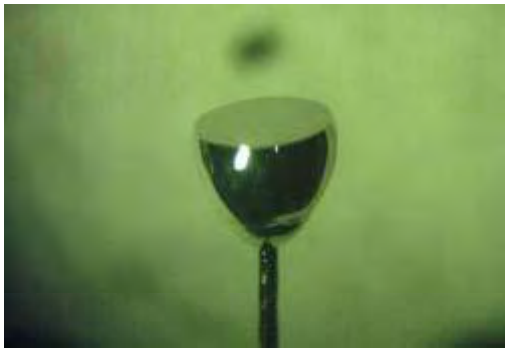
Electrodes

Working Electrode:
monocrystal Au (111)



Working Electrode:
monocrystal Pt (111)

Working:
∅ 4-15 mm (Au 111),
Pt (111), HOPG, polished
polycrystalline metals)

Counter: Cu, Pt, Au-wire

Reference: Cu, Pt, Au-wire,
Ag/AgCl (Cypress system)

Working Electrode:
HOPG (0001)

Reference Electrode:
Ag/AgCl (Cypress
System)

Electrolyte:
H_2SO_4 (50mM) + $CuSO_4$ (1mM)
or any suitable electrolyte

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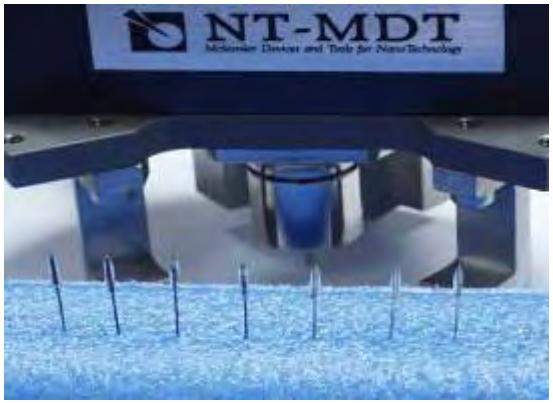
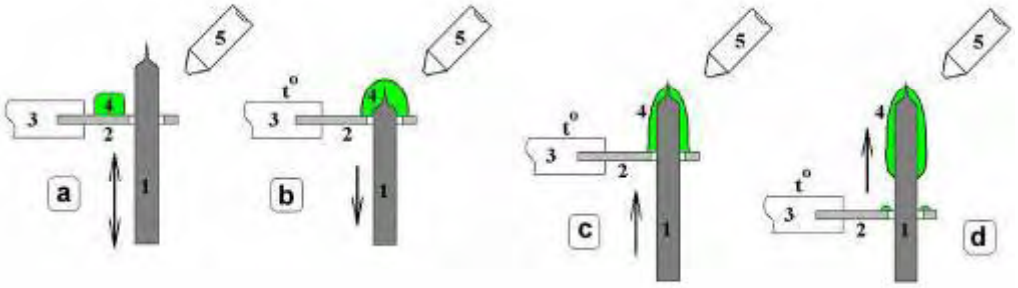
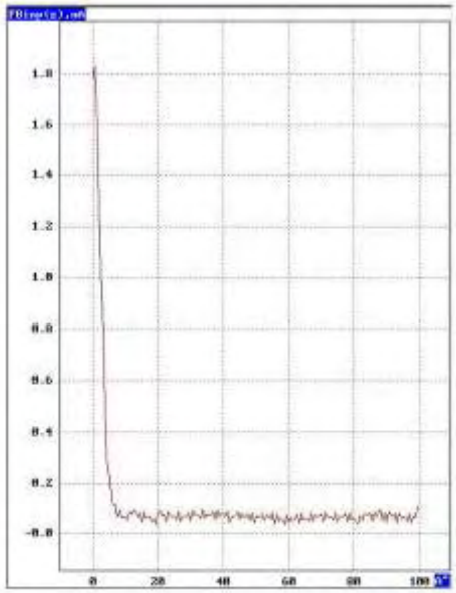
STM Electrochemical Tips



Technological Scheme of Tip Insulation Process





Probe Spectroscopy

- Material: W, Pt-Ir (10-25%)
- Size: ∅ 0.4-0.5 mm,
  max length 20 mm
  (insulated part 5-7 mm)
- Sharpening: electrochemical,
  mechanical
- Insulation: “Apiezon Wax”,
  polyethylene

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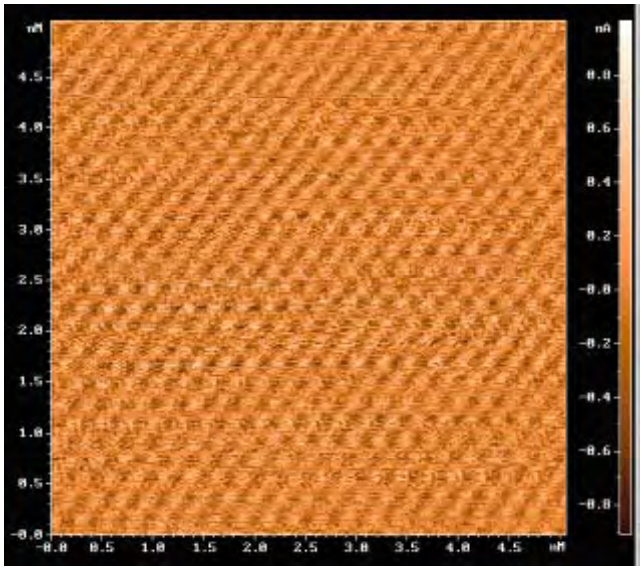
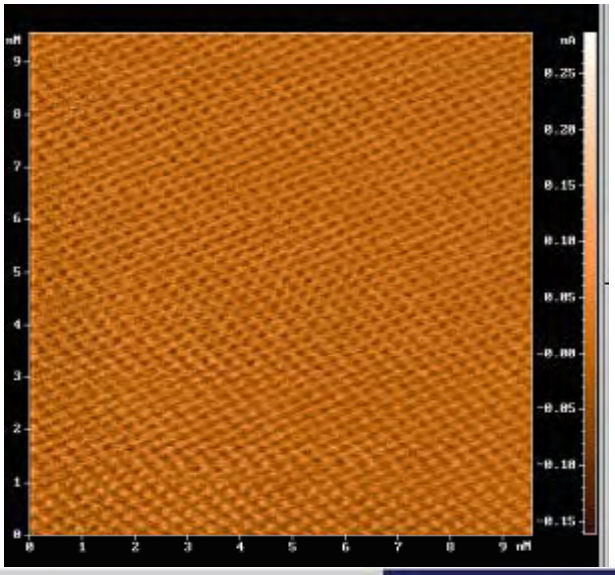
Results

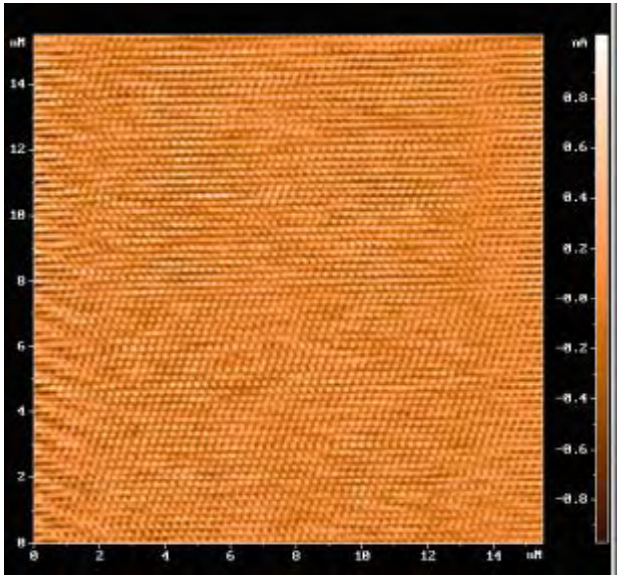
STM Image of Graphite (on air)



Scan size: *5 × 5 nm*

Scan size: *10 × 10 nm*





Scan size: *15 × 15 nm*

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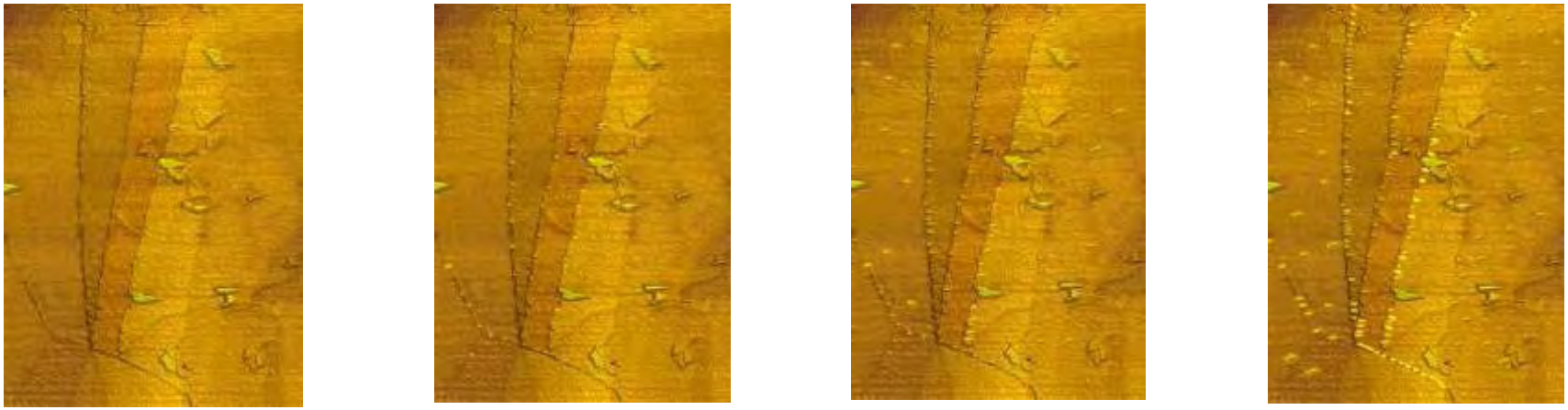
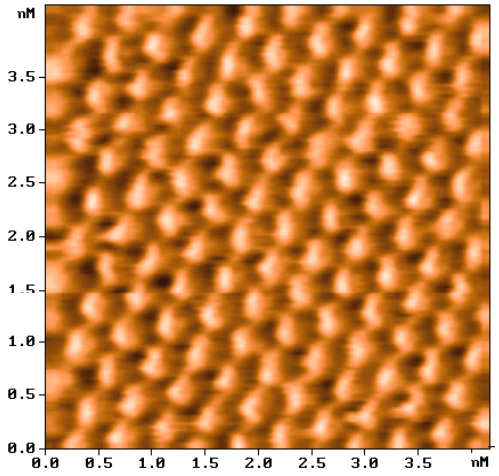
Results

STM Image of Graphite (in solution)

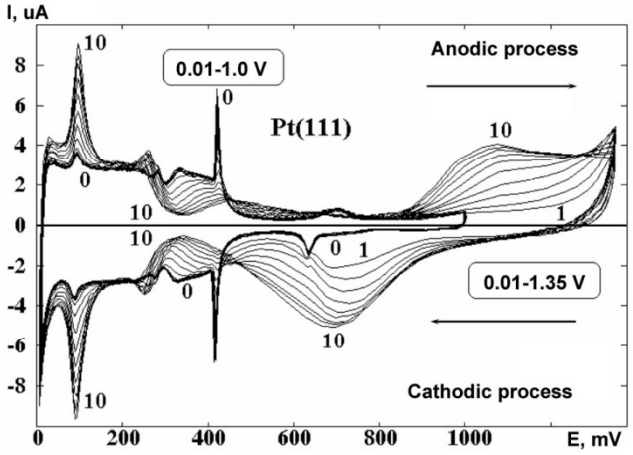


Scan size: *0.8 × 1.1 µm*
Graphite surface decoration by copper clusters during dynamic electro deposition process

Scan size: *4.1x4.1 nm*
Atomic resolution of HOPG in Electrolyte solution (0.05 M H2SO4 + 1 mM CuSO4) under potential.



Results (Cu/Pt)



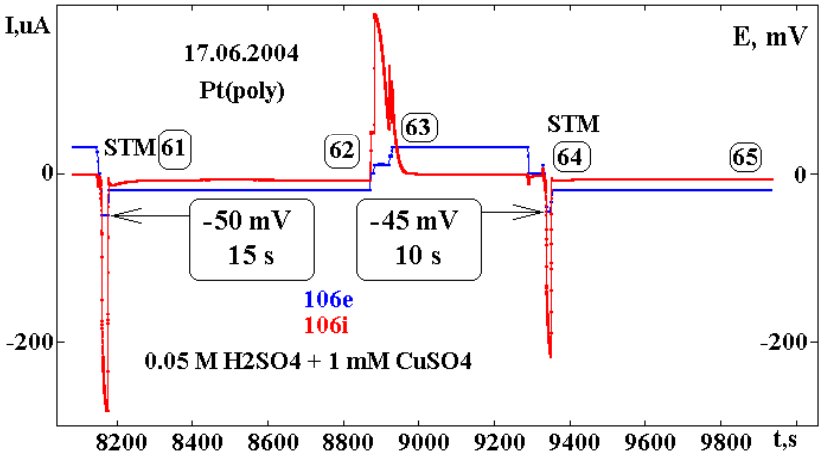
Cyclic voltammogram of the Pt electrode

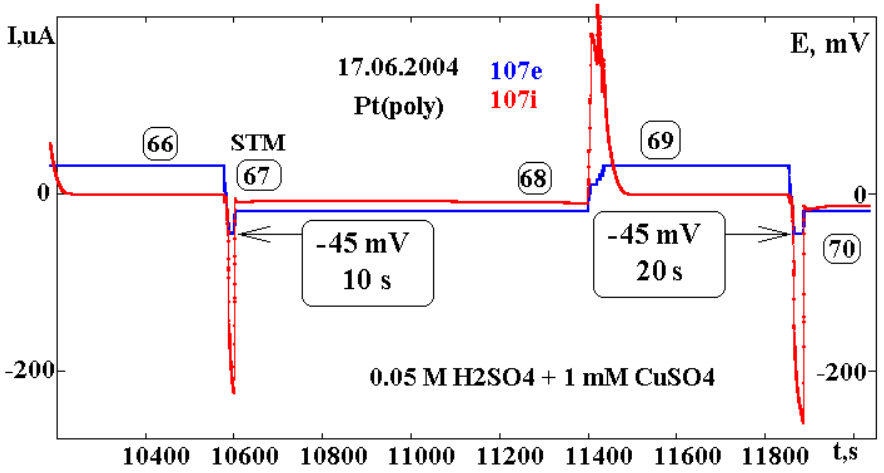
A piece of Cu wire was used as the quasi reference electrode and counter electrode. Tungsten tips, which were etched in 2M KOH and subsequently coated with "Apiezon Wax" were used as tunneling probes. The Faradaic background current through the tip was below 10 nA.The Pt poly crystal was 3 mm in diameter. Prior to each experiment, the Pt electrode was flame annealed in flame for a few minutes.

The electrolyte was 50 mM H_2SO_4 containing 1 mM $CuSO_4$. Periodically the electrolyte was changed at the upper and lower potential limits. After this procedure the voltammetric response of the electrode was in reasonable agreement with the commonly accepted voltammogram of the Pt in 50 mM H_2SO_4.

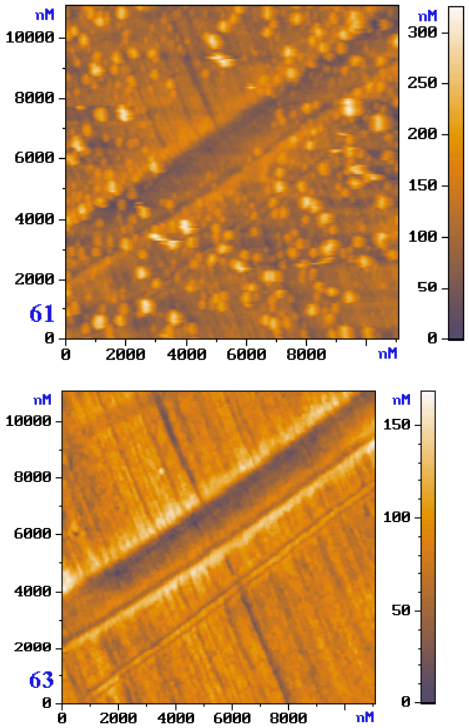
Applied potentials and numbers of STM images are presented in figures below.

STM images are shown on next slide.

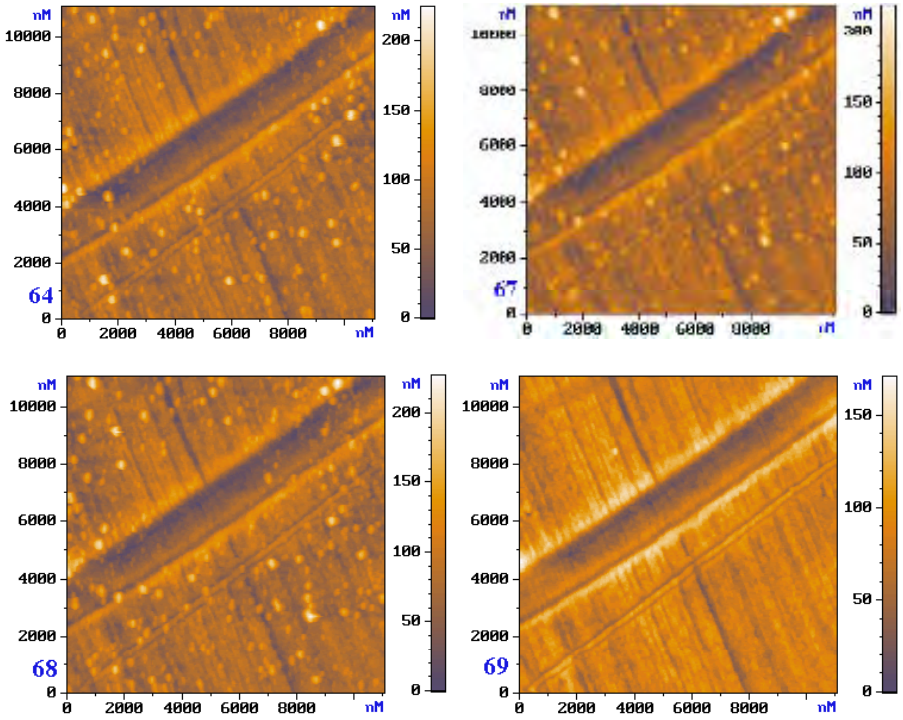




Results (Cu/Pt)

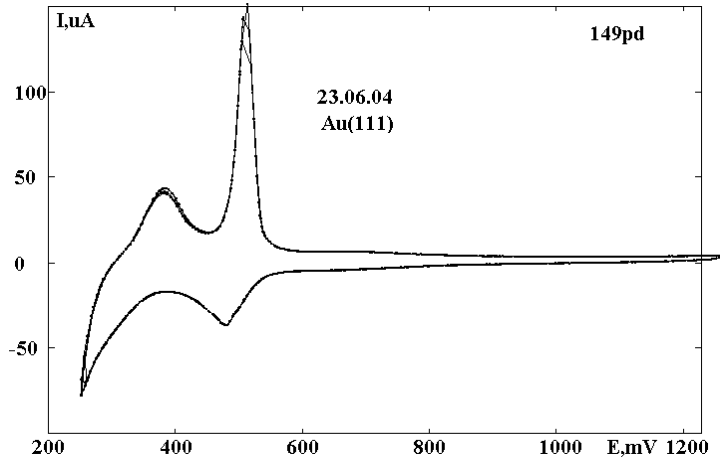


STM images (61) and (62) show nucleus growth. These images were recorded at -50 mV.
STM image 63 shows nucleus dissolving at +30 mV ("clear surface").



STM images (64), (67) and (68) show nucleus growth at other potential (-45 mV). It can be seen that number of nucleus are considerably reduced. Nucleus arrangement are changed.
STM image (69) shows nucleus dissolving at +30 mV ("clear surface").

Results (Cu/Au)

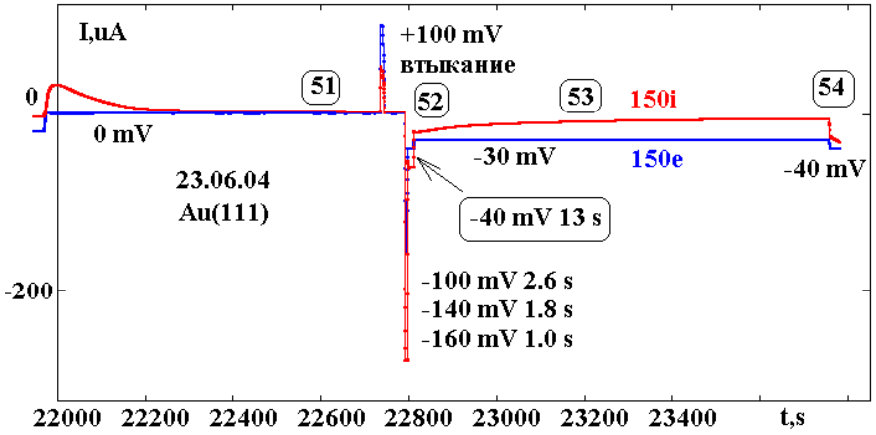


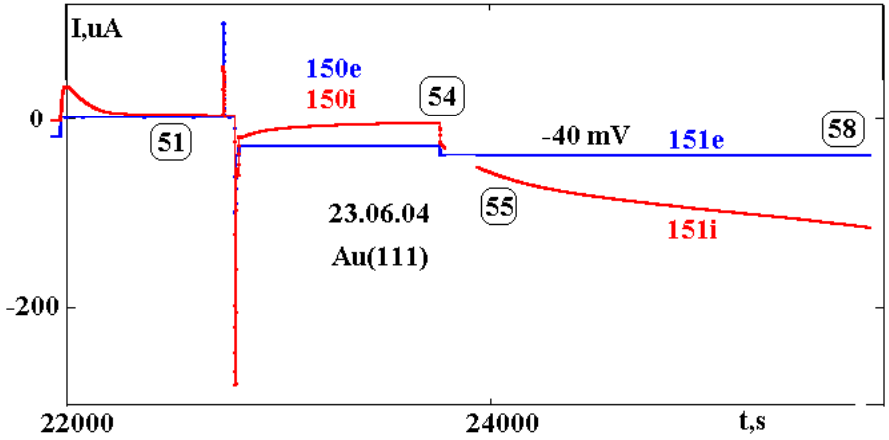
Cyclic voltammogram of the Au electrode

A piece of Cu wire was used as the quasi reference electrode and counter electrode. Tungsten tips, which were etched in 2M KOH and subsequently coated with "Apiezon Wax" were used as tunneling probes. The Faradaic background current through the tip was below 10 nA. The Au monocrystal was 10 mm in diameter. Prior to each experiment, the Au electrode was flame annealed in flame for a few minutes.

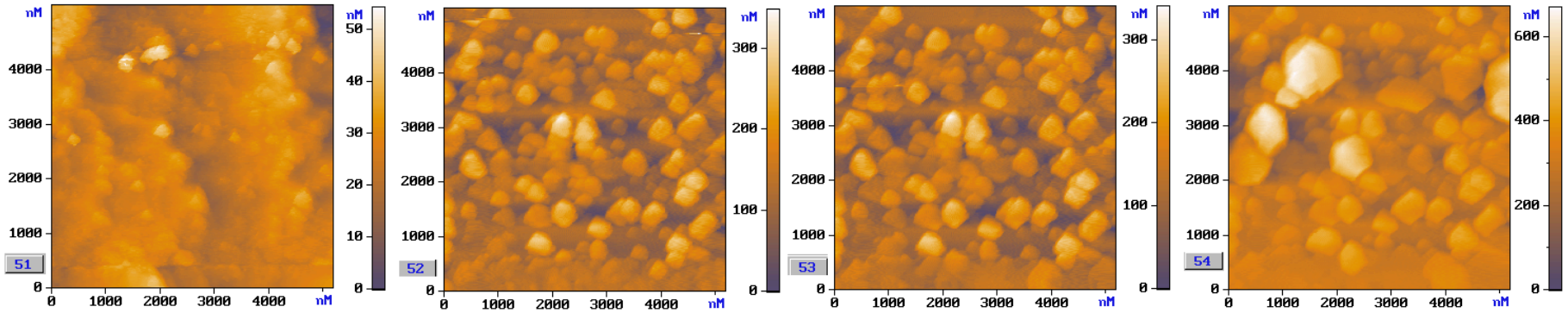
The electrolyte was 50 mM H_2SO_4 containing 1 mM $CuSO_4$. Periodically the electrolyte was changed at the upper and lower potential limits. After this procedure the voltammetric response of the electrode was in reasonable agreement with the commonly accepted voltammogram of the Au in 50 mM H_2SO_4.

Applied potentials and numbers of STM images are presented in figures below. STM images are shown on next slides.

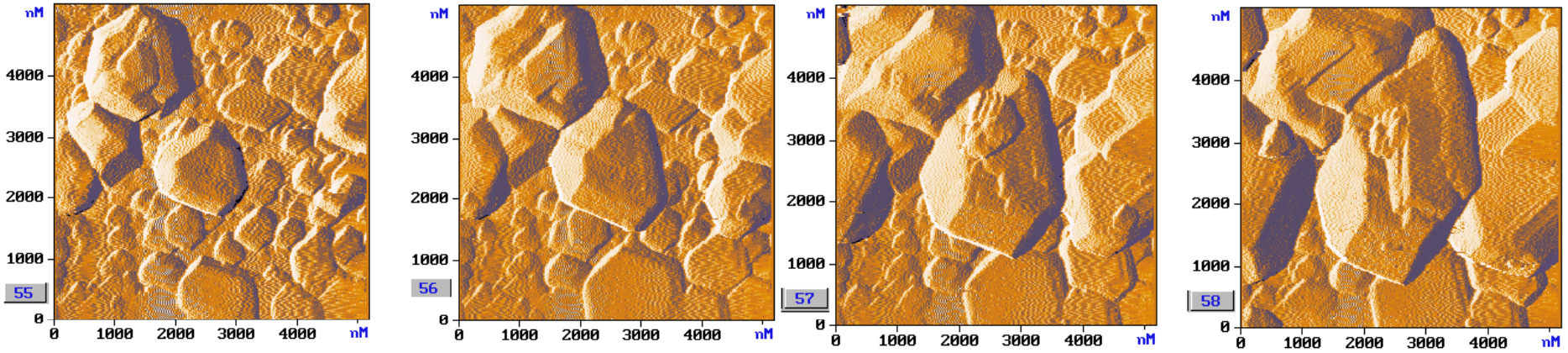




Results (Cu/Au)

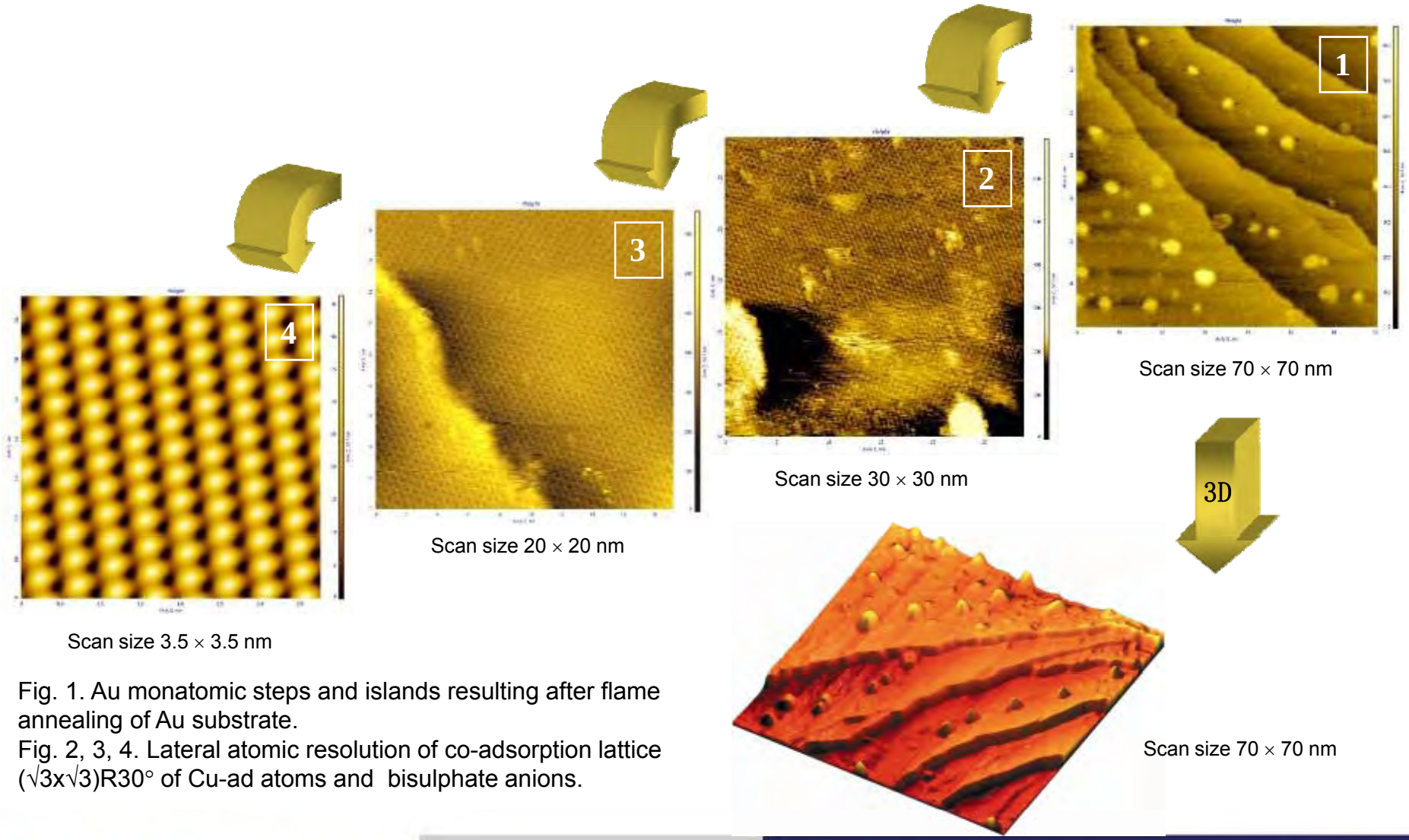


STM Images (51)-(54) show Cu dissolving. There are fair amount small nucleus. Their size is 0.2-0.4 μm.



STM Images (56)-(58) show Cu monocrystals growth. It can be seen facets of Cu (111) monocrystal. There are growth steps on big crystals.

Results (Cu/Au)



Scan size 70 × 70 nm

Scan size 30 × 30 nm

Scan size 20 × 20 nm

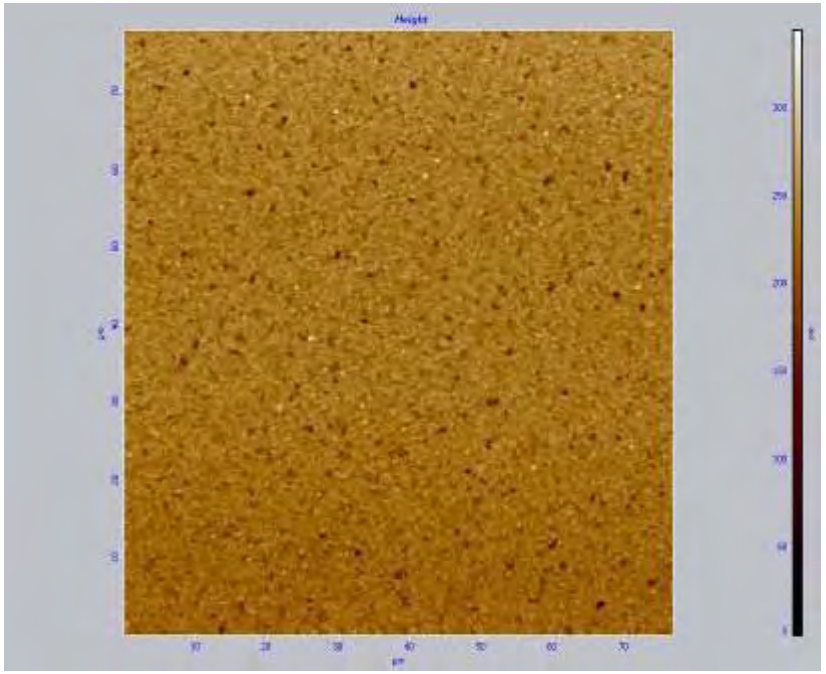
Scan size 3.5 × 3.5 nm

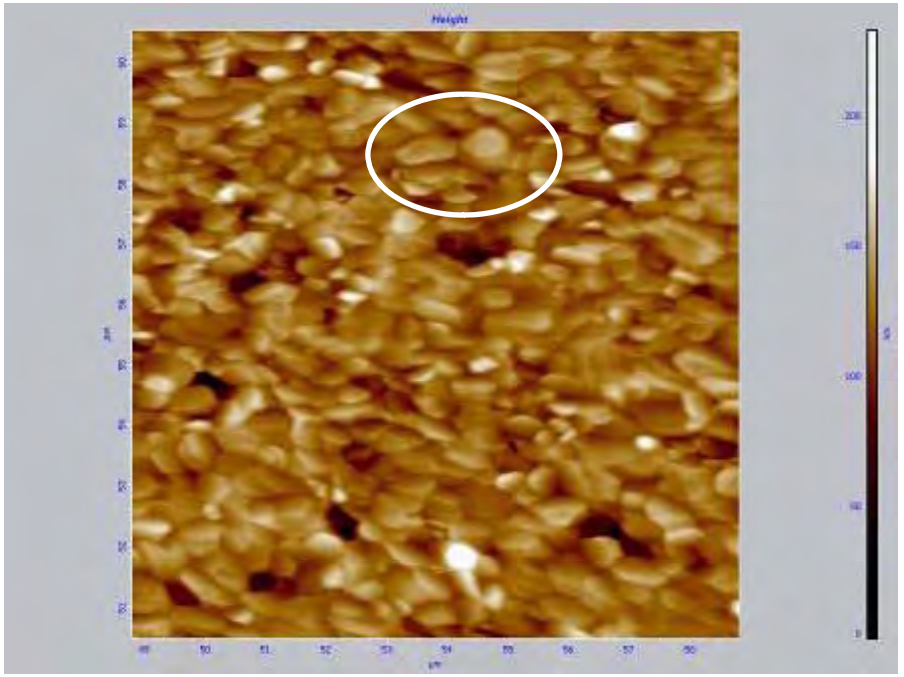
Scan size 70 × 70 nm

Fig. 1. Au monatomic steps and islands resulting after flame annealing of Au substrate.
Fig. 2, 3, 4. Lateral atomic resolution of co-adsorption lattice (√3x√3)R30° of Cu-ad atoms and bisulphate anions.

Nanoporous alumina surface

Nanoporous alumina surface

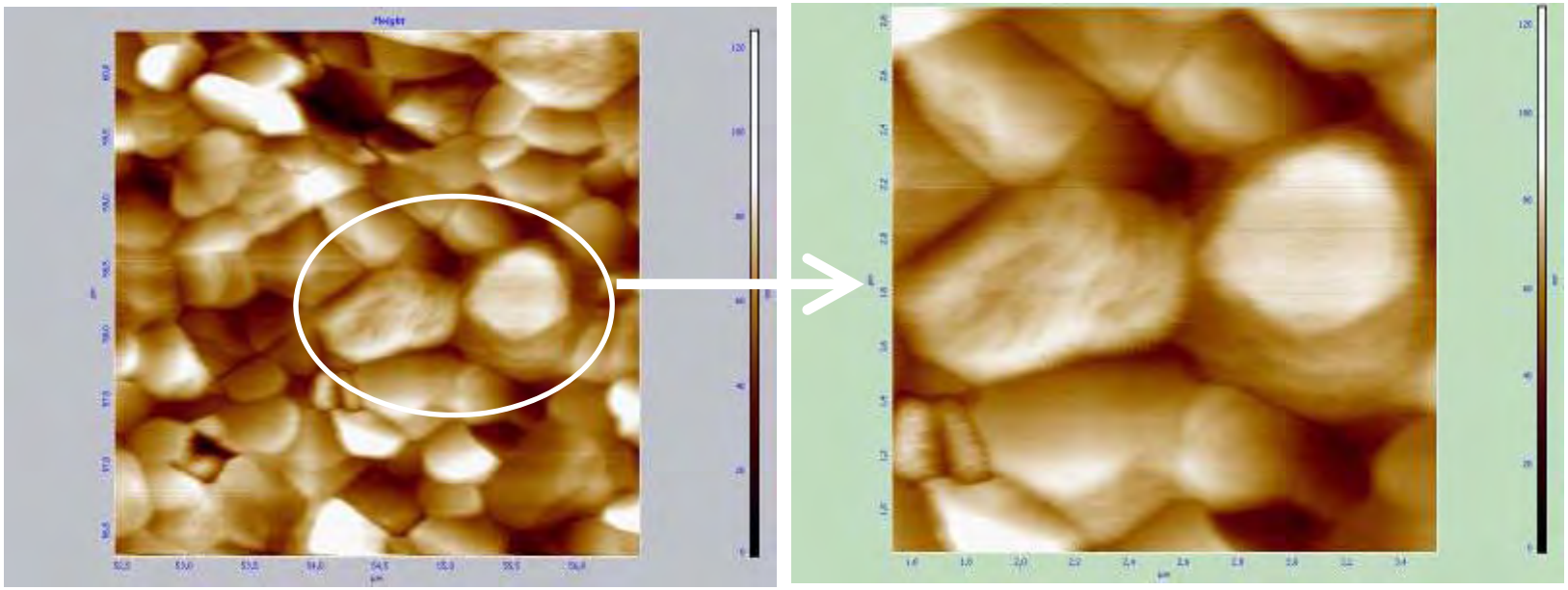




Substrate: silicon wafer with alumina layer.

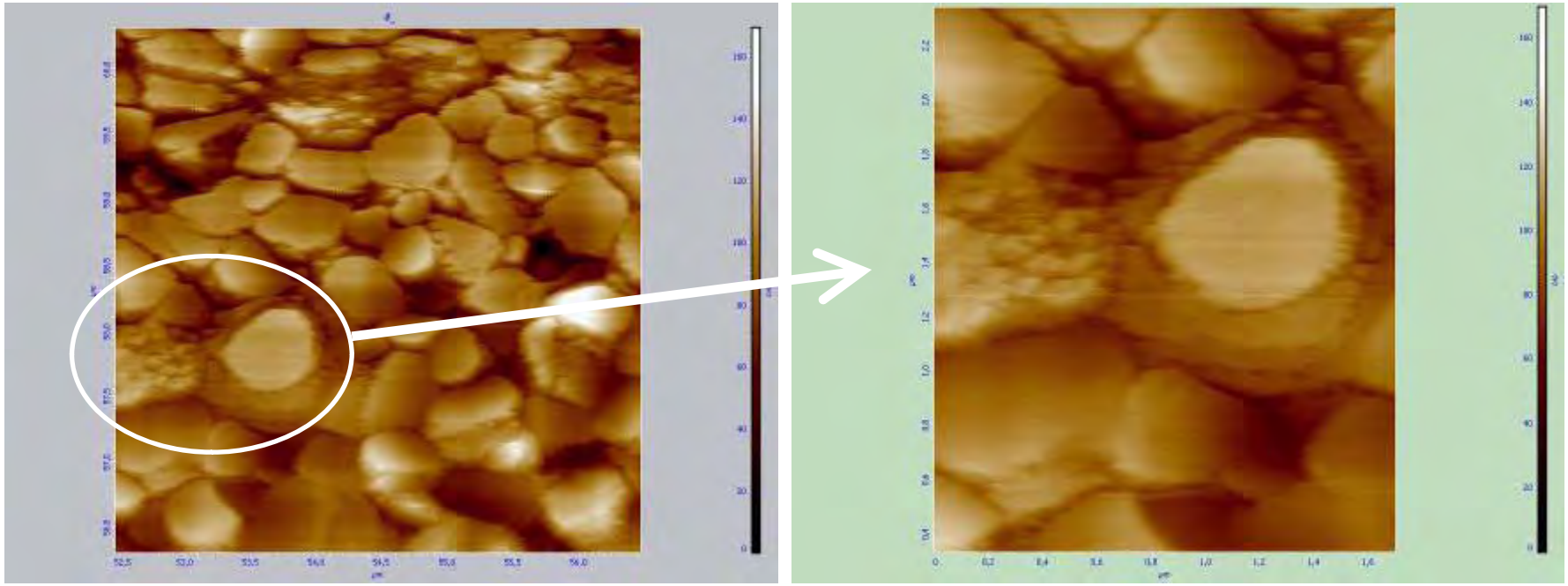
To characterize the porous surfaces Atomic Force Microscope and electrochemical cell are used.

Nanoporous alumina surface



Potential = 0 V

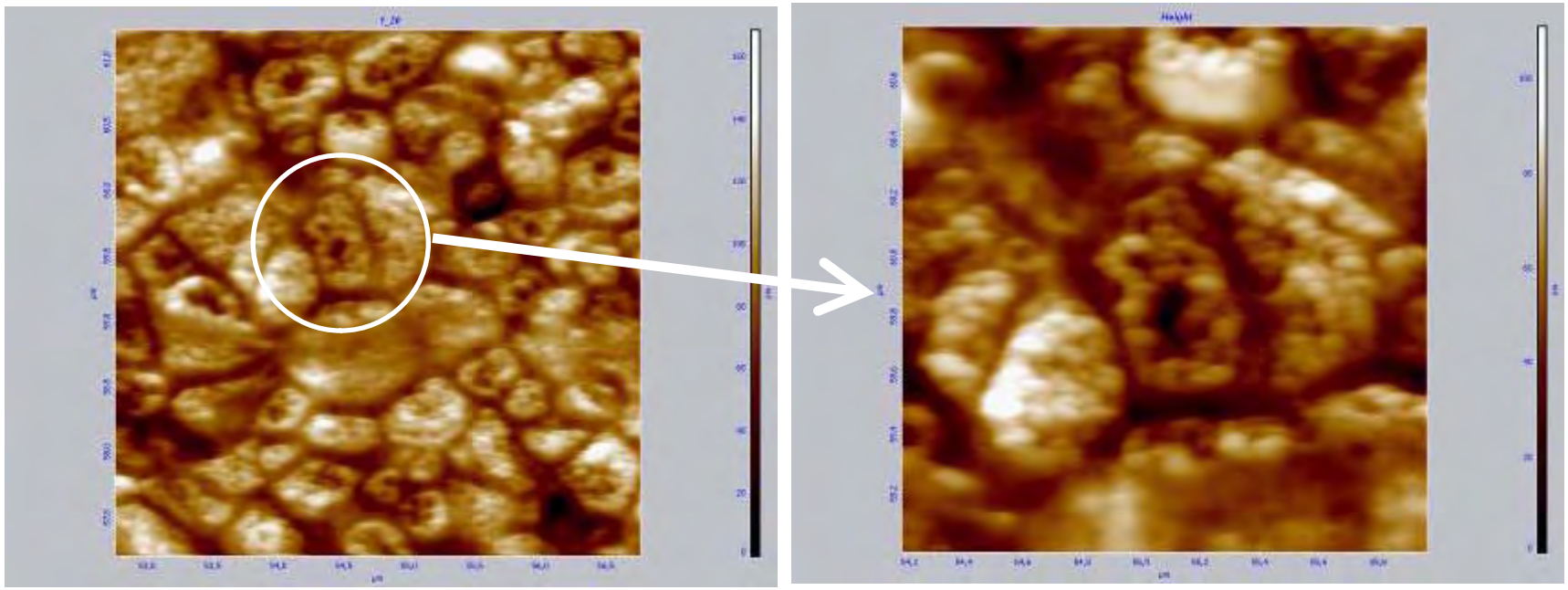
Nanoporous alumina surface



t = 10 s

Anodization is done by applying an electrical current to a part of aluminum in a acidic electrolyte (6wt% phosphoric acid). Anodization leads to an alumina layer with a porous surface.

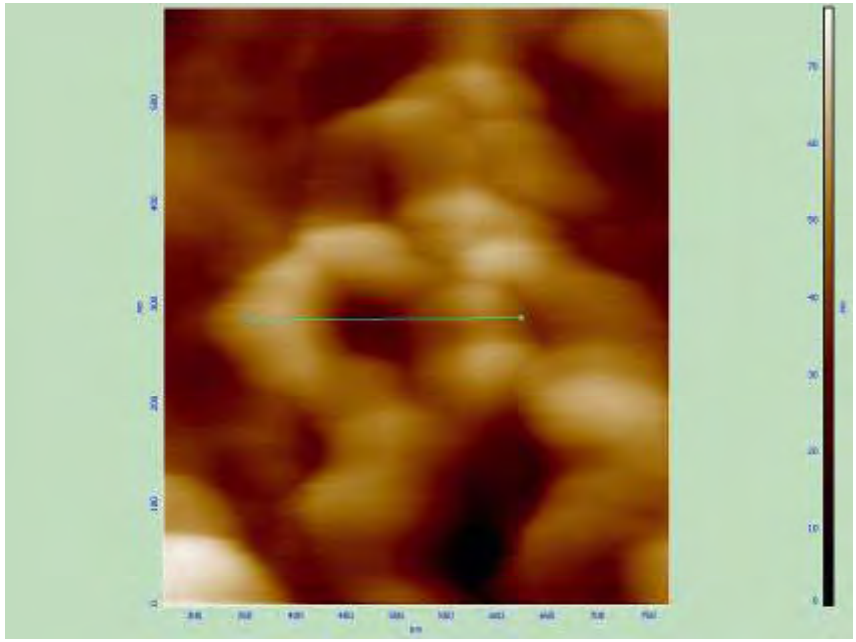
Nanoporous alumina surface



t = 60 s

At the beginning of anodization process, the pores are randomly distributed on the surface.

Nanoporous alumina surface



t = 120 s

During pores growth into the bulk material they arranged in a hexagonal pattern due to a process a self-organization. This can be utilize to create a surface with ordered pores.

Highlights

1. Easy set up and clearance TEFLON cell.
2. Flexible design allowing various modifications.
3. Cell design allows mounting a wide range of samples with different thickness and shapes (hemispherical is possible). Flow trough possibility, heating, cooling.
4. Insulating medium (purified inert gas) is used to prevent electrolyte contamination.
5. Sample is separated from the piezotube to prevent any scanner damage.
6. A wide range of electrode types.
7. High resolution (up to atomic)
8. EC device is based on the NTEGRA platform.

THANK YOU!

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