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Visualization of conducting channels in polymer layers by atomic force microscopy with a conducting probe

© V.M. Kornilov,[1] A.N. Lachinov,[2] A.R. Yusupov[1]

[1] Bashkir State Pedagogical University named after M.Akmulla,
450008 Ufa, Russia
[2] Institute of Molecule and Crystal Physics, Ufa Federal Research Centre, Russian Academy of Sciences,
450054 Ufa, Russia
e-mail: kornilov@anrb.ru

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The results of an experimental study of the local electrophysical properties of ultrathin polymer films by atomic force microscopy with a conducting probe are presented. It is established that visualization of current flow sites (conducting channels) is possible in areas from which the surface layer has been mechanically removed. The conducting channels in the current image have the form of individual points with a height corresponding to the locally flowing current. It is found that the location of the observed channels correlates well with the model of conductivity along the grain boundaries of the supramolecular structure of the polymer.

Keywords: thin polymer films, atomic force microscopy with a conducting probe, conducting channels, supramolecular structure.

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Introduction

Development of modern micro- and nanoelectronics is mainly caused by the demands of the modern information technologies, that require development of increasingly more spacious and quick-operation devices for information recording and storing with a possibility of rewriting and energy independence. Along with traditional types of memory devices (dynamic, static and flash drives) there is an increasing attention to resistive memory, that combines benefits of quick random access memory with energy independence of a programmable memory. This type of memory is based on metal-insulator-metal structure, in which the reversible and sharp change of dielectric layer conductivity can be implemented — the resistive switching effect. Described effects were observed and researched in many composition classes, including non-organic [1–4] and polymeric layers of sub-micron thickness [5,6].

Literature analysis shows that only resistive switching caused by electric voltage is described in papers (transition into high-conduction state). In review [7] the results of research of resistive switching effects in sub-micron polyheteroarylene films, induced not only by electrical field, but also by uniaxial pressure, traps thermoionization, electronic or ionic radiation, magnetic field, change of boundary conditions on metal-polymer interface, are presented. Potential of usage of such thin-film elements, electrical conductivity of which can be controlled with small external influence, in electronics is obvious. At the same time the issue of resistive switching mechanism in dielectric (polymer) films is directly related, first of all, to quality and internal structure of the film, and, secondly, to injection and contact phenomena on electrode-polymer interfaces.

The resistive switching mechanism, involving conducting cords (filaments) forming in dielectric layer, was proposed for the first time in [8]. Cords may break and no longer contribute to conductivity, under appropriate conditions the cords may re-appear, and this provides the main property of resistive switching: the reversible transition from low conducting to high conducting state. By now the assumption on current filamentation during switching is considered common almost for all materials, in which the resistive switching is observed [9]. Historically, several terms were used in books for designation of conducting sections in dielectric layer: cords, threads, filaments, channels. In this paper we use the „conducting channels“term.

Therefore, there was a task to experimentally research the local electrophysical properties of ultrathin dielectric polymer films by atomic force microscopy (AFM) with a conducting probe. This method allows to perform simultaneous mapping of a surface morphology and registration of electrical inhomogeneity in polymer films [10,11]. The intention was to understand if there are initially any specifics in polymer layer, favorable to current flow at resistive switching, or charge transfer starts as a result of external influence on polymer. Therefore, at this step the polymer film, that was not exposed to additional influence, has been researched. Of course, it is impossible to exclude factors, caused by scanning parameters: force of contact interaction of the probe with a sample and applied voltage, they should be considered at results interpretation.

1. Experimental procedure

Electrical parameters research modes are made as a set of additional software and hardware means, that are connected to basic systems of scanning multi-microscope SMM-2000T. As a result, simultaneously with registered topographic map the point-to-point reading of additional maps, corresponding to this topography, is performed. Additional maps contain information on electrical potentials or electrical conductivity with localness of data reading up to Angstrom units. Standard single-pass procedure of topography scanning in contact mode with simultaneous measurement of current, flowing through cantilever, was implemented. During experiment the AFM-cantilevers of „GOLDEN“ CSG10 series with conducting coating PtIr, intended for operation in contact mode and made by NT-MDT company, were used. Cantilever is mounted on AFM-stage of SMM-2000 microscope, electrically isolated from the device housing. Voltage supplied to the sample by the basic microscope system was controlled from a control panel of STM mode in a range from -5 to $+5$ V with accuracy of up to 1 mV. In each scan point the current was measured, in correspondence with which the current map was formed (i.e. image that is obtained simultaneously with basic AFM-image).

For research using AFM method the polymer films of polydiphenylenephthalide (PDP) on polished substrates of stainless steel were manufactured using procedure described in [12]. Films thickness was set by polymer concentration in a solvent — cyclohexanone. For determination of films thickness and their internal structure the deepening was made to substrate surface using copper micro-cutter. Deepening wall was made as a step with a height equal to the required thickness.

2. Research results

At the first stage the initial sample surface images were observed, made simultaneously in AFM mode (constant force maintaining) and current registration mode for current, flowing in the place of conducting cantilever contact with the sample. As a result of multiple researches it was observed that in constant force maintaining mode the current specifics are not registered in the area under research. This is because the initial polymer film (sample) is complete and uniform in terms of thickness (in this experiment – 115 nm) and exhibits good dielectric properties. Therefore, during operation in the mode of maintaining the constant force of cantilever interaction with the sample, current does not flow through the film and current specifics are not registered on current flow map.

Therefore, the attempt was made to artificially create the deformed sections of polymer film not on full depth. This would allow to obtain the image of not a surface, but internal structure of a polymer. Properties of surficial region of polymer layers usually differ from properties of polymer inside the layer. In particular, it is known that side functional groups of polymers are oriented mainly normally to polymer-air interface. It was assumed that removal of the surficial layer allows to observe the distribution of flowing currents in the mode of constant force of cantilever interaction with the sample.

Fig. 1, *a* shows the appearance of the deformed section of polymer film (surface morphology). Left and lower parts of the image correspond to metal substrate, that became visible after removal of polymer film part as a result of mechanical deformation. In the upper right part there is a polymer film section, remaining on substrate surface. Cross-section profile along measuring line (shown on the image) allows to define the height difference between substrate surface and film surface, i.e. film thickness (114 nm in this experiment). Fig. 1, *b, c* shows images obtained simultaneously from the magnified section of Fig. 1, *a*. Image in Fig. 1, *b* is typical for internal (supramolecular) structure of polymer film. The corresponding cross-section profile allows to define the geometrical dimensions of the structure elements inside the film. Fig. 1, *c* is a map of a flowing current distribution. It can be observed that there are specifics on the current image, looking like small bright dots. There are no such dots on the geometrical image (Fig. 1, *b*), arrangement of dots correlates with the boundaries of the image element, shown on both figures.

Image in current mode is a two-dimensional distribution of flowing current value for the whole array of surface dots under research. Current specifics of the image are presented as sharp spikes, which height corresponds to the flowing current value. Fig. 1, *d* shows the magnified image of the section with conducting channels and cross-section profile. Maximum current value is 14.37 nA, channel cross-section is about 4.5 nm. Under multiple scanning, especially when image is magnified, there is a change of current specifics value and their arrangement shape (Fig. 1, *e*). Apparently, it is caused by degradation of polymer layer at repeated, although small influence of the cantilever. Value of current measured in one of the peaks was 69.13 nA, channel cross-section is about 4.5 nm.

3. Results discussion

Thus the experimental study of ultrathin polymer films on metal was performed using atomic force microscopy method with the conducting probe. AFM-image is a result of simultaneous conduction of several processes. Some processes are set by hardware and can be controlled (presence or lack of feedback, value of force of cantilever interaction with the sample, value of voltage on the conducting probe, scanning speed, etc.). There are also several factors, that impact the final image and that are caused by the specifics of the objects under research.

It was observed that polymer film thickness is about 115 nm, and structure element size in the deformed region is about 90 nm (Fig. 1, *a, b*), that agrees with the results,

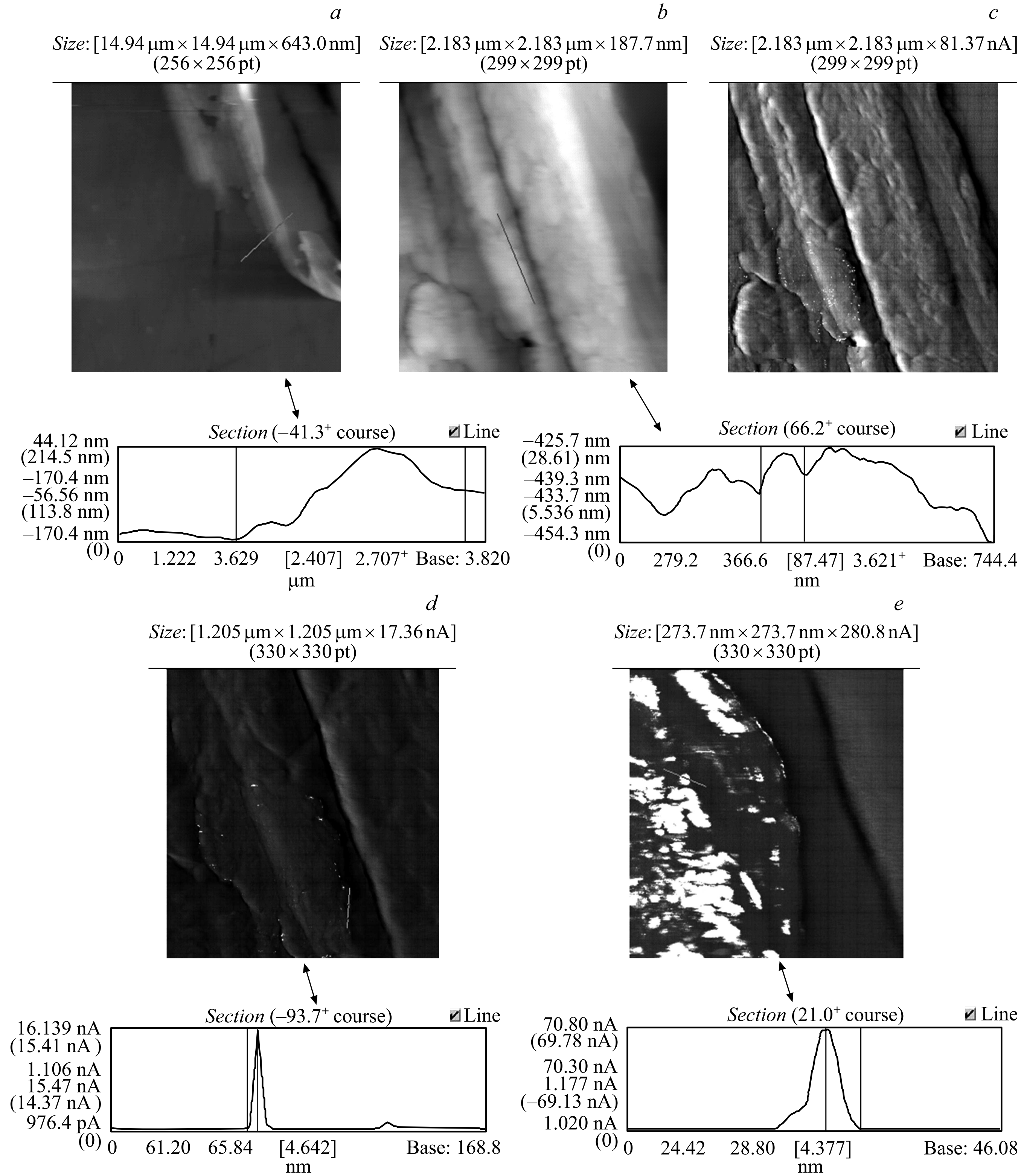

Figure 1. Series of AFM-images of deformed polymer film at various scale of magnification: *a* — general view of deformed section and cross-section profile, polymer film thickness is 114 nm; *b* — magnified view of internal structure of polymer film and the corresponding profile, structure element size is 87.5 nm; *c* — image of conducting channels on current map, corresponding to the surface topography in Fig. 1, *b*; *d* — magnified view of a section with conducting channels and cross-section profile; *e* — the next stage of image magnification and cross-section profile.

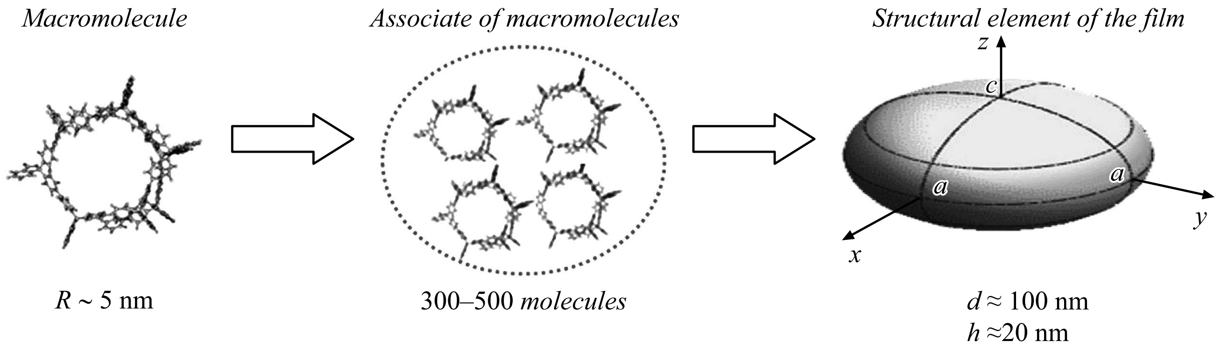

Figure 2. Assumed process of supramolecular structure forming.

observed earlier, in terms of the order of value [13]. To observe the current specifics inside the polymer layer in the mode of the constant interaction force maintaining, the deformed sections of polymer film were artificially made not on full depth of polymer film, i.e. the surface layer was removed. In this case it was possible to register the current specifics as bright dots located nearly within the image section (Fig. 1, *c*-*e*). Arrangement of the current specifics (conducting channels) is mainly remained at scaling and repeated scanning. Value of current, measured in a separate conducting channel, significantly changes, while channels cross sectional dimensions remain within 4–5 nm. At larger magnification of the image the measured current value does not change, but the image becomes unstable and poorly reproduced. Apparently, this is caused by increase of intensity of cantilever interaction with the sample and degradation of polymer surface.

With polymer film thickness of 115 nm and voltage of 5 V applied to cantilever tip there is no film electric breakdown. Values of currents, flowing through the separate channel, are within a range from fractions of nA to dozens of nA. The approximate evaluation of value of current density, locally flowing through a certain conducting channel (image and profile in Fig. 1, *c*), gives a value of about 10^9 A/m^2. Electrical resistance of this channel is 347 MΩ, while specific resistance is 0.033 Ωm. It should be also noted that the current specifics are located only within a surface section of about $0.8 \times 0.5\,\mu$m, while their configuration and intensity do not depend on polymer layer thickness. It can be said that inside the polymer film (after surface layer removal) the sections of submicron size are registered, within which there are nanosized conducting channels. However the influence of the conducting probe of the microscope does not result in generation of new channels, the boundary between the section with conducting channels and surrounding dielectric matrix is clearly detected at image upscaling.

Since the measurements of conductivity of the sample under research were performed under normal conditions, the presence of water film on polymer surface and voltage applied on the tip, significantly exceeding 0.5 V, can result in local electrochemical reactions [14], that, in their turn, can be one of the reasons of the observed variations of the measured current flowing map at repeated scanning. The more precise evaluation of electrochemical reactions influence for the purpose of its complete elimination will be the one of the tasks for the further experimental studies.

According to the modern classification the resistive switching can be described in terms of conducting path type [9]. The first type corresponds to threadlike (filamentary) conducting path, under which the resistive switching is performed as a result of appearing and breaking of conducting threads in an insulating matrix. The second type of conducting path corresponds to the interface type mechanism, under which the resistive switching is performed at the interface between metal electrode and dielectric. This switching mechanism is usually related to resistive switching of bipolar type observed in semiconductor oxides. Change of macromolecule conformations is also considered as switching mechanism in polymeric resistive memory devices jcite6. Some non-conjugated polymers, containing carbazole groups in a side chain, such as derivatives of poly(N-vinylcarbazole), can demonstrate electrically induced conformational changes between random and regioregular structure, thus resulting in change of conductivity state [15].

In any case the conducting channels forming is surely caused by the structure and properties of the corresponding dielectric (polymeric in our case) matrix. Studies [12,13] show that in case of smooth and even external surface the polymer film of PDP is internally structured, while internal structure (supramolecular structure) of films is associated with macromolecules association in initial solution. Before that, using mathematical model methods, it was observed that the most energetically favorable configurations of PDP macromolecules are linear syndiotactic and spiral isotactic. Polymer molecules with spiral structure in initial solution combine into associates with the preferred orientation of side fragments on the surface of the associate. Particularly, for polyheteroarylenes the side fragment is a phthalide one, one of bonds of which can be polarized at low energy electron capture.

Fig. 2 shows the schematic representation of the process of supramolecular structure forming in PDP film.

When forming a film from a solution, under quick solution evaporation the associate structure is fixed, while boundaries between associates act as interfaces between polymer surfaces with the preferred orientation of dipole moments. Processes, performed in such structures, are currently actively studied in non-organic and organic crystals, as well as on polymer-polymer interfaces. Interfaces of complex oxides demonstrate a wide range of effects [16], such as high mobility of carriers and high values of carriers concentration; superconductivity and giant magnetoresistance are also observed. As it was observed earlier [17], many things in the observed effects are defined by the mechanisms of interface region forming, including the sequence of atomic layers and related nature of dipole alignment near interface [18]. Model of „polarization catastrophe“, used for explanation of conditions for two-dimensional free electron gas appearing, appeared to be sufficiently credible and efficient [17]. Particularly, the studies were published, where the similar effects were observed along interface of organic crystals [19] and amorphous polymer films [20, 21].

Within the interface, existing at boundary line of two PDP films, the layer appears with anomalously high conductivity, that is caused by two-dimensional electronic system, formed by the layer of surface-oriented side phthalide groups with high dipole moment. The defining mechanism in conducting interface forming at boundary line of two polymer dielectrics is a surface polarization caused by spontaneous dipole alignment of side phthalide groups. Local field, formed by these dipoles, creates favorable conditions for charge transfer in interface area, as evidenced by high mobility values [22]. Charge transfer through nanosized conducting channels is apparently implemented in correspondence with general idea on injection current filamentation [23]. Visualization of conducting channels is a good basis for detailed research of electrophysical properties of a separate channel, and this is a subject of further studies.

Conclusion

The study allowed to receive new experimental data on local electrophysical properties of thin polymer layers. We visualized the nanosized conducting channels in dielectric polymer matrix. Methods of AFM with the conducting probe allowed to define linear dimensions of conducting channels, value and density of current in channels.

Simultaneous observation of places of current flowing and polymer supramolecular structure allowed to use the model of conducting interface forming at polymer dielectrics boundary for the effect describing. Observed data are important for results interpretation of electrophysical measurements in submicron polymer films and allow to make an intentional influence on composition and supramolecular structure of polymer during resistive switching properties studying.

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Conflict of interest

The authors declare that they have no conflict of interest.

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