PROBE TECHNOLOGY APPLICATIONS AND MOLECULE-BASED DEVICES

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As early as in 1987 the first in Russia technological STM has been created by collaborators of our centre which allowed not only to carry out visualization of a conducting surface, but also to realize its modification. By means of this device it was already possible to observe responses of separate atoms of crystal lattice of high oriented pyrolytic graphite in ambient conditions. For the present moment the centre has the whole range of scanning probe microscopes which mainly is given by the Russian company NT-MDT, one of the world leader in this area. Among thr centre equipment the scanning probe microscope (later SPM) for carrying out of precision lithography (it is supplied by active system of drift struggle), three universal SPM, five scientific training SPM "Nanoiducator" composing unique laboratory class for the students work, two home-made scanning tunneling microscopes till now allowing students to obtain the atomic resolution on a HOPG, equipment of molecular conductors formation and other. In the near future the installation of the first in the centre ultra high vacuum SPM in structure of nanotechnology facility "NANOFAB" with focused ion beam (FIB) and molecular beam epitaxy (MBE) blocks is planned.

Before to pass to centre achievements in the field of probe nanotechnology, we will pay attention to the most obligatory component of these technologies – to the probes itself. The probe is our intermediary in the nanoworld, and its parameters and properties define problems that accessible to our solving. On character of interaction with investigated object two most basic types of probes are allocated: atomic force and tunnel probes. The first necessarily have a cantilever beam as an element sensitive to force of interaction. Its typical material is silicon. Special coverings, such as platinum or cobalt, are usually applied to maintain conductivity or magneto sensitivity correspondingly. The preparation method is etching from silicon substrate and it provides the typical curvature radius on the order of 10 nm. For aspect ratio increase the nanotube-based probes are applied. Platinum/iridium probes prepared mechanically and tungsten probes prepared by a method of electrochemical etching basically are used as tunnel probes. Platinum/iridium probes have such advantages as simplicity of preparation, and absence of surface oxides, however the geometry of their top in general is arbitrary, while tungsten probes have reproducible curvature radius and aspect ratio. For tungsten probes obtained in our conditions the curvature radius and aspect ratio are on the order of 15 nanometers and 30 degree correspondingly . Probes of all listed types are used in our center.

The first on time of appearance, but not the last on importance probe technology application is visualization of objects in micro and nanoscale. Here the atomic force microscopy (later AFM) has that advantage that allows to work anyhow practically with any objects on any substrates while the scanning tunneling microscopy (later STM) require exclusively conducting objects, however provides ultra high resolution.

The next most obvious, that probe technologies allow to do, it to pass from visualization (small intensity of interaction) to a manipulation by objects (by increasing of interaction intensity). For a tunnel microscopy it can be capture and transportation along a substrate of separate atoms or molecules, however, for conditions of room temperature and atmospheric pressure, more suitable an example of nanotube manipulation in atomic force mode. By means of probe it is possible to move, to bend nanotubes, to create local defects in them, down to full break. Creation of electric contacts between nanotubes and conducting paths is one of the interesting examples of such manipulation.

In that case when the probe of atomic force microscope exerts the influence under which the object of manipulation undergoes irreversible changes, the special term - " force lithography " is used. By means of force lithography it is possible "to print" images on substrates whose hardness concedes to hardness of material of the probe. Often force lithography is necessary for opening internal properties of a sample (as example - breaking up of one of the knobs shows the viscous state of knobs' inside, that indicated by sudden change of adhesion on the phase scan). Another Interesting example of force lithography application is modifying a catalyst film with the purpose of creation of mechanically intense areas which would be the center of NT growth at the subsequent catalytic pyrolysis of coaly gas.

Except for mechanical influence in case of force lithography, the probe can exert electrochemical influence on the sample, causing the anodic oxidation in the localized area. It is remarkable, that the given operation is accessible both for conducting atomic force and for tunnel probes. Depending on an the oxidized material, result of oxidation can be in creation of areas with oxide or areas with removed material. The last in case of volatile oxidation products witch take place for example in carbon oxidation. Natural air adsorbate always presenting on surfaces in ambient conditions plays the important role during oxidation process since it serves as a source of oxygen ions. Therefore there is a tendency of increase of oxidation process intensity with increase of relative humidity of air.

Having applied the local anodic oxidation, it is possible to obtain the structures of reduced dimension from standard lithography prepared paths, in particular quasione-dimensional channels whose conductivity shows sensitivity to external electric fields. The experimental device has been developed which can be considered as the prototype of a field effect transistor on the quantum wire basis. The quasione-dimensional channel is obtained by cutting side areas of an initial metallic thin-film cross. The isolated areas of the cross can play a role of side gates.

The results considered above were reached by means of atomic force microscopy. Use of tunnel microscopy favours achievement of greater resolution. At the same time high oriented pyrolitic graphite represents special interest as modified object since its layers represent the extremely ordered structures of the lowered dimension with the ballistic mechanism of conductivity (I.e. have the same advantages as carbon nanotubes only in the unrolled variant). It is necessary only to cut out from them the structures of required geometry. Attempts of such cutting by methods of tunneling microscopy have led to achievement of greater resolution then in atomic force mode.

In the world scientific search there is a promising direction based on attempts to use separate molecules as element base of electronic devices. The interest to this direction is caused by unique perspectives which open in case that molecular assemblies can be really used as functional elements. So the extremely high degree of integration and frequency of work are predicted. Besides molecules in itself are already a product of processes of self-organizing and having applied them as functional elements we obtain ideal reproducibility of the lasts. In order to create molecular conductor in polymeric matrix using an external electric field, it is necessary to provide for several conditions. First, the dipole-dipole interaction energy must exceed the energy of thermal breakage of the molecular channel, which implies that there exists a critical field for the channel formation. Second, the electric field must have a "channel-like" or axis configuration whereby the longitudinal field component is maximum at the axis and rapidly decays in the radial direction. Third, it is necessary that the linear molecules would possess reactive ends and be capable for formation of long conducting channels owing to dipol-dipol interection. Such conditions were provided between a flat metal substrate surface and a tungsten probe with a tip radius below 20 nm in a drop of epoxy diane resin. Epoxy resin is liquid dielectric and consists of sufficiently long extended molecules with two benzene rings per monomer. It possesses a residual bulk resistivity on the order of 1010 Ohm·cm. By gradually moving the probe away from the substrate, it was possible to grow vertical molecular conductors up to 500 nanometers in length. had been obtained by the above described method. Its resistance has from 1 up to 10 Ohm depending on geometry of the probe and the mode of germ formation. If to estimate the equivalent conductivity of such channels the value obtained at least on 20 orders will exceed conductivity of an initial polymeric matrix.

Hardening of polymeric matrix excludes destruction of the molecular channel by thermal movement, and also allows to exert on it the certain mechanical influence, by means of volumetric expansion of the matrix at its heating by an external source. On the time dependences corresponding to the given process the series of spontaneous step switchings of structure resistance were observed, consistently translating structure from low to high-resistance state. Characteristic features of the switchings well agree with the assumed mechanism of channel formation from a set of parallel molecular bridges which serial switching causes observed step changes of resistance. Each step, thus, holds the information on the contribution to the general conductivity of the channel of the corresponding molecular bridge (or groups of bridges if switching was collective). The obtained resistance of one molecular bridge is sufficiently agrees with fundamental quantum of ballistic resistance $h/2e^2 \approx 13$ Kohm. There is also another evidences of ballistic conductivity in this molecular bridges concerned with joule heating estimations and resistance-length independence.

In order to obtain planar molecular conductors, we used multiwalled carbon nanotubes (or their bundles) as electrodes providing the conditions formulated above. These nanotubes were placed between conductive paths and cut (mechanically or electrically) with the aid of the probe of an atOmic force microscope. The obtained gaps ranged from 20 to 500 nm. The field between such electrodes had the required “channel” configuration. After epoxy resin penetration into the structure application of a potential difference of up to 10 V to the gap between nanotubes led to the appearance of electric current in the circuit, which indicated that a molecular conductivity channel was created in the gap. Owing to a planar character of the channel, the molecules constituting this channel are subjected to orienting action of the substrate. This factor accounts for the stability of the channel in the absence of a drain-source voltage. Since the diameter of nanotube electrodes is on the order of 10 nm and the applied voltage is on a level of several volts, the fields generated at the ends of such electrodes reach 108-109V/m and are sufficient to provide the cold electron emission at a high current density. Electrons emitted with an energy exceeding 5 eV can produce rupture of the intramolecular bonds of the epoxy resin. TherefOre, it is not excluded that the molecular chan- nel formed between carbon nanotubes may contain fragments of the molecules of the epoxy resin and residual impurities. It was found that the conductivity of the molecular channel could be controlled using the third electrode situated under a silicon oxide layer of the substrate so that the experimental device exhibits the properties of a field-effect transistor. It should be noted that multiwall carbon nanotubes played the role of electrodes and did not show any significant ability to control the regime. Upon a sharp change in the control field (e.g., switching the gate voltage from -20 to +20 V with a transient time on the order of 0.1 ms) the conductivity disappeared. In order to restore the conductivity, it was necessary to apply again a drain- source voltage of about 10 V. In these regimes, the experimental device exhibited the properties of an energy-independent memory cell or molecular switch. We believe that the observed experimental behaviour can be explained by considering the micromechanics of molecules in external electric fields. The longitudinal electric field aligns macromolecules and favours the formation of linear conducting molecular bridges (evidence for rather high linearity is provided by the ballistic transport regime observed in an analogous vertical structure). The transverse field of the gate probably produces partial reorientation of the molecules. However, questions concerning the particular mechanism of conductivity modulation in the molecular channel still remain open.