Formation of metal catalytic centers from atomic flows of matter for the growth of carbon nanostructures using PECVD method

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Abstract. Consider formation of nickel catalytic centers from atomic flows obtained by the method of vacuum resistive evaporation. A model of formation kinetics of catalytic centers of nickel from atomic flows has been constructed. A complete model of theoretical studies of the formation of catalytic centers of nickel on a silicon surface is shown. A dependence of cluster concentration on normalized formation time is obtained. According to the results of theoretical studies, it was learned that flux of nickel atoms to substrate is \( F = 1.296 \times 10^{18} \), residence time of nickel atom on substrate in adsorbed state is \( t_g = 5.135 \times 10^{-7} \), and concentration of adsorbed atoms as a function of time is \( N = 6.657 \times 10^{11} \).

1. Introduction
Currently, carbon nanostructures are structural basis for many micro and nanoelectronic devices. Each of modifications which has its own individual properties and possible prospects. So carbon nanotubes have been used for quite some time in transistors, diodes, memory elements, nanocathodes, storage batteries and others [1-10]. However, although many publications indicate experimental confirmation of these applications and confirmations of formation of carbon nanostructures that satisfy specified process parameters, theoretical basis of process of growth and formation of carbon nanotubes is still a weak point of nanotechnology [11-15]. This work is aimed at carrying out theoretical studies of formation kinetics of catalytic centers from atomic flows of matter for oriented growth of carbon nanotubes.

2. Discerption of investigation
Formation of catalytic centers from transition metals on surface of substrate is initial and one of the most important stages in technology for producing carbon nanotubes by plasma chemical vapor deposition. The consideration was based on the formation of catalytic centers of nickel.

In further considerations, it is assumed that nickel catalytic center is a single crystal with an axis [100] parallel to the axis of nanotube and a base face (001) on which acetylene does not decompose and carbon is not deposited [16-27]. According to growth mechanisms considered earlier, there is a difference in activity of dissociation at different faces of nickel single crystal. With the single crystal structure of the catalytic center, complete dissociation of acetylene occurs on Ni (100) faces, while molecular desorption is observed on Ni (110) and Ni (111) faces.

Consider the formation of nickel catalytic centers from atomic flows obtained by the method of vacuum resistive evaporation. The initial data used in the calculations: binding energy of two nickel
atoms adsorbed on surface of substrate $W_g = 1.6 \text{ eV}$, the residence time of atom on substrate is $t_0 = 10^{-13} \text{ sec}$, evaporation temperature is $1200 \text{ K}$, and the substrate temperature is $750 \text{ K}$.

Figure 1 (a, b). AFM (a) and SEM (b) images of catalytic centers formed on the Ni / V / Si structure at a temperature of 600 °C.

So, for example, in the model, intensity of the particle evaporation flow, taking into account assumption that there is no reevaporation of adsorbed single atoms, can be estimated based on the kinetic theory of sublimation according to the Knudsen equation [25]:

$$F = \frac{P}{\sqrt{2\pi mkT}}$$  \hspace{1cm} (1)

where $m$ is mass of molecule, $P$ is equilibrium vapor pressure at evaporation temperature $T$.

The equilibrium vapor pressure is determined by formula (2)

$$P = 10^{(\frac{E}{A+19^S}})$$  \hspace{1cm} (2)

where $A$ and $B$ are constants for nickel, $T$ is the temperature of the substrate.

The residence time of an atom on a substrate in an adsorbed state is determined by the expression.

$$\tau_E = \tau_0 \exp\left(\frac{E_R}{kT}\right)$$  \hspace{1cm} (3)

where $\tau_0$ is the residence time of the atom on the substrate; $E_R$ is the binding energy of two nickel atoms adsorbed on the surface of the substrate.

An atom arriving at the surface is adsorbed by the surface and remains in a bound state for some time.

The binding energy of the atom with the substrate $E_R$ is quite low, so the atom has a certain degree of mobility. By migrating over the surface in an adsorbed state, an atom can either desorb back into vacuum, or when colliding with another atom, form a complex of 2 atoms. Since the complex is bound to the substrate by two atoms, it is less mobile and its evaporation energy doubles. To determine the dependence of the concentration of adsorbed atoms on time, we use the expression for the surface density of atoms:
According to the atomic theory of condensation, the surface density of atomic clusters that can serve as catalytic centers is determined by the expression:

\[ N_i = F \star \tau_B \]  
(4)

According to the atomic theory of condensation, the surface density of atomic clusters that can serve as catalytic centers is determined by the expression:

\[ n_i(x) = \frac{N_i}{2} \left[ 1 - e^{-x} \left( \sum_{i=1}^{k-2} \frac{x^i}{i!} \right) \right], k \geq 2 \]  
(5)

where \( i \) is count of atoms in clusters; \( x = \omega \int_0^t n_i(x) \star dt \) is normalized cluster formation time, \( n_i \) is concentration of atoms on the surface of the substrate \( n_i(x) = N_i = F \star \tau_B \).

3. Results and Discussion

The model obtained in the course of theoretical studies, formed on expressions (1) - (5), allows us to evaluate the dynamics of the formation of catalytic centers taking into account their sizes.

Figure 2. Dependence of the concentration of atomic clusters on the formation time for a different number of atoms in a cluster (i = 2, 5, 10, 20).

Figure 2 shows the results of calculations according to model (1) - (5) of the dependences of the concentration of atomic clusters on the formation time for a different number of atoms in a cluster (i = 2, 5, 10, 20).

According to the results of the analysis, the following values of the flux of nickel atoms to the substrate were \( F = 1.296 \times 10^{18} \), the residence time of the nickel atom on the substrate in the adsorbed state was \( \tau_g = 5.135 \times 10^{-7} \), and the concentration of adsorbed atoms as a function of time \( N = 6.657 \times 10^{11} \).

The theoretical results obtained in this work contribute to deepening knowledge in the field of processes of formation of carbon nanoscale structures in order to match the elements obtained with the given process parameters, which allows not only to simplify the mechanism of their production, but also to find new applications in other areas of micro- and nanoelectronics.
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