Influence of ammonia flow and sublayer material on adhesion properties of carbon nanotubes

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Abstract. The results of experimental studies of the effect of the sublayer material and the ammonia buffer gas flow on the adhesion force of carbon nanotubes (CNTs) are presented. It is shown that the best adhesion is shown by CNT arrays grown on a chromium sublayer, which is due to the hierarchy of their structure. The influence of ammonia flow on the geometric parameters of CNT is shown. The nonlinear dependence of CNT adhesion force on ammonia flow is established. The results obtained can be used to create adhesive coatings of high strength.

1. Introduction
Carbon nanotubes (CNTs) are a promising material for the creation of coatings with the effect of "dry glue" due to the high adhesion and elasticity values [1-3]. The main parameters influencing the adhesion value are the CNT alignment to the substrate and the geometric dimensions of the nanotubes [4]. At the same time, the plasma enhanced chemical vapor deposition (PECVD) method allows controlling the size and alignment of CNTs [5, 6]. An important factor influencing CNT parameters in the PECVD method is the ratio of carbon-containing:buffer gas flows [7]. As a buffer gas, H₂, NH₃, etc. are often used, which allows to restore oxidized catalytic centers and reduce their diameter in the synthesis of CNTs. To avoid chemical interaction between the material of the catalytic layer (Ni) and the substrate, a barrier layer based on films of metals or dielectrics is formed in the structure [8]. However, when heated, diffusion mass transfer is initiated between the layers. As a result, in the volume of layers and in the contact area of the substrate, the component composition changes, and the outer surface of the structure changes its profile. In this case, different combinations of materials "catalyst/sublayer" affect the geometric dimensions of CNTs [9].

The aim of this work is to study the dependence of the adhesion force of carbon nanotubes on the sublayer material and the value of the buffer gas flow NH₃.

2. Experimental studies
CNT arrays grown by PECVD method on Si substrates with different sublayer materials (TiN, SiO₂ and Cr) at NH₃ buffer gas flows were used as test samples: 6, 35, 70, 105, 140 cm³/min. Catalytic centers (CC) of CNT growth were formed by heating a continuous Ni film with a thickness of 10 nm to 660 °C in 20 minutes. CNT growth was also carried out at a temperature of 660 °C in an atmosphere of argon and ammonia at a pressure of 4.5 Torr. Acetylene (70 cm³/min) was used as a carbon-containing gas. The growth time was constant for each sample and was 15 min. To create a vertical alignment of CNT growth relative to the substrate, a plasma was initiated using a high-voltage DC source. Images of CNT arrays obtained using a scanning electron microscope (SEM) are shown in Figure 1.

Research of CNT adhesion force were carried out by force spectroscopy of atomic force microscope (AFM) using the technique described in [4]. Colloidal probe of CPC_SiO2-20 brand with radius 20±3...
μm and force constant 0.3 N/m and silicon probe with platinum coating of NSG10/Pt brand with radius 20 nm and force constant 12 N/m were used as probes. Earlier we showed that the radius and material of AFM probe significantly affect the results of adhesion measurement [4, 6]. Thus, a silicon probe of a small radius is allowed to measure the adhesion force of single nanotubes, and a spherical colloidal probe of a larger radius is required to assess the adhesion forces of CNT arrays [4, 6].

![Image of SEM images of CNT arrays grown at different NH₃ flow values.](image)

**Figure 1.** SEM images of CNT arrays grown at the NH₃ flow value 6, 35, 140 cm³/min.

3. Results
Analysis of SEM images of experimental samples showed that an increase in the flow of buffer gas NH₃ leads to an increase in the etching rate of Ni CC and a decrease in CNT density (Table 1). High temperature (660 °C) and plasma decompose the carbon-containing gas into reactive ions. At the same time, the formation of undesirable amorphous carbon occurs in the flow of C₂H₂ weakly diluted NH₃. When the ratio of C₂H₂:NH₃ flows is 70:6 cm³/min, it is seen that the encapsulation of Ni CC by carbon and the growth of amorphous carbon on the walls of the formed CNTs. An increase in ammonia flow accelerates the etching of Ni CC, but the etching is not accompanied by a linear decrease in CNT diameter. This is due to the fact that as a result of etching under the action of ammonia, the CC is predominantly reduced in diameter. However, as a result of surface diffusion, a gradual union of smaller
CCs into larger ones occurs, which leads to an increase in the CNT diameter and a decrease in their density.

When the structure “catalyst/sublayer/substrate” is heated, diffusion mass transfer is initiated between the layers. Due to the difference in the thermal expansion coefficients of the substrate and sublayer materials, mechanical thermal stresses occur during the heating process. Depending on the type of sublayer material, the outer surface of the structure changes its profile in different ways. Therefore, at the same process parameters for different sublayer materials, the rate of CNT density reduction varies.

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

| Number of samples | Sublayer material | Diameter of CNTs (nm) | Density of CNTs (μm²) | Adhesion force Colloid probe (nN) | Silicon probe (μN) |
|-------------------|-------------------|-----------------------|----------------------|----------------------------------|--------------------|
| 1                 | TiN               | 1165                  | 12                   | 20±11                            | 4±3                |
| 2                 | SiO₂              | 1136                  | 9                    | 13±3                             | 4±2                |
| 3                 | Cr                | 936                   | 5                    | 127±34                           | 3±1                |
| 4                 | TiN               | 57                    | 70                   | 163±112                          | 18±5               |
| 5                 | SiO₂              | 129                   | 73                   | 21±4                             | 12±1               |
| 6                 | Cr                | 52                    | 84                   | 217±122                          | 24±4               |
| 7                 | TiN               | 104                   | 56                   | 119±49                           | 20±5               |
| 8                 | SiO₂              | 123                   | 69                   | 42±33                            | 39±13              |
| 9                 | Cr                | 42                    | 126                  | 257±38                           | 21±5               |
| 10                | TiN               | 118                   | 46                   | 62±35                            | 14±2               |
| 11                | SiO₂              | 71                    | 58                   | 81±62                            | 36±12              |
| 12                | Cr                | 37                    | 83                   | 269±74                           | 20±5               |
| 13                | TiN               | 79                    | 42                   | 23±6                             | 29±8               |
| 14                | SiO₂              | 69                    | 30                   | 94±80                            | 18±3               |
| 15                | Cr                | 41                    | 76                   | 309±128                          | 35±7               |

The analysis of the results of measuring the adhesion forces of experimental samples showed that the dependence of the adhesion forces on the NH₃ flow is nonlinear and significantly depends on the type of AFM probe (figure 2). Thus, for an array of CNTs grown on a TiN sublayer, with an increase in NH₃ flow, the value of the adhesion force first increases to 163 nN, and then decreases to 23 nN (figure 2). The initial increase in the adhesion force is due to the formation of CNTs with a high content of amorphous carbon, formed at a flow of NH₃ 6 cm³/min (Figure 2). When the NH₃ flow is more than 40 cm³/min, the decrease in the CNTs array adhesion is associated with the active union of nanotubes into bundles (Figure 1). At the same time, the measurements obtained by the AFM silicon probe showed an increase in the adhesion value at the NH₃ flow of 6 cm³/min, which is associated with a sharp decrease in the CNT diameter (Table 1). Colloidal probe studies did not show this change, because they reflect changes in the adhesion value of the entire array of united in bundles CNTs. For CNT arrays grown on SiO₂ sublayer, adhesion forces increased nonlinearly from 13 to 94 nN, which is associated with a decrease in CNT diameter (Table 1). At the same time, measurements of single CNTs obtained by the AFM silicon probe showed the maximum value of the adhesion force at the NH₃ flow of about 80 cm³/min (Figure 2 b). This fact is associated with the formation of a branched CNT structure at ammonia flow in the range from 70 to 105 cm³/min. For CNT arrays grown on the Cr sublayer, the highest

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adhesion values were observed, increasing from 127 to 309 nN (Figure 2 a). This fact is associated with an increase in the hierarchy of the CNTs array structure with an increase in NH₃ flow (Figure 1). At the same time, measurements of single CNTs showed a decrease in the adhesion force at NH₃ flow from 50 to 100 cm³/min (Figure 2 b), which is probably due to the localization of the AFM probe on the side wall of the nanotube, and not its top due to the increase in hierarchy and branching of the structure.

![Image](image_url)

**Figure 2 (a, b).** Dependence of CNT adhesion forces on the NH₃ flow value obtained by a (a) colloid probe and a (b) silicon probe.

It should be noted that the measurement results obtained by the silicon probe were two orders of magnitude higher than those obtained by the colloidal probe (Table 1). This fact is due to the different contact area of the AFM probe with the array surface and the type of interaction between the probe and nanotubes [4, 6]. The obtained results are in good agreement with the previously established regularities [4, 6].

4. Conclusion

Thus, in this work, the dependence of the adhesion forces of CNT arrays and single CNTs on the value of the buffer gas flow NH₃ and the sublayer material were obtained. The necessity of diluting the carbon-containing gas with ammonia (or hydrogen) is shown. It is established that the maximum adhesion force of CNT array is observed when using chromium as a sublayer. The value of the adhesion force of CNT array increases with increasing NH₃ flow, which is associated with decreasing diameter of the nanotubes and the increase of hierarchy of the array as a whole. It is shown that the measurements obtained by the AFM silicon probe are more sensitive to changes in the geometric parameters of single CNTs. But to assess the adhesion strength of the CNT array as a whole, the use of a colloidal AFM probe is preferable. The results obtained can be used to create coatings with the effect of "dry glue" on the basis of arrays of 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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