Influence of annealing temperature and activation time on the catalytic centers formation for carbon nanostructures growth

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Abstract. Experimental studies of the effect of annealing temperature and time of the PECVD process activation stage on the formation of catalytic growth centers of carbon nanostructures were carried out. The dependences of the diameter and height of the catalytic centers on the annealing temperature are obtained. It has been established that exposure in an ammonia atmosphere leads to additional etching of nickel and a decrease in their diameter and height. It has been established that the most optimal temperature for creating with the smallest dispersion of the geometric parameters of the catalytic centers is 750 °C.

1. Introduction
The unique properties of nanostructures based on carbon nanotubes (CNTs) make them a promising material for creating new elemental base of micro- and nanoelectronics, nanopiezotronics [1-3]. However, for instrument applications, oriented CNT arrays are of interest. One of the most promising methods for the synthesis of oriented CNT arrays is plasma enhanced chemical vapor deposition (PECVD) [4, 5]. The growth of CNT arrays by the PECVD method requires the presence of catalytic centers (CC) based on transition metals. The most frequent formation of CC is carried out by annealing of films of Ni, Fe, Co, etc. Parameters of catalytic centers (size, dispersion, chemical composition, etc.) determine the parameters of carbon nanotubes (diameter, height, chirality, electrical properties, growth kinetics), which underlie their instrument application.

2. Experiments and methods
In this paper, studies of the effect of annealing temperature and activation time on the formation of catalytic centers of growth of CNT have been carried out. Samples with Ni (10 nm)/Cr (20 nm)/Si structure were heated in the temperature range of 700-800 °C with simultaneous feeding of an inert gas (QAr = 40 cm³/min) and ammonia (QNH₃ = 15 cm³/min) into the chamber. Argon is used to displace residual air from the chamber, and ammonia creates a reducing atmosphere that prevents oxidation of the catalytic film.

The activation consisted in holding the samples obtained at the heating stage in an NH₃ atmosphere (210 cm³/min) with and without plasma initiation. Formed 6 batches of samples for which the heating stage was carried out to a temperature of 750 °C for 20 minutes, in a stream of Ar (40 cm³/min) and NH₃ (15 cm³/min). Upon completion of the heating stage, the activation stage began, during which only NH₃ (210 cm³/min) was fed into the chamber, while the heating temperature did not change. For samples № 1-3, the gas supply time was 1, 3 and 5 minutes without plasma initiation, for № 4-6 the time was the same, but with plasma initiation.
The study of the obtained catalytic centers was carried out using atomic force microscopy (AFM) using the Ntegra Nanolaboratory (NT-MDT, Russia) and scanning electron microscopy (SEM) using a Nova Nanolab 600 microscope.

We investigate the phase composition of the structure of the nickel catalytic layer by X-ray absorption spectroscopy (XANES, EXAFS) at a specialized source of synchrotron radiation (SIC "Kurchatov Institute", Moscow, Russia). The obtained X-ray absorption spectra were compared with reference samples.

3. Results and discussion

The dependences of the catalytic centers diameter and height on the annealing temperature (Fig. 1a) and EXAFS spectra (Fig. 1b) of the Ni/Cr/Si structure after heating to 750 °C were obtained. The difference between the temperature coefficients of expansion of the Si substrate and the Cr sublayer contributes to the appearance of a strong mechanical stress on the film/substrate contact during annealing, and, as a result, fragmentation and rupture of the metal film into separate islands — catalytic centers (Fig. 2).

![Figure 1](image)

Figure 1(a, b). (a) Dependence of the catalytic centers diameter and height on the annealing temperature; (b) EXAFS spectra of the Ni/Cr/Si sample after heating to 750 °C

CC formed at a temperature of 700 °C characterized by a large scatter of geometric parameters, which is associated with the initiation of the film breakdown process and insufficiently intense surface diffusion of Ni atoms. As the temperature rises to 750 °C, diffusion exchange of atoms is activated through the contact plane between the film and the substrate. As the plasticity of the metal increases, a combination of small CC into larger ones with a decrease in the scatter of their height is observed. When the temperature rises above 750 °C, there is a simultaneous process of sublimation and surface diffusion, which leads to a decrease in the diameter and height of the CC, while there is a decrease in the number of small CC, which were observed at a temperature of 700 °C.

The results of an X-ray absorption spectroscopy show that in structures obtained by heating to 750° C, Ni is mainly in the oxidized state (the volume of pure Ni is ~30%). Due to the necessity of forming catalytic centers from pure Ni, for subsequent growth of CNTs, it is necessary to “activate” centers to reduce Ni from NiO before starting the process of CNT synthesis.

The results obtained from an experimental study of the effect of the “activation” process showed that this stage has a significant impact on the evolution of catalytic centers, with the greatest contribution being made by the effect time, and not by the presence of plasma in the process.

Comparison of dependencies (Fig. 3) shows that exposure in an ammonia atmosphere leads to additional etching of Ni catalytic centers and decrease their diameter and height. At the same time, more ordered and homogeneous catalytic centers arrays are formed in comparison with arrays those obtained at the heating stage. It is shown that, with an increase in the catalytic centers processing time during the “activation” stage, it is possible not only to reduce the size of the CC from 122 ± 19 to 65 ± 9 nm (in the range of processing time 1–5 min), but also to increase their homogeneity.
Figure 2(a, b, c). SEM-images of CC, formed at temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C.

Figure 3(a,b). Dependencies of the catalytic centers diameter (a) and height (b) on activation time

The results of EXAFS spectroscopy (Fig. 4) show that Ni on the samples almost completely recovered, with a metal purity of 90-95%, which confirms the necessity of "activation" step prior to the growth stage.
Figure 4. EXAFS spectrum of the sample after activation in plasma

It has been established that exposure in an ammonia atmosphere leads to additional etching of Ni and a decrease in their diameter and height. In this case, a more ordered and homogeneous CC array is formed, compared to the heating stage.

As a result of research on the effect of heating temperature on the formation of CC, it has been established that the most optimal temperature for creating CC with the smallest dispersion of geometric parameters is 750 ºС. At the same time, as the activation time increases, it becomes possible to reduce the size, increase homogeneity, and restore oxidized catalytic centers.

The results can be used to create elements and devices of micro- and nanoelectronics, sensitive elements of gas sensors, energy harvesting.

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