Impact of the piezoelectric response of carbon nanotubes on their memristive properties

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Abstract. The experimental studies of the piezoelectric response of aligned carbon nanotubes (CNT) with different geometric parameters are presented. It is shown that the magnitude of the piezoelectric response increases with decreasing diameter and length of the CNT. It is established that CNT memristive properties improve with an increase of piezoelectric response. The results can be used in the development and creation of energy-efficient storage devices and nanogenerators.

1. Introduction
One of the main factors affecting the development of wearable electronics is the time of autonomous work of devices [1-3]. The time of work increase occurs both by increasing the capacity of energy storage elements, and by creating new electronic components with lower energy consumption [4]. One of the promising non-volatile memory elements is a memristor [5]. Earlier studies have shown that the use of vertically aligned carbon nanotubes (CNTs) will allow the creation of memristor structures with scale close to the diameter of the nanotube [6, 7]. The creation of such memristor structures is possible due to the anomalous manifestation of the piezoelectric properties in CNTs [8, 9]. However, at present the piezoelectric properties of CNTs and their effect on the memristor effect have not been sufficiently studied and requires many studies.

The aim of this work is studying the effect of carbon nanotubes piezoelectric response on their memristor effect.

2. Experimental studies
Arrays of vertically aligned carbon nanotubes grown by plasma-chemical vapor deposition using the multifunctional nanotechnological complex NANOFAB NTK-9 (NT-MDT, Russia) were used as experimental samples. The geometric parameters of the grown nanotube arrays were controlled using a Nova NanoLab 600 scanning electron microscope (SEM) (FEI, Netherlands). The average height of the CNT for samples No. 1-5 were 8.6; 8.2; 8; 24.2; 19.7 μm, respectively (Figure 1). The average diameter of the CNT for samples No. 1-5 were 43; 58; 63; 59; 34 nm, respectively (Figure 1).
The experimental studies of the piezoelectric and memristive properties were carried out using atomic force microscopy (AFM) using the Ntegra probe nanolaboratory (NT-MDT, Russia). A cantilever of the HA_NC / Pt brand with a force constant of 12 N / m was used as an AFM probe. All CNT arrays were pre-scanned in AFM semi-contact mode. As a result of scanning and interaction with the AFM probe, the nanotubes formed CNT bundles under the influence of van der Waals forces [10]. The magnitude of the piezoelectric response of CNTs was determined based on a previously developed technique using the AFM force spectroscopy mode with external force of 3.6 μN [8]. At the first stage of the AFM force spectroscopy, the probe created an additional compression strain in the nanotubes (Figure 2, red curve in the insets). At the second stage (during the removal of the AFM probe from the bundle surface), the nanotubes underwent tensile deformation. So the tops of the CNTs were held for some time on the AFM probe under the influence of the van der Waals forces (Figure 2, blue curve in the insets). The mechanical deformation of the CNT bundle led to generation of a piezoelectric current, the magnitude of which was detected using the digital oscilloscope (Figure 2).

The memristor properties of CNT arrays were evaluated in the AFM current spectroscopy mode using a sawtooth voltage pulse with an amplitude from ± 1 to ± 10 V. The obtained current-voltage characteristics (CVC) at a pulse amplitude of ± 7 V for each CNT array are presented in Figure 3. Resistance ratio in high resistance and low resistance states (R_{HR}/R_{LR}) CNTs were calculated at a fixed voltage of 2 V.

3. Results
The study of the piezoelectric response of CNTs showed that the magnitude of the piezoelectric current for samples No.1-5 was 22; 20.5; 19; 18; 16 nA, respectively (Figure 2). An analysis of the results showed that the magnitude of the piezoelectric response of CNTs depends on the length, diameter of the CNTs and the structure of the CNT array. So, there was a tendency to decrease of the piezoelectric current magnitude with an increase of the nanotube height and diameter. This dependence is associated with a decrease in the magnitude of their relative deformation under mechanical effect of the AFM probe. In this case, an increase in the density of CNTs in the array (from 42 to 76 μm\(^2\) for samples No.1-5) also led to a decrease in the piezoelectric response from 22 to 16 nA. This dependence is associated
with a decrease in the diameter of the bundle formed during preliminary scanning of the array in the semi-contact AFM mode. In addition, the deviation of the orientation of the CNTs from the vertical also led to a decrease in the piezoelectric response, which is associated with the predominant formation of bending deformations of CNTs during AFM force spectroscopy.

An analysis of the CVCs of deformed CNT bundles showed that the $R_{HR}/R_{LR}$ resistance ratios for samples No.1-5 were 3; 7; 8; 13; 18, respectively (Figure 3). It should be noted that the CVC of the studied samples obtained at amplitudes of less than $\pm 5$ V did not show the presence of hysteresis characteristic of memristor switching. It may be due to the insufficient value of the external electric field to compensate for the internal piezoelectric field arising during the formation of a CNT bundle [4].
Figure 3. Current-voltage characteristics for each CNT array at a pulse amplitude of ± 7 V.

Based on the obtained results, the dependence of the resistance ratio $R_{HR}/R_{LR}$ on the piezoelectric current value was constructed (Figure 4). The analysis of the obtained dependence showed that the resistance ratio $R_{HR} / R_{LR}$ increased from 3 to 18 with an increase in the piezoelectric response of CNTs from 16 to 22 nA, respectively (Figure 4). This dependence is associated with an increase in the internal field of CNTs, determined by the magnitude of the piezoelectric properties. As a result, an increase in the resistance of CNTs in a high-resistance state is observed. This leads to a hysteresis loop increase of the CNTs CVC and an increase in the value of $R_{HR}/R_{LR}$. 
4. Conclusion

Thus, it is shown that memristive properties of the CNTs improve with increasing value of its piezoelectric response. This dependence is fully consistent with the previously proposed memristive switching mechanism of a deformed CNT [4]. The obtained results can be used to develop the nanopiezotronics devices based on vertically aligned carbon nanotubes. 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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