Piezoelectric response of aligned carbon nanotubes depending on sublayer material

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Abstract. The results of experimental studies of the effect of the sublayer material on the piezoelectric response and sensitivity to mechanical deformations of aligned carbon nanotubes (CNTs) are presented. It is shown that the highest piezoelectric response (136 nA at a pressing force of 4 µN) and best sensitivity are demonstrated by CNTs grown on a Mo sublayer. This dependence is probably due to the geometric parameters of CNTs and the structure of the CNT array as a whole. The results obtained can be used to develop energy-efficient nanogenerators based on CNT arrays.

1. Introduction

Currently, there is an active development of wearable electronics, which requires the search for suitable energy sources capable of ensuring their autonomous operation. An attractive direction in this area is the ability to use mechanical energy of the environment (ambient noise, vibration, human body activity, etc.) as power sources. One of the devices capable of converting nanoscale deformations and vibrations into electrical energy is a nanogenerator [1, 2]. In this connection, there is an active search for functional nanostructures capable of providing the highest sensitivity to external nanoscale deformations and maximum power [3].

Recent studies show that carbon nanostructures are capable of exhibiting anomalous piezoelectric properties as a result of violation of their centrosymmetric structure through the introduction of defects or the formation of non-uniform deformations [4-7]. Particular attention is attracted by vertically aligned carbon nanotubes (CNTs) due to the ability to transform nanoscale deformations into a surface potential, which leads to the generation of an electric current [7-9]. This makes vertically aligned CNTs one of the most attractive materials for creating energy efficient nanogenerators [10]. However, work in this direction is at an early stage and requires wide research. The aim of this work is to study the effect of the sublayer material of the CNTs on their piezoelectric response and sensitivity to mechanical deformations.

2. Experimental studies

To establish this dependence, a series of 4 arrays of vertically aligned CNTs was grown by the plasma-chemical vapor deposition method [11]. As sublayer materials were used Ti, Mo, TiN and Cr. The growth temperature was 645 °C. The thickness of the catalytic nickel layer was 5 nm. Scanning electron
microscopy (SEM) images are shown in Figure 1. Experimental studies of the piezoelectric response of CNT arrays were performed by atomic force microscopy (AFM) using a previously developed technique [8, 12]. As a piezoelectric response, we detected the current arising as a result of the formation of the surface potential of CNTs during their deformation upon pressing the AFM probe with a force of 4 µN. The top electrode was a commercial NSG10/Pt probe with platinum coating and with force constant 8 N/m. It should be noted that the AFM ammeter operates linearly in the range from 10 to -10 nA, and for large values, the logarithmic transformation is turned on. The values of the piezoelectric response of CNTs are recalculated taking into account this transformation.

![SEM images of the CNT arrays grown on a Ti (a), Mo (b), TiN (c) and Cr (d) sublayer materials.](image)

**Figure 1.** SEM images of the CNT arrays grown on a Ti (a), Mo (b), TiN (c) and Cr (d) sublayer materials.

3. Results and discussion

Analysis of the geometric parameters of CNTs showed that the sublayer material affects the length, diameter and density of CNTs in the array (Figure 1). The average heights of CNTs ranged from 6.6 to 12.9 µm. The average diameters of CNT ranged from 35 to 72 nm. On the Mo sublayer, the growth of separately standing vertically aligned CNTs with a density of 1 µm\(^{-2}\) was observed. The growth of vertically aligned CNTs with a high density in the array (26 and 22 µm\(^{-2}\)) was observed on the TiN and Ti sublayer respectively. On the other hand, on the Cr sublayer CNTs grew combined into bundles, with a density of 10 µm\(^{-2}\).

Results of the AFM studies have shown that the geometric parameters of CNTs, in turn, have a significant effect on their piezoelectric response of CNTs. So, the value of the piezoelectric response increased from 2 to 39 nA with an increase in the pressing force from 0 to 4 µN for the CNT array grown on a Ti sublayer. For the CNT array grown on a Mo electrode, the piezoelectric response increased from...
40 to 136 nA under the same influences. For the CNT array grown on a TiN sublayer, on the contrary, an insignificant decrease in the piezoelectric response from 18 to 13 nA was observed. The CNT array grown on a Cr sublayer showed the smallest piezoelectric response (10 ± 2 nA), which weakly depends on the pressing force. These dependences are probably due to the influence of the geometric parameters of CNTs and the structure of the CNT array as a whole. Thus, a decrease in the piezoelectric response of the CNT array grown on a TiN sublayer is due to a high aspect ratio of the CNT length to diameter (~360), which led to large deviations of the CNT from its axis and the formation of bundles during the measurement. The formation of CNT bundles, in turn, caused a decrease in the total piezoelectric potential due to the compensation of positive and negative charges with each other. A similar situation was observed for the CNT array grown on a Cr sublayer, which was initially combined into CNT bundles (Figure 1d). A gradual increase in the piezoelectric response for CNT arrays grown on Ti and W sublayers is due to an increase in the CNT deformation. In this case, a greater value of the response for CNTs on a Mo sublayer is associated with a lower value of the aspect ratio (~92) compared to CNTs on a Ti sublayer (~223), which led to a greater relative deformation of the CNTs at a given pressing force. It should be noted that the work function of electrons from Ti, Cr, and Mo is similar (4.5 - 4.6 eV) and could not have a decisive influence on the obtained results.

Further, studies of the influence of the sublayer material on the "sensitivity" (the ratio of the piezoelectric response to the amount of deformation) to external mechanical influences were carried out (Figure 2). For this, the AFM probe was gradually shifted into the CNT array to a depth of 500 nm, which led to the formation of 3.5, 7.5, 1.5, and 7% deformation of CNTs grown on Ti, Mo, TiN, and Cr sublayers, respectively.

![Figure 2](image_url) Dependence of the piezoelectric response of CNTs grown on various sublayers on deformation. The graph shows the values obtained directly from an AFM ammeter with a built-in logarithmic converter for currents greater than ± 10 nA.

As a result, it was found that nanotubes grown on a Cr sublayer are not very sensitive to deformations up to 7%. Thus, with an increase in deformation from 0 to 500 nm, the generated current signal was quite noisy and amounted to -7 ± 5 nA in the entire deformation range (Figure 2). This dependence is associated with the fact that nanotubes were combined into bundles during growth, which significantly reduced their "sensitivity" to external mechanical influences. For CNTs grown on a TiN sublayer, at a deformation of less than 200 nm (0.6%), a noisy current signal of -8 ± 5 nA was also observed. With a further increase in deformation, a stable current signal was observed, increasing from -23.3 to -49.7 nA.
with an increase in deformation from 200 to 500 nm (from 0.6 to 1.5%) (Figure 2). For CNTs grown on a Ti sublayer, an increase in current from 0 to -27.35 nA was observed in the entire range of deformations from 0 to 3.5% (Figure 2). With a deformation of 1.5%, the current was -15.34 nA. The highest current was detected for CNTs grown on the Mo sublayer, both in the region of small and large deformations (Figure 2). The magnitude of the current increased from 0 to -89.2 nA with deformation from 0 to 7.5%, respectively. In this case, at a deformation of 1.5%, the current reached -49.7 nA, similar to the value for CNTs grown on a TiN sublayer. However, at a deformation of less than 1.5%, nanotubes grown on the Mo sublayer, in contrast to those grown on the TiN sublayer, also demonstrated a stable current signal, which increased with increasing deformation.

Analysis of the results obtained allows us to conclude that the "sensitivity" of CNTs to external mechanical influences is determined by their aspect ratio of length to diameter and vertical orientation in the array. Thus, in the region of small deformations (up to 1.5%), the highest "sensitivity" is demonstrated by not bundled nanotubes with an aspect ratio of no more than 200. In the region of large deformations (more than 1.5%), the magnitude of the piezoelectric response increased with an increase in the aspect ratio. At the same time, the tendency of CNTs to combine into bundles significantly reduces their "sensitivity" to external mechanical influences.

4. Conclusion
Thus, it has been shown that vertically aligned carbon nanotubes grown on the Mo sublayer exhibit the maximum piezoelectric response with the best «sensitivity». However, further research is required to investigation of the effect of the sublayer material on the structure of CNTs and their piezoelectric response. The results obtained can be used to develop energy efficient nanogenerators based on vertically aligned CNTs. The results were obtained using the equipment of the Research and Education Center “Nanotechnologies” of Southern Federal University.

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