ISSN 1063-7842, Technical Physics, 2015, Vol. 60, No. 7, pp. 1044–1050. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © O.A. Ageev, O.I. Il'in, M.V. Rubashkina, V.A. Smirnov, A.A. Fedotov, O.G. Tsukanova, 2015, published in Zhurnal Tekhnicheskoi Fiziki, 2015, Vol. 85, No. 7, pp. 100–106.

PHYSICS OF NANOSTRUCTURES

# Determination of the Electrical Resistivity of Vertically Aligned Carbon Nanotubes by Scanning Probe Microscopy

**O. A. Ageev*, O. I. Il'in, M. V. Rubashkina, V. A. Smirnov, A. A. Fedotov, and O. G. Tsukanova**

*Southern Federal University, Institute of Nanotechnologies, Electronics, and Equipment Engineering, Nekrasovskii per. 44, Taganrog, 347900 Russia*
**e-mail: ageev@sfedu.ru*

Received September 1, 2014

**Abstract**—Techniques are developed to determine the resistance per unit length and the electrical resistivity of vertically aligned carbon nanotubes (VA CNTs) using atomic force microscopy (AFM) and scanning tunneling microscopy (STM). These techniques are used to study the resistance of VA CNTs. The resistance of an individual VA CNT calculated with the AFM-based technique is shown to be higher than the resistance of VA CNTs determined by the STM-based technique by a factor of 200, which is related to the influence of the resistance of the contact of an AFM probe to VA CNTs. The resistance per unit length and the electrical resistivity of an individual VA CNT 118 ± 39 nm in diameter and 2.23 ± 0.37 μm in height that are determined by the STM-based technique are 19.28 ± 3.08 kΩ/μm and $8.32 \pm 3.18 \times 10^{-4}$ Ω m, respectively. The STM-based technique developed to determine the resistance per unit length and the electrical resistivity of VA CNTs can be used to diagnose the electrical parameters of VA CNTs and to create VA CNT-based nanoelectronic elements.

**DOI:** 10.1134/S1063784215070026

## INTRODUCTION

Owing to a unique combination of electrical, mechanical, and geometric properties, vertically aligned carbon nanotubes (VA CNTs) are widely used to create promising nanoelectronic devices, such as field-emission emitters, transistors, memory elements, and interconnections [1–3]. As a rule, the main properties of VA CNTs that determine the parameters of such devices are electrical resistivity and resistance per unit length. It is difficult to determine these VA CNTs parameters by standard methods because of the vertical orientation of nanotubes and their high aspect ratio. For example, the two- and four-probe methods that are widely used to study the electrical properties of microstructures need contact pads several microns in size at the top of a VA CNT array, which significantly limits the possibilities of application of these methods to determine the electrical parameters of individual vertically aligned nanotubes because of their small sizes [4]. The problems related to the development of new techniques of nanodiagnostics to determine the electrical parameters of vertically aligned nanotubes become challenging due to the necessity of controlling and studying the electrical parameters of individual VA CNTs and construction and device elements based on them and due to the requirements of developing the metrology of nanotechnologies.

Scanning probe microscopy (SPM), which can be used to measure the *I*–*V* characteristics of nanotubes, is a precision method for studying the electrical properties of individual carbon nanotubes (CNTs) [5, 6]. This method does not require additional fixation of VA CNTs and the formation of contact pads at their top. However, when VA CNTs are studied by SPM, difficulties related to the mobility of nanotubes during contact with a probe and the formation of VA CNT bundles in an applied electric field arise [6]. Moreover, the determination of the electrical resistivity of CNTs from the *I*–*V* characteristics obtained by SPM requires an analysis of the measurement of *I*–*V* characteristic and the related development of a technique to find the electrical parameters of VA CNTs with allowance for the specific features of SPM.

The purpose of this work is to develop an SPM technique to determine the electrical resistivity and the resistance per unit length of VA CNTs.

## EXPERIMENTAL

A sample with a VA CNT array was grown by plasma-enhanced chemical vapor deposition in a multifunctional NANOFAB NTK-9 (NT-MDT, Russia) nanotechnology facility. VA CNTs were grown on a silicon wafer containing catalytic nickel centers on its surface. A 20-nm-thick titanium film was used as a lower conducting and adhesion layer on the silicon wafer.

The geometric parameters of the VA CNT array were studied by a Nova NanoLab 600 (FEI, the Netherlands) scanning electron microscope (SEM). The VA CNT diameter and height were 98 nm and 2.2 μm, respectively, and the nanotube density in the array was 8 μm$^{-2}$ (Fig. 1).

The electrical properties of VA CNTs were studied by an Ntegra (NT-MDT, Russia) scanning probe laboratory by contact atomic force microscopy (AFM) in the current spectroscopy mode and by scanning tunneling microscopy (STM) in the STM spectroscopy mode at a distance of 0.5 nm between an STM probe and VA CNTs. As the AFM probe, we used a commercial cantilever with an NSG11/Pt platinum coating. As the STM probe, we used a tungsten probe 52 nm in radius, which was sharpened by an electrochemical method [7]. To localize a probe at the top of VA CNTs, we performed preliminary scanning of the array surface using AFM in the tapping mode and using STM in the dc mode. The AFM and STM images of the VA CNT array are shown in Figs. 2a and 3a, respectively. The VA CNT diameter was determined by processing the AFM and STM images using the Image Analysis (NT-MDT, Russia) software package (Figs. 2b, 3b). During statistical processing of the STM image by the Grain Analysis function, a cut plane was drawn parallel to the vertices of VA CNTs in order to determine the cross-sectional area and the diameter of each nanotube cut by this plane (Fig. 3b).

The *I–V* characteristics of VA CNTs obtained by AFM and STM spectroscopy are shown in Figs. 2c and 3c (solid lines), respectively. The scheme of measuring the *I–V* characteristic of VA CNTs by contact AFM is shown in Fig. 4a, and the scheme of STM measurement is similar with allowance for the fact that tunneling contact is formed between an STM probe and VA CNTs.

The resistance of the probe/conducting layer/VA CNT array/contact system was additionally measured using the circuit presented in Fig. 4c to exclude the resistances of the probe material, the conducting layer, the contact, and the array of the nanotubes under it from the total resistance of the probe/VA CNT/conducting layer/VA CNT array/contact system. To measure this resistance, we preliminarily performed force lithography of the VA CNT array by AFM using the technique from [8]. Figure 5 shows AFM and SEM images of the modified region in the sample. When analyzing the AFM image by the technique described in [8], we were able to find the average VA CNT height (2.23 ± 0.37 μm), which correlates with the results of analysis of the SEM image (Fig. 1). Figures 2c and 3c show the *I–V* characteristics of the modified region obtained by AFM and STM spectroscopy (dotted lines), respectively.

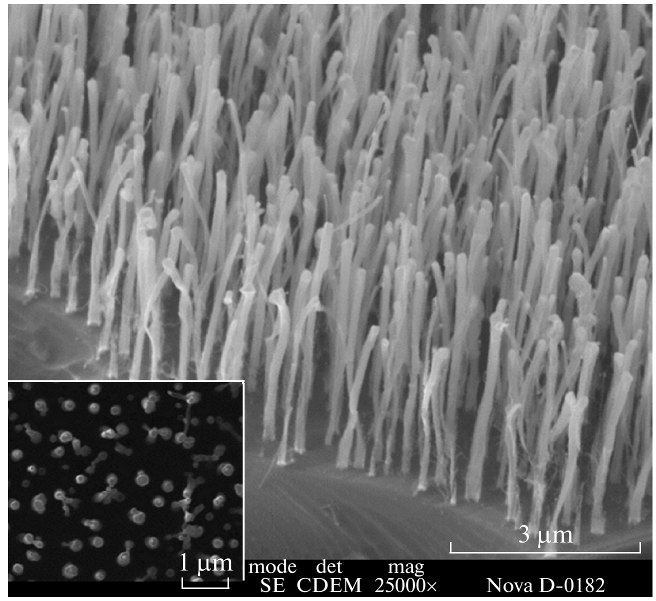


**Fig. 1.** SEM image of a VA CNT array: (inset) top view.

## RESULTS AND DISCUSSION

An analysis of the AFM image of the VA CNT array taken in the tapping mode demonstrates that individual nanotubes are joined into bundles 320–650 nm in diameter during mechanical interaction with the AFM probe, which hinders the investigation of the electrical properties of individual nanotubes (Fig. 2a). The mechanism of formation of VA CNT bundles and the techniques of determining their geometric parameters when a VA CNT array is studied by AFM in the tapping mode were described in [8]. Figure 2c (solid line) shows the *I–V* characteristic of a bundle of VA CNTs 612 nm in diameter consisting of eight individual nanotubes. The VA CNT bundle has the following two states of conduction: a high-resistance state when the voltage changes from 0 to 10 V and a low-resistance state when the voltage changes from 10 to 0 V, which is associated with the resistance properties of VA CNTs [9]. To determine the resistance of VA CNTs, we used the *I–V* characteristic that corresponds to the low-resistance state of the VA CNT bundle, since no additional resistance related to the internal field in nanotubes appears in VA CNTs in this case [9].

An analysis of the measurement of the *I–V* characteristic of the VA CNT bundle showed that the AFM probe/VA CNT/conducting layer/VA CNT array/contact system can be represented by the equivalent circuit shown in Fig. 4b. The total resistance of this system $R_{\mathrm{tot}}^{\mathrm{AFM}}$ is

$$R_{\mathrm{tot}}^{\mathrm{AFM}} = R_0^{\mathrm{AFM}} + R_{\mathrm{bundle/sub}} + R_{\mathrm{bundle}} + R_{p/\mathrm{bundle}}, \quad (1)$$

$$R_0^{\mathrm{AFM}} = R_{\mathrm{Me}} + R_{\mathrm{CNTs/Me}} + R_{\mathrm{CNTs}} + R_{\mathrm{CNTs/sub}} + R_{\mathrm{sub}} + R_p^{\mathrm{AFM}}, \quad (2)$$

where $R_0^{\mathrm{AFM}}$ is the total resistance of the conducting layer ($R_{\mathrm{sub}}$), the contact material ($R_{\mathrm{Me}}$), the AFM probe material ($R_p^{\mathrm{AFM}}$), the nanotube array under the contact and the contacts to it ($R_{\mathrm{CNTs/Me}}$ + $R_{\mathrm{CNTs}}$ +

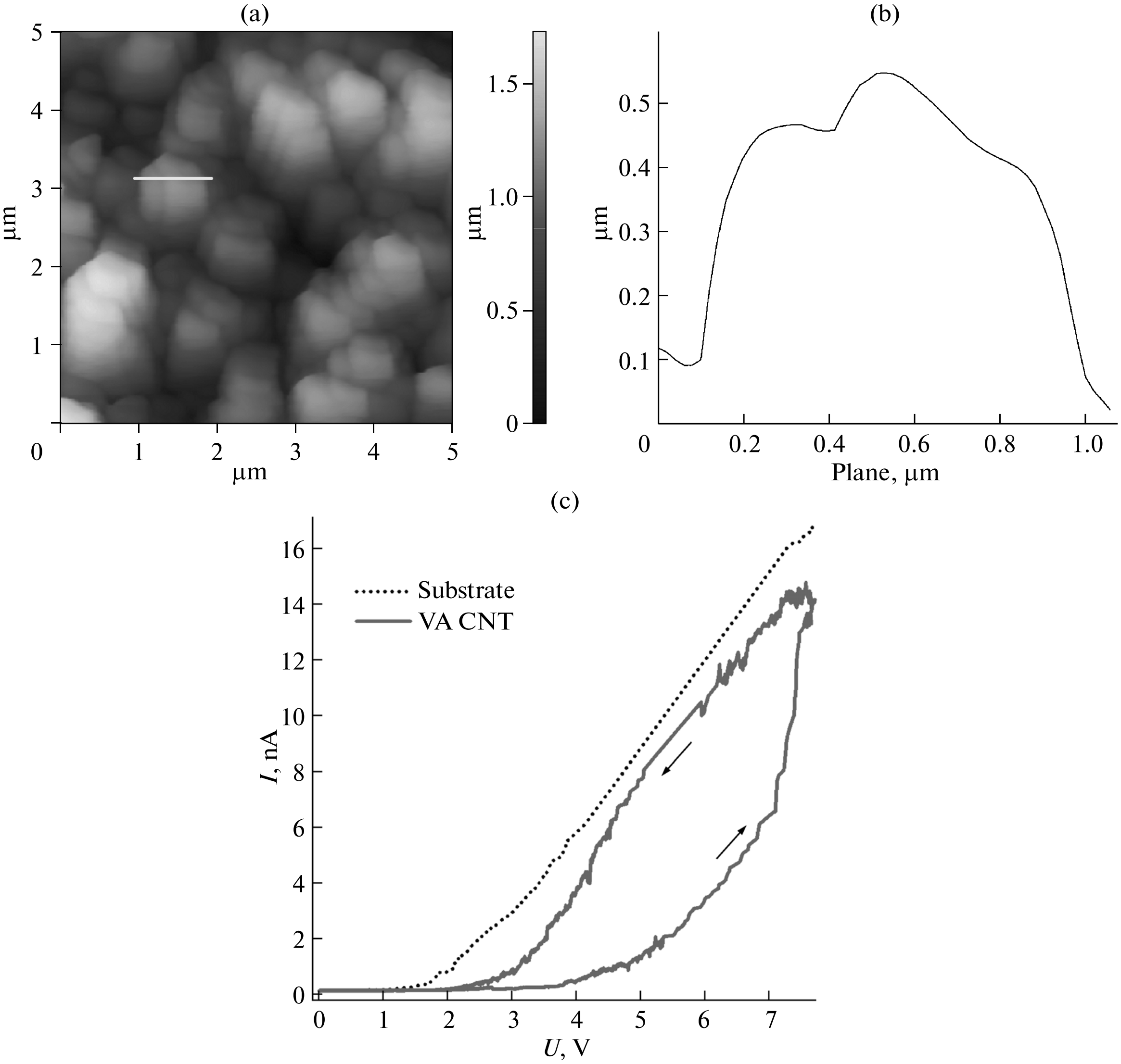


**Fig. 2.** AFM study of a VA CNT array: (a) AFM image of a VA CNT array, (b) profilogram along a line, and (c) $I$–$V$ characteristics of (solid line) nanotube bundle and (dotted line) substrate.

$R_{\mathrm{CNTs/sub}}$); $R_{\mathrm{bundle/sub}} + R_{\mathrm{bundle}} + R_{p/\mathrm{bundle}}$ is the resistance of the VA CNT bundle and the contacts to it.

Resistances $R_{\mathrm{tot}}^{\mathrm{AFM}}$ and $R_0^{\mathrm{AFM}}$ are determined by an analysis of the linear segments of the $I$–$V$ characteristics obtained by AFM spectroscopy on the VA CNT bundle and on the VA CNT array region modified by force lithography (Fig. 2c). An analysis of the measurement of the $I$–$V$ characteristic of the modified region in the VA CNT array showed that the AFM probe/conducting layer/VA CNT array/contact system can be represented by the equivalent circuit represented in Fig. 4d. Resistance $R_0^{\mathrm{AFM}}$ is found to be 452 MΩ on the assumption that the resistance of the contact of the AFM probe with the metallic film of the conducting layer meets the relations $R_{p/\mathrm{sub}} \ll R_{p/\mathrm{bundle}}$, $R_{p/\mathrm{sub}} \ll R_{\mathrm{bundle}}$, and $R_{p/\mathrm{sub}} \ll R_{\mathrm{bundle/sub}}$. Resistance $R_{\mathrm{tot}}^{\mathrm{AFM}}$ for the low-resistance state of the VA CNT bundle is 533 MΩ (Fig. 2c). Therefore, the resistance of the VA CNT bundle and the contacts to it is

$$R_{\mathrm{bundle/sub}} + R_{\mathrm{bundle}} + R_{p/\mathrm{bundle}} = R_{\mathrm{tot}}^{\mathrm{AFM}} - R_0^{\mathrm{AFM}}. \quad (3)$$

Since VA CNTs are joined into bundles during an AFM investigation (Fig. 2a), the resistance of one nanotube and the contacts to it ($R_{\mathrm{CNT}}^{\mathrm{AFM}}$) can be written as

$$R_{\mathrm{CNT}}^{\mathrm{AFM}} = \frac{R_{\mathrm{tot}}^{\mathrm{AFM}} - R_0^{\mathrm{AFM}}}{N}, \quad (4)$$

where $N$ is the number of nanotubes in the VA CNT bundle. According to Eq. (4), resistance $R_{\mathrm{CNT}}^{\mathrm{AFM}}$ is 10.1 MΩ. This VA CNT resistance is overestimated, since it includes both the VA CNT resistance and the

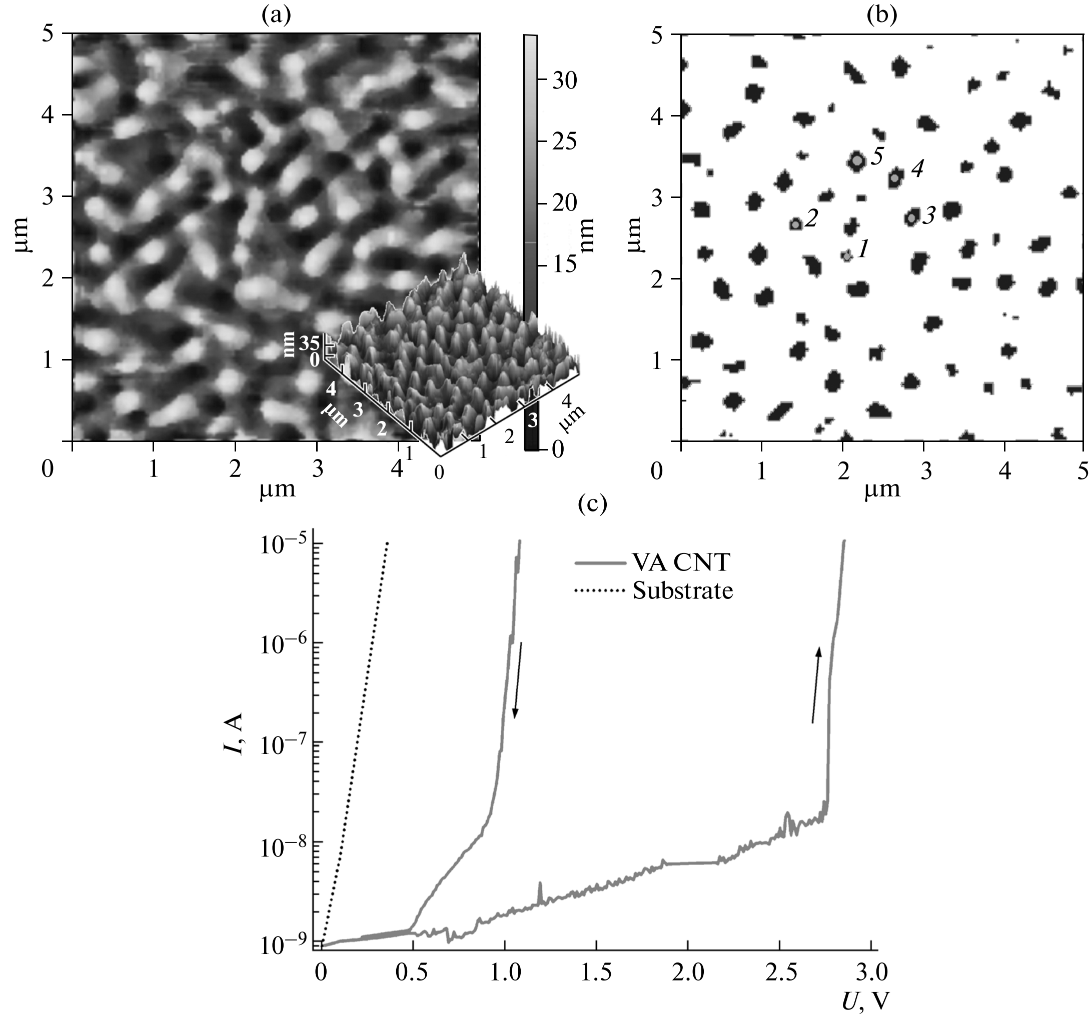


**Fig. 3.** STM study of a VA CNT array: (a) STM image of a VA CNT array, (b) profilogram along a line, and (c) *I–V* characteristics of (solid line) an individual nanotube at point *3* and (dotted line) substrate.

resistance of the contact of the AFM probe to the top of the VA CNT bundle ($R_{p/\mathrm{bundle}}$) and the contact to the conducting layer ($R_{\mathrm{bundle/sub}}$). As was shown in [10], the resistance of the contact of an AFM probe with a platinum coating to the top of VA CNTs can reach several hundreds kiloohms. It should also be noted that the resistance of a VA CNT bundle differs from the sum of the resistances of its individual nanotubes because of the van der Waals interaction between CNTs [11]. Moreover, nanotubes in a bundle differ from each other in the geometric parameters, which also affects the resistance of VA CNTs determined by AFM spectroscopy.

To exclude the resistance of the contact of the probe with the top of a VA CNT bundle ($R_{p/\mathrm{bundle}}$), we performed similar measurements of the *I–V* characteristic of VA CNTs by STM spectroscopy (Fig. 3). An analysis of the obtained STM image of a VA CNT array showed that (Fig. 3b), in contrast to the results shown in Fig. 2a, the individual nanotubes are not joined into VA CNT bundles because of a low CNT density in an array and the VA CNT diameter is 118 ± 39 nm, which makes it possible to study the electrical properties of individual VA CNTs. Based on the *I–V* characteristic of an individual VA CNT (Fig. 3c), we can conclude that an individual VA CNT also has two states of conduction and that the *I–V* characteristic that corresponds to the low-resistance state of VA CNT should be used to determine the VA CNT resistance [9].

An analysis of the measurement of the *I–V* characteristic of an individual VA CNT by STM showed that the measurement system can be represented by the equivalent circuit represented in Fig. 6a. The total resistance of the system ($R_{\mathrm{tot}}^{\mathrm{STM}}$) is

$$R_{\mathrm{tot}}^{\mathrm{STM}} = R_0^{\mathrm{STM}} + R_{\mathrm{CNT/sub}} + R_{\mathrm{CNT}} + R_{\mathrm{tun}}, \tag{5}$$

$$R_0^{\mathrm{STM}} = R_{\mathrm{Me}} + R_{\mathrm{CNTs/Me}} + R_{\mathrm{CNTs}} + R_{\mathrm{CNTs/sub}} + R_{\mathrm{sub}} + R_p^{\mathrm{STM}}, \tag{6}$$

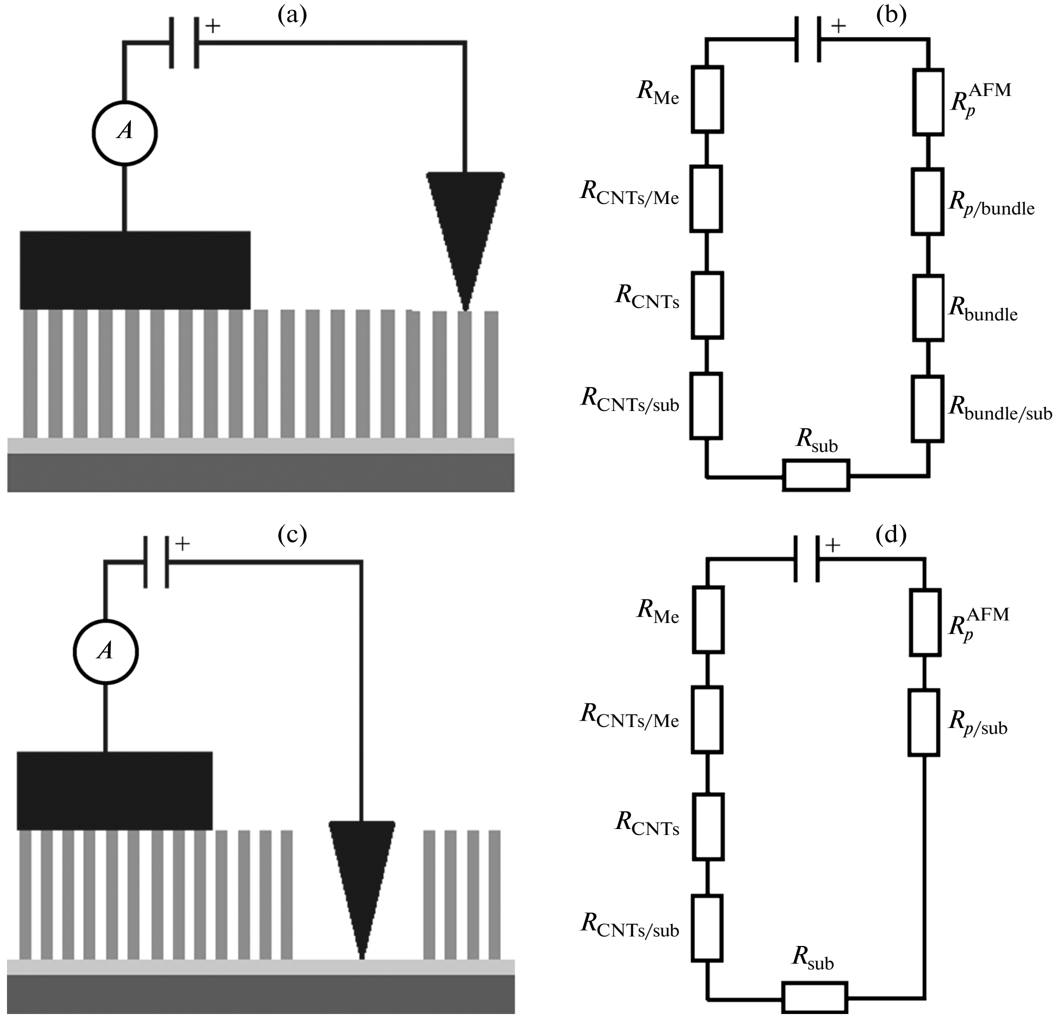


**Fig. 4.** AFM measurement of the electrical parameters of VA CNTs: (a) schematic of measuring the total resistance, (b) equivalent circuit corresponding to Fig. 3a, (c) schematic for measurement without the resistance of a VA CNT bundle and the contacts to it, and (d) equivalent circuit corresponding to Fig. 3c.

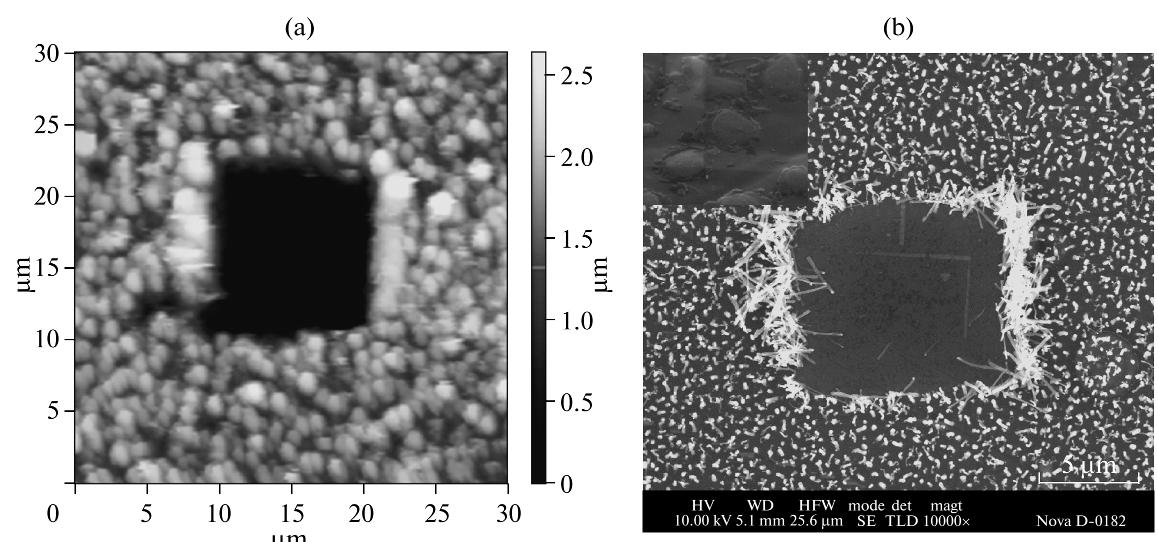


**Fig. 5.** VA CNT array after performing force lithography: (a) AFM image of a VA CNT array and (b) SEM image. (inset) Substrate region without VA CNTs 1 × 1 $\mu m^2$ in size.

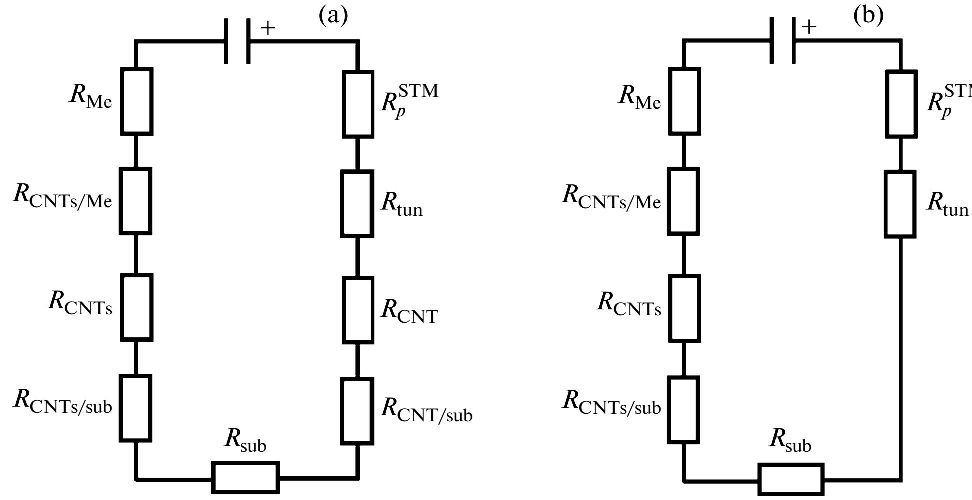


**Fig. 6.** Equivalent circuits for STM measurement of the electrical parameters of VA CNTs: (a) total resistance and (b) without regard for the resistance of an individual VA CNT bundle and its contact to the conducting layer.

where $R_0^{STM}$ is the total resistance of the conducting layer ($R_{sub}$), the contact material ($R_{Me}$), the STM probe material ($R_p^{STM}$), and the nanotube array under the contact and the contacts to this array ($R_{CNTs/Me}$ + $R_{CNTs}$ + $R_{CNTs/sub}$), which is determined by STM spectroscopy of the VA CNT array region modified by force lithography; $R_{tun}$ is the resistance of the tunneling contact between the STM probe and VA CNT; and $R_{CNT}$ + $R_{CNT/sub}$ is the total resistance of an individual VA CNT and the contact between the VA CNT and the conducting layer.

When determining the electrical parameters of materials by STM, the authors of [12] showed that the contribution of the resistance of the tunneling contact decreases with increasing electric field and that it can be assumed $R_{tun} \sim 0$ in a high field. Therefore, the total resistance of an individual VA CNT and the contact to the conducting layer can be written as

$$R_{CNT}^{STM} = R_{tot}^{STM} - R_0^{STM}. \quad (7)$$

Resistance $R_{tot}^{STM}$ was determined from the *I–V* characteristic recorded by STM spectroscopy for an individual VA CNT, and it was found to be 108 kΩ for the low-resistance state (Fig. 3c). Resistance $R_0^{STM}$ was determined using the equivalent circuit of measurement at $R_{tun} \sim 0$ (Fig. 6b) and the *I–V* characteristic recorded for the modified region in a VA CNT array (Fig. 3c); it was found to be 41 kΩ. Therefore, the total resistance of an individual VA CNT and the contact to the conducting layer is $R_{CNT}^{STM}$ = 67 kΩ (Fig. 3b, point *1*).

To determine the transition resistance of the contact of the VA CNT with the conducting layer ($R_{CNT/sub}$), we measured the *I–V* characteristic of VA CNTs with a diameter $D$ = 96, 118, 124, 132, and 157 nm (Fig. 3b; points *1–5*, respectively). Resistance $R_{CNT}^{STM}$ for these VA CNTs was calculated by Eq. (7); it was found to be 67, 63, 47, 22, and 14 kΩ, respectively. Figure 7 shows $R_{CNT}^{STM}$ versus $1/D$. According to the technique in [13], this dependence can be approximated by the function

$$Q = a_1 + a_2 x, \quad (8)$$

where $Q = R_{CNT}^{STM}/D$, $a_1 = \rho B/2$, ρ is the electrical resistivity of VA CNT, $B$ is a correcting coefficient, $a^2 = 4\rho_c/\pi$, $\rho_c$ is the transition electrical resistivity of the

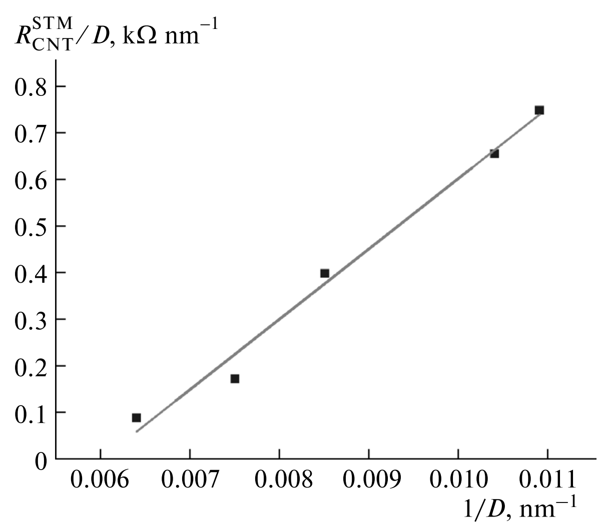


**Fig. 7.** $R_{CNT}^{STM}/D$ vs. $1/D$ for determining the transition resistance of the contact of a VA CNT to the conducting layer.

contact of the VA CNT with the conducting layer, and $x = 1/D$.

An analysis of the dependence of $R_{\mathrm{CNT}}^{\mathrm{STM}}/D$ on $1/D$ (Fig. 7) using the technique from [13] showed that $\rho_c = 118.6$ kΩ nm$^2$ ($1.186 \times 10^{-9}$ Ω cm$^2$). Therefore, the resistance of the contact for the VA CNTs under study changes in the range $R_{\mathrm{CNT/sub}} = 4.1$–$12.8$ Ω. Thus, we have $R_{\mathrm{CNT/sub}} \ll R_{\mathrm{CNT}}^{\mathrm{STM}}$ and this resistance weakly contributes to the resistance of VA CNTs determined by the STM technique.

With allowance for the geometric parameters of VA CNTs, resistance per unit length $r$ and electrical resistivity ρ of VA CNTs are $19.28 \pm 3.08$ kΩ/μm and $8.32 \pm 3.18 \times 10^{-4}$ Ω m, respectively. These values of resistance per unit length and electrical resistivity of multilayer VA CNTs agree well with the data in [14, 15].

## CONCLUSIONS

The electrical properties of VA CNTs were studied by AFM and STM. Based on the obtained results and using force lithography, we developed techniques to determine the resistance per unit length and the electrical resistivity of an individual VA CNT. When the resistance of a VA CNT was determined by AFM, the resistance per unit length and the electrical resistivity of VA CNTs were shown to be higher than those known from the literature, which is likely to be related to the effect of the contact of an AFM probe to the top of VA CNTs and the appearance of an additional resistance in the measuring system. Moreover, it was shown that VA CNT bundles form when preliminary scanning is performed by AFM in the tapping mode in order to position the AFM probe at the top of VA CNTs. These bundles hinder the investigation of the electrical properties of an individual nanotube.

When determining the resistance of an individual VA CNT by STM, we were able to overcome these difficulties, since the resistance of the tunneling contact of an STM probe with the top of VA CNTs becomes insignificant at a voltage higher than 1 V and weakly affects the total resistance of the STM probe/VA CNT/conducting layer/VA CNT array/contact system. Moreover, VA CNT bundles do not form during preliminary STM scanning of the surface of the VA CNT array under study. It was shown that the transition electrical resistivity of the contact of an individual VA CNT to the conducting layer is $1.186 \times 10^{-9}$ Ω cm$^2$ and can be omitted in determining the resistance of VA CNTs. The values of the resistance per unit length and the electrical resistivity of VA CNTs calculated by the developed STM technique were found to be $19.28 \pm 3.08$ kΩ/μm and $8.32 \pm 3.18 \times 10^{-4}$ Ω m, respectively, which agree well with the reported data.

Thus, the developed STM technique of determining the resistance per unit length and the electrical resistivity of VA CNTs can be used to find the electrical parameters of an individual VA CNT without additional fixation of a nanotube and preliminary formation of contact pads to it. In addition, it can be applied to diagnose the electrical parameters of VA CNTs and to create nanoelectronic elements based on them.

## ACKNOWLEDGMENTS

The experimental results were obtained on the equipment of the Center of Collective Use and the Scientific-Education Center Nanotechnologies of Southern Federal University.

This work was supported by the Ministry of Science and Education of the Russian Federation (project nos. 1936, 16.1154.2014/K), project 14.575.21.0045 (unique identifier RFMEFI57514X0045), and the Russian Foundation for Basic Research (project nos. 14-07-31322mol_a, 14-07-31162mol_a).

## REFERENCES

1. Y. Lan, Y. Wang, and Z. Ren, Adv. Phys. **60,** 553 (2011).
2. X. V. Lu and J. Y. Dai, Appl. Phys. Lett. **88**, 113104 (2006).
3. H. Li and K. Banerjee, IEEE Trans. Electron Devices **56**, 2202 (2009).
4. N. Chiodarelli, S. Masahito, Y. Kashiwagi, Y. Li, K. Arstila, O. Richard, D. J. Cott, M. Heyns, St. Gendt, G. Groeseneken, and Ph. M. Vereecken, Nanotechnology **22**, 085302 (2011).
5. K. Ichimura, M. Osawa, K. Nomura, H. Kataura, Y. Maniwa, S. Suzik, and Y. Achiba, Physica B **323**, 230 (2002).
6. O. A. Ageev, Yu. F. Blinov, O. I. Il'in, A. S. Kolomiitsev, B. G. Konoplev, M. V. Rubashkina, V. A. Smirnov, and A. A. Fedotov, Tech. Phys. **58**, 1831 (2013).
7. B. G. Konoplev, O. A. Ageev, A. S. Kolomiitsev, V. A. Smirnov, and N. I. Serbu, Mikroelektronika **41**, 47 (2012).
8. O. A. Ageev, O. I. Il'in, A. S. Kolomiitsev, B. G. Konoplev, M. V. Rubashkina, V. A. Smirnov, and A. A. Fedotov, Mikro-Nanosist. Tekh., No. 3, 9 (2012).
9. O. A. Ageev, Yu. F. Blinov, O. I. Il'in, M. V. Rubashkina, V. A. Smirnov, and A. A. Fedotov, in *Proceedings of the International Symposium "Physics and Mechanics of New Materials and Underwater Applications," Thailand, 2014,* p. 12.
10. Q. Ngo, D. Petranovic, Sh. Krishnan, A. M. Cassell, Q. Ye, J. Li, M. Meyyappan, and C. Y. Yang, IEEE Trans. Nanotechnol. **3**, 311 (2004).
11. G. Kim, J. Bernholc, and Y.-K. Kwon, Appl. Phys. Lett. **97**, 063113 (2010).
12. H. Won and R. F. Willis, Surf. Sci. **604**, 491 (2010).
13. Yu. D. Chistyakov, V. V. Baranov, and A. P. Dostanko, Obz. Electron. Tekh., Ser. Poluprovod. Prib., No. 7 (143), 364 (1973).
14. B. Vivo, P. Lamberti, G. Spinelli, and V. Tucci, Rom. J. Inf. Sci. Tech. **13**, 33 (2010).
15. D. Fathi and B. Forouzandeh, *Carbon Nanotubes*, Ed. by J. M. Marulanda (InTech., 2010), pp. 275–297.

*Translated by K. Shakhlevich*