The influence of the temperature and Ti and TiN sublayer material on carbon nanotubes growth

N N Rudyk, O I Il’ in, M V Il’ ina, O I Osotova, A A Fedotov
Southern Federal University, Institute of Nanotechnologies, Electronics and Equipment Engineering, Taganrog, 347922, Russia

Abstract. The influence of the temperature and Ti and TiN sublayer material on the height, diameter, density, and uniformity of carbon nanotubes (CNTs) growth is studied. It was found that on the TiN sublayer, CNTs form an array with a more uniform diameter distribution of CNTs than on the Ti sublayer (minimum dispersion 5.6 nm versus 8.1 nm). It is shown that for the Ti sublayer, with an increase in the growth temperature, an almost linear increase in the CNT height occurs. It was found that an increase in the CNT height is accompanied by a decrease in their diameter for both sublayers. For a given thickness of Ni, arrays with a density of 3–18 μm–2 were obtained on the Ti sublayer, and on a TiN sublayer in the range of 8–21 μm–2. The greatest uniformity of the surface distribution of CNTs is showed at 660 °C. CNT arrays on the Ti sublayer are characterized by a lower concentration of bundles than on the Ti sublayer.

1. Introduction
The unique properties of carbon nanotubes (CNTs) have long attracted the interest of scientists for their device application [1]. However, at present CNTs have not found mass application in modern micro- and nanoelectronics devices. This problem is mainly associated with a high dispersion of the geometric dimensions of CNTs, which do not allow ensuring the stability of the developed devices. For device applications, CNTs must be grown on an electrically conductive contact sublayer. In this case, the parameters of the technological process, as well as the material of the sublayer [2, 3], have a significant effect on the geometric dimensions of CNTs and their uniformity. The aim of this work was to research the influence of the growth temperature and the material of the Ti and TiN sublayer on the height, diameter, density and uniformity of CNTs in the array.

2. Experiments and methods
Experimental studies were carried out on the Ni/Ti/Si and Ni/TiN/Si structures. The formation of catalyst films (Ni, 10 nm) and a sublayer (Ti and TiN, 100 nm) was provided by magnetron sputtering on Auto500 (BOC Edwards, UK). In these structures, the sublayer acts as a conductive material, and the Ni film acts as a catalytic material for the CNTs growth.

The formation of CNTs was carried out in the temperature range of 615–690 °C with a step of 15 °C. Heating to a set temperature was conducted in Ar (40 sccm) and NH3 (15 sccm) flows for 20 minutes. CNTs were grown by the PECVD method for 15 min in the ammonia (210 sccm) and acetylene (70 sccm) flows with plasma initiation (40 W). Throughout the process, a pressure of 4.5 Torr was maintained. The study of the geometric dimensions and density of the grown CNTs was carried out by SEM on a Nova Nanolab 600 (FEI, Netherlands).
For the instrumental use of vertically oriented CNTs, a different character of their distribution over the substrate surface may be required. When creating and studying memristors, previously used carbon nanotube bundles [4], as well as freestanding CNTs [5]. Therefore, the effect of the temperature of the PECVD process on the uniformity of distribution of CNTs over the surface was also investigated.

The uniformity of the distribution of CNTs in the array was estimated by formula:

\[ U = \frac{\mu}{\sigma} \]

where \( \mu \) - expectation of the distance from each tube to 6 neighbors, \( \sigma \) – standard deviation. This parameter allows to quantitatively characterize the degree of integration of vertically oriented CNTs into bundles.

3. Results and discussion

Due to the action of plasma at the growth stage, the obtained CNTs have a pronounced perpendicular orientation with respect to the substrate (Figure 1).

![Figure 1(a,b). SEM images of the obtained CNT on the TiN sublayer: a) surface; b) cross-section.](image)

The analysis of SEM images showed that the formation of CNTs occurred according to the «tip-growth» mechanism, and the nature of the change in the geometric parameters of CNTs (Figure 2) did not vary with temperature for different materials of the Ti and TiN sublayer.

For the Ti sublayer, with an increase in the growth temperature, an almost linear increase in the CNT height occurs (Figure 2, a). This may be due to the fact that during the growth of CNTs by the «tip-growth» mechanism, the catalyst become estranged from the substrate. With an increase in the length of the CNTs, the estrangement of the catalytic particle leads to its gradual cooling and loss of catalytic ability. An increase in temperature can lead to the maintenance of catalytic activity at large distances with an increase in the total length of CNTs. The minimum height dispersion for the Ti sublayer was provided at 630 °C and was 10.05 ± 0.63 μm.

The height of CNTs grown on the TiN sublayer was significantly higher than on the Ti sublayer. In this case, a section with an almost linear decrease in height in the temperature range 630–675 °C was accompanied by an almost linear increase in the diameter of the CNTs. Also interesting is the fact that an increase in the height of CNTs is accompanied by a decrease in their diameter (Figure 2, b). This may be due to the loss of the volume of the catalytic particle inside the CNT cavity during growth. Also, it was found significantly more uniform distribution of the diameter of CNT grown on the TiN sublayer as compared to a sublayer Ti (minimal dispersion 5.6 nm compared to 8.1 nm).
Figure 2(a,b). Dependence of the height (a) and diameter (b) of the CNTs on the growth temperature.

The obtained dependences of the distribution density of CNTs in the array showed that their character is similar for both sublayers (Figure 3). With an increase in the synthesis temperature from 630 °C, a decrease in the density of CNTs is observed. For the Ti sublayer, the density maximum is observed at a temperature of 630 °C and amounts to 17.6 μm². For the TiN sublayer, the highest density was also achieved at a temperature of 630 °C, but amounted to 20.6 μm². A decrease in the density of CNTs on the TiN sublayer may be due, inter alia, to an increase in the diameter of CNTs (Figure 2, b). The different density of CNTs on the sublayers can be explained by the features of the chemical interaction between the catalytic layer and the material of the sublayer, which is reflected in the distribution of the formed CCs.

Figure 3. Dependence of the surface density of CNTs on the growth temperature.

The decrease in density on both sublayers at a temperature of 615 °C can be associated with a high heterogeneity of the diameter of the CNTs (Figure 2, b). Ni islands formed at the heating stage cannot actively sublimate. The movement of Ni atoms between individual CCs along the surface of the sample is also hindered by the lack of thermal energy. In this regard, CCs of various sizes formed at the initial stage do not have the ability to be modified. The large scatter in the diameter of nanotubes from 12 to 100 nm, which is a consequence of this, is accompanied by their combination into bundles around larger diameter CNTs. This circumstance can also complicate their differentiation and
calculation. It can be concluded that arrays with a density of 3÷18 \( \mu m^2 \) can be obtained on the Ti sublayer at a given thickness Ni, and on the TiN sublayer in the range of 8÷21 \( \mu m^2 \).

The results of calculations of the uniformity \( (U) \) of the distribution of CNTs over the surface showed that the process temperature affects the bundle concentration (Figure 4). The data obtained were normalized to the maximum \( U \) value (TiN sublayer, 660 °C). A higher uniformity value corresponds to better isolated CNTs in the array, while a small \( U \) indicates the formation of CNT bundles of different sizes.

![Figure 4. Dependence of the uniformity of the CNTs on the growth temperature.](image)

Figure 5 demonstrates CNT arrays on a TiN sublayer with different values of \( U \). It can be seen that at \( U = 0.7 \) (Figure 5, a) nanotubes on the surface interact quite strongly with each other, uniting into agglomerates. Typically, smaller diameter CNTs are attracted to larger diameter CNTs by Van der Waals forces. In an array with \( U = 1 \) (the maximum value in this experiment) (Figure 5, b), CNTs interact much weaker with each other and are therefore better isolated.

![Figure 5(a,b). SEM images of the obtained CNT on the TiN sublayer: a) \( U = 0.7 \); b) \( U = 1 \).](image)

It was found that for both sublayers in the temperature range 645 - 660 °C the greatest uniformity (the lowest concentration of bundles) is observed. It should also be noted that CNTs on the TiN sublayer demonstrate better uniformity compared to CNTs on the Ti sublayer.
The obtained results can be used for creating elements and devices of micro- and nanoelectronics, nanopiezotronics, sensitive elements of gas sensors, as well as materials with increased adhesive ability.

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