Probe modifications and development of model samples for use in chemical force microscopy

S.G. Bystrov, A.A. Shakov, A.V. Zhikharev

Physical Technical Institute UrBr RAS, 132 Kirov str., Izhevsk, 426001 Russia, Phone (4312)212655, Fax. (3412)250614, E-mail: uds@pti.udm.ru

Various information on the structure and characteristics of substances can be derived by means of the AFM-technique, though it is generally agreed that the information thus obtained is scarce [1]. Considerable attention in recent years has been given to the intensively developing chemical force microscopy, CFM, which is capable of presenting information on the local chemical structure of matter. The technique consists in different ways of enhancing chemical contrast of AFM-images, such as physico-chemical modification of tips or sample surfaces, selection of measuring modes, etc.

The previously published methods of depositing self-assembling surfactant layers onto the tip [2] are hard to realize (sputtering of adhesive gold sublayers onto the tip is required, besides, special reagents of high grade purity should be used). Furthermore, the resultant layers are abrasion-unstable so that the measurements might be poorly reproducible. An attempt has been made here to alter the tip surface energy both by its treatment in plasmas of different gases and by deposition of plasma-polymerized coatings onto the tip. Since very small area of the probe tip is dealt with silicon plates simulating the tip surface (sample 1) have been used to refine the preparation methods and to study the characteristics of the resultant coatings. The plasma-treatment of samples was performed in a tube-type reactor with the displacement of 20 cm^3. Low-temperature plasma (LTP) was excited by alternating electromagnetic field with the frequency of 40.68 MHz. Residual air (sample 2), nitrogen (sample 3), and octane (sample 4) were used as plasma-stimulating gas. The gas pressure was 10 Pa (oil-free pumping), the source specific power was 3,5 Wt per cm$^{3.}$ P47- NT MDT probe microscope was used to investigate the morphology and characteristics of samples. The curvature radius of the silicon probes of the same company did not exceed 10 nm and a force constant made up 5.5 N/m. The sample surface energy was estimated by means of contact angle measurements (distilled water was used). It has been stated that root mean square deviation of surface roughness Rq for samples 2 and 3 grow insignificantly as compared with sample 1 (Fig.1a). This means that no intense etching of the silicon surface takes place during plasma-treatment, implying the initial sharpness of the modified tips.

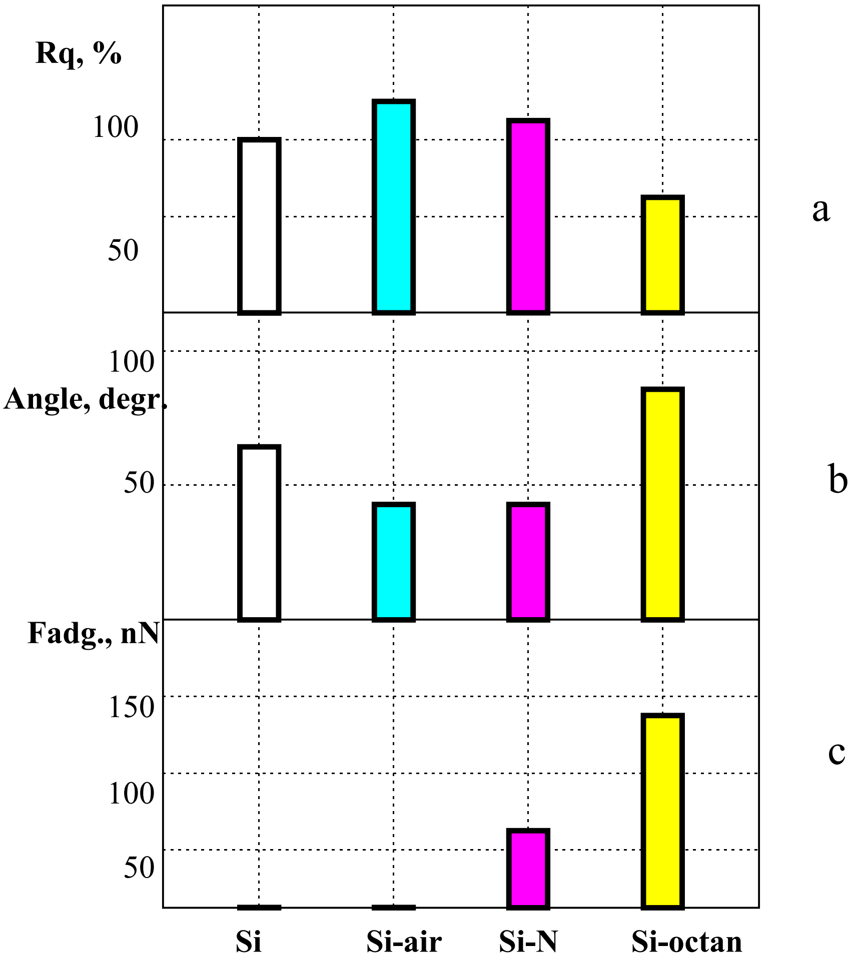

Fig.1. The propertys of intial silicon (Si), silicon after treatment in plasma of residual air (Si-air), silicon ufter treatment in plasma of nitrogen (Si-N) and silicon ufter treatment in plasma of octane (Si-octan).

a - root mean square deviation of surface roughness data;

b - contact angle data;

c - adhesion force data.

As is seen from the contact angle data, in comparison with sample 1, the post-modification surface energy of samples 2 and 3 increases, with its sharp decrease in sample 4 (Fig. 1b). Hence, by changing plasma-treatment conditions we will be able to obtain tips with different surface energies.

The measurement of force-distance curves (Fig.1c) indicated a very poor adhesion between the tip and the initial silicon. Note that no adhesion changes occurred after silicon treatment in plasma of air while after nitrogen plasma treatment (sample 3) the increase in the tip-sample detachment force was observed. The reason may be the formation of a more hydrophylic surface in the latter case that results in adhesion increase due to capillary forces. The adhesion growth is even higher in the case of sample 4, although its surface energy is low. The specific chemical interaction between the organic film on the sample surface and the tip might apparently be the explanation.

The scratch-depth method was used to measure the thickness of the organic film on the sample 4 surface. The film appeared to be in the order of 60 nm thick, it was fairly smooth and strong (no film rupture was observed after $2.5*10^2$ nN loading had been applied to the probe). By decreasing plasma-treatment time it is possible to obtain a thinner film on the tip, with good strength characteristics.

Most important here is the availability of standardized test samples that include the areas of definite sizes with completely different chemical structure. It is important for the sample surface to be smooth so that the contribution of topography in the resulting images is less developed. The areas should be limited by the dimensions of 10-100 nm. We suggest that test samples are manufactured by creating a multilayer of alternating polymer layers with different chemical structure. Having cross-sectioned such a composite we obtain the required test sample. Film thickness can be controlled by changing concentration of polymer solutions.

The work has been performed under the sponsorship of RFFI (projects 01-03-96461, 01-03-96463, 01-02-96463, 00-02-17426).

1. S.Speller, W.Heiland, M.Schleberger. Surface Characterization:Composition Structure and Topography/ Experimental Methods in the Physical Sciences, vol.38, Academic Press, 2001, p.99.
2. A.-S. Duwez, C.Poleunis, P.Bertrand and B.Nysten. Chemical Recognition of Antioxidants and UV-Light Stabilizers at the Surface of Polypropylene: Atomic Force Microscopy with Chemically Modified Tips/ Langmuir 2001, 17, p. 6351-6357.