The study of electrical conductivity of DNA molecules by scanning tunneling spectroscopy

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Abstract. An interest to the processes of charge transport in DNA molecules is very high, due to perspective of their using in nanoelectronics. The original sample preparation for studying electrical conductivity of DNA molecules by scanning tunneling spectroscopy has been proposed and tested. The DNA molecules immobilized on gold surface have been imaged clearly and their current-voltage curves have been measured.

1. Introduction

The use of DNA molecules in nanoelectronic devices is very promising [1, 2] since it may cause significant interest to the processes of charge transport in these molecules. Although the double helix DNA form was discovered more than 60 years ago [3], the correct relationship between its structural, chemical, and electrical properties is not established yet. One of the problems is that attempts to measure the electrical resistance of DNA resulted in contradictory conclusions: the molecule can demonstrate dielectric [4, 5], semiconductor [6], conductor [7-9], and even superconductor [10] properties. Fink and Schonenberger [7] have shown that current-voltage curves of λ–DNA molecules of 1 µm length are linear and their resistivity $\rho \sim 10^{-4} \, \Omega \cdot cm$. Porath et al. [6] have described current-voltage curves with a clear gap of around 2 V and a resistance of 3 GΩ at a voltage of 4 V for Poly(G)-Poly(C) DNA sequence length of 10 nm ($\rho \sim 10 \, \Omega \cdot cm$). The reasons of such results ambiguity can be attributed to a complex structure of the DNA molecule, as well as uncertainty in treatment of the experimental results. In addition, the sample preparation and research methodology that influence the conductivity mechanism in DNA are also important.

There are two main approaches for conductivity research of the DNA molecule. First, the isolated DNA molecule is placed between two electric contacts [11-13]. The distance between electrodes should be small (about 1-10 nm), but sufficient enough to interfere with tunneling of charges. Such experiment is rather hard to carry out and extremely difficult to control.

Second approach is based on the use of a scanning tunneling microscope (STM) [14, 15]. First experiments with STM have shown that it is the most suitable research tool for both single DNA molecules and molecules in monolayer films [16, 17]. However, qualitative experimental measurements of charge transport through a single molecule by means of STM as well as interpretation of the results are extremely difficult. A great experimental problem is arranging the contacts to a single molecule. The accuracy of such manipulation is very important for charge transport.
2. Materials and methods
We have used scanning probe microscope Solver P47 and Probe nanolaboratory Ntegra-Prima («NT-MDT», Zelenograd, Russia) for the AFM/STM study and for scanning tunneling spectroscopy (STS) of DNA molecules. All investigations were carried out in air. The deionized distilled water MilliQ (Millipore, France) was used in preparation of all solutions.

Specimens were 20-mer oligonucleotide ("Syntol", Moscow, Russia) and the 5-thiol modified oligonucleotides. The following reagents were used also: 1 mM 2-mercaptoethanol, the hybridization buffer is 100 mM Tris.HCl/100 mM NaCl, the solution for washing 100 mM Tris HCl/300 mM NaCl. A plate of silicon Si (111) alloyed with phosphorus with a specific resistance of 1.6 Ω·cm (the nominal concentration of the current carriers ~ 8·10^{17} cm^{-3}) was used as an initial substrate material. After degreasing in toluene, the silicon substrates have been washed in ultrasonic bath with acetone, and then by deionized water. Next, we have carried out the thermal deposition of gold onto the silicon substrate.

The next stage of the experiment was the modification of the gold surface to bind with the studied oligonucleotides. Chemical modification included the creation of the covalent bond of chemically polarized groups of thiols with a clean metal surface. Adsorption of DNA was carried out by the Coulomb interaction of a molecule with a tightly packed monomolecular film of thiol oriented by its positive functional groups to the DNA molecule. 5'-thiol modified oligonucleotides were dissolved in water. Then, 5 µl of this solution was dropped on a gold substrate, which was placed in a Petri dish with moist atmosphere, created using the cuvette and water with and aged for 16 hours at 50°C. After that, the substrate was washed twice by water and a solution of 2-mercaptopethanol. This solution allowed increasing the availability of immobilizing samples to complementary sequences. Finally, the substrate was placed back into the Petri dish, kept for 2 hours at 40°C, and washed by water.

Oligonucleotides in the concentration of 1 µM were placed for 10 minutes in the solution for hybridization at 80°C. Immediately after this process, 5 µl of this solution was dropped on the substrate, which was then incubated for 1 hour in air at 40°C. Then it was washed in the buffer for rinsing and afterwards with clean water. The prepared substrates were dried at room conditions.

3. Results and discussion
AFM study revealed DNA molecules rarely located on the sample surface (Fig. 1a) [18]. We needed to obtain the STM image for identification of DNA molecules on the substrate in order to measure the current-voltage curves. It is known that the DNA molecules are represented as the dark spots in the STM image, due to lower electrical conductivity as compared to gold.

STM-study of the gold surface with immobilized DNA molecules was performed at the constant tunneling current mode. On the STM image (Fig. 1b), dark objects of the small diameter – DNA molecules are observed with lateral dimensions similar to the dimensions of DNA on the AFM image.

Figure 1. Images of DNA molecules on the gold surface: (a) AFM, (b) STM.
The DNA molecules were identified on STM images and the current-voltage curves were measured by scanning tunneling spectroscopy mode in dark locations (Fig. 2). The voltage $U$ applied between the gold substrate and the STM tip ranged from -1.5 V to +1.5 V.

The symmetric current-voltage curve with pronounced manifestation of nonlinearity and the growth of a tunnel current dispersion of fluctuations have been observed. The obtained current-voltage curves were compared with the approximated ones for semiconductor, dielectric, and conductor. We have found out that our approximation curves have the most similarity with the current-voltage curves of the semiconductor.

4. Conclusion
For investigating the dependence of the tunneling current through the DNA molecule on the magnitude of the applied voltage between the gold substrate and the STM tip, the current-voltage curves have been measured by scanning tunneling spectroscopy method. The study of electrical conductivity has crucial importance in the development of biosensors.

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