ATOMIC FORCE MICROSCOPY

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Abstract: Since the invention of the Scanning Tunneling Microscope (STM), a number of related surface probing techniques have been developed, capable of resolving single atoms or molecules at a free surface. In particular, the Atomic Force Microscopy (AFM) is well recognized as a promising tool for observing nanometer-scale structures of non-conductive surfaces, soft matter objects like single organic molecules, polymers, biological tissues, etc. Basic principles of operation of various Surface Probe Microscopy techniques application in various fields are discussed. Application of AFM Force Spectroscopy on polymer-coated surfaces is described.

Mikroskopija na atomsko silo

Ključne besede: STM mikroskopija skanirna tunelna, sila atomska, AFM mikroskopija sile atomske, spektroskopija sile, AFM spektroskopija, topografija površine, SPM mikroskopija s sondo skanirno, EFM mikroskopi s silo električno, MFM mikroskopi s silo magnetno, SNOM mikroskopi skanirni optični s poljem bližnjim, PWB plošče ožičenja tiskane

Izvleček: V letih po odkritju vrstičnega tunelskega mikroskopa (Scanning Tunneling Microscope, STM) je bilo razvitih veliko podobnih tehnik mikroskopiranja površine, katerih ločljivost je velikostnega reda dimenzij posameznega atoma ali molekule. Med njimi posebno mesto zavzema mikroskop na atomsko silo (Atomic Force Microscope, AFM), ki je zaradi enostavnosti delovanja in visoke ločljivosti postal nepogrešljivo orodje pri analizi topografije neprevodnih površin, mehke snovi, polimerov in bioloških snovi. V članku bom opisal osnove delovanja STM in AFM, njuno uporabo na različnih raziskovalnih področjih in še posebej predstavil spektroskopijo sile na polimernih površinah.

1. Introduction

The Atomic Force Microscope (AFM), as first described by Binnig et al. /1/ in 1986, is by now a well established tool for the studies of surface topography and surface forces in a variety of condensed matter systems, such as solid crystals, polymers, biological systems, molecular crystals, etc. The principle of operation of an AFM /2/ is based upon the measurement of the attractive or repulsive forces between the nanometer-sharpened tip and the substrate. This allows for the observation of either (i) **the surface topography**, or (ii) **the distance-dependence of the forces** between the tip and the surface. In combination with different materials for the surface-sensing tip (metal, isolator, ferromagnet, etc.) one can test and observe a wide variety of interfacial forces acting between the tip and the substrate and can therefore extract a qualitatively different information on the surface structure. These two basic modes of operation of an AFM can be used in very different environments, as we can perform the AFM experiments at ambient conditions, in vacuum and even in the presence of liquids. This makes an AFM a powerful experimental tool for very different fields of surface science.

2. Principles of operation of surface probe microscopes

The principle of operation of a Surface Probe Microscope (SPM) is simple: a small (i.e. submicron) probe is scanned across the surface and is held in close proximity to the surface by a feedback-loop electronics, as shown in Fig. 1. The close proximity between the probe and the surface is sensed by a specific interaction between the probe and the surface. Regarding to the type of this interaction, the class of SPM devices can be divided as follows:

(i) **Scanning Tunneling Microscope** (STM). In this instrument, an electron tunneling current is measured between a very sharp metallic tip with a radius of curvature of less than 10 nm and a metallic surface. When the separation between the metallic tip and a conductive surface is less than 1 nm, a quantum electron tunneling current appears across the gap. As the tunneling current increases exponentially with decreasing separation, one can position the tip very accurately. As a consequence of the exponential dependence of the tunneling current, the electrons are tunneling to the surface via the orbital of the atom, that is closest to the surface. This results in extremely high lateral resolution of an STM, which can routinely image single atoms or molecules. The disadvantage of an STM is the inability to image non-conductive surfaces.

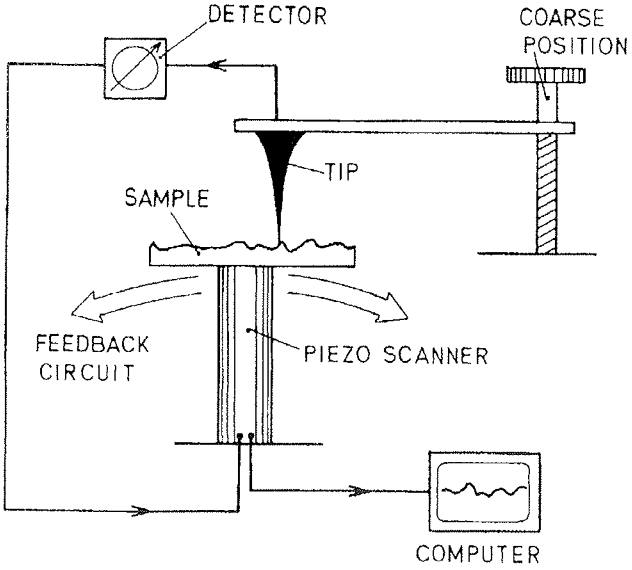

Fig.1. In an SPM, a small probe is scanned across the surface and is held in the close proximity to the surface. The distance between the probe and the surface is sensed and this information is sent to the feedback electronics. A piezoelectric scanner is used to position the sample, and the electronics adjusts in real time the vertical position of the sample, as the probe is scanned across the surface. The positioning signal is recorded as a function of the lateral position of the sample and this is a record of the sample topography in a single scanning line.

(ii) **Atomic Force Microscope** (AFM). In this instrument, the forces between a sharp tip and a surface are monitored as a function of the separation between a tip and a surface /3/. The AFM can therefore be used to image both conductive and non-conductive surfaces. At large separations, the force is zero. By approaching, we always reach a regime of some attractive (i.e. van der Waals) or repulsive (i.e. electrostatic) forces on the tip. The tip is mounted on a flexible micro-cantilever (see Fig. 2), and the bending of the cantilever is monitored by means of a deflection of a focused laser light (see Fig. 3). The force on the tip is calculated from the deflection of the cantilever, once we know the elastic constant of the cantilever. By further approaching the surface, a repulsive regime is reached, where the tip is in "hard contact" with the surface and Pauli exclusion principle gives rise to strong repulsion. The AFM can operate in two regimes: contact and non-contact. In the contact regime, the tip is in hard contact with the surface. The resolution of the AFM is in this case very high, although somewhat lower than in STM and one can routinely image flat surfaces with an atomic resolution (see Fig.4.). The non-contact regime is more suitable for soft surfaces. Here, the forces on the surface are smaller, but also the resolution is lower.

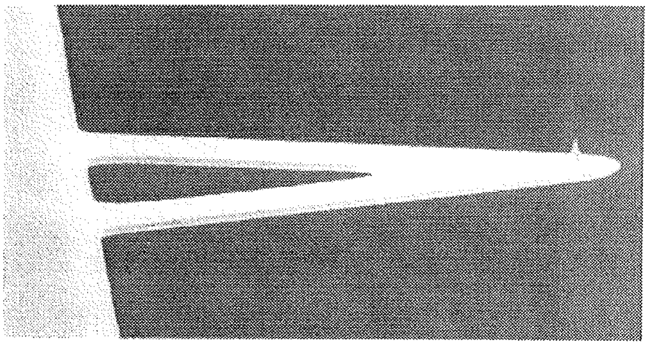

Fig. 2. AFM tip is mounted to a flexible cantilever (courtesy Park Scientific Instruments). The curvature radius of the tip is 10-20 nm

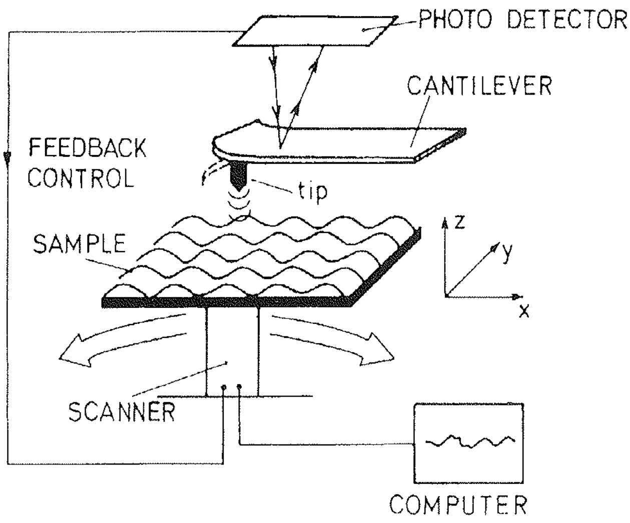

Fig. 3. The bending of the AFM cantilever is monitored via the deflection of a focused laser beam. A four-quadrant photodiode can monitor the deflection of the cantilever with an atomic resolution.

(iii) **Electric and Magnetic Force Microscope** (EFM and MFM). In this version of the AFM, the tip is made or coated either by conductive (i.e. highly doped Si) or ferromagnetic (Fe, Co) material. In the EFM, the voltage is applied to the conductive tip and one can measure the electrostatic forces due to charges on the surface. This particular technique is very suitable in the studies of fer-

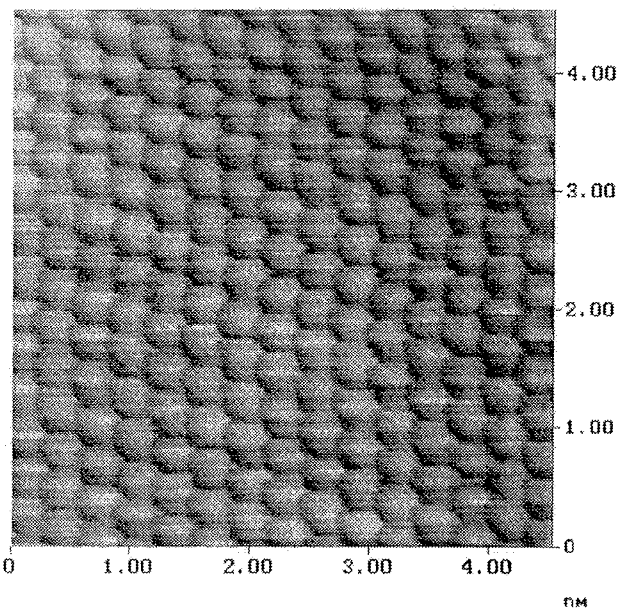

Fig. 4. Atomic resolution of an AFM on a freshly cleaved surface of $NbSe_2$*. Dimensions of the image are 4.5nm x 4.5nm. One can clearly see Se atoms. The image has not been filtered or modified graphically.*

roelectric and piezoelectric materials and one can image ferroelectric and piezoelectric properties of these surfaces with submicron resolution. The technique can also be used in testing electrical connections in microelectronic circuits. In the MFM, magnetic forces are measured between the ferromagnetic tip and the magnetic surface. The technique allows for submicron detection of ferromagnetic domains. We should also mention the Magnetic Resonance Force Microscope (MRFM) /4/ which was developed with the aim to spatially resolve chemical constitution of the surface. Here, the magnetic force is mediated by nuclear magnetization of specific nuclei, which is induced by NMR technique.

(iv) **Scanning Near-Field Optical Microscope** (SNOM) /5/. Here, a very sharp tip of an optical fiber is scanned at a close proximity to the surface. Optical signal from a transparent sample is collected by some mechanism, as for example near total internal reflection at a surface of the sample. One can therefore monitor variations of the dielectric constant of the surface with submicron resolution.

Whereas the mechanism of surface detection is different for the above mentioned microscopes, all of them reconstruct the image of the surface from data collected during regular scanning of the probe above the surfaces under imaging. Usually, the probe transverses the sample in a "zigzag" fashion, and the data are collected at regular time intervals. The scan rate (i.e. the inverse time for a single scan) can vary from 1 s to 1/100 of a second in commercial microscopes. In some cases, real-time imaging can be performed with a rate of several frames per second. The number of points, collected during a single scan is typically 512, so that an image can be taken typically in a time of one to several minutes.

3. Force spectroscopy in colloidal systems

Whereas imaging of surfaces is of prime importance for the monitoring of surface quality and topography, an Atomic Force Microscope is a powerful tool for measuring forces between surfaces in the presence of liquids. As an example, I shall here describe the application of AFM force spectroscopy to the forces in colloidal systems and to the study of mechanism of deposition of nano and microparticles from colloidal solution to the polymer surface. The technological problem is the production of conductive layers on printed wiring board (PWB) laminates, which are used during the through-hole metallization process in printed wiring board (PWB) laminates. The primary conductive coatings are usually chemically deposited and result in substantial production of hazardous waste. Water-based deposition of conductive coatings formed by densely packed mesoscopic particles of carbon black or graphite onto printed wiring board (PWB) laminates is a promising candidate for environment-friendly technology of PWB mass production /6,7/. There are two competing physical mechanism that have to be controlled in the process of deposition: (i) On one hand, the water dispersion of mesoscopic conductive particles has to be stable. For this purpose, surfactants are used, which adsorb onto the surfaces of particles. Due to dissociation, these surfactants become charged in aqueous solution and the resulting electrostatic repulsive forces between equally charged surfaces leads to stabilization of dispersion against van der Waals attraction. (ii) On the other hand, the electrostatic properties of particles in dispersion have to be near the point where the particles can approach the polymer surface to a certain minimum distance, so that coagulation and adsorption onto a surface can occur. This point is

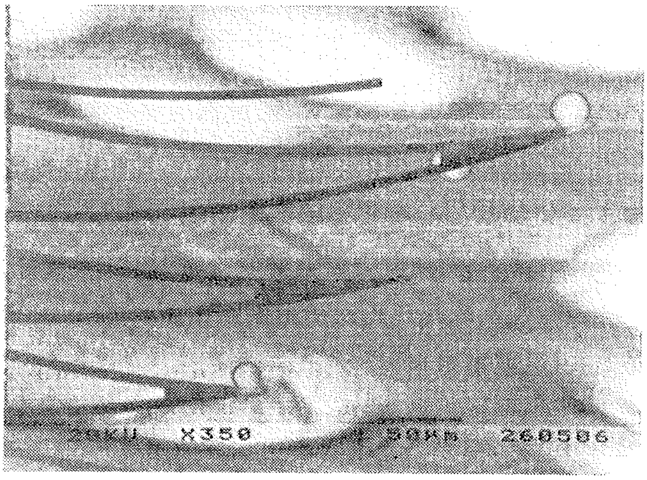

Fig. 5. For the study of colloidal forces, glass microspheres are attached on the AFM cantilever. The surface of the glass spheres can be coated or chemically modified.

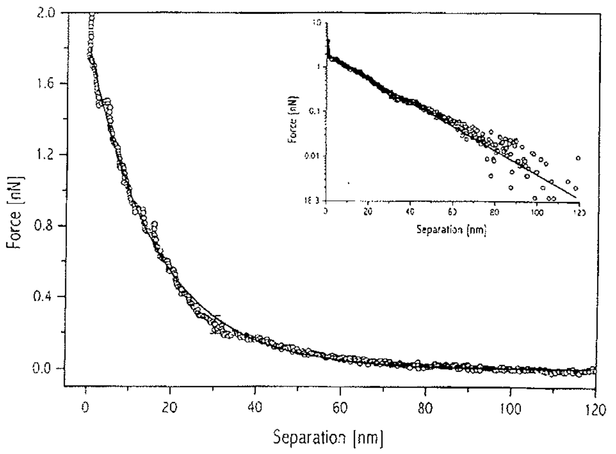

Fig.6. *Electrostatic double-layer repulsive force as a function of separation between the surfaces of a glass microsphere and mica in pure water. The inset shows the same data in log-lin scale with a linear fit yielding Debye screening length of 16.4(1±0.02)nm and the force amplitude 1.8(1±0.01)nN.*

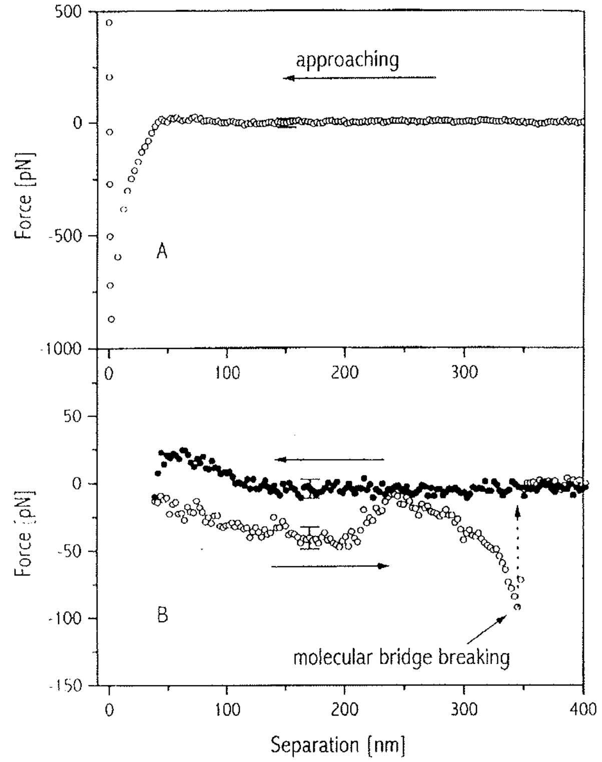

Fig.7. *The forces between gelatin-coated 15 μm glass sphere mica surface in pure water. (A) When full approach of the two surfaces is performed, one can observe electrostatic attractive double-layer force. (B) In the "fly fishing mode", approach of the two surfaces is stopped at a separation of 50-100 nm. When retracting, one can observe irregular, saw-tooth-like molecular bridging force between the two surfaces, mediated by the gelatin molecules.*

controlled by the appropriate addition of a salt (i.e. charged ions), which screens the electric field of the surfaces and allows particles to approach to shorter distances during their Brownian motion.

In the studies of forces in colloidal systems, the forces to the AFM tip are far too small to be measured very accurately. For this purpose, a microsphere made of glass or some other material is attached onto the cantilever (see Fig. 5) and the forces on this microscopic object are measured as a function of separation between the sphere and the surface. Fig. 6. shows the force between a 15 μm soda-lime glass sphere, attached to a AFM tip and a freshly cleaved mica surface in the presence of pure water. The force is electrostatic repulsive and decays exponentially with increasing separation. The surfaces of glass and mica are both negatively charged in pure water and the corresponding electrostatic force is repulsive. In the next step, a thin layer of gelatin was adsorbed onto the glass sphere. The interaction forces between a freshly cleaved mica surface and gelatin-coated sphere in pure water are shown in Fig. 7. Here, the so-called "fly fishing mode" approach of the sphere was applied, where the approaching was stopped at a given separation to the surface and the AFM probe was then retracted. Although the two surfaces obviously did not come into a hard contact, there is some small attractive force between the two surfaces, when the sphere is moved away. This force is interpreted as a molecular bridging force, mediated by the gelatin macromolecules. The gelatin layer on the glass surface is "hairy" and expands with randomly coiled loops and tails deep into water. When this "hairy" interface is brought into a certain minimum distance from the bare mica surface, gelatin molecules are adhered to the mica surface and create molecular bridges between a sphere and a surface. These bridges are observed upon retracting the sphere from the surface, as they are irreversibly broken by the external pulling force and the heat is dissipated at the interface. In spite of relative weakness of this molecular bridging force, the range of the force is as large as several hundreds of nanometers, and a binding energy for a micrometer sphere is several thousands of k_BT.

This simple example clearly shows the power of force spectroscopy in colloidal systems. In my opinion, many interesting applications of force spectroscopy will be developed in near future. In particular, molecular-specific interaction and molecular recognition on the basis of force spectroscopy will play a very important role in biosensors and molecular-specific devices /8/.

4. Conclusions

It is not easy to give any conclusions in the field, which is so rapidly developing, as the SPM community over the past ten years. However, it is more or less clear, that several important fields are emerging, that would play substantial role in tomorrow high technology: (i) SPM methods in micro and nanoelectronics will play the role of a basic tool for testing and controlling the technological parameters. (ii) piconewton and sub-piconewton force-oriented devices and sensors will play an important role in molecular recognition, detection and imaging. (iii) SPM oriented devices and methods will play an important role in nanotechnology. Molecular structures

will be tailored, produced and analyzed with subnanometer precision. (iv) SPM based nanodevices for high density information storage will be developed. For more specific information, the reader is advised to visit:
http://www.di.com/;
http://www.nanonics.co.il/fs _products.html;
http://www.pacificscanning.com/;
http://www.molec.com/.

5. ACKNOWLEDGMENT

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