Effect of surface modification with ZnO films on aligned carbon nanotubes properties

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Abstract. The results of experimental studies of the piezoelectric response and memristor effect of aligned carbon nanotubes conformally coated with ZnO film are presented. It is shown that the surface modification of the carbon nanotubes with ZnO films leads to a decrease of the memristor effect and piezoelectric response of nanotubes due to an increase their stiffness and a decrease the strain value upon the application of an external field. The results can be used to develop the storage devices based on aligned carbon nanotubes.

1. Introduction
One of the main directions of development of modern electronics is nanopiezotronics – a field of science studying the piezoelectric and semiconductor properties of nanostructures to create new electronic devices and elements [1-5]. Special attention in this area is paid to carbon nanotubes (CNTs) due to the high values of elasticity, strength and anomalous piezoelectric properties [6, 7]. However, the study of the piezoelectric properties of carbon nanotubes and the process of generating current and potential during deformation are at the initial stage. Recent studies in this field shown that carbon nanotubes demonstrate a memristor effect associated with non-uniform strain of CNTs and their piezoelectric properties [7, 8]. In this connection, an assumption has arisen that the memristor effect and piezoelectric response of CNTs is enhanced due to the camphor coating of their surface with a piezoelectric material.

The aim is to study the effect of surface modification of aligned CNTs with ZnO films on their piezoelectric response and memristor properties.

2. Experimental studies
As the experimental sample we used a vertically aligned CNTs array grown by plasma-enhanced chemical vapor deposition [9-11]. A diameter, length and density of a CNT in an array were 35±3 nm, 980±70 nm and 147 μm⁻², respectively (Figure 1). The surface modification of the carbon nanotubes with ZnO films was carried out using a Pioneer 180 (Neocera Co., USA) [12]. The ZnO film was conformally deposited at laser radiation energy of 160 mJ and a pulse number of 10 000 with a repetition rate of 10 Hz. The substrate temperature was 300 ºC. The pressure in the chamber was 10⁻³ Torr.

Studies of the vertically aligned CNTs were carried out by the atomic force microscopy (AFM) using the Ntegra probe nanolaboratory (NT-MDT, Russia). A commercial cantilever with a platinum coating NSG11/Pt was used as the AFM probe. A preliminary a scanning of the CNT array was carried out in the semi-contact AFM mode for the formation of non-uniform strain in the nanotubes [7]. As a result of scanning the individual CNTs were combined into bundles of non-uniformly strained CNTs under the action of van der Waals forces. It was a necessary condition for the
manifestation of the memristor effect in the CNTs [13]. The AFM images of the CNT array before and after the modification are presented in Figure 2.

Figure 1. SEM image of the vertically aligned CNTs array.

Figure 2 (a, b). AFM image of the CNTs array before (a) and after (b) the surface modifying with ZnO films.

Studies of the piezoelectric response of CNTs were carried out on the basis of a previously developed technique [7]. The maximum penetration of the AFM probe into the CNTs array did not exceed 50 nm relative to the top of the CNT. The current flowing in the “bottom electrode / CNT / AFM probe” system during CNT deformation was detected using an Ntegra oscilloscope. The current-time dependences of the process of CNTs deformation before and after the surface modifying with ZnO films are shown in Figure 3.

The current-voltage characteristics (CVCs) of strained CNTs were measured by the AFM in current spectroscopy mode when a saw tooth voltage pulse of amplitude ±10 V and duration 0.5 s was applied.

3. Results
An analysis of SEM images showed no visible changes before and after CNT modification due to conformal ZnO deposition. However, the AFM images showed changes in the geometric parameters of CNTs bundles after modification (Figure 2). Thus, the diameter of the CNT bundles formed during the AFM probe action was 800 ± 50 nm before modification (Figure 2a) and 450 ± 50 nm after modification (Figure 2b). The decrease in the CNT diameter is probably due to an increase in the
stiffness of the CNT and a decrease in the van der Waals forces between the nanotubes after coating with ZnO films.

Studies of the piezoelectric response of the CNTs array showed that in the “lower electrode / CNTs / AFM probe” system a current flows to 19 nA when the AFM probe approaches the top of the CNT bundle (Figure 3a). The generation of current prior to the application of pressing force is due to the initial deformation of the CNTs forming the bundle [7]. Then, the current value varied from 0 to 21 nA, when the pressing force on the CNT bundle varied from 0 to 0.4 μN, respectively (Figure 3a). The piezoelectric response of modified CNTs decreased in the amount of current flowing during the strain of the CNT by more than 3 times as compared to pure CNTs (Figure 3b). Thus, there was no current when the AFM probe was approached to modified CNTs due to a decrease in the deformation of the CNTs forming bundle (Figure 3b). Then the current value reached 6 nA when the pressing force was 0.4 μN (Figure 3b). This fact is also associated with an increase in the stiffness of the CNT coated with ZnO films and as a consequence a decrease in the value of the CNT deformation at the same pressing force.

In addition, it was experimentally established that the modification of CNT with ZnO films leads to a decrease in the memristor effect of (Figure 4). The ratio between high- and low-resistance states of carbon nanotubes obtained before and after the modification decreased from 32 to 1, respectively (Figure 4). It should be noted that the saturation section on the CVCs is related to the features of the Ntegra measuring system in the current spectroscopy mode (built-in current preamplifier after 25 nA).

Figure 3 (a, b). The current-time dependences of the deformation process of CNTs before (a) and after (b) the surface modifying with ZnO films.

Figure 4 (a, b). CVCs of the CNT bundle before (a) and after (b) the surface modifying with ZnO films.
The decrease in the memristor effect of CNT after surface modification with ZnO films is due to an increase in the stiffness and consequently a decrease in the deformation and piezoelectric response of the nanotubes after the coating [8, 14, 15]. Thus, it has been shown that surface modifying of the CNTs with a ZnO film does not enhance the memristor effect of CNT due to the ZnO piezoelectric properties, but, on the contrary, reduces this effect by reducing the mobility and deformation of the CNT.

The obtained results can be used in the development of promising nanoelectronics devises based on aligned carbon nanotubes in particular memory elements and high-efficiency nanogenerators. The results were obtained using the equipment of the Research and Education Center and Center of Common Using “Nanotechnologies” of Southern Federal University.

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