Critical pressure during the formation of carbon nanotubes by the method of plasma chemical vapor deposition

V S Klimin^12, A A Rezvan^1, J V Morozova^1

^1Department of Nanotechnology and Microsystems, Southern Federal University, Taganrog 347922, Russia
^2Research and Education Center “Nanotechnologies”, Southern Federal University, Taganrog 347922, Russia

Abstract. The critical pressure of acetylene required for the formation of nanotubes on nickel catalytic centers of a given size was calculated by plasma chemical vapor deposition. It has been established that for a stable growth of carbon nanotubes on a catalytic center with a diameter of 20 nm, the critical pressure of acetylene should be 1.9 Pa, while the growth time of carbon nanotubes in length of 5 μm is 131 sec. Nickel was used as a material for the formation of catalytic centers. In the calculations, the averaged parameters of carbon nanotubes were used. This analysis allowed to form a number of criteria for the materials of the underlayer and catalytic centers, to obtain an array of carbon nanotubes with a high degree of verticality.

1. Introduction
The increased interest in the study of carbon nanotubes is due, on the one hand, to their unique physicochemical properties, thanks to which they are an attractive object of basic research, and, on the other hand, to broad prospects for applied use [1-5]. The development of technologies for producing arrays oriented carbon nanotubes with controlled parameters opens up wide possibilities for their application in microelectronic sensors for creating sensitive elements of gas sensors. Such sensitive elements can reduce the operating voltage and improve the weight and size characteristics of the devices [6-12]. To implement practical developments using carbon nanotubes, selective synthesis of nanotubes with a controlled structure and properties is required [13-18]. One of the most promising methods of such synthesis is chemical vapor deposition initiated by plasma. The plasma chemical vapor deposition method allows to obtain oriented arrays on various substrates. A feature of this method is the use of catalytic centers. However, to obtain carbon nanotubes with the required geometric and electrical parameters requires a clear understanding of the processes and their precise control. In this connection, the study of the critical pressure of acetylene and its influence on the growth of carbon nanotubes on nickel catalytically layers is important [19-25].

2. Materials and Methods
This technique is consistent with the following points, namely, silicon substrates were used in the studies, the surface of which was cleaned by the method of liquid polishing. Nickel was used as a material for the formation of catalytic centers. The calculation method is based on the Knudsen theory and the basic equations of solid-state physics, which allows analyzing the diffusion of the carbon flow presented in Figure 1.

The calculations were performed using the averaged parameters of carbon nanotubes, which resulted in the calculation of the resulting single carbon nanotube (1).
There is the length, \( d_1 \), \( d_2 \) are the inner and outer diameters, respectively. The inner diameter of the nanotube is assumed to be equal to the size of the catalytic center \( d_k \).

The number of atoms that make up a carbon nanotube is defined as (2):

\[
N_H = \frac{M_N}{M_C} N_A
\]

\( M_N = V_M M_C \) – carbon nanotube molar mass, \( V_M = (V/V_C) \) – carbon nanotube molar volume, \( V_C \) – molar volume of carbon, \( M_C \) – molar mass of carbon; \( N_A \) – Avogadro’s number.

On fig. 1 (a, b) shows a scheme of a diffusive flow of carbon through a nickel catalytic center with the growth of carbon nanotubes.

Determine the molar concentration of carbon that is released during the dissociation of acetylene and dissolves on the surface of the nickel catalytic center:

\[
\Delta C = 10^{-5} \frac{n_C}{V_{Ni}} \frac{M_{Ni}}{M_C}
\]

\( V_{Ni} \) – molar volume of Ni; \( M_{Ni} \) - molar mass of Ni; \( n_C \) – carbon limit concentration, which, without entering into chemical interaction, dissolves in nickel at the temperature of growth of carbon nanotube (1023 K). Know the concentration of carbon dissolved on the surface of the catalytic center, one can estimate the molar flux of carbon to the base of the growing nanotube:

\[
F \simeq D * \frac{\Delta C}{L_D}
\]

There \( D \) - carbon diffusion coefficient and \( L_D \) – diffusion length.

Using (3) and (4), the time of nanotube formation can be estimated as:

\[
\tau = \frac{V_M}{F * A}
\]

\( A \simeq \pi d^2 / 4 \)

There \( A \) – the area of the catalytic center through which carbon diffuses to the base of the nanotube, assuming that the catalytic center has a spherical shape. Then the growth rate of carbon nanotube can be estimated as:

\[
\omega = \frac{l}{\tau}
\]

The number of carbon atoms arriving at the base of the nanotube per unit of time is determined by the formula:

\[
\omega_A = D * \frac{\Delta C}{L_D} * N_A * A
\]

There the area of the base of the nanotube is equal to the area of the catalytic center \( AH = A \).

For a stable growth of carbon nanotubes, it is necessary that the acetylene molecules on the surface of the catalytic center dissociate at the same rate. Considering that as a result of the decomposition of acetylene \( \text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2 \), two carbon atoms are released, the steady growth of carbon nanotubes will be maintained if the dissociation rate balances the outflow of carbon to the base of carbon nanotube:

\[
\omega_d = \omega_A / 2
\]

From this it follows that per unit of surface area of the catalytic center per unit of time during the dissociation of acetylene appears

\[
\omega^* = \omega_d / A
\]
Then it is possible to calculate the total number of dissociation centers \( N^* \) on the surface of the catalytic center.

![Diagram of the diffusion flow of carbon through the nickel catalytic center with the growth of carbon nanotube.](image)

**Figure 1 (a, b).** Diagram of the diffusion flow of carbon through the nickel catalytic center with the growth of carbon nanotube

In this case, \( V_d \) dissociation will occur on the surface of the catalytic center per unit of time, and after each interval of time \( t_d \) two new carbon atoms will appear, that is \( \text{C}_2\text{H}_2 \) dissociation reaction is carried out. Thanks to a series of transformations, the following form was obtained for determining the magnitude of the critical pressure (11).

\[
P = \frac{w}{2(2\pi mkT)^{-1}}
\]

(11)

3. Results

The obtained values of the average parameters, as well as the constructed mode of formation of carbon nanotubes, were used to obtain an array on the catalytic nickel centers in the Ni/Ti/Si and Ni/V/Si system.

![SEM images of CNT arrays obtained on structures with different underlayer materials: a) Ni/Ti/Si; b) Ni/V/Si](image)

**Figure 2 (a, b).** SEM images of CNT arrays obtained on structures with different underlayer materials: **a**) Ni/Ti/Si; **b**) Ni/V/Si
4. Discussion and Conclusions

At the end of the analysis, taking into account the results obtained, the mode of the process of growing carbon nanotubes by the method of plasma chemical vapor deposition was formed and tested. Also, this analysis allowed us to form a number of criteria for the materials of the underlayer and catalytic centers, to obtain an array of carbon nanotubes with a high degree of verticality.

Calculations showed that for sustainable growth of carbon nanotubes on catalytic centers with a diameter of 20 nm, the critical pressure of acetylene should not be less than 1.9 Pa. The number of dissociation of acetylene molecules per unit of time per unit area of the catalytic center was \(1.777 \times 10^{22} \text{ m}^{-2}\text{s}^{-1}\), the formation time of carbon nanotubes was 131 seconds with an average speed of 2.3 \(\mu\text{m/min}\).

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