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Investigation of Synthesis of Carbon Nanowalls by the Chemical Vapor Deposition Method in the Plasma of a Radio Frequency Capacitive Discharge

Didar Batryshev, Yerassyl Yerlanuly, Tlekkabul Ramazanov, and Maratbek Gabdullin

***Abstract*— In this paper, the synthesis of carbon nanowalls (CNWs) by the chemical vapor deposition method in the plasma of a radio frequency (RF) capacitive discharge is considered. The so-called "CNWs" are one of the allotropes of carbon, which are interesting from both the practical and theoretical points of view. Because of their large surface, CNWs are a perfect electrode material for electronic devices. CNWs were synthesized at relatively low values of RF power, and it was found that an increase in the discharge power caused a decrease in the height of CNWs and an increase in their thickness. The study of graphitization of the CNW structure showed that synthesized CNWs had a low number of defects in the structure. The obtained results could be useful for the low-cost production of CNWs by the plasma-enhanced chemical vapor deposition (PECVD) method.**

***Index Terms*— Atomic force microscopy (AFM), carbon nanowalls (CNWs), plasma, radio frequency (RF) discharge.**

I. Introduction

TODAY, the theoretical and experimental studies of plasma properties and plasma technologies are especially important as their results play a significant role in their practical applications in the future. The areas of their applications include power generation in fusion reactors [1]–[3], the use of plasma in medicine [4], practical application of plasma technologies in the surface treatment of materials [5]–[7], and so on. Plasma technologies are also widely used to obtain various carbon nanomaterials, in particular, carbon nanoparticles, carbon nanotubes, carbon nanowalls (CNWs), and graphene. The process of synthesis of these carbon nanomaterials in the plasma medium depends on the plasma parameters such as discharge power, temperature, pressure, and gas mixture, which enable scientists to control formation of nanostructures and types of obtained products [8]. An intensive study of the synthesis process of such nanostructures is caused by a wide use of these structures, for example, carbon nanoparticles are used for water purification [9], carbon nanotubes are used as reinforcing elements for the production of high-quality construction materials [10], as well as for targeted drug delivery [11], graphene is used for production of highly sensitive sensors and semiconductor elements [12], CNWs can be used as an absolutely blackbody material for bolometers [13], solar cells [14], and also as electrodes for supercapacitors [15]. CNWs can be considered as a walllike graphite nanostructure with a high-aspect ratio, a large surface area, high chemical stability, and mechanical strength. However, in order to fully use their potential, it is necessary to carry out further experimental investigations to determine how to control the nanostructure characteristics and to find optimal synthesis parameters.

In [16] devoted to the study of CNWs synthesis in the plasma of radio frequency (RF) discharge, it was found that an increase in the discharge power caused agglomeration of nanowalls into nanoclusters with the formation of defects in the structure. In this paper, we will try to explain in more detail the influence of RF discharge on the growth mechanism of CNWs. This paper presents the results of the experimental study of the CNW synthesis by the chemical vapor deposition method in the plasma of an RF capacitive discharge.

II. Experiments

The experiments were conducted in a horizontally parallel-plate RF plasma of methane (CH_4) and argon (Ar) gases with RF power of 8–14 W, a total pressure of 1.9 torr, the gas temperature of 700 K, and flow rates of CH_4/Ar: 1/7 sccm. A more detailed description of the experimental setup is given in [16].

The recent investigations of the CNWs synthesis by the plasma-enhanced chemical vapor deposition (PECVD) method [17]–[19] showed that formation of high-quality CNWs depends on gas flow rate, temperature, discharge power, growth time, gas pressure, the source of carbon, and other factors. All these works were carried out at relatively high values of the discharge power, higher than 100 W. The main difference of this paper from the previous ones is an

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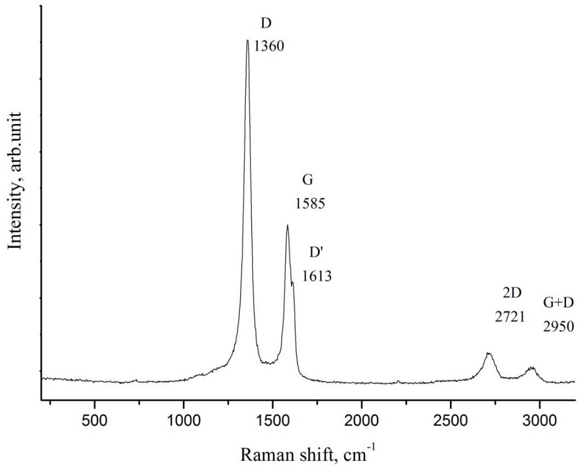

Fig. 1. Raman spectrum of obtained CNWs at RF power of 10 W.

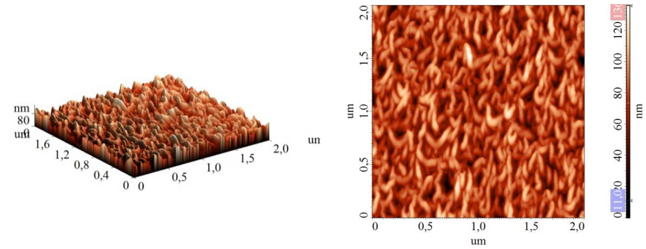

Fig. 2. AFM topography (left) and phase map (right) of synthesized CNWs (sample No. 1) at RF power of 8 W.

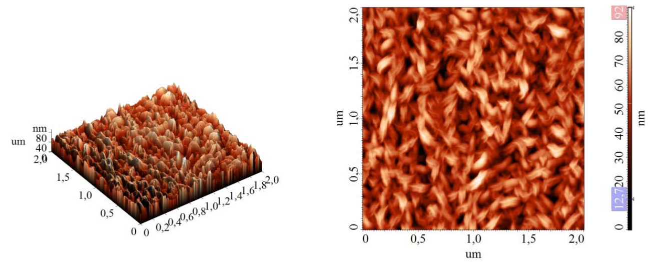

Fig. 3. AFM topography (left) and phase map (right) of synthesized CNWs (sample No. 2) at RF power of 10 W.

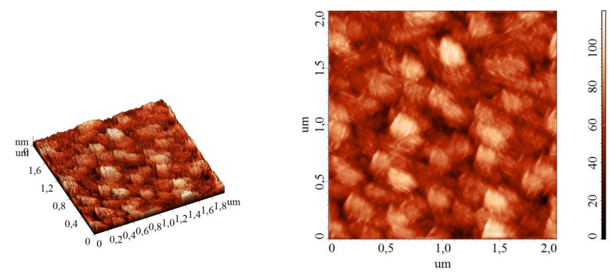

Fig. 4. AFM topography (left) and phase map (right) of synthesized CNWs (sample No. 3) at RF power of 12 W.

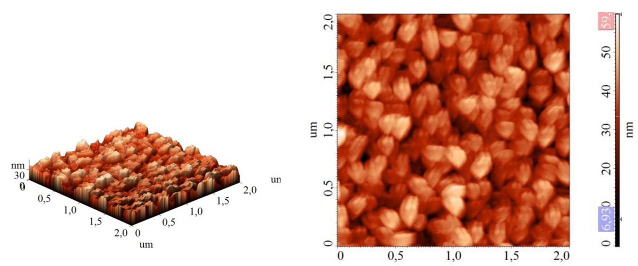

Fig. 5. AFM topography (left) and phase map (right) of synthesized CNWs (sample No. 4) at RF power of 14 W.

investigation of the PECVD synthesis of CNWs at lower values of RF power in order to find an opportunity for the low-cost production of CNWs.

CNWs were synthesized on silicon (Si) substrates with nickel (Ni) catalytic nanolayer. Before the RF synthesis, the Si/Ni substrate was annealed in Ar RF plasma at a temperature of 500 K for 15 min, then the temperature was raised up to 700 K and CH_4 gas was injected into the RF reactor with Ar. The PECVD process in which CNWs were synthesized lasted 25 min.

The morphology of the synthesized CNWs was studied by atomic force microscopy (AFM), and graphitization of their structures was studied by the Raman spectroscopy with a laser wavelength of 473 nm. The AFM measurement of the obtained CNWs samples was made in the semicontact mode.

III. Results and Discussion

Fig. 1 shows a typical Raman spectrum of CNWs consisting of three dominant Raman modes D, G, and D', and less intense 2-D and G + D modes. The D-mode is caused by a disordered structure in graphene, the G-band is related to the C–C vibrational mode, the D'-peak corresponds to the appearance of the graphene edge, the 2-D-peak is the second-order of D-mode, and the G + D-peak is a combination band of G and D peaks. Usually, to estimate the structure quality of graphitelike materials, the intensity ratio between D and G peaks is used. The I_D/I_G ratio indicates the defectiveness of the graphite structure, and as the average value for the obtained samples is 1.8, it means that synthesized CNWs have a small number of defects in the structure.

The AFM analysis of the obtained samples showed that the shape of the walls changed as the RF power increased. Indeed, the corresponding AFM images are shown in Figs. 2–5. It was found that an increase in the RF power leads to a decrease in the height of CNWs and an increase in their thickness. The estimated average thickness values for the samples obtained at RF power of 8, 10, 12, and 14 W are 44, 85, 185, and 150 nm, respectively, whereas their heights decrease from 80 to 30 nm (Table I). It seems that increasing RF power leads to the formation of wide walls splitting into several small walls, which look like a "squama" structure.

The mechanism of CNWs growth on the substrate surface is well known [20]–[22]. At the first step of the CNWs nucleation process, Ni nanoislands are formed on the Si substrate,

TABLE I
Characteristics of CNWs Obtained at Different Values of Discharge Power

Samples	RF power	Height of CNWs	Thickness of CNWs	I_D/I_G
No. 1	8	~ 80	44	1.64
No. 2	10	~ 60	85	1.67
No. 3	12	~ 30	185	1.84
No. 4	14	~ 30	150	1.81

and as the synthesis time increases, these nanoislands cover the whole surface of the substrate, forming a thin interface layer. Subsequently, small 2-D carbon nanoflakes grow on the aggregations of nanoislands, and then randomly oriented carbon flakes start to grow mainly in the vertical direction.

Thus, few vertical CNWs grow continuously. In this growth mechanism, Ar ion irradiation (ions flux and energy) plays an important role [21], [22] in the formation of nanoislands and dangling bonds on the growing surface, resulting in the formation of nucleation sites. Moreover, Ar ion irradiation enhances surface reaction in the growth phase, including the adsorption of hydrocarbon radicals in the nucleating sites, whereas the increasing ion irradiation (higher RF power) inhibits the growth of CNWs due to etching effects. For this reason, the heights of CNWs decrease with an increase in RF power. Also, at the first sight, it seems that increasing RF power enhanced the thickness of CNWs, which increased from 44 to 185 nm. However, a more detailed analysis of AFM images (Figs. 3–5) shows that each CNW consists of 2, 3, or even more walls of approximately the same thickness. This means that the increasing RF discharge does not significantly affect the thickness of each wall, but increases the ion bombardment, and hence, the number of defects in the growing surface, which leads to the creation of more nucleation sites and, as a consequence, small walls. The corresponding changes (increase) in the I_D/I_G values are presented in Table I. Thus, the previous result [16] of CNWs agglomeration into nanoclusters with increasing RF power can be explained by the above-mentioned process of creation of more defects on the growing surface, resulting in the formation of more nucleation sites, which are further agglomerated into nanoclusters.

Note that this paper is performed at quite high pressure (1.9 torr). At this pressure, the formation of nanoparticles has sometimes been reported in Ar/CH4 RF discharges, as in [23]. The difference in this paper is using a high-gas temperature of 700 K. At such high-gas temperature (relatively from room temperature), the carbon nanoparticles nucleation process is much delay in the plasmas [24], [25], even if the nucleation phase of nanoparticles has occurred, the nanoparticles would not reach the size comparable with CNWs for their observation.

IV. Conclusion

In this paper, the process of synthesis of CNWs by the chemical vapor deposition method in the plasma of an RF capacitive discharge was considered. The CNWs were obtained at different values of RF power and it was found that increasing RF power caused a decrease in the height of CNWs and an increase in their thickness. The study of graphitization of the CNW structure showed that synthesized CNWs have a small number of defects in their structure. The obtained results could be used for low-cost production of CNWs by the PECVD method.

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Authors' photographs and biographies not available at the time of publication.