Atomic Force Microscopy experiments with amino-functionalized silicon AFM tips and samples

lsirghi@uaic.ro

Lucel Sirghi and Alexandra Besleaga

Iasi Plasma Advanced Research Center (IPARC), Faculty of Physics," Alexandru Ioan Cuza" University, Iasi, 700506, Romania

Abstract

•In this work we used plasma technology in combination with wet-chemistry functionalization methods to functionalize silicon atomic force microscopy (AFM) probe and sample surfaces with amino (-NH_2) chemical groups. Plasma cleaning, oxidation, and hydroxylation processes are used to chemically activate silicon or silicon nitride surfaces by generating surface silanol (Si-OH) groups. This process is followed by self assembled monolayer (SAM) deposition of ethanolamine to generate surface amino groups. The amino-functionalized AFM probes and samples were used in atomic force spectroscopy measurements that confirmed successful functionalization by chemical force titration.

Material and methods

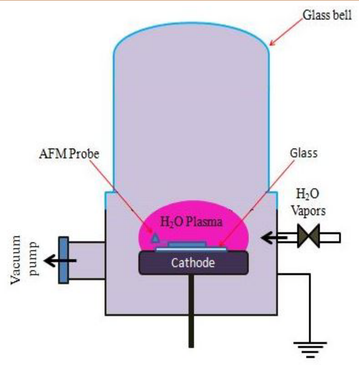

Fig. 1 The plasma reactor used to hydroxylation the AFM probe.

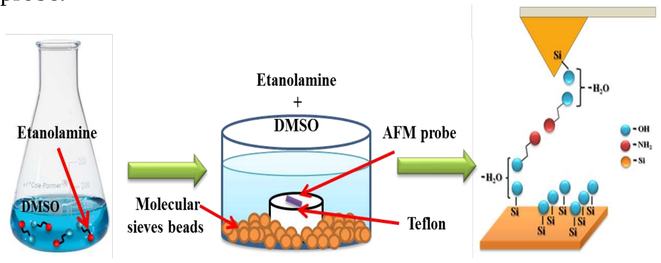

Fig. 2 Schematic representation of amino-functionalization procedure

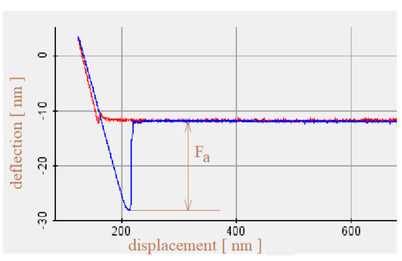

Fig. 3 Force (arb. u.) versus probe displacement (nm) acquired with amino-functionalized AFM tip and sample at pH = 4.5

Hydroxylation of Atomic Force Microscopy probes

❖Before, plasma hydroxylation, the as-received AFM probes were washed in chloroform (Sigma-Aldrich, ≥98.5%) to remove large dust particles from the surface. Then, the AFM probes were exposed for 3 minutes to the negative glow plasma of a d. c. discharge in a mixture of air and water vapor at 40 Pa. The discharge current intensity and voltage were maintained constant at 3 mA and 470 V, respectively. This treatment removes the surface contaminant molecules from the AFM probe surface and generates surface silanol (Si-OH). After plasma treatment, the AFM probes were used immediately in SLB indentation experiments.

Amino-functionalization by ethanolamine hydrochloride

❖The hydroxylated surfaces of the AFM probes and samples were functionalized by amino functional groups of ethanolamine. For this purpose we dissolved ethanolamine in dimethyl sulfoxide (DMSO) (0.5 g/mL) by gentle heating to approximately 70°C in a crystallization dish. Subsequently, after complete dissolution and cooling at room temperature, a Teflon block was immersed in the centre of the crystallization dish and molecular sieve beads (4Å) were added (about 25% of the volume of the solution) around the Teflon block. Then, the crystallization dish was placed in desiccators for 30 minutes to remove the dissolved air by degassing. Then, the AFM probes and samples were placed on the Teflon block and incubated in the ethanolamine solution overnight. Following the incubation, the AFM probes were washed in DMSO (3×1min) and ethanol (3×1min), and dried in a gentle stream of nitrogen gas.

Force spectroscopy measurements of amino-functionalized AFM tip and samples

❖The AFM force spectroscopy measurements were performed at room temperature in buffer solutions with various pH values (from 2.7 to 10.5) using a commercial AFM apparatus (XE-100 from Park Systems, South Korea). We used commercial AFM probes (MLCT from Bruker) with very flexible silicon nitride cantilevers (nominal force constant of 10 pN/m) and sharpened tips (nominal radius < 10 nm). The probes and silicon wafers Si(100) were functionalized with amino groups by procedure described above. The AFM force-displacement curves (Fig. 3) were acquired at a constant speed of scanner extension (1μm/s). The cantilever deflection versus scanner extension curves acquired in the experiments were calibrated and transformed in force versus tip displacement (tip-sample distance). The tip-sample adhesion force was measured as maximum force required for detachment of the AFM tip from the sample surface.

RESULTS AND DISCUSSION

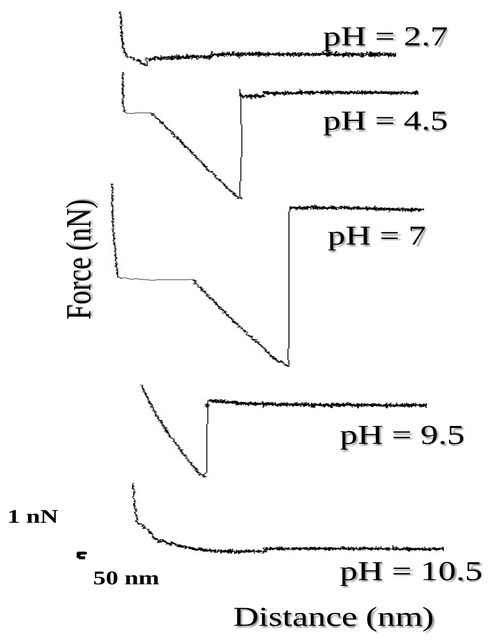

Fig. 4 Examples of force-distance curve recorded during retraction of the amino-functionalized AFM tip from the amino-functionalized sample surface in buffer solutions with various pH values.

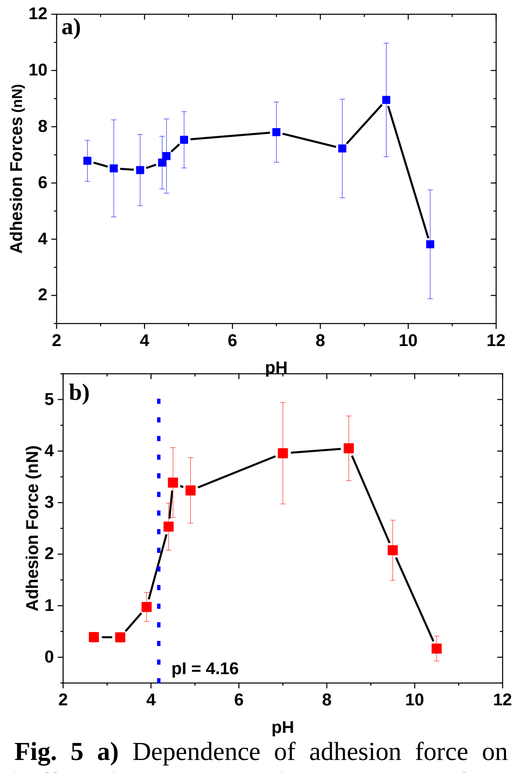

Fig. 5 a) Dependence of adhesion force on pH of buffer solution in control experiment performed with as-received AFM probe and silicon sample.
b) Dependence of adhesion force on pH of buffer solution in titration experiment performed with amino-functionalized AFM probe and silicon sample.

➢The presence of –NH_2 groups on the AFM probe and sample surfaces was evaluated by chemical force titration experiments, which probe the electrical charging of the surfaces under different pH conditions. Results of control experiment performed with as-received AFM probe and samples are presented in Fig. 5a.

➢Force-displacement curves (Fig. 4) were acquired on an arrays of 8 × 8 equidistant points on a area of 0.5 μm × 0.5 μm for each value of pH, the adhesion force values being used to determine the average and standard deviation values.

➢Figure 5b shows the results of chemical force titration experiment for AFM tip and sample, both modified with ethanolamine.

➢At low pH, a small adhesion (< 1 nN) is observed. A sudden increase of the adhesion force between amino-functionalized AFM tip and silicon sample was recorded at isoelectric point (pI = 4.2).

➢With increase of pH, the amino groups become deprotonated, a larger adhesion arises because of the hydrogen bound formation between neutral amino groups on the tip and sample surface.

➢For pH > 9 the adhesion force start to decrease and approaches zero above pH = 11. A simple explanation this behavior is that at low pH, the amino group on both tip and sample surfaces are protonated (NH_3^+) and the net positive charge results in the formation of electric double layers on both surfaces which leads to an electrostatic repulsion. At very high pH, the adhesion force falls to zero and this drop could be explained by electrostatic repulsion between two surfaces.

CONCLUSION

- ✓ Surfaces of silicon samples and silicon nitride AFM probes were hydroxylated in water vapor plasma and amino-functionalized by SAM deposition of ethanolamine.
- ✓ The success of amino-functionalization process was confirmed by the results of chemical force titration experiments consisting in measurements of tip-sample adhesion force in buffer solutions with pH varying from 2.7 to 10.5
- ✓ The chemical force titration experiments showed a sudden increase of adhesion force at the isolelectric point pI = 4.16, which is in agreement with the isoelectric point of amino surface groups.