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Scanning Probe Techniques for Characterization of Vertically Aligned Carbon Nanotubes

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Abstract

This chapter presents the results of experimental studies of the electrical, mechanical and geometric parameters of vertically aligned carbon nanotubes (VA CNTs) using scanning probe microscopy (SPM). This chapter also presents the features and difficulties of characterization of VA CNTs in different scanning modes of the SPM. Advanced techniques for VA CNT characterization (the height, Young's modulus, resistivity, adhesion and piezoelectric response) taking into account the features of the SPM modes are described. The proposed techniques allow to overcome the difficulties associated with the vertical orientation and high aspect ratio of nanotubes in determining the electrical and mechanical parameters of the VA CNTs by standard methods. The results can be used in the development of diagnostic methods as well as in nanoelectronics and nanosystem devices based on vertically aligned carbon nanotubes (memory elements, adhesive structures, nanoelectromechanical switches, emission structures, etc.).

Keywords: nanotechnology, carbon nanotube, scanning probe microscopy, resistivity, Young's modulus, adhesion, piezoelectric response

1. Introduction

Precise parameters of vertically aligned carbon nanotubes (VA CNTs) control geometric parameters, resistivity, Young's modulus, adhesion, strength, and so on, and are a prerequisite for the devices of nanoelectronics and nanosystems creation on their basis with reproducible and stable characteristics [1–4]. However, the determination of these parameters in

the carbon nanotubes (CNTs) by standard diagnostic methods is difficult due to the vertical orientation and the high aspect ratio of the nanotubes.

Thus, the application of traditional experimental methods for determining mechanical parameters (direct tensile load, pulsed dynamic method, etc.) is complicated due to the size of the VA CNT and also because of the need to fasten nanotubes on the substrate. In addition, as shown by the analysis of published data, the Young's modulus (one of the main mechanical parameters of CNTs) has a wide range of values in the range 0.4–6.85 TPa [5–13]. The values of the Young's modulus obtained experimentally are 2–3 times smaller [5, 7–10] calculated on the basis of theoretical models [11–13]. This may be due to the fact that the Young's modulus of CNTs depends essentially on the thickness of the CNT wall, which in practice is several times larger than values used in theoretical calculations [14].

The most widely used methods for investigating the electrical properties of microstructures require the formation of contact areas of several micrometers in size at the tops of the VA CNTs. This fact significantly limits the possibilities of using these methods to determine the electrical parameters of individual vertically aligned nanotubes because of their small transverse dimensions [15]. The work on quantitative evaluation and study of VA CNT adhesion to substrate is not numerous due to the complicated nature of interaction between the substrate, the catalytic center and the nanotube during the growth of the carbon nanotubes and also the need to manipulate individual nanotubes during experimental studies [16–18].

Thus, the tasks associated with development of new nanodiagnostic techniques to determine the geometric, mechanical and electrical parameters of VA CNTs are relevant in connection with the need to control and study parameters of individual vertically aligned carbon nanotubes, elements and devices on their basis and also in connection with requirements for development of metrological support for nanotechnologies.

A promising method for developing such nanodiagnostic techniques is a scanning probe microscopy (SPM) method [19–25]. This method does not require additional fixation of VA CNTs, special sample preparation and formation of contact areas on their tops. However, the determination of quantitative values of individual carbon nanotube parameters based on results obtained by SPM requires analysis of measurement process and development on its basis of techniques for determining parameters of CNTs taking into account the features of the SPM method.

This chapter describes unique techniques for determining the height, Young's modulus, bending stiffness, resistivity and adhesion to a substrate of vertically aligned carbon nanotubes, based on the methods of scanning probe microscopy. Described techniques can be used for nanodiagnostics of parameters of individual vertically aligned carbon nanotubes and for creation of nanoelectronic elements and devices on their basis [1, 11, 21, 23, 25–29].

2. Scanning probe techniques for characterization of vertically aligned carbon nanotubes

2.1. Experimental samples and equipment

The experimental samples of vertically aligned carbon nanotubes were grown using the NANOFAb NTC-9 nanotechnology multi-functional complex (NT-MDT, Russia) using the

plasma-enhanced chemical vapor deposition (PECVD) method [2, 25, 30, 31]. A silicon wafer with a deposited titanium film and a nickel catalytic film with thicknesses of 20 and 10 nm, respectively, was used as the initial substrate. Acetylene was used as the reaction gas. The growth of VA CNT arrays was carried out at a pressure of 4.5 Torr and a temperature of 750°C. The growth parameters for experimental samples were characterized by the growth time, the acetylene feed rate and current flowing in the system. The structural analysis of the VA CNT arrays was conducted by the transmission electron microscopy (TEM) using Tecnai Osiris (FEI, Netherlands) and the Raman spectrometer Renishaw InVia Reflex (Renishaw plc, UK). Analysis of TEM images and Raman spectra showed that the experimental samples were multi-walled carbon nanotubes [3]. Surface investigations of the obtained VA CNT arrays were carried out using a scanning electron microscope (SEM) Nova Nanolab 600 (FEI Company, Netherlands).

Experimental studies of geometric, mechanical, electrical and adhesive properties of VA CNT arrays were carried out using the Ntegra probe nanolaboraty (PNL) (NT-MDT, Russia). To process the experimental data, the ImageAnalysis application package was used. A commercially available silicon cantilever of the NSG 20 brand was used as the probe of the atomic force microscope in developing the technique for determining the height of the VA CNT array. Investigations of the mechanical properties of carbon nanotube were carried out at Ntegra PNL by an integrated scanning hardness nanotester. The indenter was a diamond triangular pyramid of Berkovich with an angle at the vertex between the edge and height $\theta = 70^\circ$. Investigations of the electrical parameters of VA CNTs were carried out by scanning tunneling microscopy (STM) method in spectroscopy mode with a distance between the STM probe and the VA CNT top equal to 0.5 nm. A tungsten probe made by an electrochemical method was used as a STM probe. Experimental studies of the VA CNT adhesion to a substrate were carried out by atomic-force microscopy (AFM) in current spectroscopy mode, with a distance between CNT top and an AFM probe equal to 1 nm. Experimental studies of piezoelectric response of VA CNT were performed by the AFM method in force spectroscopy mode. A commercially available silicon cantilever with a platinum coating of NSG11/Pt brand with a tip radius of 20 nm was used as an AFM probe.

2.2. A technique for determining the height of a vertically aligned carbon nanotube array

One of the promising methods for studying nanoscale structures is the atomic force microscopy, which allows one to determine the parameters of nanostructures without special sample preparation and to modify them by probe nanolithography methods [25]. The main difficulty in the study of VA CNT arrays by the AFM method is the mobility of nanotubes in their interaction with the probe. In addition, at a high density of carbon nanotubes in the array, the depth of penetration of the AFM probe between the individual nanotubes is limited by the parameters of the probe itself (the radius of curvature and aspect ratio of tip sides), which can lead to the display on AFM images of nonindividual nanotubes in the array and their bundles [25].

The study of influence of AFM scanning mode (contact, semi-contact and noncontact) on the quality of the image obtained on the surface of VA CNT array (with a diameter $D = 80$ nm, length $L = 2$ μm and density of nanotubes in the array $n = 30$ μm^{-2}) shows that the carbon nanotubes “detach” from substrate-surface VA CNTs in AFM contact mode (**Figure 1a**). As a result, the AFM contact mode cannot be used for nanodiagnostics and for determining the

VA CNT geometric parameters [25]. The study of the VA CNT array in the semi-contact mode shows that the individual VA CNTs are combined into bundles when the probe is exposed (**Figure 1b**). The main disadvantage of AFM images of VA CNT array obtained in a semi-contact mode is the presence of a number of scanning artifacts caused by the high mobility of nanotubes during mechanical contact with the probe, and as a consequence, the relatively low resolution of this AFM mode (**Figure 1b**).

In addition, a partial destruction of the VA CNT array is possible when scanning in a semi-contact mode with a pressing force of the AFM probe to surface more than 10 μN and scanning frequency more than 1 Hz (**Figure 2**).

The usage of the AFM noncontact mode at which the probe interacts with the array surface only due to van der Waals forces [32] made it possible to obtain AFM images of bundles of vertically aligned carbon nanotubes with a higher resolution, without explicit artifacts (**Figure 1c**). In the noncontact mode, the individual nanotubes were also combined into bundles with a diameter of about 300 nm (**Figure 1c**) under the action of van der Waals forces [25]. Statistical processing of AFM images showed that the maximum height of the bundle was 2.52 μm , the average height was $1.27 \pm 0.35 \mu\text{m}$ and the density of individual VA CNT bundles in the array was about $1.68 \mu\text{m}^{-2}$ [25].

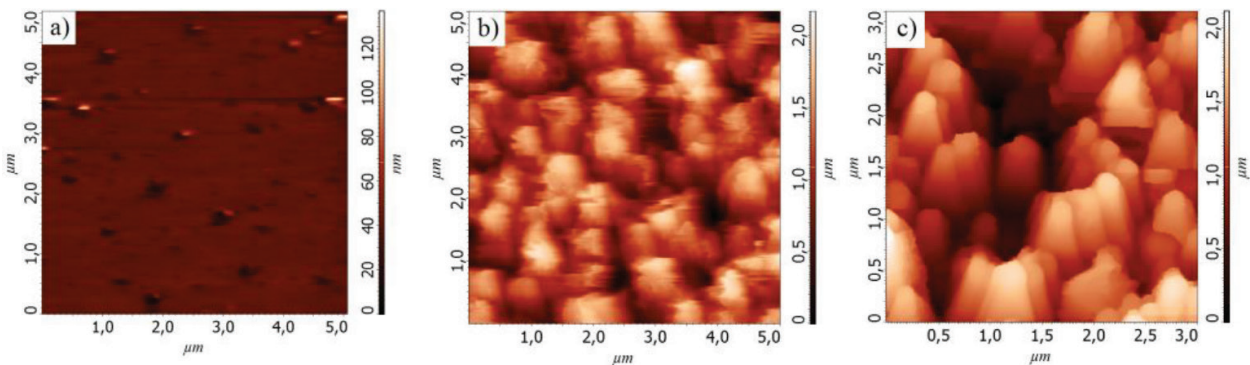


Figure 1. AFM images of the surface of the VA CNT array obtained by AFM: (a) in contact mode, (b) in semi-contact mode and (c) in noncontact mode [25].

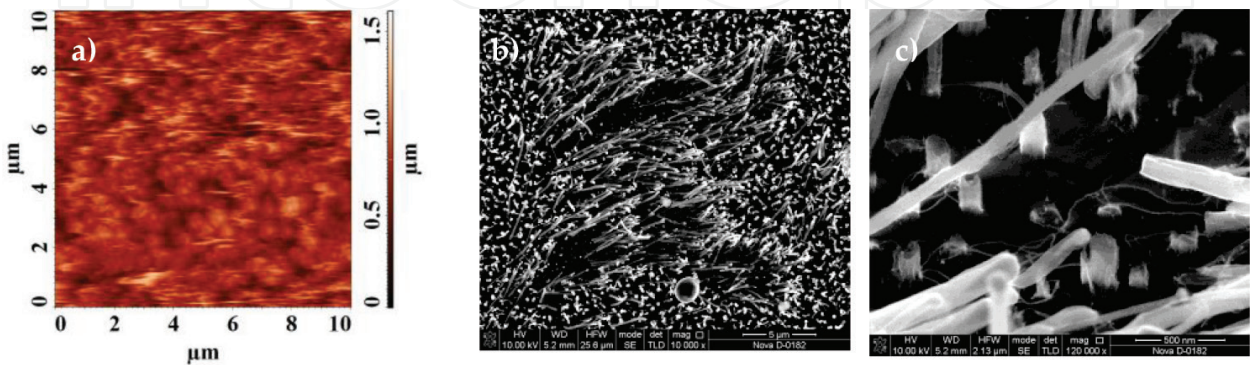


Figure 2. The images of the VA CNT array obtained after scanning in a semi-contact mode with a pressing force of the AFM probe to surface more than 10 μN : (a) AFM images; (b) and (c) SEM images.

Thus, it has been shown that the optimal scanning mode for determination of the geometric parameters of vertically aligned carbon nanotubes is the AFM noncontact mode, which allows one to obtain AFM images with a higher resolution resolving and without destroying the VA CNT structure. The results obtained by the AFM noncontact mode correlate well with the values of the geometrical parameters of the VA CNT determined by the SEM method.

Based on the obtained results, a technique for measuring a VA CNT array height was developed. This technique was based on sequential scanning in contact, then in semi-contact or non-contact modes of a VA CNT array with different areas [25]. So, the VA CNT array were scanned with an area of $10 \times 10 \mu\text{m}^2$ and then $30 \times 30 \mu\text{m}^2$ (**Figure 3a, b**). The analysis of the profilogram of the scanning area allowed to determine the maximum height of the VA CNT array equal to $1.98 \mu\text{m}$ and the average height of VA CNTs in the array equal to $1.12 \pm 0.45 \mu\text{m}$ (**Figure 3c**).

The developed technique for measuring the VA CNT array height allows to determine the height value with a higher reliability than a semi-contact or noncontact mode in that the measurement of this parameter is made relative to substrate's surface and not the greatest penetration depth of the AFM probe into the array. Moreover, the developed technique makes it possible to obtain and automatically process a statistical set of the geometric parameters' values of carbon nanotubes in contrast to the SEM method.

2.3. A technique for determining the Young's modulus and bending stiffness of vertically aligned carbon nanotubes

One of the promising methods for determining the Young's modulus of vertically aligned CNTs is the nanoindentation method based on indenting a solid needle (indenter) into the array by applying an external load and obtaining the dependence of the penetration depth of the indenter into the array from nanoindentation force [11, 22]. A schematic process of nanoindentation of a vertically aligned carbon nanotubes array is shown in **Figure 4**. Initially, the indenter is in the approached state, then the load is applied and the indenter interacts with the array surface and touches the first VA CNT at the depth h_1 ; with a further increase in the load, the first nanotube begins to bend and the indenter touches the second tube at the depth h_2 (**Figure 4a**). At a given depth h , the indenter interacts with the i -number of VA CNTs, each of which is deflected by a distance w_0 (**Figure 4b**), depending on the initial touch depth of the indenter with the i -tube and the geometry of the indenter [13]:

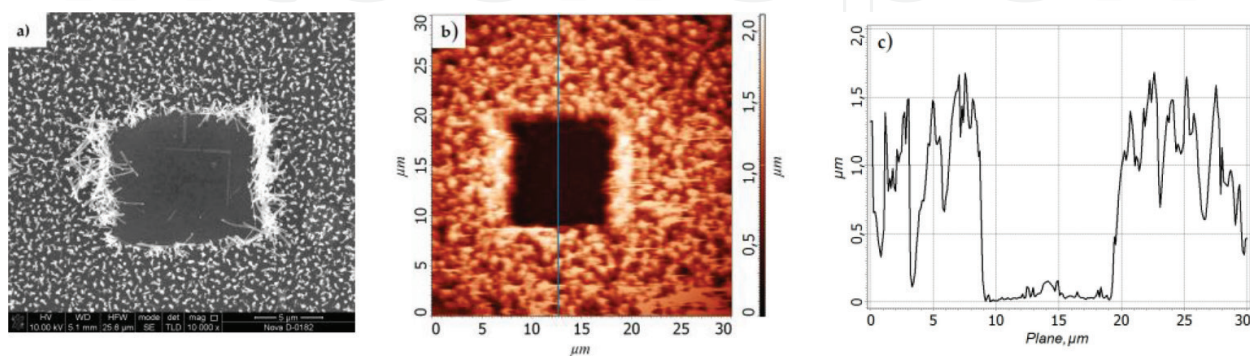


Figure 3. Measuring a VA CNT array height based on developed technique: (a) SEM image, (b) AFM image and (c) profilogram along the line [25].

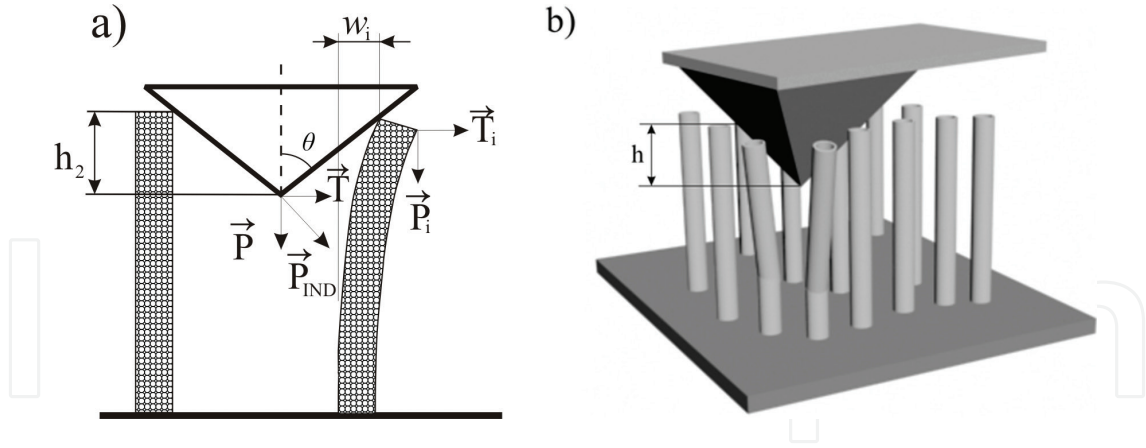


Figure 4. Schematics of the nanoindentation process of the VA CNT array: (a) the deflection of the first nanotube and the touching of the second nanotube of the indenter with increasing applied force; (b) the interaction of the indenter with i nanotubes at depth h [29].

$$w_0 = (h - h_i) \tan \theta. \quad (1)$$

On the other hand, the nanoindentation process can be considered using a micromechanical model. This model is based on the beam theory, according to which an individual vertically aligned nanotube is an elastic hollow cylindrical rod fixed at one end. In this case, the elastic deflection w_0 of a carbon nanotube with an outer diameter D and a height L when an external load is applied is described by the equation [11]:

$$w_0 = \frac{T}{P} \left(\frac{\tan kL}{k} - L \right), \quad (2)$$

where P and T are the forces acting on the nanotube parallel and perpendicular to its axis, respectively (**Figure 4a**); $k = (P/(EI)_{\text{eff}})^{1/2}$, $(EI)_{\text{eff}}$ is the effective bending stiffness of a VA CNT with an effective moment of inertia equal to $I_{\text{eff}} \approx \pi D^4/64$ [11].

Earlier, a method was developed for determining the mechanical parameters of a VA CNT based on the nanoindentation using a micromechanical model [11]. The main shortcoming of this method was the use of bending stiffness as a rigidity parameter of theoretical and experimental dependencies, from which the value of the Young's modulus of the VA CNT is calculated [11]. This fact significantly reduced the reliability of the obtained results. To eliminate this shortcoming, we proposed a technique for determining the bending stiffness $(EI)_{\text{eff}}$ for each i -tube interacting with the indenter using experimental dependencies [22, 28, 29]. For this the force P acting on one CNT was represented as [22]:

$$P = (P_{\text{IND}} - P_i) \cos \theta / i, \quad (3)$$

where P_{IND} is the indentation force representing the vector sum of the forces P and T (**Figure 4a**), P_i is the indentation force corresponding to the depth h_i of touching of the i -tube and i is the number of nanotubes interacting with the indenter at the P_{IND} . The values of the P_{IND} and P_i forces are determined from the experimental dependencies obtained in the nanoindentation process of the VA CNT array.

Thus, Young's modulus is determined from the following expression based on the technique developed by us [22]:

$$Y = \frac{64(P_{IND} - P_i) \cos \theta}{\pi i D^2 k^2}. \quad (4)$$

The number of nanotubes i interacting with the indenter for a given indentation force is defined as the product of the total interaction area of the indenter S at penetration depth h and density of the VA CNTs in an array. The total area S is the sum of the cross-section area of the indenter S_{ind} at depth h , the interaction area by the perimeter of indenter S_{per} and the cross-sectional area of the nanotube S_{CNT} . Due to the fact that the Berkovich indenter is a regular triangular pyramid with the angle at the vertex $\theta = 70^\circ$, the height of the triangle lying at the base of the pyramid is $a = 1.5 h \cdot \tan 70^\circ$ and the value of the edge of the base is $c = 2a \cdot \tan 30^\circ$. The interaction area of the indenter S at the penetration depth h with one tube is [22]:

$$S = i/n = S_{ind} + S_{per} + S_{CNT} = 9.853 h^2 + 14.355 h D_0 + 3.141 D_0^2/4. \quad (5)$$

This dependence allows us to determine not only the number of tubes interacting with the indenter at a depth h but also the depth h_i at which the indenter touches the i -tube.

The technique proposed by us technique makes it possible to calculate the Young's modulus of individual VA CNT directly from a set of the experimental dependences obtained in the nanoindentation process [22]. The limits of applicability of the technique are determined by the aspect ratio of vertically aligned carbon and the nanotube deflection value. The maximum value of the deflection of CNTs in the nanoindentation process, in which the interaction of the indenter with the VA CNT array is still described by the beam theory, depends on the length of the carbon nanotube and is determined by the following expression [22]:

$$w_{\max} = (0.2L - h_i) \tan \theta, \quad (6)$$

where $0.2L$ is the maximum penetration depth determined from the experimental dependences.

For the approbation of the developed technique, three experimental samples of VA CNT arrays with various geometric parameters were studied (**Figure 5**). Analysis of SEM images made it possible to estimate the diameter and height of carbon nanotubes, as well as the density of nanotubes in the array. The values of these parameters are presented in **Table 1**.

Using the obtained values of the geometric parameters of carbon nanotubes, their mechanical properties were investigated by the developed technique. The maximum value of an indentation force was 100 μ N. The nanoindentation was carried out at six different points separated from each other by a distance of about 5 μ m for each VA CNT array. **Figure 6** shows the experimental dependences obtained for three arrays of VA CNT.

Analysis of the dependences showed that the curve of the penetration depth of the indenter into the array on the indentation force is nonlinear. Two sections of the curve can be distinguished: the elastic (from 0 to 250 nm for the first mass, from 0 to 175 nm for the second mass, and from 0 to 250 nm for the third one) and inelastic (from 250 to 330 nm for the first array, from 175 to 275 nm for the second one and from 250 to 600 nm for the third one) interaction. Therefore, only the first section of the curves was used to calculate the Young's modulus of

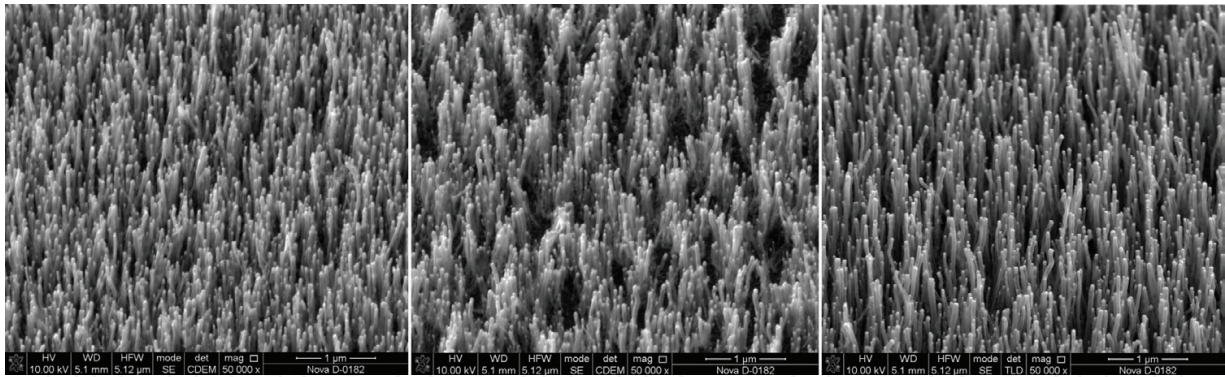


Figure 5. SEM images of the investigated arrays of vertically aligned carbon nanotubes: (a) VA CNTs No 1, (b) VA CNTs No 2 and (c) VA CNTs No 3.

VA CNTs as the beam theory describes only small elastic deflections. Based on this, the total penetration depth of the indenter into the first array h was 250 nm, into the second one was 175 nm and into the third one was 250 nm. The corresponding indentation forces of P_{IND} were about 8, 10 and 3 μN , respectively (**Figure 6**).

Using the developed technique, the bending stiffness and Young’s modulus were determined for each i-nanotube of the VA CNT interacting with the indenter at a depth h and the average values of these parameters were obtained for each VA CNT arrays. The results are shown in **Table 2**. The obtained values of the mechanical parameters of the VA CNT correlate well with the literature data [5–7, 9, 11, 22, 28].

An analysis of the results showed that the Young’s modulus of a VA CNT increases with the increase in its length. This fact can be associated with decreasing the structural defects of the nanotube with increasing length. Analysis of the bending stiffness values showed that the value of this parameter increases with increasing diameter of the nanotubes. This is probably due to an increase in the number of inner layers in multi-walled carbon nanotubes and an increase in Van der Waals forces between layers, which leads to an additional resistance of the carbon nanotube to bending deformations during indentation [14].

Thus, the developed technique can be successfully used to measure the mechanical parameters of vertically aligned carbon nanotubes by the nanoindentation, as well as to study the effect of the geometric parameters of VA CNT on their Young’s modulus [22, 28]. The developed technique can be used to determine the mechanical properties of nanotubes and nanowires from other materials [21].

Parameter	VA CNTs No 1	VA CNTs No 2	VA CNTs No 3
Height L , nm	650	1210	930
Diameter D , nm	44	36	51
Aspect ratio H	15	34	13
The VA CNTs density in array n , μm^{-2}	82	72	69

Table 1. Geometric parameters of the VA CNTs determined by the SEM method.

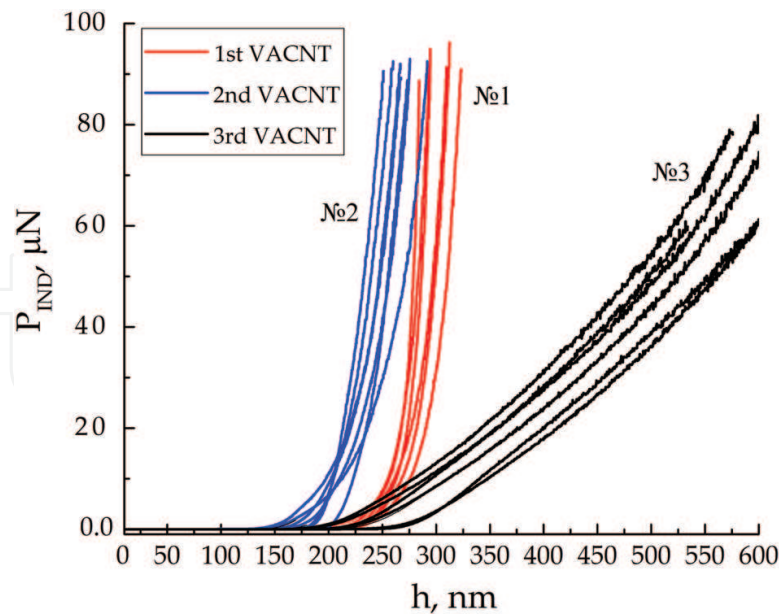


Figure 6. Experimental dependences obtained by the nanoindentation of the VA CNT arrays.

2.4. A technique for determining the resistivity of vertically aligned carbon nanotubes

Scanning probe microscopy is a precision method for studying the electrical properties of horizontal carbon nanotubes [33–35]. However, the study of vertically aligned carbon nanotube has difficulties due to the mobility of nanotubes upon contact with the SPM probe and the formation of VA CNT bundles on the application of an electric field [36]. In addition, the determination of the VA CNT resistivity based on the current–voltage characteristics (CVC) obtained by the SPM method requires an analysis of the measuring process the CVCs and the development of a technique taking into account the features of the SPM [23]. Earlier, it was shown that the value of the VA CNT resistivity obtained on the basis of CVCs obtained by the AFM method is higher [23] than the value presented in the literature [37]. This is due to the influence of contact of the AFM probe on the VA CNT top and the appearance of additional resistance in the measuring system. In addition, as a result of preliminary scanning of the VA CNT array in an AFM semi-contact mode, nanotubes form bundles, which makes it difficult to localize the probe over an individual VA CNT top and to study its electrical properties. The determination of the resistance of an individual VA CNT by the scanning tunneling microscopy (STM) method allows to overcome these difficulties because the resistance of the tunnel contact of the STM probe with the VA CNT top at a voltage of

Mechanical parameters	VA CNTs No 1	VA CNTs No 2	VA CNTs No 3
Bending stiffness, N·nm ²	0.112 ± 0.004	0.106 ± 0.005	0.195 ± 0.007
Young's modulus, TPa	1.15 ± 0.05	1.29 ± 0.08	0.59 ± 0.12

Table 2. The geometrical and mechanical parameters of the nanotubes in the VA CNT array determined by the AFM and the nanoindentation.

more than 1 V becomes insignificant and does not significantly affect the overall resistance of the system “STM probe/VA CNT/conductive layer/VA CNT array/contact.” In addition, the formation of VA CNT bundles does not occur during the preliminary scanning by the STM method [23].

The schematic and the equivalent circuit of the measuring system of the VA CNT by the STMs method are shown in **Figure 7**. According to **Figure 7b**, the total resistance of the system R_{tot}^{STM} is [23]:

$$R_{tot}^{STM} = R_0^{STM} + R_{CNT/sub} + R_{CNT} + R_{tun'} \quad (7)$$

$$R_0^{STM} = R_{Me} + R_{CNTs/Me} + R_{CNTs} + R_{CNTs/sub} + R_{sub} + R_p^{STM}, \quad (8)$$

where R_0^{STM} is the total resistance of the conductive layer R_{sub} , the contact materials R_{Me} and the STM probe R_p^{STM} , as well as the array of nanotubes under contact $R_{CNTs/Me} + R_{CNTs} + R_{CNTs/sub}$ determined by STM spectroscopy of the array area without the VA CNTs (**Figure 7c, d**); $R_{tun'}$ —resistance of the tunnel contact between the STM probe and VA CNT; $R_{CNT} + R_{CNT/sub}$ is the total resistance of an individual vertically aligned carbon nanotube and the contact between the VA CNT and the conductive layer [23].

Earlier, it was shown that the contribution of the resistance of the tunnel contact decreases with increasing electric field strength and at large values of the strength one can take $R_{tun} \sim 0$ [38], where the total resistance of the individual VA CNT and the contact to the conductive layer can be taken as [23]:

$$R_{CNT}^{STM} = R_{tot}^{STM} - R_0^{STM}. \quad (9)$$

The resistance R_{tot}^{STM} was determined on the basis of the CVC obtained by STM spectroscopy on an individual VA CNT. The resistance R_0^{STM} was determined on the basis of the equivalent circuit for $R_{tun} \sim 0$ (**Figure 7d**) and the CVC obtained at the modified area of the VA CNT array. The resistivity of an individual VA CNT was defined as $\rho_{el} = R_{CNT}^{STM} \cdot S/L$.

The experimental approbation of the proposed technique was carried out on an experimental sample of VA CNT array ($D = 70\text{--}120\text{ nm}$, $L = 2.2\text{ }\mu\text{m}$, $n = 8\text{ }\mu\text{m}^{-2}$). The distance between the

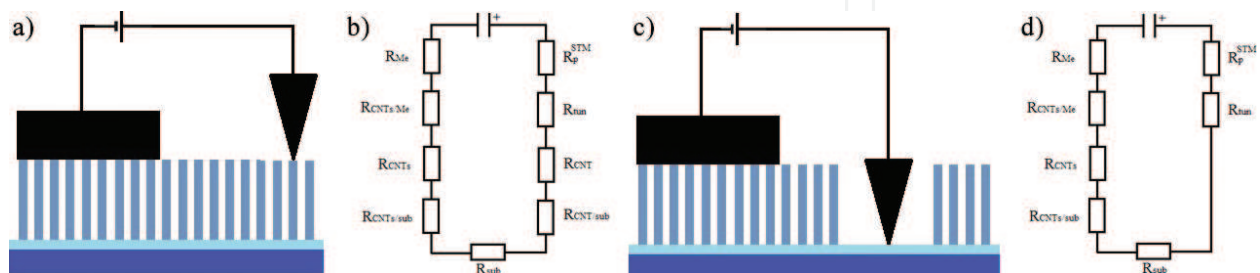


Figure 7. Measurement of the electrical parameters of the VA CNT by the STM method: (a, b) a schematic and equivalent circuit of measuring the total resistance; (c, d) a schematic and equivalent circuit without resistance of the VA CNT and its contacts [23].

STM probe and the VA CNT top was 0.5 nm. To localize the probe at the VA CNT top, a preliminary scanning of the array surface was performed using the STM method. The resulting STM image and the CVC of the VA CNT (solid line) are shown in **Figure 8**. The resistance of the “STM probe/conductive layer/VA CNT array/contact” system (**Figure 7c**) was measured additionally to exclude the resistance of the STM probe, the conductive layer, the contact material and the nanotube array below it from the total resistance system. To measure this resistance, the VA CNT array was previously scanned in the AFM contact mode using the technique presented in Section 2.2. The CVC of the modified area is shown in **Figure 8b** (dashed line).

Analysis of the obtained STM image of the VA CNT array showed that individual nanotubes are not combined into bundles due to the low density of VA CNTs in the array (**Figure 8a**). It allows investigating the electrical properties of individual VA CNTs. The diameter of the VA CNT is 118 ± 39 nm. The height of the VA CNT is not displayed correctly on the STM image due to the peculiarities of measuring the VA CNT array by the STM [36]. Based on the CVC of the individual VA CNT (**Figure 8b**), it can be concluded that the individual VA CNT exhibits two conduction states: high resistance when the voltage is varied from 0 to 10 V and low resistance when the voltage varies from 10 to 0 V, which is due to the manifestation of a memristor effect in VA CNT [3, 26, 29, 39, 40]. The low-resistance state of the VA CNT was used to determine the resistance of the nanotube, since there is no additional resistance in VA CNT associated with the internal electric field in the nanotube [3, 40].

The resistance of R_{tot}^{STM} was determined on the basis of the CVC, an individual VA CNT in low-resistance state, and was 108 k Ω (**Figure 8b**). The resistance R_0^{STM} was determined on the basis of the CVC obtained at the modified area of the VA CNT array (**Figure 8b**) and was 41 k Ω . From there, the total resistance of the individual VA CNT and the contact to the conductive layer R_{CNT}^{STM} was 67 k Ω . It was previously shown that a transition electrical resistivity of the contact of the VA CNT with the conducting layer is about 118.6 k Ω nm² ($1.186 \cdot 10^{-9}$ Ω cm²) [23]. Therefore, the resistance of the contact for the VA CNTs under study changes in the range $R_{CNTs/sub} = 4.1\text{--}12.8$ Ω . Thus, we have $R_{CNTs/sub} < R_{CNT}^{STM}$ and this resistance weakly contributes to the resistance of VA CNTs determined by the STM technique. Taking into account the geometric parameters of VA

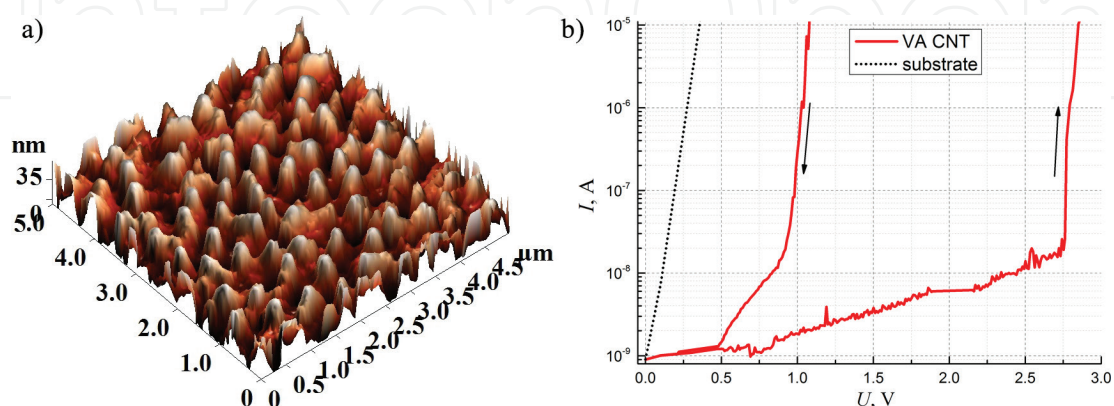


Figure 8. Investigation of the VA CNT array by the STM method: (a) 3D STM image of the VA CNT array; and (b) CVCs of an individual nanotube (solid line) and substrate (dashed line) [23].

CNT, the resistivity of VA CNT was $(8.32 \pm 3.18) \cdot 10^{-4} \Omega\text{m}$. The obtained value of the resistivity of multi-walled VA CNT correlates well with the literature data [41].

2.5. A technique for determining the adhesion of vertically aligned carbon nanotube to a substrate

The adhesion of VA CNT to a substrate W_a quantitatively characterized by the work of breaking the adhesive bond per unit area was assumed to be equal to the work of the internal elastic forces arising at the base of the VA CNT at the moment of detachment from substrate [42]:

$$W_a = \sigma \frac{\Delta L_0}{x_0} x_0 = \sigma \Delta L_0, \quad (10)$$

where $\sigma = k\Delta L_0/S$ —mechanical stress arising in a VA CNT as a result of elongation; ΔL_0 is a VA CNT elongation at the point $x_0 = 0.01 L$ at $t = t_0$.

From a practical point of view, the adhesion strength and the corresponding detachment force (the maximum force that can be applied along the axis of the nanotube without detaching it from the substrate) are of great importance. These parameters allow optimizing the design and operating parameters of emitters and memory elements based on VA CNT to prevent a VA CNT detaching from the substrate. The adhesion strength f_0 was defined as the force required for breaking the adhesive bond of the VA CNT with the substrate referred to the area of the adhesive contact. The value of adhesive strength is sensitive to the determination method and depends on the type of external load causing destruction of the adhesive contact. When applying a mechanical load to the VA CNT, the external force is expended on the deformation of VA CNT (F_x) and the break of the adhesion bond with the substrate ($F_a = W_a \cdot S / \Delta L_0$), and the adhesion strength of the VA CNT bond to the substrate is determined as [42]:

$$f_0 = (F_x(L, t_0) + F_a) / S = F_0 / S. \quad (11)$$

When applying an external electric field, the adhesive strength f_0' is higher than adhesion strength f_0 by applying a mechanical load due to the attraction force $F_{at}(t)$ arising under the action of an external electric field which is expended not only on the deformation of VA CNT and the break of adhesive bond with the substrate but also on the polarization and creation of the conduction current VA CNT. The adhesive strength f_0' is determined as [42]:

$$f_0' = F_{at}(t_0) / S. \quad (12)$$

Thus, the value of the maximum force that can be applied to the “VA CNT/substrate” system without its destruction will be different for devices functioning in the field of mechanical loads of high electric field.

Experimental studies of adhesion were carried out on a VA CNT array ($D = 70\text{--}120 \text{ nm}$, $L = 2.2 \mu\text{m}$ and $n = 8 \mu\text{m}^{-2}$) when voltage pulses U were applied with an amplitude of 10 V to 30 V and duration of 1 s. The detachment of the VA CNT from the substrate was fixed by the absence of current on the reverse branch of the CVC (with the voltage from the maximum value to zero) obtained in the “substrate/VA CNT/AFM probe” system in the AFM spectroscopy mode (Figure 9). The nanotube is retained on the surface of the AFM probe by the van der Waals forces

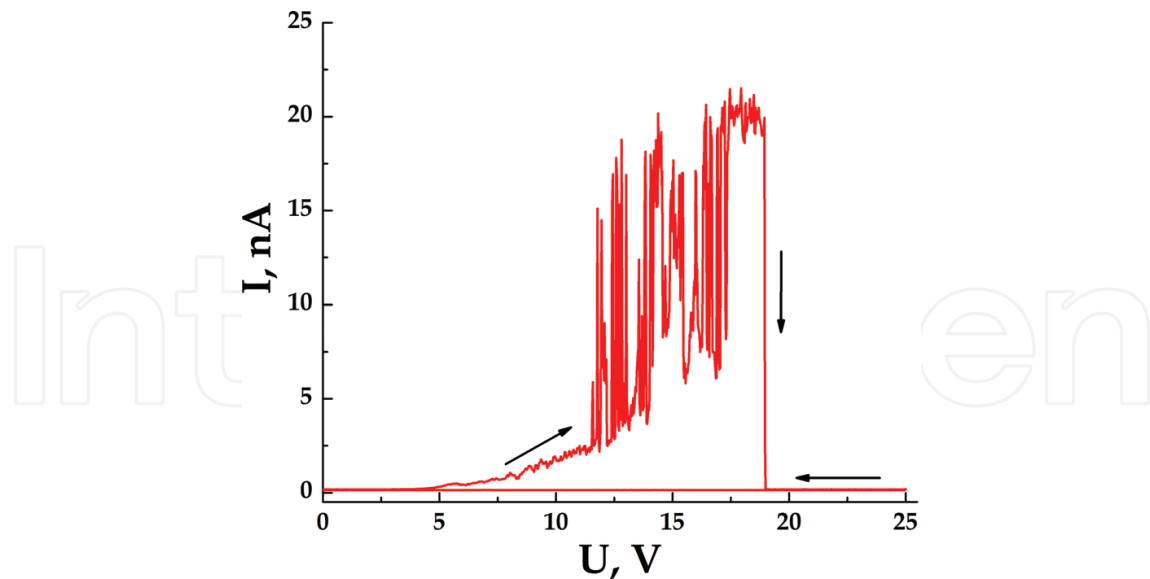


Figure 9. A CVC of the VA CNT during detachment from the substrate by AFM current spectroscopy.

after removal of the external electric field [19]. This effect was used to create critical-dimension atomic-force microscopy (CD-AFM) probes by depositing a carbon nanotube from a VA CNT array on the tip [19]. As shown by experimental studies, the detachment of a vertically aligned carbon nanotube from the substrate did not occur at $U = 10$ V; a single nanotube was detached with a reproducibility of about 30% at $U = 15$ V; a constant detachment of one or two VA CNTs was recorded at $U = 20$ V; several nanotubes were detached at $U > 20$ V. The voltage at which the detachment of a single VA CNT from the substrate was observed was likely to vary with the diameter of the nanotube. It should be noted that only van der Waals forces (~ 15 nN [3]).

Further, a modeling of the VA CNT deformation under the action of an external electric field was carried out to determine the quantitative values of the adhesion of VA CNTs to the substrate [3, 29, 40]. The results of the modeling showed that the VA CNT deformation increases with increasing voltage from 10 V to 30 V. So the elongation at the VA CNT base ($x = 0.01 L$) ΔL_0 is 0.037, 0.0391, 0.0404, 0.0419, 0.0441 and 0.0445 nm for a VA CNT with $D = 70, 80, 90, 100, 110$ and 120 nm, respectively, at corresponding voltage at the detachment (**Figure 10**). The elongation at the VA CNT top ($x = L$) ΔL_{max} is 1.25, 1.31, 1.36, 1.41, 1.48 and 1.49 nm, respectively (**Figure 10**). An analysis of the dependence of the elongation of a vertically aligned carbon nanotube (at $x = L$) on its diameter showed that at a voltage of 15 V ΔL_{max} of the VA CNT with a diameter of 70 nm is 1.24 nm and the ΔL_{max} increases to 1.49 nm with an increase in the diameter of VA CNT to 120 nm. Thus, voltage at the detachment of a VA CNT with $D = 80$ nm is equal to 16.3 V; with $D = 90$ nm, $U = 17.5$ V; with $D = 100$ nm, $U = 18.7$ V; with $D = 110$ nm, $U = 19.6$ V and; with $D = 120$ nm, $U = 20$ V (**Figure 10**) [42].

Taking into account the results of modeling, the adhesion of VA CNT ($D = 70 - 120$ nm) W_a increases from 0.55 to 1.19 mJ/m² with the increase in diameter according to Eq. (10). This fact probably connected with the increase in the number of carbon atoms interacting with the substrate per unit area of the adhesive contact, when the diameter of the VA CNT is increased and as a result of the increase in the layers of the multi-walled carbon nanotube. The corresponding adhesion force F_a of the individual VA CNT with increasing diameter varied from 92.5 nN to 226.1 nN. According to Eq. (11), the adhesive strength of the VA CNT to the substrate f_0 is 714.1 ± 138.4 MPa when a

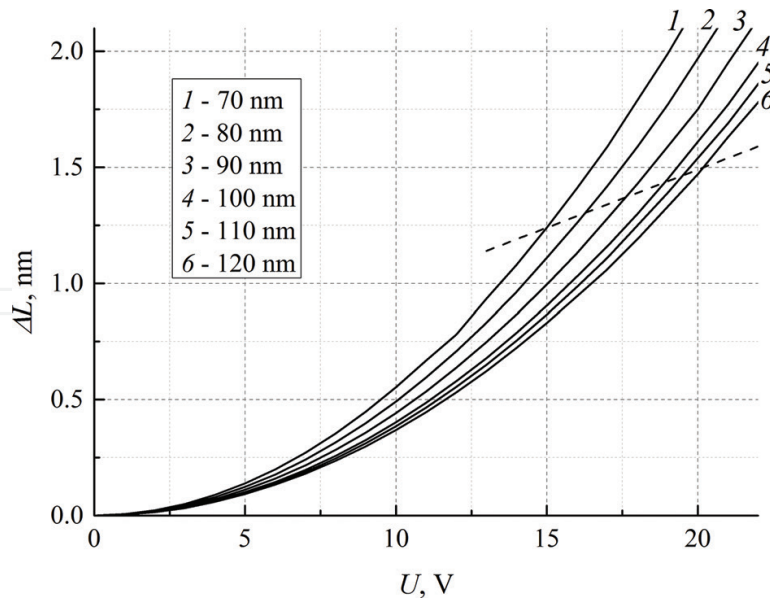


Figure 10. Dependence of the VA CNT elongation with a diameter of 70–120 nm (at $x = L$) on the voltage at time $t = t_0$. The dotted line indicates an elongation at which the VA CNT can be detached from the substrate [42].

mechanical load is applied. The corresponding detachment force F_0 varies from 1.93 to 10.33 μN depending on the diameter of the VA CNT (**Figure 11**, dependence 1).

The detachment force F_0 exceeds the adhesion force F_a by tens of times due to the considerable internal elastic forces arising in VA CNT under tension. According to Eq. (12), the adhesion strength of the VA CNT to the substrate f_0 is 1.43 ± 0.29 GPa when applying the external electric field. The corresponding detachment force is equal to the attractive force $F_{at}(t_0)$ at the moment of nanotube detachment from the substrate (varies from 3.83 μN to 20.02 μN for VA CNT with a diameter of 70–120 nm) (**Figure 11**, the dependence of 2) [42].

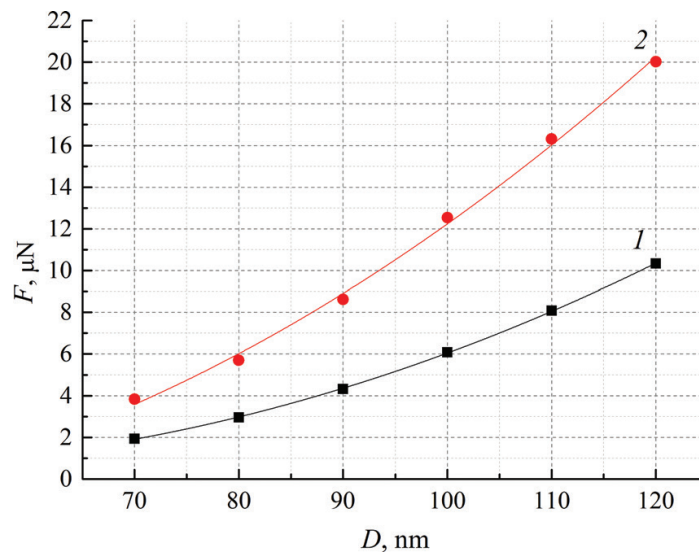


Figure 11. Dependence of the maximum force that can be applied along the axis of VA CNT without its detachment from the substrate, on the diameter of the nanotube: 1—When applying a mechanical load; and 2—When applying an external electric field. The points correspond to the values calculated on the basis of experimental and theoretical data; the solid line is the approximation of the obtained values [42].

Thus, the adhesion strength of a VA CNT to the substrate when applying an external electric field f_0 exceeds by almost two times the adhesion strength when applying mechanical load f_0 . It allows using a VA CNT with diameter from 70 to 120 nm grown by PECVD in the development and creation of emitters and memory elements with an electric field strength up to 10^{10} V/m. The calculated adhesion force and adhesion strength are well correlated with available literature data [17, 18], which confirms the reliability of the results obtained.

2.6. A technique for determining the piezoelectric response of vertically aligned carbon nanotubes

Recent work in the field of investigation of electromechanical properties of carbon nanostructures has shown the possibility of manifesting flexoelectric and piezoelectric effects in them [3, 43–46]. In this connection, an urgent task was the development of a technique for determining the piezoelectric response of vertically aligned carbon nanotubes because the use of the piezoresponse force microscopy in this case is difficult.

To study the piezoelectric response of VA CNT, we proposed a technique based on AFM power spectroscopy with parallel detection of a current flowing in the “lower electrode/VA CNT/AFM probe” system using an AFM oscilloscope. As a result, deformation of VA CNTs was formed in the AFM force spectroscopy mode by mechanical pressing of the probe to its top and the current value generated by VA CNT was detected at a known mechanical load. Schematic of the measurement process is shown in **Figure 12a**.

The results of study of the VA CNT array ($D = 34 \pm 3$ nm, $L = 370 \pm 40$ nm and $n = 47 \mu\text{m}^{-2}$) on the basis of the proposed technique showed that the current in the “lower electrode/VA CNT/AFM probe” system did not flow when an AFM probe is approached to an individual nanotube; with increasing the pressing force of the probe from 0 to 0.5 μN , a current appeared the value of which varied from 0 to -24 nA, respectively; the current value decreased back to zero at the subsequent removal of the pressing force (**Figure 12b**).

To exclude the influence of the measurement system and the substrate on the measurement results, it is also necessary to carry out similar measurements on a substrate mechanically purified from VA CNT using the AFM contact mode. For this sample, the measurements of

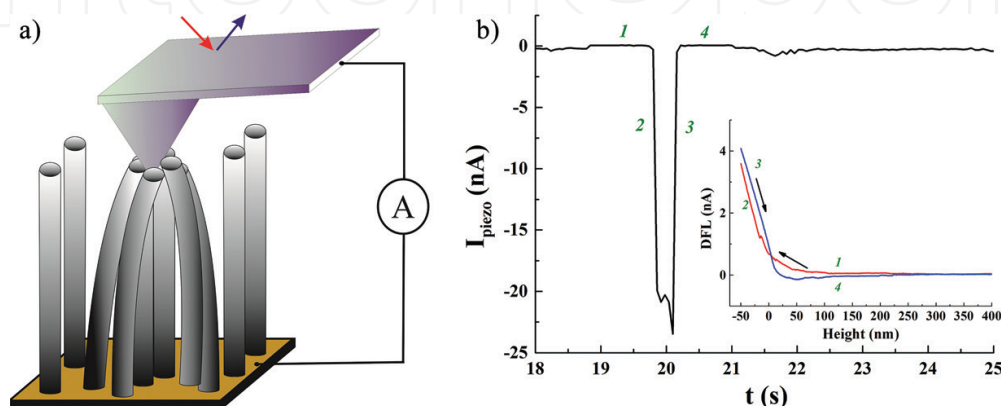


Figure 12. Study of the piezoelectric response of the VA CNT: (a) schematic of the measurement process; and (b) current-time dependence of a VA CNT and the corresponding AFM force spectroscopy [46].

the substrate showed the absence of a piezoelectric response when it deformed. The current flowing in the measurement system was constant and amounted to about 60 pA, which can be attributed to the systematic error of the PNL Ntegra measurement system.

Thus, the developed technique allows us to experimentally estimate the value of a current generated by deforming a carbon nanotube as a result of a direct piezoelectric effect. The obtained results correlate with the experimental and theoretical studies carried out by us earlier [3, 44].

3. Conclusion

Thus, unique techniques for nanodiagnostics of geometric, mechanical, electrical and adhesion properties of vertically aligned carbon nanotubes have been developed. The developed techniques were used for experimental investigations of the VA CNT. The obtained values of Young's modulus, bending stiffness, resistivity and adhesion of VA CNTs correlate well with the published data [5–7, 9, 11, 17, 18, 22, 28, 41], which confirm the reliability of the developed techniques. The developed techniques do not require additional sample preparation and can be used as express techniques for quality control of grown VA CNTs and elements of nanoelectronics and nanosystems based on them. The obtained results can be used for the development of nanodiagnostic methods, as well as for the design and fabrication of resistive energy-efficient memory elements with a high density of cells, adhesive structures, nanoelectromechanical switches and emission structures based on vertically aligned carbon nanotubes. Application of the developed techniques at the stage of interoperational control of the technological process of manufacturing such devices will increase reproducibility of their parameters and stability of operation.

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Conflict of interest

The authors declare no conflict of interest.

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