Piezoelectric effect in non-uniform strained carbon nanotubes

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Abstract. The piezoelectric effect in non-uniform strained carbon nanotubes (CNTs) has been studied. It is shown that the magnitude of strained CNTs surface potential depends on a strain value. It is established that the resistance of CNT also depends on the strain and internal electric field, which leads to the hysteresis in the current-voltage characteristics. Analysis of experimental studies of the non-uniform strained CNT with a diameter of 92 nm and a height of 2.1 μm allowed us to estimate the piezoelectric coefficient 0.107 ± 0.032 C/m².

1. Introduction

The transition of electronics into the nanoscale area has led to the fact that the surface piezoelectric and flexoelectric effects have a significant impact on the electrical properties of the nanostructures [1, 2]. These effects were not taken into account in bulk materials because of the small values of the surface-to-volume ratio and the strain gradients. However, in the nanostructures the surface-to-volume ratio and the strain gradients can reach high values [1].

A new science direction – nanopiezotronics, which studies the flexo- and piezoelectric properties of nanostructures, has developed [3]. The fundamental principles of nanopiezotronics were formulated less than ten years ago [3]. However, the search for materials for its practical implementation continues at present. Currently, there are reports that carbon nanostructures can exhibit flexo- and piezoelectric properties [4-6], which opens a wide field for their application in nanopiezotronics and nanoelectronics at high strength and elasticity.

The aim of this work is to study a piezoelectric effect in non-uniform strained carbon nanotubes (CNTs) and to determine their piezoelectric coefficient using scanning probe microscope.

2. Experimental studies

2.1. Experimental sample

An array of vertically aligned CNTs grown by plasma chemical vapor deposition using nanotechnology complex NANOFAB NTC-9 (NT-MDT, Russia) was studied. CNTs were grown by a vertex mechanism using Ni catalyst particles. Figure 1a shows the sample image obtained by scanning electron microscope (SEM) Nova NanoLab 600 (FEI, Netherlands). Structural analysis by Raman spectroscopy showed presence of D- and G-mode characteristic of carbon nanotubes and absence of RBM mode in the range of 0-200 cm⁻¹, indicating that they were multi-walled. Analysis of transmission electron microscopy (TEM) image showed that the experimental sample represented multi-walled carbon nanotubes with bamboo-like defects (Fig. 1b).
2.2. Methods
To study the piezoelectric effect in CNTs, a scanning of the array surface by atomic force microscopy (AFM) in a tapping mode was carried out on the first pass (Fig. 2a). As a result, the CNT bundles having non-uniform bending strain were formed by van der Waals forces [7]. During the second pass, the surface potential of the strained CNT bundles at a distance of 12 nm from the array surface was measured. The surface potential of strained CNTs was studied by Kelvin probe mode using the probe nanolaboratory Ntegra (NT-MDT, Russia). The NSG11/Pt cantilever was used. The image of the distribution of the surface potential of the CNT bundles is shown in Figure 2b.

To determine the piezoelectric coefficient of CNT, a controlled non-uniform strain was formed in it and the current-voltage characteristics (CVCs) were measured. Controllable non-uniform strain in CNTs was formed under the action of a local electric field in scanning tunnel spectroscopy mode [6]. The strain value of CNT from 0.2 to 3.0 nm was controlled by feedback system of the scanning tunneling microscope (STM). The strain of CNT was maintained by van der Waals forces between STM probe and nanotube top after removing the external electric field [8]. CVCs of the strained CNTs were measured by applying a saw tooth voltage pulse with amplitude of 8 V and duration of 1 s. Upper electrode was a tungsten STM probe. Lower electrode was conductive layer on a substrate with CNTs.

![Figure 1](image1.png)

**Figure 1.** The experimental sample of CNT: SEM (a) and TEM (b) images.

![Figure 2](image2.png)

**Figure 2.** Investigation of the surface potential of non-uniform strained CNTs forming a bundles: the surface topology (a), the potential distribution (b), and sections along the lines (c, d).
3. Results and discussion

Analysis of the AFM images shows that a negative surface potential of up to -42 mV is observed at the tops of the CNT bundles up to 500 nm in diameter (Fig. 2c). A positive potential of up to 40 mV is observed near the bundles bottom (Fig. 2d). Thus, the magnitude of the surface potential depends on the diameter of the bundle and the strain value of nanotube in it (Fig. 2c, d). The potential at the tops of individual nanotubes is close to zero (Fig. 2d). The presence of a surface potential on bundles of the strained CNTs agrees with the results of the previous studies [9, 10] and confirms the possibility of the piezoelectric effect in carbon nanotubes.

The measuring of CVCs of the non-uniform strained CNT with a diameter of 92 nm and a length of 2.2 µm shows that the largest loop is observed for the CNT having a strain at 1 nm (Fig. 3a) due to the fact that for a given strain an internal electric field in the CNT is formed; it is completely redistributed when the voltage (8 V) is applied due to the piezoelectric effect [6]. As a result, the resistance of the CNT in the low-resistance state ($R_{LR}$) is determined by resistivity of the nanotube.

The hysteresis of CVCs decreases in the deviation from this strain value (Fig. 3a). This is due to the fact that the internal electric field of the CNT becomes insufficient to form a high-resistance state ($R_{HR}$) at a lower strain of the nanotube (less than 1 nm). An increase in the CNT strain value, on the contrary, led to an increase in the internal electric field, as the resistance of the CNT in the low-resistance state increased sharply (Fig. 3a). Thus, the ratio of the resistances of the CNT in the high-resistance and low-resistance states ($R_{HR}/R_{LR}$) was maximal at a strain equal to 1 nm and decreased as it increased or decreased (Fig. 3b).

We can conclude that the internal electric field of CNT with a diameter of 92 nm and a length of 2.1 µm is close to zero, when its strain is 1 nm and the voltage of 8 V is applied. Therefore, the intrinsic resistance of the CNT is about 25 MΩ (Fig. 3a). Then the resistance $R_{LR}$ of the CNT increases from 202 to 285.7 MΩ with an increase in strain from 1.5 to 2.0 nm, respectively. If we assume that the increase in the CNT resistance is due to the growth of its internal electric field by reason of the appearance of a piezoelectric effect, then the piezoelectric coefficient of the CNT with a diameter of 92 nm and a length of 2.1 µm is $0.107 \pm 0.032$ C/m². Our previous calculation using the classical equations of the piezoelectric effect showed a lower value of the piezoelectric coefficient of the CNT, which was $0.048$ C/m² [6]. The difference in the obtained values may be due to the non-uniform strain of the CNT and the increase in the internal electric field of the nanotube due to the manifestation of the flexoelectric effect in it [4, 5].

4. Conclusion

In summary, the obtained experimental results confirm the manifestation of the piezoelectric effect in multi-walled carbon nanotubes. It is shown that under the action of mechanical stresses the CNTs are
polarized and the internal electric field is formed, which leads to a change in their resistance. Analysis of experimental studies of the non-uniform strained CNT allowed us to estimate the value of the piezoelectric coefficient $0.107 \pm 0.032 \text{ C/m}^2$.

The obtained results can be used in the development and the fabrication of nanoelectronics devices based on carbon nanotubes.

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