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## SURFACE PHYSICS AND THIN FILMS

# Study of the Resistive Switching of Vertically Aligned Carbon Nanotubes by Scanning Tunneling Microscopy

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**Abstract**—The effect of an external electric field on the electromechanical properties and regularities of the resistive switching of a vertically aligned carbon nanotube (VA CNT) has been studied experimentally using scanning tunneling microscopy. It has been shown that the VA CNT resistivity ratio in the high- and low-resistance states is higher than 25 as the distance between the scanning tunneling microscope (STM) probe and the VA CNT is 1 nm at a voltage of 8 V and depends on the voltage applied between the probe and the VA CNT. The proposed mechanism of resistive switching of VA CNTs is based on an instantaneous deformation and induction of a VA CNT internal electric field as a result of the sharp change in the time derivative of the external electric field strength. The obtained results can be used for the design and fabrication of resistive energy-efficient memory elements with a high density of storage cells on the basis of vertically aligned carbon nanotubes.

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## 1. INTRODUCTION

At the present time, the resistive switching effect in nanomaterials and nanostructures, which manifests itself in resistance switching of a material between the low-resistance ($R_{LR}$) and high-resistance ($R_{HR}$) states under action of an external electric field, has been extensively studied theoretically and experimentally. A promising application of the effect is the design of elements of energy-efficient resistive random-access memory (ReRAM) with high speed and high density of recording of information [1, 3].

Main part of reports on the design of ReRAM is devoted to the studies of the resistive switching processes in structures based on metal oxide thin films ($TiO_2$, ZnO, etc.) [3–5]. However, much attention is also focused on studies of the resistive switching processes in nanostructured materials (nanoparticles, nanorods, and nanotubes), which is due to the necessary of decreasing memory cell sizes to 10 nm and lower [2, 6–8].

Vertically aligned carbon nanotubes (VA CNTs) are of special interest for the design of elements of resistive random-access memory with high density of memory cells, because the vertical orientation of nanotubes provides a significant decrease in the memory cell area as compared to the standard ReRAM elements, and the technology of preparing VA CNTs based on plasma-enhanced chemical vapor deposition (PECVD) makes it possible to locally grow nanotubes during a process compatible with the silicon technology [9, 10].

The importance of the resistive switching in a VA CNT structure was demonstrated [11] when studying an array of VA CNTs by scanning tunneling microscopy (STM). The resistivity ratio in the high- and low-resistance states of a bungle of VA CNTs was 28 [11]. Similar resistive switching effect in VA CNTs was observed during studying the emission properties of an array of VA CNTs by atomic-force microscopy [12]. The effect was observed with applying a voltage about 200 V and at the distance between the probe and the sample of 350 nm, and it was explained by a deformation of VA CNTs during measurements of current–voltage characteristics. The deformation of oriented carbon nanotubes under action of an external electric field was demonstrated experimentally in [13]. However, the mechanism of the resistive switching in a structure based on VA CNTs remains poorly understood, and the further studies are necessary.

The aim of this work is to study the effect of an electric field on the electromechanical properties of vertically aligned carbon nanotubes by scanning tunneling microscopy and to study the resistive switching process in a structure based on VA CNTs when applying an external electric field.

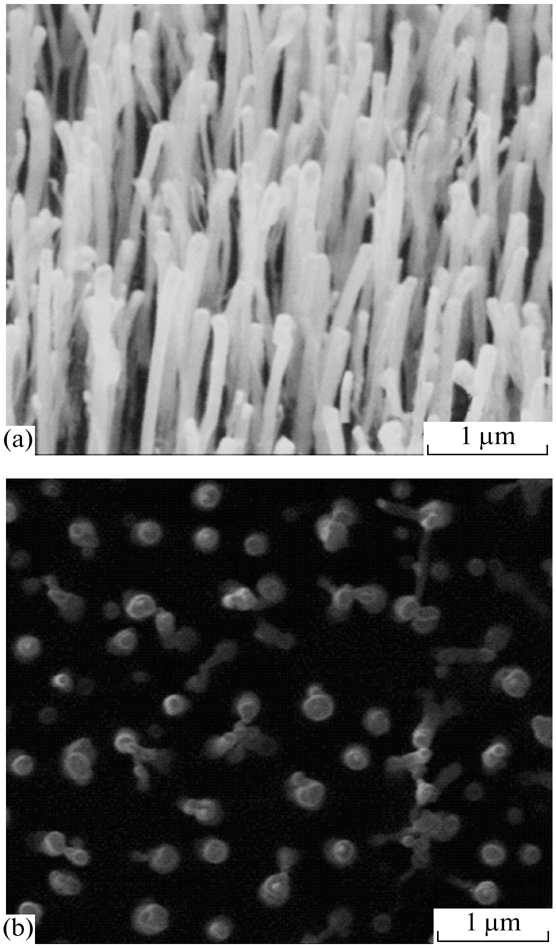

**Fig. 1.** SEM image of an array of VA CNTs: (a) side view and (b) top view.

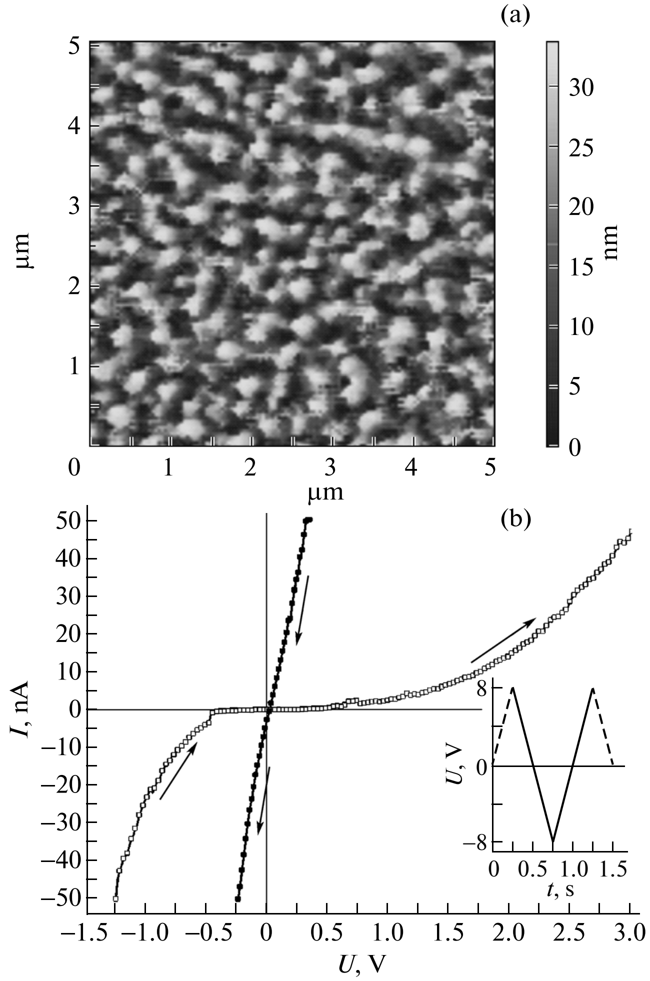

**Fig. 2.** STM study of an array of VA CNTs: (a) STM image obtained at $U = 0.1$ V, the distance between the probe and the VA CNT is 1 nm; (b) CVC of an individual nanotube corresponding to the voltage pulse shown in the inset.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

We studied a sample that was an array of vertically aligned carbon nanotubes grown by plasma-enhanced chemical vapor deposition (PECVD) in an NT-MDT NANOFAB NTC-9 nanotechnological unit. The synthesis of the vertically aligned carbon nanotubes was performed according to the tip-growth mechanism (Fig. 1a). The substrate used was a silicon plate at whose surface a two-layer structure was formed consisting of a 20-nm-thick titanium film and 10-nm-thick nickel film.

The studies of the array of the VA CNTs on a FEI Nova NanoLab 600 scanning electron microscope (SEM) (The Netherlands) made it possible to estimate the diameter, height, and the density of VA CNTs in the array, which were 95 nm, 2 μm, and 8 $\mu m^{-2}$, respectively (Fig. 1).

The electrical and geometric properties of the array of vertically aligned carbon nanotubes were determined by scanning tunneling microscopy using an NT-MDT Solver P47 Pro scanning probe microscope (Russia). The tungsten STM probe 52 nm in diameter was prepared by electrochemical etching. The STM study results of the array of VA CNTs are shown in Fig. 2. The carbon nanotube diameter of the experimental sample was determined by statistic processing of obtained STM images using the Grain Analysis functions of the Image Analysis 3.5 program package. During processing the STM images, we built a secant plane parallel to tops of VA CNTs to determine the cross-section area and the diameter of each of nanotubes intersected by this plane. The current–voltage characteristics (CVCs) of VA CNTs were measured in the STM-spectroscopy mode. Figure 2b shows the characteristic CVC of an individual vertically aligned carbon nanotube measured in the case of applying the voltage pulse shown in the inset to the probe at the distance between the STM probe and a VA CNT of 1 nm.

To study the effect of the rate of changing the external electric field strength ($dE/dt$) on the electrome-

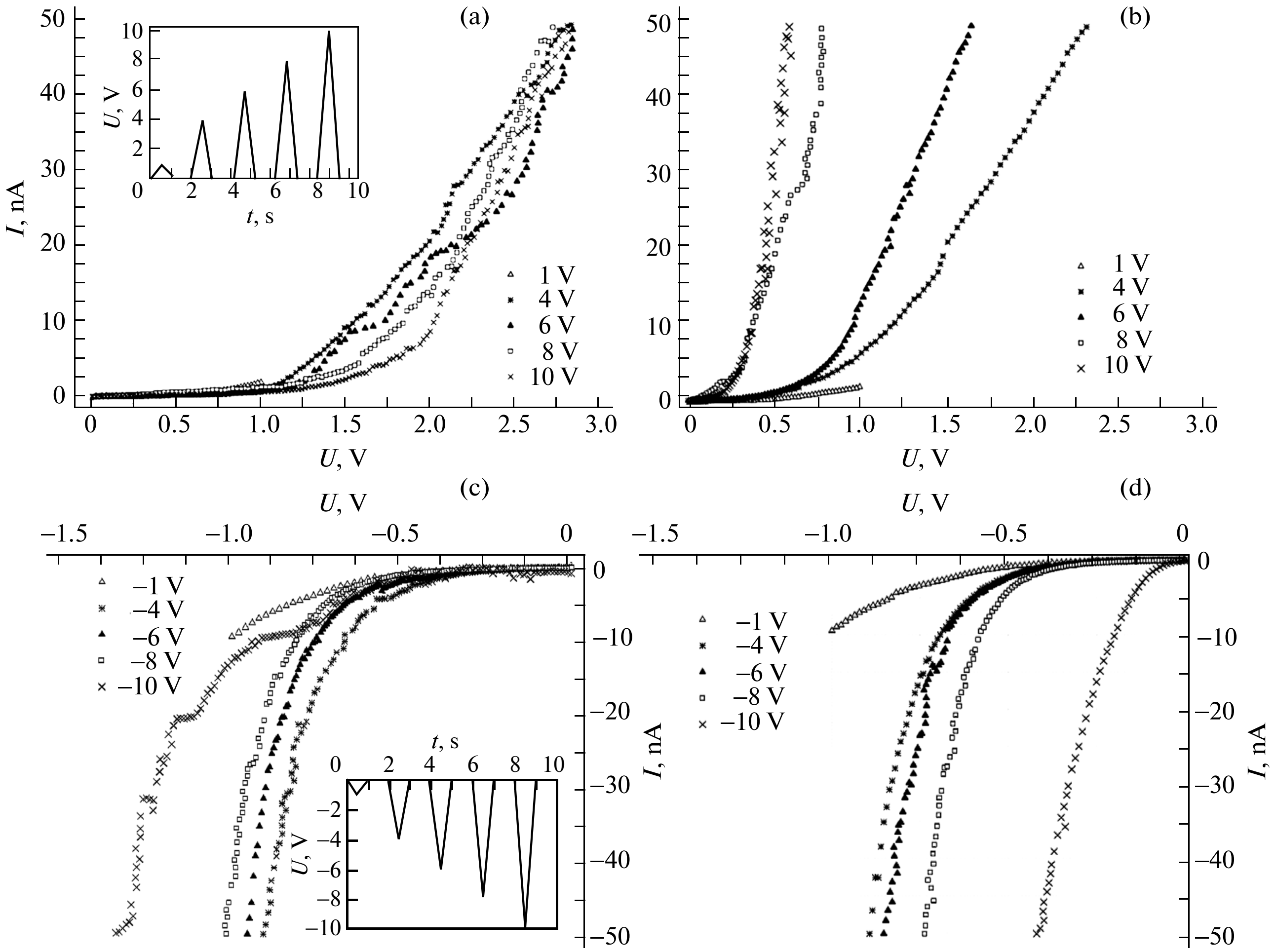

**Fig. 3.** Current–voltage characteristics of the VA CNT measured by the STM method: (a) at rising *dE*/*dt* (the inset shows the pulses of applied positive voltage); (b) at decreasing *dE*/*dt*; (c) at rising –*dE*/*dt* (the inset shows the pulses of applied negative voltage); and (d) at decreasing –*dE*/*dt*.

chanical properties of a vertically aligned carbon nanotube, we used STM spectroscopy at the distance between the STM probe and the VA CNT 1 nm to measure the current–voltage characteristics of the VA CNT as a saw-tooth voltage pulses (Fig. 3) were applied to the probe and the current–time characteristics of the VA CNT as rectangular voltage pulses were applied to the probe (Fig. 4). The current–voltage characteristics of the vertically aligned carbon nanotube corresponding to the increase in *dE*/*dt* ($0 < t < 0.5$ s and so on) are shown in Figs. 3a and 3c, and those corresponding to the decrease in *dE*/*dt* ($0.5 < t < 1$ s and so on) are shown in Figs. 3b and 3d. Using the experimental CVCs, we obtained the dependence of the resistivity ratio in the high-resistance and low resistance states of VA CNT $R_{HR}/R_{LR}$ on the positive potential on the STM probe (Fig. 5). It is necessary to note that the current characteristics of the VA CNT are given in the range from 0 to 50 nA, which is due to a specific feature of the measurement system of the scanning tunneling microscope.

## 3. RESULTS AND DISCUSSION

An analysis of the obtained STM-image of the array of the VA CNTs (Fig. 2a) using the Grain Analysis function shows that the diameter of vertically aligned carbon nanotubes is 108 ± 29 nm, the density of the nanotubes in the array of VA CNTs is 7 ± 2 μm$^{-2}$, which correlates well with the results of estimating the data obtained by the SEM method. This fact allows the conclusion that, during the STM studies, individual nanotubes are not combined into bundles of VA CNTs because of low density of the nanotubes in the array, unlike the results presented in [11], and it makes possible to study the electromechanical properties of individual VA CNT. An analysis of CVC of the individual nanotube (Fig. 2b) shows that the VA CNT resistance is changed from the high-resistance to low-resistance state under action of an external electric field; i.e., the resistive switching effect is observed.

The experimental studies of the influence of the value and sign of *dE*/*dt* in the case, when a positive voltage is applied between the STM probe and VA

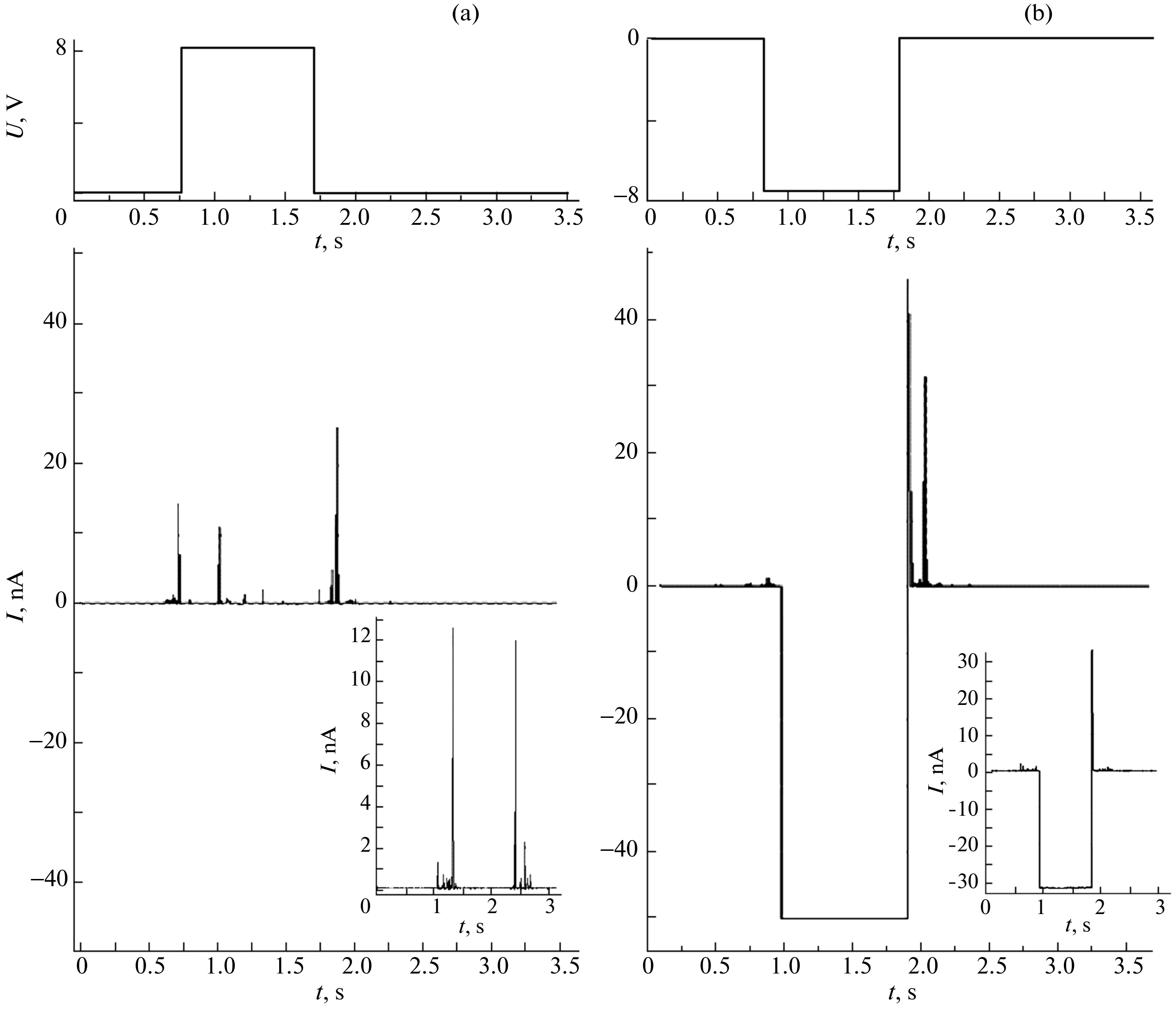

**Fig. 4.** Time dependences of the current and the voltage in the STM probe/VA CNT system: (a) at the probe potential of +8 V (in the inset, at +0.1 V); (b) at the probe potential of –8 V (in the inset, at –0.1 V).

CNT (inset in Fig. 3a) show that $R_{HR}$ is almost independent of the derivative value at $dE/dt > 0$ and is 540 MΩ at $U = 1$ V (Fig. 3a). At $dE/dt < 0$, $R_{LR}$ decreases with increasing $dE/dt$ (Fig. 3b). So, at $U = 1$ V, the VA CNT resistance $R_{LR} = 156$ MΩ after applying 4 V to the probe and $R_{LR} < 20$ MΩ after applying 8 V (Fig. 3b). Thus, ratio $R_{HR}/R_{LR}$ increases with the rate of decreasing the external electric field strength and is larger than 25 at $U = 8$ V (Fig. 5). Similar dependences were also observed when applying saw-tooth pulses of negative voltage to the probe (Figs. 3c, 3d).

It should be noted that the resistive switching effect in the VA CNT-based structures is observed at the instants of time $t = 0.5$, 2.5, 4.5 s, and so on, which corresponds to a sharp changes in $dE/dt$ (Fig. 3). To study the effect of the jump of $dE/dt$ on the electrical properties of VA CNTs, we measured the time dependence of the current flowing in the STM probe/VA CNT system when applying the rectangular voltage pulse (Fig. 4).

An analysis of the experimental dependences obtained in the case when a rectangular pulse of positive voltage with pulse duration 1 s and an amplitude from 0.1 to 10 V shows that no current flows in the STM probe/VA CNT system and only the current jumps were observed in the instants of sharp changing $dE/dt$ (Fig. 4a). When we applied a rectangular pulse of negative voltage (with amplitude from –0.1 to –10 V), a significant current flowed in the STM probe/VA CNT system (Fig. 4b); in this case, the current jumps corresponding to the forward front of the voltage pulse were insignificant. Similar dependences were also obtained for the pulse duration 1 ms.

In addition, the experimental study of the influence of the distance between the STM probe and VA CNT on the obtained dependences showed that as a rectangular pulse of a positive voltage is applied to the probe at the distances larger than 2 nm, the flowing current is a few nanoampers; and, as the voltage applied to the probe is negative, the current is a few tens of nanoampers, as is the case at the distance 1 nm. Thus, as the distance between the STM probe and VA CNT increases, the current increases when applying a positive voltage to the probe, and this fact indicates the absence of the correlation of the observed effect with the autoelectronic emission in the gap between the STM probe and VA CNT.

To explain the observed dependences, we propose a mechanism of resistive switching of VA CNTs. According to the mechanism, the dependence of the current flowing in the STM probe/VA CNT system on the strength of external electric field is related to deformation of VA CNT as a result of polarization of the nanotube [14] and the appearance of the surface attractive force between the STM probe and nanotube $F_{at}$ [11]

$$F_{at} = \frac{1}{2}\varepsilon_{\|}\varepsilon_0 E^2 S, \tag{1}$$

where $\varepsilon_{\|}$ is the longitudinal permittivity of VA CNT, whose value was found based on the data of [14] and was ~87; $S$ is the VA CNT cross-sectional areas. At voltage $U = 1$ V and the distance between the STM probe and VA CNT of 1 nm, the external electric field strength $E$ is $\sim 1 \times 10^9$ V/m, with allowance for the probe geometry, [15], and the corresponding force $F_{at} \sim 3.5$ μH.

The longitudinal elongation of a VA CNT under action of surface attractive force $F_{at}$ depends on its geometric and mechanical properties

$$\frac{\Delta L}{L} = \frac{F_{at}}{YS}, \tag{2}$$

where $Y$ is the Young's modulus of the VA CNT. The Young's modulus of VA CNT was obtained experimentally using the technique of determining the mechanical properties of VA CNT based on the nanoindentation method [16], and its value is $Y = 1.2$ TPa. The nanotube elongation $\Delta L$ is 0.63 nm at voltage $U = 1$ V and corresponding force $F_{at} \sim 3.5$ μH. The relative elongation of VA CNT was measured from 0.03 to 3% at the applied voltages from 1 to 10 V, respectively.

Since the correlation between the deformation and the electric field strength is quadratic, the direction of the VA CNT deformation is independent of the potential sign at the STM probe. In this case, the surface attractive force $F_{at}$ is always directed to the region of the highest field strength, i.e., to the STM probe, and the VA CNT is attracted to the probe at both positive and negative potentials; this is, the VA CNT deformation is always positive. The elongation of VA CNTs during applying a potential to the probe was also observed experimentally in [13].

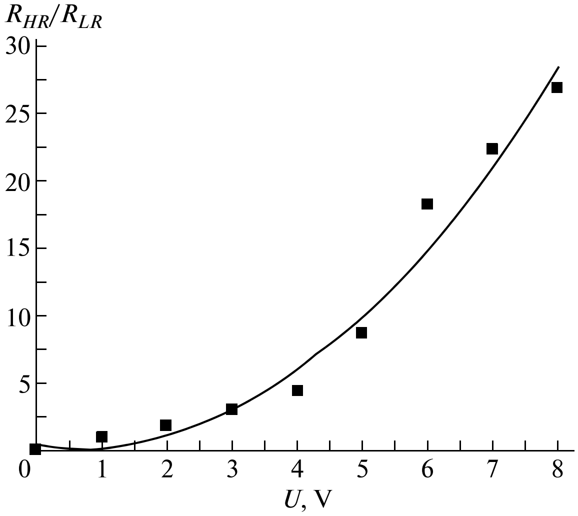

**Fig. 5.** Dependence of $R_{HR}/R_{LR}$ on the probe potential $U$.

Because no current flows in the STM probe/VA CNT system when applying a rectangular voltage pulse at a positive potential on the probe, and the current is fairly significant at a negative potential, we can suppose that an internal field strength $E_{\text{def}}$ is induced in the nanotube as a result of instantaneous deformation at the moment of sharp changing $dE/dt$, and the field is co-directed with the deformation

$$\frac{\Delta L}{L} \approx \beta E_{\text{def}}, \tag{3}$$

where β is the coefficient of proportionality.

In addition, electric-field strength $E_P$ related to the VA CNT polarization and directed oppositely to external field $E$ is induced in the nanotube; i.e., at the moment of applying a rectangular voltage pulse, internal electric field strength $E_{\text{CNT}}$ that is the sum of electric field strength $E_{\text{def}}$ caused by an instantaneous deformation of the nanotube and electric field strength $E_P$ related to the polarization is induced in the vertically aligned carbon nanotube. In this case, internal electric field strength $E_{\text{CNT}}$ decreases as the STM probe/VA CNT distance increases, because a part of the external electric field begins to decrease in the gap between the probe and VA CNT and, therefore, the deformation and the polarization of the nanotube decrease under action of the external electric field.

Thus, as a positive potential is applied to the STM probe, internal electric field in the VA CNT $E_{\text{CNT}}$ compensates external electric field $E$ (Fig. 6a); as a negative potential is applied to the probe, internal electric field of VA CNT $E_{\text{CNT}}$ is insignificant, and a

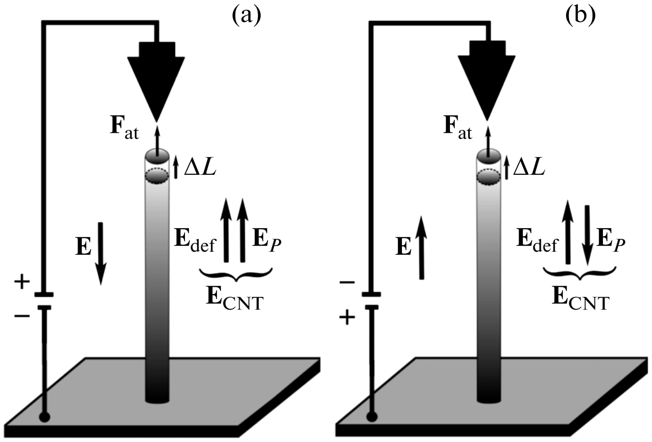

**Fig. 6.** Schematic drawing of the distribution of the field strengths when interacting VA CNT with the STM probe: (a) at a positive probe potential and (b) at a negative probe potential.

current flows in the STM probe/VA CNT system under action of external electric field $E$ (Fig. 6b). This effect is observed most clearly at the distances between the CTM probe and VA CNT smaller than 2 nm.

If we take that $E_{def} \sim 1/2E$, it follows from Eq. (3) that coefficient $\beta > 30 \times 10^{-12}$ m/V. This value is comparable to the values of the piezoelectric modulus of nanowires of ZnO and a number of other piezoelectric materials [17, 18]. This circumstance allows the conclusion that vertically aligned carbon nanotubes exhibit piezoelectric properties. According to the theory of piezoelectric effect, force $F_{at}$ induces surface charge $Q$ [18]:

$$Q = \beta F_{at}. \tag{4}$$

Surface charge $Q$ is positive, since force $F_{at}$ is always positive, and, with allowance for Eqs. (2) and (3), we have

$$Q = \beta YS\frac{\Delta L}{L} = \beta^2 YSE_{def}. \tag{5}$$

Because the charge is distributed over entire external surface of VA CNT, area $S$ in Eq. (5) should be considered as the external surface area of VA CNT.

The formation of surface charge $Q$ explains the existence of jumps of positive current corresponding to the sharp change in $dE/dt$ (Fig. 4). The current jumps corresponding to the positive voltage pulse rise (Fig. 4a) are due to insignificant inertia of the VA CNT deformation process and accumulation of charge $Q$. The current jumps corresponding to the pulse decay of both positive and negative voltage (Figs. 4a, 4b) are due to the ejection of the charge accumulated in VA CNT after switching off the external electric field. There is no current jump corresponding to the negative voltage pulse rise (Fig. 4b), because it is compensated by the summary current flowing in the STM probe/VA CNT system.

Similar processes also proceed in the point corresponding to the change in the sign of $dE/dt$ when applying saw-tooth voltage pulses (Fig. 3). The appearance of internal electric field strength of VA CNT $E_{def}$ also leads to asymmetric CVCs for the positive and negative voltages (Figs. 2b, 3).

In addition, the application of a saw-tooth voltage pulse to the STM probe/VA CNT system leads to a gradual deformation of VA CNT, whose result is current $I_Q$ related to a change in charge $Q$ in time:

$$I_Q = \frac{dQ}{dt} = \beta^2 YS\frac{dE_{def}}{dt}. \tag{6}$$

Summary current $I$ flowing in the STM probe/VA CNT system when applying a saw-tooth voltage pulse is the sum of the conduction current of free charges $I_C$ and current $I_Q$ related to the change in the surface charge

$$I = I_C + I_Q. \tag{7}$$

At $dE/dt$, the deformation of VA CNT increases ($0 < t < 0.5$ s and so on), current $I_Q$ is directed oppositely to the free charge conduction current $I_C$, because the electric field strength of the nanotube $E_{def}$ is co-directed to the deformation of VA CNT and decreases summary current $I$ in the STM probe/VA CNT system. In this case, the contribution of current $I_Q$ is most substantial in the point corresponding to the initial moment of applying the external electric field, since current $I_Q$ increases slowly with farther increasing external electric field strength $E$, because of induced elastic forces preventing increase in electric field $E_{def}$, which brings about the formation of a high-resistance state of the conduction in the STM probe/VA CNT system (Figs. 3a, 3c).

At the instants of time $0.5 \text{ s} < t < 1$ s and so on, $dE/dt$ becomes negative, the VA CNT deformation begins to decrease, current $I_Q$ changes its direction to the opposite and is summed with free charge conduction current $I_C$, and, as a result, summary current $I$ increases. The contribution of current $I_Q$ is also most substantial in the point corresponding to the change in the sign of $dE/dt$, which brings about the formation of a low-resistance state of the conduction in the STM probe/VA CNT system (Figs. 3b, 3d).

In the case of a rectangular voltage pulse, current $I_Q$ does not influence the system conductivity, because the external electric field strength and, as a result, the deformation of VA CNT are unchanged in time.

It also should be noted that, as VA CNT is deformed under action of a saw-tooth pulse of an external electric field, the piezoresistive effect of VA CNT is observed whose result is a change in the internal resistance of the nanotube [19] and, as a result, current $I$ in the STM probe/substrate system decreases as the rate of the external field strength rise increases (Fig. 3).

## 4. CONCLUSIONS

The effect of an external electric field on the electromechanical properties of vertically aligned carbon nanotubes was experimentally studied by scanning tunneling microscopy to elucidate the mechanism of the resistive switching in the structure based on VA CNTs. The resistivity ratio of VA CNT in the high- and low-resistance states $R_{HR}/R_{LR}$ is shown to increase with the voltage applied to the STM probe/VA CNT system and is higher than 25 at $U = 8$ V.

We proposed the mechanism of resistive switching of VA CNTs related to the internal electric field strength of a nanotube $E_{\text{def}}$ induced as a result of the instantaneous deformation of VA CNT upon sharp changing the time derivative of an external electric field. When applying a rectangular voltage pulse, the internal electric field strength in the VA CNT $E_{\text{def}}$ brings about the formation of two stable states of conduction of VA CNT: no current flows in the STM probe/VA CNT system as a positive potential is applied to the probe, and a significant current flows as a negative potential is applied to the probe.

When applying a saw-toothed voltage pulse, a current occurs in a VA CNT under action of the time derivative of an external electric field; the current is due to the change in the surface charge of the VA CNT. The change in the sign of the external electric field strength leads to the change in the resistance of the structure based on the vertically aligned carbon nanotube and the formation of a hysteresis in the current–voltage characteristics of VA CNT.

Thus, the summary current flowing in the STM probe/VA CNT system is dependent on the sign and the magnitude of the time derivative of the external electric field strength, i.e., on the shape of the signal of applied voltage.

The results can be used in the design and fabrication of resistive energy-efficient memory elements with a high density of cells based on vertically aligned carbon nanotubes.

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