Adhesive coatings based on aligned arrays of carbon nanostructures

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Abstract. The article presents the results of establishing the influence of the carbon nanotubes growing modes by plasma enhanced chemical vapour deposition method on their geometric dimensions and adhesion properties. The results of experimental research of the activation time, plasma power, temperature, and growth time effects on the parameters of carbon nanotubes are presented. It is shown that control of growth technological modes makes it possible to create carbon nanotubes arrays of various types: bundled, individual, branched, and disoriented. The adhesion of experimental samples was investigated by atomic force microscopy. The greatest value of the adhesion force (11.12 μN) is demonstrated by aligned arrays of carbon nanotubes, which during the growing process were grouped into bundles with the diameter of individual nanotubes 51 nm, height 0.69 μm, and density 69 μm⁻¹.

1. Introduction

The development of nanotechnologies and the possibility of creating spatially oriented nanoscale structures have generated a wide interest in research for creating not only promising devices for nanoelectronics [1-3], but also artificial bio-like structures. Reproduction of parameters of biological objects [4-7] allows solving a number of problems in the field of mechanical contacts of high strength and repairing materials with "dry" adhesion working in vacuum. Among the artificial biomimetic nanostructures, carbon nanostructures based on arrays of vertically aligned carbon nanotubes (VA CNT) possess the best adhesion characteristics [4,8-11], which is associated with an increase in the adhesion force due to an increase in the number of nanostructures contacting the surface [12]. For controlled growth of CNTs with specified characteristics, the most promising method is plasma enhanced chemical vapour deposition (PECVD) [13,14]. However, a large number of parameters of the PECVD method require establishing the relationship between their influence on the growth of CNTs with controlled parameters.

The aim of this work is establishing the influence of the CNTs growing modes by PECVD method on their geometric dimensions and adhesion properties.

2. Experiments and methods

Si/TiN/Ni structure was used for creating experimental samples. VA CNT were grown by PECVD using specialized module cluster complex nanotechnological NANOFAB NTC-9 (NT-MDT, Russia). To provide different CNT parameters, values of the activation time, plasma power, temperature, and growth time were changed during PECVD process. The samples with 4 types of VA CNT were grown: bundles (Fig. 1a), individual (Fig. 1b), branched (Fig. 1c), and disoriented (Fig. 1d).
Cultivation of CNTs was carried out in 3 stages: "heating", "activation", and "growth". In the "heating" stage, the formation of Ni catalytic centres from a continuous film of a catalytic material was carried out by annealing the samples at specified temperatures for 20 minutes under argon atmosphere (40 sccm) and ammonia (15 sccm) at a pressure of 4.5 Torr. After that, the "activation" stage was carried out – exposure of the substrates in the ammonia atmosphere (210 sccm). Depending on the type of grown samples, plasma could also be initiated using a high-voltage DC source. At the stage of "growth", acetylene (70 sccm) was fed into the chamber together with ammonia. To create a vertical directional growth of CNTs relative to the substrate, plasma was initiated. CNTs grew by top-mechanism. The values of the activation time ($t_{act}$), plasma power ($W$), temperature ($T$), and growth time ($t_{growth}$) were varied to create samples with different parameters of CNTs. The estimation of the geometric parameters of the CNT arrays experimental samples was carried out using a scanning electron microscope (SEM) Nova NanoLab 600 (FEI, The Netherlands). Growth parameters of the CNT arrays and their geometric dimensions are presented in Table 1.

Investigation of the adhesion strength of the experimental samples was carried out using a probe nanolaboratory Ntegra (NT-MDT, Russia). A colloid probe of the CPC_SiO$_2$-20/Au series was used with a radius of 20 μm and a stiffness coefficient $k = 0.3$ N/m. Measurements of the adhesion value were carried out at 10 points of the array of each experimental sample in the force spectroscopy mode. During the process, the dependence of the cantilever bending value ($J_{DFL}$ signal) on the degree of extension of the $x$-piezoelectric element of the scanner (signal $h$) in direct (solid line) and the inverse (dashed line) cantilever courses was measured. The experimental dependence $\Delta J_{DFL}(h)$ for samples with individual VA CNT is shown in Figure 1e.

Using the resulting force spectroscopy dependencies, the array of adhesion force $F_a$ of VA CNT to the surface of the probe was evaluated by the method described in Ref. [15]:

$$F_a = \Delta J_{DFL} (dh / dJ_{DFL}) k,$$

where $\Delta J_{DFL}$ is the difference of $J_{DFL}$ signal at the point of complete detachment of the probe from the CNT array and the one at the point of the maximum negative value of the $J_{DFL}$ signal.

Figure 1. SEM images of (a) CNTs bundles, (b) individual VA CNTs, (c) branched VA CNTs, (d) disoriented CNTs. (e) Experimental dependence $\Delta J_{DFL}$ for individual VA CNTs. Scale segment 500 nm.
3. Results and discussion

Analysis of SEM images of experimental samples A1-A3 has shown that, with the parameters presented in Table 1, exposure in ammonia plasma leads to etching of Ni catalyst centres and reduces their diameter from 44 to 36 nm in samples A1 and A2, respectively. However, as the activation time increases, the probability of combining small catalytic centres (CCs) into larger ones due to surface diffusion increases, which leads to an increase in diameter and a decrease in density of CNTs in A3 sample. Also, the CNT growing modes with the "activation" time of less than 1 min promote to the formation of CNT bundles.

In B1-B3 samples, the increase in the activation time was also accompanied by combining small CCs into larger ones with increasing diameter and decreasing density. At the same time, an increase in the plasma power up to 40 W contributed to the complete removal of small CCs and a higher electric field strength, which made it possible to obtain arrays of individual VA CNTs.

One of the specificity of the CNT growth by PECVD is that the temperature value at the stage of "heating" is retained at the "activation" and "growth" stages. Thus, with a change in the growth temperature from 645 to 675°C on the SEM images of C1-C3 samples the integral effect of temperature can be seen associated with the two processes:

1) formation of CCs at the stages of "heating" and "activation";
2) the growth of CNTs on CCs formed at a given temperature.

At the same time, a short activation time promotes an increase in the adhesion of the CCs to the substrate. As a result, there is a growth both top- and base-growth mechanisms with the formation of arrays of branched CNTs. With increasing temperature up to 675°C, there is the simultaneous occurrence of sublimation and surface diffusion processes, which reduces the diameter, height, and density of CNTs. Also, an increase in temperature leads to an acceleration of the desorption of acetylene from the sample surface and the carbon-containing gas is evacuated by the vacuum system without reacting with the CCs.

### Table 1. Parameters of CNTs and calculated values of adhesion of experimental samples.

| Sample | Diameter, nm | Height, μm | Density, μm⁻¹ | CNT growth parameters | Adhesion force, μN |
|--------|-------------|-----------|----------------|-----------------------|------------------|
|        |             |           |                | Constant               | Variable         |
| A1     | 43.8        | 0.65      | 82             | T = 660°C,            | 20               | 5.03            |
|        |             |           |                | W = 25 W, Tact = 12 min | 40               | 8.53            |
| A2     | 35.6        | 1.21      | 72             | W = 40 W, Tact = 8 min | 60               | 11.12           |
| A3     | 51          | 0.69      | 69             | W = 50 W, Tact = 12 min | 240              | 1.56            |
| B1     | 44.1        | 0.35      | 95             | T = 660°C,            | 120              | 2.30            |
| B2     | 62          | 0.28      | 54             | W = 40 W, Tact = 8 min | 180              | 0.67            |
| B3     | 63.2        | 0.65      | 38             | t_growth = 12 min,    | 240              | 1.56            |
|        |             |           |                | t_growth = 12 min     |                  |                 |
| C1     | 42.1        | 0.42      | 71             | t_ax = 5 s,           | 645              | 3.22            |
| C2     | 50.1        | 15.97     | 44             | W = 50 W, T = 660°C   | 660              | 6.42            |
| C3     | 44.7        | 12.45     | 26             | t_growth = 12 min     | 675              | 2.24            |
| D1     | 34.6        | 2.11      | 89             | T = 660°C,            | 4                | 1.09            |
| D2     | 28.7        | 2.87      | 52             | t_act = 60 s, t_growth = 8 min | 8               | 7.38            |
| D3     | 28.8        | 3.07      | 45             | W = 0 W               | 12               | 2.70            |

For the experimental samples D1-D3, plasma was not initiated during the growth. The absence of a vector of electric field strength, which determines CNT growth direction, led to the formation of CNTs disoriented array. The increase in the growth time from 4 to 12 min allowed obtaining CNT arrays with a height from 2.11 to 3.07 μm.

Adhesion values shown in Table 1 were calculated based on the formula (1). Analysis of the measurement results has shown that the largest average values of the adhesion strength (8.22 μN) are demonstrated by A1-A3 experimental samples. This effect can be due to the fact that during the measurement, the longitudinal deformation of the CNT predominated and there was no additional adherence of the nanotubes to each other when interacting with the probe.
Individual VA CNT of B1-B3 experimental samples showed the lowest adhesion value among all series of samples (1.51 μN), which might be due to the prevalence of transverse CNTs deformation and their coalescence during measurement. It should be noted that among B1-B3 samples, VA CNT adhesion strength increases with increasing aspect ratio and their density in the array.

Analysis of the results of adhesion measurements in samples with branched (C1-C3) and disoriented (D1-D3) CNTs showed that the average adhesion strength was 3.96 and 3.72 μN, respectively. It is seen that the adhesion strength of these samples is lower than that of A1-A3 samples, but exceeds the adhesion value of B1-B3 samples (Table 1). This dependence can be due to the fact that during the measurement of C1-C3 and D1-D3 samples, the probe interacted not with the top of the nanotubes, but with their side walls, in contrast to the measurements of A1-A3 samples. However, there was no sticking of the CNTs tops with each other, in contrast to samples B1-B3.

It should also be considered that the change in the geometric parameters of the grown CNTs leads to a change in their Young's modulus, which affects the value of the adhesion strength. Thus, it is shown that the growth regimes significantly influence the parameters of CNTs, which allows controlling the value of the CNTs adhesion from 0.67 to 11.12 μN. The maximum value of the adhesion strength of 11.12 μN is achieved under the mode of growing CNT bundles at 60 sec activation time, 660 °C growth temperature, 25 W plasma power, and 12 min growth time.

In this case, the use of a 20-μm colloidal probe allows us to determine the value of the CNT macroadhesion, which is several times larger than the value of the local adhesion of CNT obtained by measuring with a standard silicon probe having radius of 20 nm [15].

4. Conclusion
In this work, an experimental research of CNT arrays growth and measuring of the adhesion strength value from the CNT parameters is carried out. It is shown that control of the activation time, plasma power, temperature, and growth time allows creating CNT arrays of various types: bundled, individual, branched, and disoriented.

It is established that the greatest value of the adhesion force is shown by CNT bundles arrays. Among individual CNTs, to achieve the maximum adhesion strength, it is necessary to grow CNTs with high aspect ratios (more than 10).

The results of the research can be used to create adhesive coatings and mechanical contacts of high strength for the space industry and robotics, as well as for the creation of carbon nanoelectronics elements.

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References
[1] Ageev O A, Blinov Y F, Ilina M V, Ilin O I and Smirnov V A 2016 J. Phys. Conf. Ser. 741 012168
[2] Avilov V I, Ageev O A, Smirnov V A, Solodovnik M S and Tsukanova O G 2015 Nanotechnologies in Russia. 10 214-9
[3] Avilov V I, Polupanov N V., Tominov R V., Smirnov V A and Ageev O A 2017 IOP Conf. Ser. Mater. Sci. Eng. 256 8-12
[4] Qu L and Dai L 2007 Adv. Mater. 19 3844-9
[5] Röhrig M, Thiel M, Worgull M and Hölscher H 2012 Small 8 3009-15
[6] Jeong H E, Lee S H, Kim P and Suh K Y 2008 Colloids Surf. A Physicochem. Eng. Asp. 313-4 359-64
[7] Majidi C, Groff R E, Maeno Y, Schubert B, Baek S, Bush B, Maboudian R, Gravish N, Wilkinson M, Autumn K and Fearing R S 2006 Phys. Rev. Lett. 97 076103
[8] Ge L, Sethi S, Ci L, Ajayan P M and Dhinojwala A 2007 Proc. Natl. Acad. Sci. USA 104 10792-5
[9] Qu L, Dai L, Stone M, Xia Z and Wang Z L 2008 Science 322 238-42
[10] Yurdumakan B, Raravikar N R, Ajayan P M and Dhinojwala A 2005 Chem. Commun. 30 3799
[11] Ageev O A, Blinov Y F, Il’ina M V., Il’in O I, Smirnov V A and Tsukanova O G 2016 Phys. Solid State 58 309-14
[12] Greiner C, del Campo A and Arzt E 2007 Langmuir 23 3495-502
[13] Il’ina M V., Il’in O I, Blinov Y F, Konshin A A, Konoplev B G and Ageev O A 2018 Materials 11 638
[14] Purohit R, Purohit K, Rana S, Rana R S and Patel V 2014 Procedia Mater. Sci. 6 716-28
[15] Il’ina M V, Konshin A A, Il’in O I, Rudyk N N, Fedotov A A and Ageev O A 2018 J. Phys. Conf. Ser. 993 012025