

Lithography with SPM

AFM Force Lithography

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With standard silicon or silicon nitride cantilevers Force Lithography is applicable for relatively soft substrates and no qualitative change of modified surface happens but only local change of surface morphology. Electrophysical properties are not changing with this method. Fig.1 shows the surface of polycarbonate film on a silicon substrate after force lithography. A regular array of pits has been created by rigid ($F_c=40\text{N/m}$) silicon cantilever operating in the semi-contact mode of AFM after the Force Lithography has been applied to points pre-set by program by bigger force under normal conditions. Distance between pits is about 25nm. This example demonstrates the possibilities of AFM to controllable modification of the surface on nanometer scale.

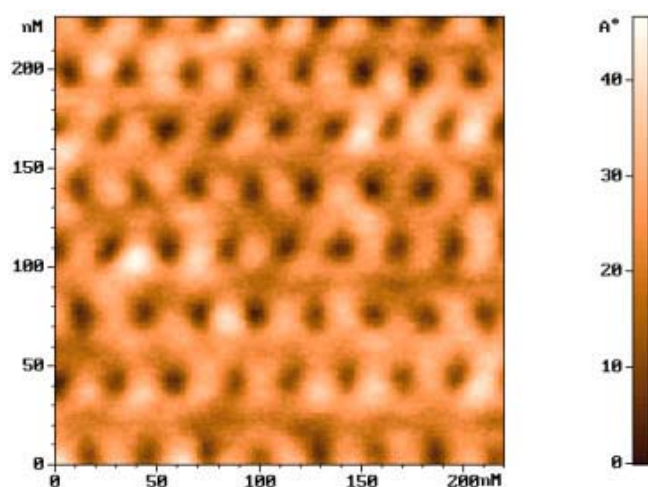


Fig. 1. AFM image of polycarbonate film surface after application of Force Nanolithography

In some cases after force lithography the convexities are observed instead of the pits. It

means that a tip extracts material of the soft sample. Fig.2 demonstrates this possibility. Drawing of the more complicated pictures is also possible. Fig.3 shows the face, which was obtained by using raster image (PCX-file). Voltage lithography provides more quality image for such complex object.

For the Force Lithography on polycarbonate film semi-contact one-beam silicon cantilevers with the force constants that range from 10 to 100 N/m are recommended. Force Lithography can be executed on the surface of hard materials when special hard cantilever is used (for example, cantilever with diamond tip).

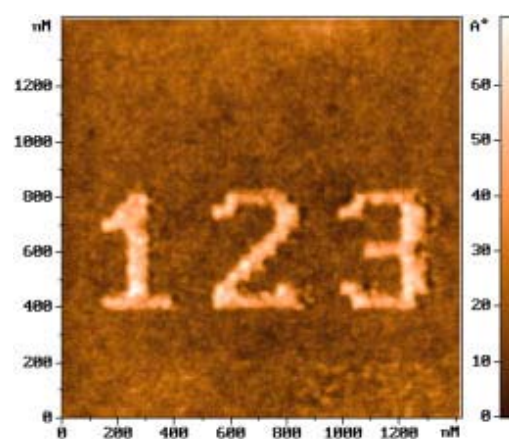


Fig. 2

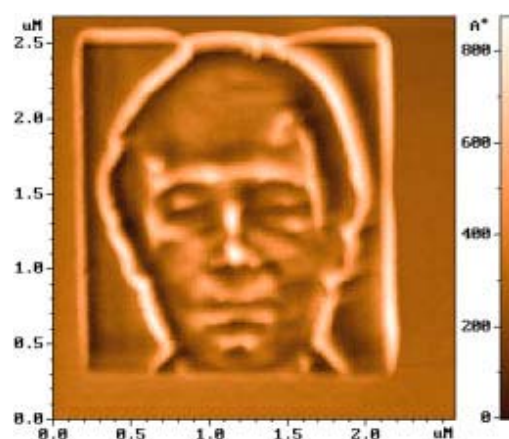


Fig. 3

AFM Current Lithography

With the help of the Voltage Lithography not only geometrical properties of the surface can be changed but also its electrophysical properties, for example, by application of voltage to conductive cantilever the electrochemical processes on the surface can be stimulated under the Probe and, thus, material will be transformed from conductor into dielectric. On Fig.1 abilities of tip-induced oxidation of the surface of hyperfine titanium film on silicon under normal conditions are demonstrated. It should be noted that the indicated surface area is 200 nm², diameter of nanoparticles is 8-10 nm by the semi-height of island. It corresponds to information recording density of 0,6 Tbit/inch²

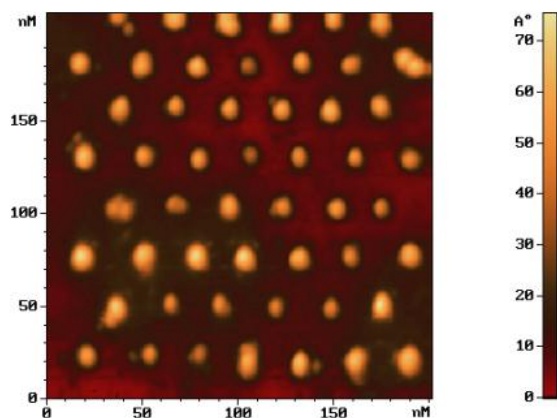


Fig. 1

Nanomodification of the surface is not limited only by formation of points. Using software we can make the Probe traveling along preset vectors and, therefore, to form lines and complex objects. Fig.2 gives example of the Vector Lithography on titanium film through its local oxidation, which is induced by conductive tip.

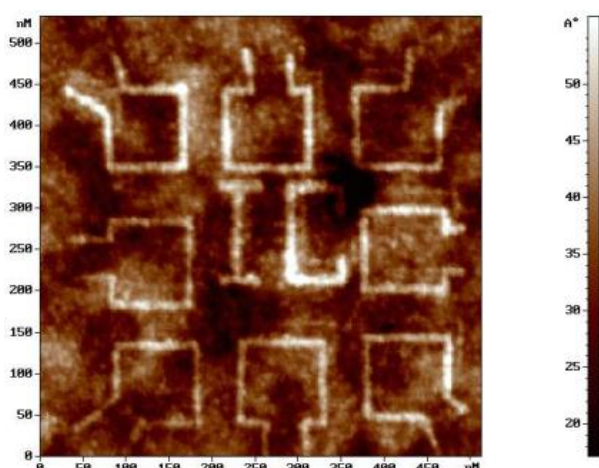


Fig. 2

The width of oxide stripe of 8-10 nanometers enables formation of tunnel-transparent barriers for electrons as well as one-electron instruments, which will operate by quantum laws even at normal indoor temperature. Lots of papers devoted to produce MIM diodes and one-electron transistors have been published [http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/text41.html#ref_1]. The process of local oxidation is based on anodization. For complex pictures Raster Lithography can be executed by using PCX-file. Difference between minimum and maximum tone voltage will be applied proportionally to brightness and, correspondingly, anode oxide will grow to a different height forming different contrast of topographical image. Examples of the Raster Voltage Lithography are shown on Fig. 3 and Fig. 4. Two Nobel Laureates A. Szent-Gyorgyi (Fig. 3) and Zh.Alferov (Fig. 4) are imaged on these figures.

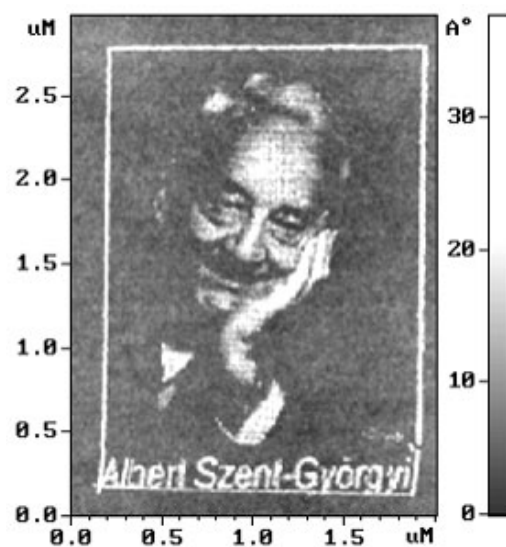


Fig. 3

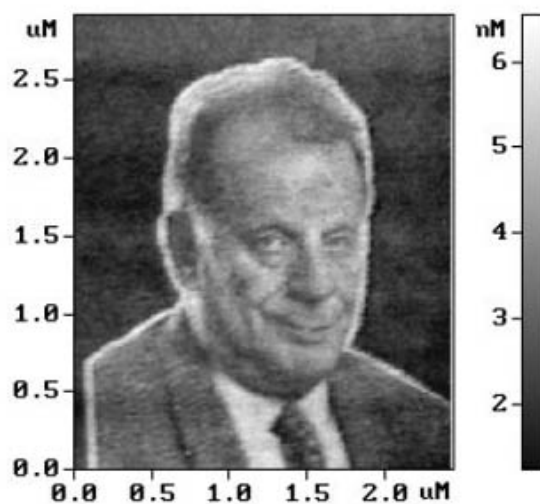


Fig. 4

■ Selection of cantilevers

To perform the Voltage Lithography on titanium film semi-contact one-beam silicon cantilever with conductive coating of high-melting alloys based on titanium and tungsten (W₂C, TiO, TiN) are recommended. Type of coating does not change significantly the Voltage Lithography mode.

■ Selection and preparation of a sample for the Electric Lithography

To test microscope and to control program in the Probe Lithography mode we recommend to use thin titanium films on thermally oxidized silicon substrate with thickness from 1 to 10 nm. Selection of titanium as test sample is specified by electrochemical potential of anodization of up to 98% as well as its use for the Voltage Lithography described in many scientific articles

[\[http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/text41.html#ref_1\]](http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/text41.html#ref_1). Of course, any material, which can be electrochemically oxidized in water can be suitable for this process. We also have performed experiments to study the process of tip-induced oxidation on semi-conductors surfaces - for example on doped silicon, gallium arsenide, heterostructures and W, Nb, Al metals. Important factor in forming of the nanopattern is initial roughness of the film, which was, in our case, 0.5-2E. Since the height of oxide lines is only 1-6 nm, therefore, for good contrast image the film should have small irregularities. To get continuous thin and smooth films of metals and semi-conductive materials we have used methods of molecular-beam epitaxy and impulse plasma deposition.

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Local Anodic Oxidation

- Direct Patterning of Titanium thin films by Local Anodic Oxidation Using AFM

■ Introduction

The term “nanolithography” is commonly used for the local change of any properties of a surface by a scanning probe microscope (SPM) tip. It is the complex technique of creating and visualizing nanometer functional elements, including individual molecules and atoms, on a surface. One of the most promising methods of local surface modification is the local anodic oxidation (LAO) process, which allows the creation of nonconductive regions on a conductive surface. In LAO knowledge about the physical-chemical reactions and process reproducibility and the factors that influence lateral resolution are crucial. A great number of publications indicate that, in the near future, the LAO method may be used for ultrahigh density storage production or in quantum electron devices

creation [\[http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/Local_Anodic_Oxidation/text106.html#ref_1\]](http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/Local_Anodic_Oxidation/text106.html#ref_1).

■ Physical-chemical model of LAO

In this note we demonstrate the facility of nanometer scale anodic oxide formation on thin titanium films and its characterization using the NT-MDT Co. Solver PRO™ AFM in contact or semicontact modes. It is well known that under the influence of an electric field that oxide films grow on the surface of different materials when the surface is positively charged against a negative charged electrode. Such electrochemical reactions are called anodization

[\[http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/Local_Anodic_Oxidation/text106.html#ref_3\]](http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography_with_SPM/AFM_Current_Lithography/Local_Anodic_Oxidation/text106.html#ref_3).

In the figure 1 a principle scheme of LAO is shown. In air or any humid atmosphere a probe and sample surface are typically covered by a thin film of absorbed water. While the tip approaches sufficiently close to the surface, these absorbed layers come in contact and form an electrolyte bridge by capillary action. With a negative voltage applied to the tip an electrochemical reaction will take place on the titanium surface under the tip.

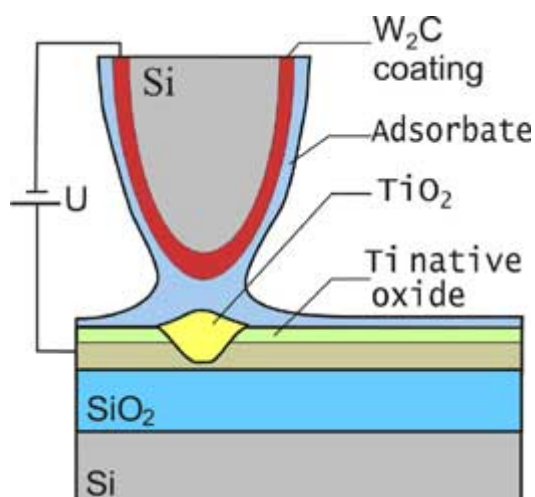


Fig.1. General concept of a local anodic oxidation method



In the course of anodization cations and anions migrate through a layer of growing anodic oxides to the oxide-surface border. Proportions of migrating ions depend on different factors such as substrate material, electrolyte and current density. Ion

transfer through the anode oxide is stimulated by the electric field which is produced between the surface and the tip. The growth speed of an anodic oxide island height mainly depends on the velocity of ions and electric field strength. The Kinetics of the electrochemical reaction can be described by the empiric relationship of Gunterschulze-Betz:

$$J = a \cdot \exp(b \cdot E)$$

In this relationship: J – electric current density, E – electric field strength, a, b are numerical constants being determined by surface materials and the electrolyte.

With constant anode potential U the field strength in the oxide will fall with the growth of anodic oxide and, therefore, the electric field is in inverse proportion to the thickness of the growing oxide island.

$$U = E \cdot h$$

Growth speed of the oxide hillock is higher at the earlier stage of anodization because the large electric field has no time to be reduced when it penetrates the ultrathin dielectric film. It can be seen that current density falls exponentially with growth of the anode film and, therefore, growth speed declines. Finally the oxide island growth stops at a certain value which is defined by the anode potential. In figure 2 a typical AFM image of modified titanium surface is demonstrated.

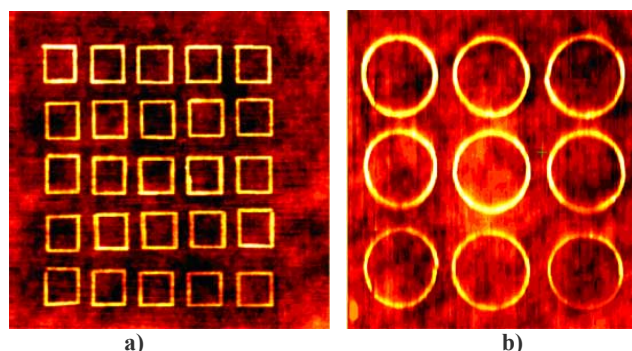


Fig 2. Semicontact mode AFM image of 10nm titanium film on silicon substrate after local anodic oxidation (Voltage on tip -10V, impulse duration 20ms). Scan size 4000x4000x7nm – a), 5000x5000x4nm –b)

■ Importance of cantilever selection and sample preparation.

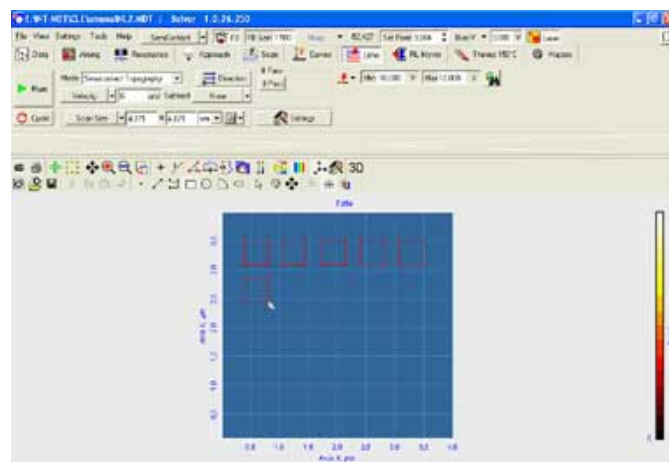
Noncontact rectangular silicon cantilevers with a force constant range of 5-30N/m were used for the LAO process realization. To decrease the water bridge diameter between the tip and surface we recommend selecting special hard coatings based on refractory compounds of W and Ti, which are characterized by hydrophilic properties. In order to reach the required characteristics we have developed TiO_x and W₂C coatings for silicon cantilevers to be used for LAO

http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography with SPM/AFM Current Lithography/Local Anodic Oxidation/text106.html#ref_4.

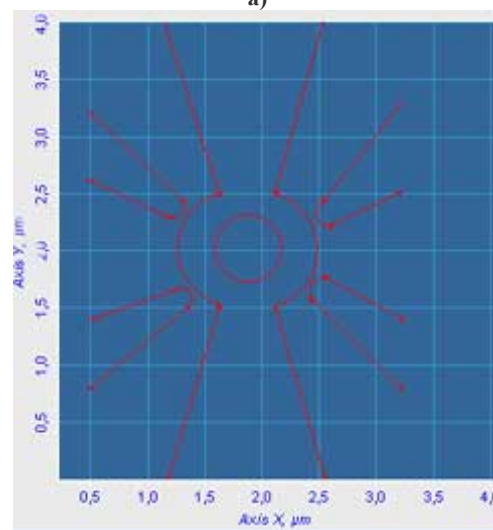
We have used the cathode arc deposition technique for thin titanium films (2 -15±1 nm) formation. Such a method allows the deposition of ultrathin continuous amorphous films with a surface roughness of about 0.1 nm. A Low value of roughness is dramatically important because the surface morphology is changed within a few nanometers during oxidation. Other low roughness thin films deposition techniques like molecular beam epitaxy can be used as well.

■ Advanced easy-to-use NANOLITH™ software

To be able to perform positioning of a tip over the surface for LAO we have used our standard software with its lithography option. A general view of the lithography window is shown in Fig. 3



a)



b)

Fig 3. AFM lithography software window a), pattern for quantum device creation b)

Using our lithography software it is possible to use a grid pad and with the PC mouse click to choose different geometrical figures and draw dots, lines, squares, rectangles, circles and arcs. The bias voltage and its impulse duration can also be varied over a wide range. The Advanced resolution mode, of up to 4096x4096 points, allows the user to write complicated patterns in large areas. It is also possible to load bitmap files or commercially available AutoCAD .dxf files.

A typical example of raster mode LAO using NANOLITH™ software is shown in figure 4. After loading a bitmap mask, during scanning, a voltage was applied proportionally between the minimum and maximum mask tones and anodic oxide was grown to different heights to give a few nanometers scale relief

http://www.ntmdt.ru/SPM-Techniques/SPM-Methodology/Lithography with SPM/AFM Current Lithography/Local Anodic Oxidation/text106.html#ref_5.



Fig 4. Semicontact mode AFM image of 10nm titanium film after raster mode LAO process (bias voltage distribution 0-10V, impulse duration in every point 10ms). Scan size 4x4,5 micrometers. Time of surface patterning 8min

▣ Advantages of closed-loop operation

Traditional piezo-tube scanners are characterized by large residual nonlinearity and creep effects. These disturbances greatly influence the performance of the lithography operations. In the Solver PRO™ AFM we solve this crucial problem. To improve the scanning performance and to expand the instrument functionality, closed-loop control with the use of the equivalent scanner technique was added. The closed loop equivalent (CLE) scanner is an external twin of the working scanner, which has capacitance sensors to register actual movement of the scanner in the X, Y and Z dimensions. The working and equivalent scanners are connected parallel to the auxiliary control unit and then to the SPM controller in order to provide movement synchronism and closed-loop control of scanning. Our experiments indicate that with closed-loop operation AFM performance in surface patterning dramatically improves. AFM images demonstrating a difference between open loop and closed-loop operations are shown in fig 5.



Closed-loop operation off



Closed-loop operation on

Fig 5. Semicontact mode AFM image of 10nm titanium film after raster mode LAO process (bias voltage distribution 0-10V, impulse duration in every point 10ms). Scan size 4x4,5 micrometers. Time of surface patterning 10min

▣ Factors that influence lateral resolution

In this work we would like to emphasize several important factors that influence the lateral resolution and growth of a thick anodic oxide in the LAO method [6]. According to the physical-chemical model of an oxidizing film the humidity, tip hydrophobic properties, film resistance, and applied voltage greatly influence the anodic oxide line width. Thus we have tried to reach a limit of lateral resolution by varying these parameters and determined that on rather thick Ti film (15nm) at 20% relative humidity it is possible to reach an anodic oxide island size of 4nm (measured on half of the height, Fig 6).

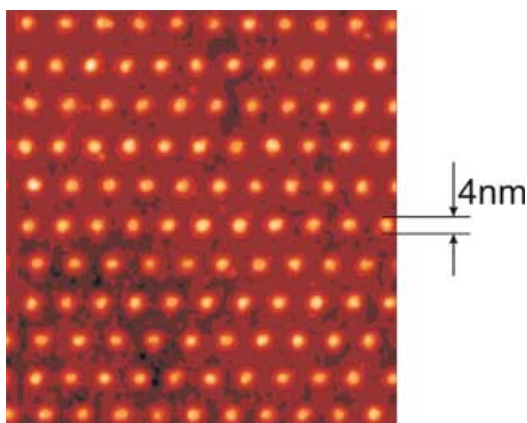


Fig 6. Semicontact mode AFM image of 15nm titanium film after raster mode LAO process (bias voltage 8V, impulse duration in every point 0,5ms). Scan size 100x100x2,6nm

References

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AFM Charge (Electrostatic) Lithography

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The electrization of some of samples is possible with use of disconnected cantilever. Example of the charge writing on the surface of standard silicon grating by silicon cantilever is discussed below. Fig.1 demonstrates the topography of grating that obtained in semicontact mode after moving of the nonvibrating tip along black arrows. Existence of the charge, which was induced by cantilever friction, can explain the holes on silicon oxide (dark tracks on convexities of the grating). These holes appeared on topography owing to strong electrostatic tip-sample interaction, which displace the cantilever resonant peak during scanning in semicontact mode. This displacement leads to the cantilever amplitude changes and corresponding changes of the Z-coordinate of scanner, which is interpreted as topography. If electrostatic tip-sample interaction is attractive (the signs of probe and sample charges are contrary) then charged areas looks like holes. Repulsive interaction gives convexities on topography for charged areas. It is seen from Fig.1 that the bulk silicon oxide (convexities of the grating) is charged contrary to cantilever.

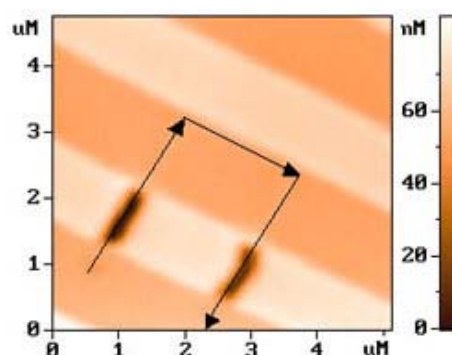


Fig. 1

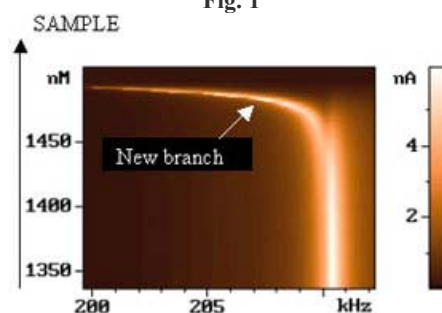


Fig. 2

Fig.2 shows changes of the resonant peak of the cantilever during approach to the sample. On this image horizontal axis corresponds to frequency, vertical axis is Z-coordinate of scanner. Brightness corresponds to the cantilever amplitude in arbitrary units. It is seen from Fig.2 that new branch appears when tip-sample distance becomes small. This new branch has strong dependence on tip-sample distance. The appearance of this branch can be connected with electrization, i.e. electrization is also available when oscillating cantilever strong interacts with the sample. The hole on topography after such procedure is shown on Fig.3. The size of this hole determines minimum possible charged area for a considered sample: 200-300nm. It is evident that minimum possible size of the charged area strong depends on material. Fig.4 shows the example of the more complex pattern: charge signature on originally uncharged flat silicon oxide. Charge Lithography was executed in resonant mode with small tip-sample distance. It should be noted that all these charge patterns only in semicontact mode are seen. The using of the contact mode makes these charged areas invisible.

Moreover, all scan will be charged after contact mode. The charged areas can be easily visualized also with Electrostatic Force Microscopy (EFM).

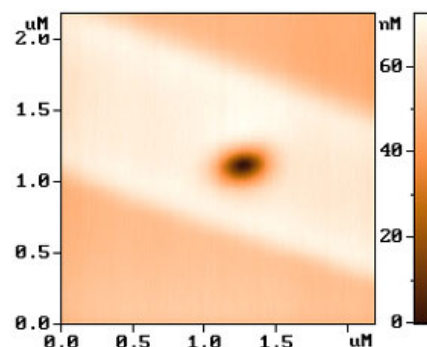


Fig. 3

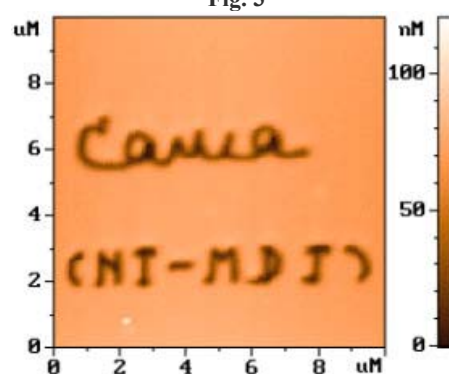


Fig. 4

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