Investigation of the influence of geometric parameters of carbon nanotube arrays on their adhesion properties

M V Il'ina, A A Konshin, O I Il'in, N N Rudyk, A A Fedotov and O A Ageev

Southern Federal University, “Nanotechnologies” Scientific and Educational Center, Shevchenko 2, Taganrog 347922, Russia

E-mail: mailina@sfedu.ru

Abstract. The results of experimental studies of adhesion of carbon nanotube (CNT) arrays with different geometric parameters and orientations using atomic-force microscopy are presented. The adhesion values of CNT arrays were determined, which were from 82 to 1315 nN depending on the parameters of the array. As a result, it was established that the adhesion of a CNT array increases with an increase in branching and disorientation of the array, as well as with the growth of the aspect ratio of CNTs in the array.

1. Introduction
The rapid development of nanotechnologies and the new opportunities for creating nanoscale structures have generated a great interest in artificial adhesion structures that mimic the parameters of biological objects (microfobs of gecko). The creation of artificial adhesion structures will solve a number of problems for micro- and nanoelectronics, as well as for the space industry.

Initially, polymeric columnar nanoscale structures were used as artificial adhesive structures. However, further studies have shown that the most promising material for creating such structures is aligned carbon nanotubes (CNTs) [1–8]. The adhesion of CNT arrays (10–500 N/cm²) is many times greater than the adhesion of artificial polymer columnar nanostructures (3 N/cm²) [1–8] due to the unique mechanical and geometric properties of nanotubes [9, 10].

The aim of this work is to study the influence of geometric parameters of CNT arrays (length and diameter of nanotubes, density and branching) on their adhesion properties.

2. Experimental details
The samples we studied were CNT arrays grown by plasma-enhanced chemical vapor deposition (PECVD) on a silicon wafer with a two-layer structure (Ni / Ti) [11]. For the study, 14 samples of four types were chosen: vertically aligned CNT bundles, individual vertically aligned CNTs, branched CNTs and disoriented CNTs, shown in figure 1 (a–d), respectively. The geometric parameters of the arrays were determined on the basis of statistical processing of scanning electron microscopy (SEM) images obtained using a Nova NanoLab 600 (FEI, Netherlands) and are presented in table 1.

The adhesion properties of carbon nanotube arrays were studied by atomic-force microscopy (AFM) using the NTEGRA Probe NanoLaboratory (NT-MDT). The AFM probe was a polysilicon probe with a conductive coating of tungsten carbide from the HA_HR/W₂C series with a radius of curvature of 35 nm and a stiffness of $k = 34$ N/m.
Figure 1 (a-d). SEM images of the four types of CNT arrays.

During the preliminary scanning of arrays in the semi-contact AFM mode, the surface of CNT arrays was determined and the measurement points were set. Then, the AFM force spectroscopy mode was used to measure two dependences: the dependence of the cantilever bending value on the degree of extension of the scanner’s z-piezoelectric element (signal $h$) on the direct cantilever course (the red dependence in figure 2) and the same for the inverse cantilever course (the black dependence in figure 2). The characteristic experimental dependences of $J_{DFL}(h)$ obtained for CNT samples of the first and fourth types are shown in figure 2.

The dependences obtained using a force spectroscopy mode allow us to evaluate the adhesion of an CNT array $F_a$ to the AFM probe surface [7]:

$$F_a = \Delta J_{DFL} \left( \frac{dh}{dJ_{DFL}} \right) k,$$

where $\Delta J_{DFL}$ is the value equal to the difference of the $J_{DFL}$ signal at the point of complete detachment of the probe from the CNT array and at the point of the maximum negative value of the $J_{DFL}$ signal.
Figure 2. The experimental dependences $J_{DFL}(h)$ for the bundles of vertically aligned (a) and disoriented (b) CNTs.

The adhesion values calculated using formula (1) for the experimental samples are presented in table 1.

### Table 1. The calculated adhesion values for experimental samples and their geometric parameters

| Number of sample | Diameter (nm) | Height (μm) | Density (1/μm²) | Adhesion (nN) | Average value of adhesion (nN) |
|------------------|---------------|-------------|-----------------|---------------|-------------------------------|
| CNT bundles      |               |             |                 |               |                               |
| 1                | 43.8          | 0.65        | 82              | 195.28        |                               |
| 2                | 35.6          | 1.21        | 72              | 255.71        |                               |
| 3                | 51            | 0.69        | 69              | 433.31        |                               |
| Individual CNTs  |               |             |                 |               |                               |
| 4                | 62            | 0.28        | 54              | 82.26         |                               |
| 5                | 56            | 0.55        | 59              | 179.58        |                               |
| 6                | 44.1          | 0.35        | 95              | 193.18        | 225.37                        |
| 7                | 63.2          | 0.65        | 38              | 260.54        |                               |
| 8                | 44.9          | 0.71        | 60              | 411.29        |                               |
| Branched CNTs    |               |             |                 |               |                               |
| 9                | 42.1          | 0.42        | 71              | 166.67        |                               |
| 10               | 50.1          | 15.97       | 44              | 1314.71       | 585.44                        |
| 11               | 44.7          | 12.45       | 26              | 274.93        |                               |
| Disoriented CNTs |               |             |                 |               |                               |
| 12               | 34.6          | 2.11        | 89              | 349.71        |                               |
| 13               | 28.8          | 3.07        | 45              | 647.61        | 633.90                        |
| 14               | 28.7          | 2.87        | 52              | 904.37        |                               |
3. Results and discussion

The analysis of the obtained results showed that the minimum value of adhesion (82.26 nN) was achieved for CNT sample 4, which is an array of individual vertically aligned CNTs with a minimum aspect ratio (the ratio of a CNT’s length to its diameter) of ~ 4.5. The maximum value of adhesion (1314.71 nN) was demonstrated by CNT sample 10, which has having a branched structure, a high density and a maximum value of the aspect ratio of ~ 320. The analysis of the measurement results has also shown that the average adhesion values of experimental samples of disoriented CNT have the greatest value of adhesion. This is probably due to the fact that the disorientation of nanotubes contributes to an increase in the contact area between the AFM probe and the CNT array.

In addition, the adhesion measurements of individual CNTs (experimental samples 4 – 8) showed that the adhesion value increases from 82.26 to 411.29 nN with an increase in the aspect ratio from 4.5 to 15.8, respectively. At the same time, sample 6 was somewhat of an outlier for this dependence, which may be due to a significant increase in the density of CNTs in the array (by more than 1.5 times) that results in an increase in the number of CNTs interacting with the AFM probe as compared to samples 4, 5, 7 and 8.

The dependence of the adhesion value on the array density is confirmed by the results of force spectroscopy of sample 1 of vertically aligned CNT bundles, shown in figure 3.

![Figure 3](image_url)

**Figure 3.** Results of the study of CNT sample 1: AFM image (a), a profilogram along the line (b) and force spectroscopy data at point 1 (c) and point 2 (d).
The obtained $J_{DFL}(h)$ dependences for bundles with diameters of 174 nm (point 1) and 452 nm (point 2) show that the adhesion of the AFM probe to a bundle of a larger diameter significantly exceeds the adhesion to a bundle of a smaller diameter (see figure 3(c-d)). In this case, the $J_{DFL}(h)$ dependence for a large-diameter CNT bundle had several peaks during both approach and retraction of the AFM probe due to the serial interaction of individual nanotubes with the AFM probe. Thus, it is shown that an increase in the number of CNTs interacting with an AFM probe leads to an increase in the adhesion of CNT arrays measured by a local method of AFM force spectroscopy.

The obtained results suggest that the adhesion of CNT arrays depends not only on the value of the aspect ratio and the structure of a CNT array, but also on the density of the array. Thus, it can be concluded that the greatest adhesion of CNT arrays to the AFM probe is observed for high density arrays of branched CNTs with high values of the aspect ratio.

4. Conclusion

This work experimentally studied the adhesion of carbon nanotube arrays of various types by using a force spectroscopy mode of AFM with a polysilicon probe with a radius of curvature of 35 nm. The value of the adhesion of CNT arrays varied from 82 to 1315 nN depending on their geometric parameters, which agrees well with the available literature data [1, 7, 8]. It is established that the maximum value of adhesion of CNT arrays to the AFM probe was achieved for the arrays that combine the branched or disoriented structure, the high density and the high aspect ratio of CNTs.

The results obtained can be used in the development of adhesion structures and elements of nanoelectronics based on carbon nanotubes.

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