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On the Contrast of the Terrace Conductivity of Graphite

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Abstract—The recently developed technique of scanning resistance microscopy (SRM) has recommended itself as a high-precision tool for the investigation of surface conductive properties. It is different from conventional atomic-force microscopy in its ability to obtain simultaneous data about both the topography and contact resistance of a probe and sample. This method was used for investigation of the conductive properties of highly oriented pyrolytic graphite (HOPG). A series of experimental facts testifies that the field of application of SRM during the performance of nanoobject research on graphite substrate is restricted by the surface of atomic plateau. This is connected with the fact that during crossing of atomic steps the state of contact of the probe and sample changes, which has a great influence on its conducting properties.

Keywords: graphite, HOPG, scanning resistance microscopy.

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INTRODUCTION

The basic and applied interest in carbon materials is connected with their unusual physical properties. In particular, graphene and carbon nanotubes, materials with unique electronic properties, are considered as an alternative to silicone, the material that is the basis of the modern electronics. With the use of carbon materials transistors, field emitters, highly sensitive sensing cells, and other devices have already been prepared [1–3]. In probe microscopy highly oriented pyrolytic graphite (HOPG) deserves special attention. Graphite crystals have a layered structure and at cleavage form atomic-smooth surfaces of significant extent that are stable in air, which can be very conveniently used as the substrates for the study of fullerenes, DNA, viruses and many other nanoobjects. Its conductivity and hydrophobicity make HOPG extremely attractive as an electrode for electropolymerization (for example, aniline [4]) and electrodeposition of nanowires of various alloys [5].

The ideal instrument for investigating the conducting properties of HOPG is scanning resistance microscopy (SRM). The principles of operation of the atomic-force microscope (AFM) are the foundation of SRM, but, in addition to topography the current flowing through the probe contact with the sample surface is measured [6]. SRM allows one to study the conducting properties of a surface with high spatial resolution. It is convenient to use it, for example, when investigating the wear of conducting films [7] or study the ageing process of Li–ionic accumulators. With the use of the scanning resistance microscopy method the difference in conductivity of atomic plateaus on graphite was detected [9]. In [10] the geometry of the contact between a probe and sample is assumed to be unchanged during scanning of HOPG, hence, the contrast of plateaus in SRM is connected with the inhomogeneity of the sample surface properties, in particular, with the difference in mobility of the electrons at various plateaus.

In the present work it was shown that for HOPG the above-mentioned assumption is not always correct. Thus, during transition through the atomic step the modification of the probe tip exists, which is one of the causes of the contrast of the atomic plateau on graphite that is observed in SRM.

EXPERIMENTAL

Freshly cleaved highly oriented pyrolytic graphite with a mosaic angle of 0.8° and 0.4° was used in the investigation. A commercial cantilever fpC-10 with Pt coating was used. According to the manufacturer's estimates, the radius of curvature of the needle is ~35 nm, with a rigidity of 0.1 N/m. Measurements of the conducting properties of the graphite surface were performed via the scanning resistance microscopy method on a FemtoScan scanning probe microscope (Advanced Technologies Center, Russia). In AFM the force of the interaction of the probe with the surface was measured by the beam flexure that was determined using a laser ray and a photodiode, and in SRM the current I flowing through the contact of the probe with the surface during sustained constant stress was inde-

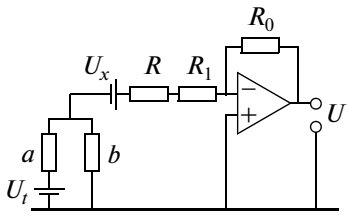

Fig. 1. Equivalent electric circuit of a microscope. U_t is a given voltage, U_x is the bias voltage that appears during contact because of the emission of electrons and the influence of laser radiation, U is the output voltage, R_0 is the feedback resistance, 1 GOhm; R is a calculated resistance, it includes the resistance of probe, contact and additionally included resistor of 1 MOhm; a = 14 980 Ohm, b = 15.8 Ohm are the resistances in the resistive divider.

pendently measured using a linear operational amplifier. Thus, we simultaneously obtained the relief and picture of the distribution of the spreading resistance for the investigated surface. Scanning was performed in the mode of constant force.

1.1. Calculation of the Measured Resistance

The electrical circuit used to measure the resistance of the contact probe–sample is presented in Fig. 1. The current flowing through the contact is connected with the output voltage by the ratio $I = U/R_0$; the circuit calculation gives

$$R = \frac{b}{a+b}\left(\frac{U_t}{I} - a\right) + \frac{U_x}{I}. \quad (1)$$

An unknown bias voltage U_x can be found taking the dependence $I(U_t)$ at the point, since $I(U_t) = \dfrac{\dfrac{b}{a+b}U_t + U_x}{R + \dfrac{ab}{a+b}}$, so at the point U_t^0, where $I(U_t^0) = 0$ we obtain $U_x = -\dfrac{b}{a+b}U_t^0$. As the experiment shows, U_x almost does not change after the setting of the laser and landing to the sample. The appearance of the bias voltage is connected with the heating of the contact area by the laser ray and the emergence of the thermal electromotive force. The measured resistance includes the following components: probe resistance, resistance of the probe and sample contact, resistance of the sample and the resistance of the remaining elements of the electric circuit, which is negligibly small.

1.2. Estimation of Probe and Sample Resistance

According to the form of the probe and the properties of its conducting coating, its contribution to the resistance can be estimated. For this we present the probe as the sequence of three resistances: beam resistance, resistance of the coating of a truncated tetrahedral pyramid, and the resistance of the contact area.

The beam resistance is

$$R_{\text{beam}} = \rho\frac{L}{Dd}, \quad (2)$$

where L is the beam length, D is its width, d is the deposition width, and ρ is a specific resistance of the conducting coating.

The resistance of the contact area is

$$R_{\text{area}} = \rho\frac{d}{\pi r^2}, \quad (3)$$

here r is the point curvature.

The resistance of the deposition on the pyramid is calculated by

$$R_{\text{pyr}} = \int_H^h \frac{\rho\,dx}{S(x)} = \int_h^H \frac{\rho\,dx}{Ax+B} = \frac{\rho}{A}\ln\left(\frac{AH+B}{Ah+B}\right), \quad (4)$$

where H is the pyramid height with the cut part, h is the cut part height, Ax is the area of the rectangles in the section of the pyramid by the horizontal plane (Fig. 2). $A = \sum d\cos\varphi_{ij}\sqrt{\tan^2 i + \tan^2 j}$ is the area of the triangles for the angles of the rectangle of the section, $B = \dfrac{d^2}{2}\sum\cos\varphi_{ij}\cos\varphi_{jk}\tan\left(\dfrac{\tan i + \tan k}{\sqrt{\tan^2 i + \tan^2 j}\sqrt{\tan^2 j + \tan^2 k}}\right)$, φ_{ij} is an angle with the vertical of the face whose edges make i and j angles with the vertical:

$$\cos\varphi_{ij} = \cos i\frac{\sqrt{\tan^2 i + \tan^2 j}}{\sqrt{\sin^2 i + \tan^2 j}}; \quad i,j = \alpha, \beta, \gamma, \delta.$$

Substituting the characteristic values of the parameters for the platinum cantilever in Eqs. (2)–(4) we obtain 35 Ohm.

The resistance of the graphite sample itself is less than 100 Ohm. The resistance measured in the experiment has characteristic values of 0.7–100 MOhm. Consequently, the main contribution is given exactly by the contact resistance.

RESULTS AND DISCUSSION

We determined that the graphite surface does not uniformly conduct, but it consists of parts with various conductivities, at various plateaus of graphite various contact resistances are observed. A typical picture of the graphite surface obtained with the use of SRM is presented in Fig. 3, the lighter parts correspond to greater height in topography, greater current and, consequently, greater conductivity in the SRM image. It was found that the distribution image of the contact resistance for the same area on the surface of graphite changes during changes of scanning direction. During forward motion the probe moves from the right to the

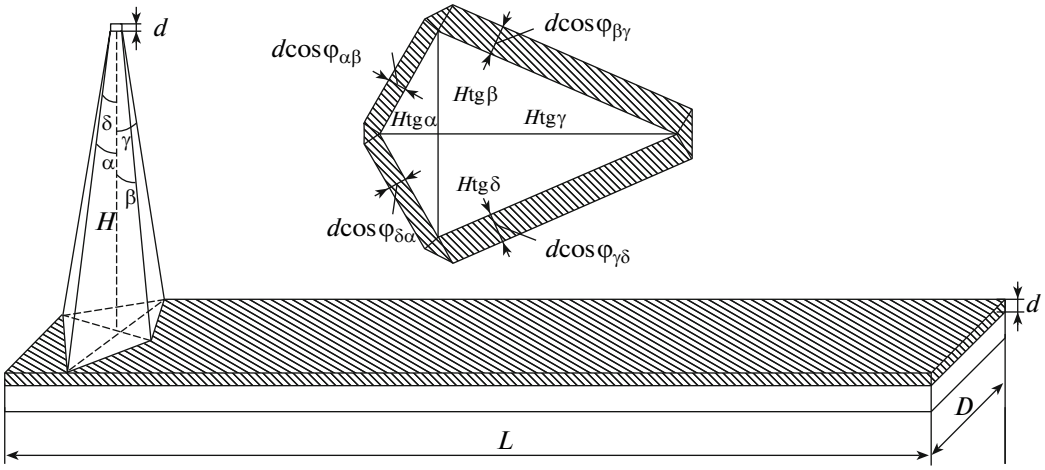

Fig. 2. The calculation of cantilever resistance. Above, the section of a pyramid by the horizontal plane at its base.

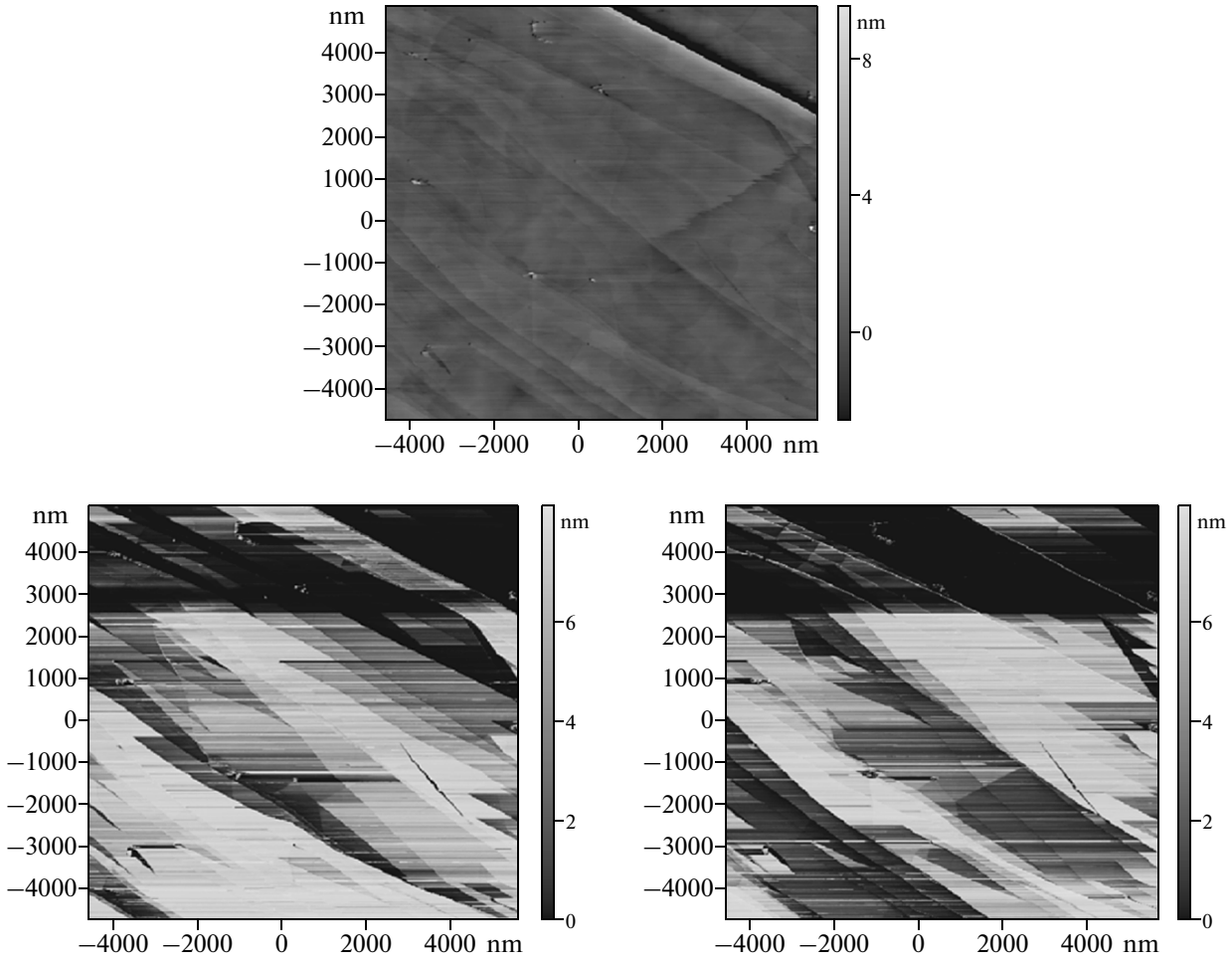

Fig. 3. Image of a HOPG 0.8 surface obtained with the use of SRM. Above, topography, at the bottom, conductivity: for forward motion (at the left) and for backward motion (at the right).

left; during backward motion it moves from the left to the right.

Analysis of the set of the obtained images showed that there is a connection between conductivity and topography. In the majority of cases the conductivity increases if the probe rises to a higher plateau from a lower one; it decreases if the probe descends from a higher plateau. Sharp changes of relief almost always

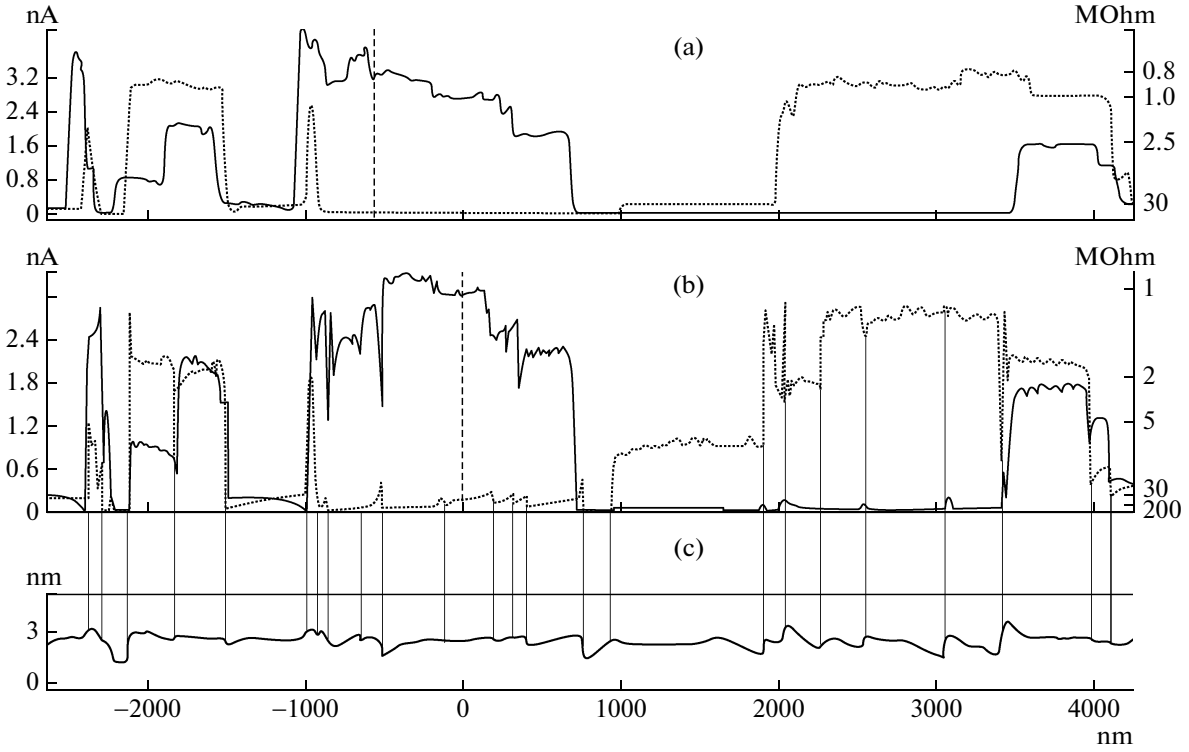

Fig. 4. a), profile of currents for big rate of scanning 7 Hz, b), profile of currents for a scanning rate of 8 mHz, and c), topography for one scanning line. Forward motion is marked by continuous line, backward motion, by dashed line. The correspondence between large steps of current and sharp changes of heights on topography is visible.

corresponds to sharp changes of conductivity, in this case the pits have high resistance and the upper plateaus have low resistance. This corresponds to the results in [10], where it was also shown that high-lying HOPG plateaus have greater conductivity. The connection of conductivity and relief is especially obviously revealed in the cases, where there is a small expressed defect on a plateau; this implies a sharp change of the resistance in the whole part of the scanning line after passing this defect. Thus, the conductivity of contact depends to a greater degree on the history of the interactions of the probe–sample than on the local changes of the surficial physical properties. Let us give two quantitative examples: on a plateau with an average resistance of 2.5 MOhm (which corresponds to a current of 5 nA) in one scanning line the current decreases to zero after passing a defect with a height of 3.8 nm; in the second case the resistance increases from 2 MOhm to 57 MOhm (the current decreases from 5.8 nA to 0.3 nA, respectively) on a defect with a height of 1.5 nm. The change of the contact resistance occurs not in the neighborhood of the defects, but exactly in the defective place.

The above data testify to the fact that during passage by the needle over defects the geometry of the contact of the probe with the sample changes. This may be connected with the change of the contact area due to the probe slope angle to the surface or with the joining of conducting carbon nanoparticles to it.

During motion along any plateau the frictional force changes insignificantly, but during passage of a step it increases by several orders of magnitude, then, on a smooth plateau it rapidly returns to the initial value. Thus, the contrast of the plateau conductivity cannot be explained by the change of the contact area due to changes of the needle slope angle to the surface, since the friction on the plateaus is approximately the same and the changes of the probe slope angle to the surface fall too fast. With an increase of the same line scanning rate the frictional force on the steps increases, but in this case the surges of the current strength values on the plateau boundaries disappear (Fig. 4). Accordingly, unambiguous connection between lateral forces and contact resistance is absent. A dependence of changes in the current strength during transition from one plateau to another on the height of the corresponding step was also not revealed.

Variations of the current strength values along the scanning line in the limits of one plateau are significantly (almost by three times) less than the variations of the current strength values across of the scanning lines, even excluding the lines passing through the defects on the surface from consideration. However, in the absence of defects on the graphite surface in the scanning field, the variations of the current strength

values are insignificant. This confirms that some random process occurs, during which the cantilever moving to a higher level collects conducting particles of graphene from the surface and moves them further on the plateau. The accumulation of such conducting particles around the probe improves the electrical contact with the surface. But the result of probe movement through a step can also be the partial or complete loss of the electrical contact between the probe and the graphite surface. The ability to recover the conducting ability of the probe by the joining to its point to graphite flakes distinguishes graphite from other materials, whose scanning leads only to gradual attrition of the probe's conducting surface.

CONCLUSIONS

For HOPG it was experimentally shown that the resistance of the conducting coating of a probe and a graphite surface can change in a wide range: from 0.7 to 100 MOhm. Based on the obtained experimental data we assume that the observed difference in the resistance of an atomic plateau on the graphite surface is connected not only with the depth of its deposition relative to each other, but with the changes in the state of the probe–surface contact during passage of steps due to the probe point modification by graphite particles. Therefore, during the use of graphite as a substrate for quantitative SRM investigations of nanoobjects, atomicly smooth parts of a surface, at which the state of the contact of a probe with a sample remains almost unchanged during scanning, should be chosen.

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