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Synthesis of carbon nanostructures on copper films by the method of oxy-acetylene torch

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ABSTRACT

The work presents the results of experiments on the synthesis of carbon nanostructures by the method of oxy-acetylene torch on the surface of pre-deposited copper thin films. The influence of the concentration ratio of oxygen and acetylene and duration of the deposition on the structure formation was investigated. According to the analysis by Raman spectroscopy and SEM methods, the obtained samples, depending on the experimental conditions, have a different structure and morphology. As a result of the experiments, monolayer graphene, nano and micro-diamonds with well-defined crystal faces and edges were obtained, as well as carbon structures, which are nanotubes. Studies using Raman scattering and scanning electron microscopy showed that synthesis of micro-diamonds occurs under certain experimental conditions.

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1. Introduction

Recent years have seen intensive development of a new direction in science and technology – nanotechnology, which allows creating new materials and structures with fundamentally new properties. Carbon nanostructures and nanodiamonds are of great interest among such structures [1].

Nanodiamonds represent one of the most complex and interesting objects of the numerous new ultradisperse materials. It is known that relatively large natural diamonds have unique physical and chemical properties. When the crystal sizes are reduced to several nanometers, diamonds not only preserve the properties inherent in macrocrystals, but also acquire completely new properties. The highly developed surface of such particles is covered with a multitude of diverse functional groups that give them various chemical, electrochemical and optical properties and open up possibilities (chemical, biochemical, physical) for controlling these properties. Therefore, nanodiamonds are used in many scientific and technical fields. High electron mobility, field electron emission and magnetic properties allow using them in electronics. High tribological and mechanical properties of nanodiamonds served as the basis for the synthesis of hard coatings in order to create a wide range of abrasive materials. Nanodiamond coatings are biocompatible with human tissues and can provide improved adhesion and low wear of implants. Such a wide range of technological applications allowed us to actively search for new, more efficient and cost effective methods for the synthesis of diamond and diamond-like materials [2].

At present, various techniques have been successfully used for the production of carbon nanostructures and nanodiamonds, such as laser ablation, synthesis in hydrocarbon flames, and chemical vapor deposition [1,3–5]. However, the electric arc discharge and various types of chemical vapor deposition (in the high-frequency and super-high-frequency discharge, DC plasma, and the hot-filament method) are the most developed and already applied methods in the large-scale production of carbon nanostructures [6]. The simplest but efficient method for producing carbon materials is the method of oxy-acetylene torch, wherein the deposition occurs at atmospheric pressure, i.e. it does not require complex vacuum and electronic equipment. This technique has several advantages compared to other methods such as high rate of synthesis, simplicity and low cost of the equipment [7,8]. Furthermore, expensive precursors as well as high purity are not required for the synthesis.

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The process of substrate preparation in the method of oxy-acetylene torch strongly affects the growth of the diamond nucleus. Many researchers have tested several substrate treatments that are effective for the growth of precipitated diamond particles. One of these methods is the surface modification of substrates with thin metal [9] or carbon (DLC) films [10]. To increase the density of nucleation in diamond deposition, transition metals (Ni, Ti, Cu, Fe, etc.) are used as catalysts [11]. In our study, copper was deposited on the surface of silicon substrates as a catalyst to increase the growth of diamond particles.

This paper presents the results of studies of carbon nanostructures and micro- and nanodiamonds obtained in the flame of oxy-acetylene torch on the surface of the copper film previously deposited on the silicon wafers by Raman scattering (RS) and scanning electron microscopy (SEM).

2. Experimental

2.1. Preparation and investigation of substrates

The monocrystalline silicon plates (analogue of brand KDB-20, manufacturer Siegert Wafer GmbH, Germany) 1 × 1 cm with orientation [1 0 0] were used as substrates and basis for copper films. The substrates were previously chemically cleaned. The treatment was carried out in a mixed solution of NH_4OH, H_2O_2 and distilled water at a volume ratio of 1:1:6.5, at a temperature of 20 °C for 10 min, using sound waves with a frequency of 850 kHz, power 250 W. Further, washout in distilled water and drying were performed.

Copper films were deposited on substrates of polished silicon plates by DC magnetron sputtering in equipment VUP-5M. Sputtering was carried out in the flow of working gas Ar at a pressure of 10^{-2} Torr. The flow rate of Ar was 6 cm^3/min and it was controlled by the gas flow controller MCV-500SCCM. Sputter deposition were conducted at a constant voltage on the anode target (740 V), the plasma current of 35 mA. The time of experiments was 60 min.

Fig. 1 show a cross-sectional SEM image of a thin copper film on the silicon substrate grown for 60 min. SEM studies showed that the thickness of the copper films deposited on silicon wafer for 60 min is 524.6 nm.

2.2. Synthesis of carbon nanostructures

Fig. 2 presents the scheme of technological equipment for synthesis of carbon materials in the flame of oxy-acetylene torch. The construction of equipment allows changing the tilting angle between substrate surface and flame direction in the range from 0° to 90° and vertical distance between them. The ratio of concentrations C_2H_2:O_2 is controlled by the standard gas flow controllers MC-10SLPM-D (manufacturer "Alicat Scientific", USA). The rate of gas supply can be varied in the range of 0–10 l/min. The diameter of the torch nozzle varies from 0.5 to 2.0 mm depending on the nozzle. The rotation of the substrate holder was provided for uniform distribution of the deposited film. The rotation speed of the substrate is set by the controller.

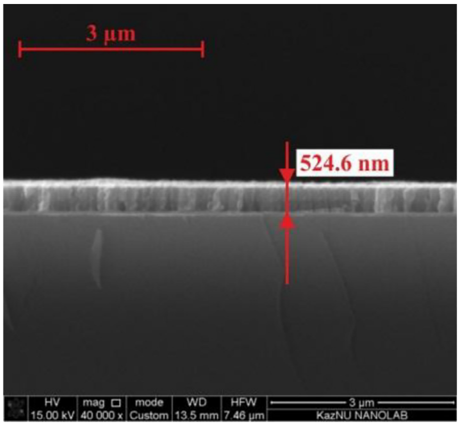

Fig. 1. Cross-sectional SEM image of thin copper film on a silicon substrate.

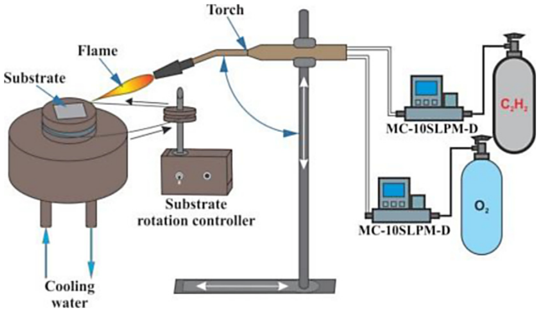

Fig. 2. The scheme of technological equipment.

A series of experiments in which the distance from the torch nozzle to the substrate (h = 4 mm) and the tilting angle between substrate surface and flame direction (α = 90°) was constant was carried out. In the first stage of the experiment, the duration of deposition was varied from 15 to 60 min in increments of 15 min and the concentration ratio of oxygen and acetylene (O_2/C_2H_2) was constant and equal to 0.94. In the second stage of the experiment, the duration of deposition was constant and equal to 5 min. The concentration ratio of oxygen and acetylene (O_2/C_2H_2) varied from 0.76 to 0.88 in 0.4 increments. All technological parameters of the experiments are shown in Table 1. The interesting results are presented below.

2.3. Characterization

The obtained samples were studied by SEM and RS. Investigation of the samples was carried out in the National nanotechnological laboratory of open type (Almaty, Kazakhstan) using spectrometer NT-MDT NTegra Spectra (laser wavelength λ = 473 nm) and Quanta 3D 200i.

3. Results and discussion

Fig. 3 shows the Raman spectra and SEM images of carbon structures obtained on Cu films grown on Si (1 0 0) for 60 min, in which the concentration ratio of oxygen and acetylene was constant and duration of deposition was changed. All spectra showed peak at 1331–1331.3 cm^{-1}, which is characteristic of the diamond phase. In samples 3*a-c* location of G group shifted to lower frequencies over time. The second order group 2D can be noticed within 2788.1–2866.1 cm^{-1} in samples 3*b and* 3*c*. The sample 3*d* shows only one peak at 1331 cm^{-1}, which corresponds to diamond phase and one can notice that the growth of diamond crystals is more massive in comparison with other experimental conditions. SEM images show that the obtained carbon structures have distinct crystallographic faces. These data are in good agreement with the results of the study by RS.

Fig. 4 shows the Raman spectra and SEM images of carbon structures obtained on Cu films grown on Si (1 0 0) for 60 min, in which the deposition time was constant and concentration ratio of oxygen and acetylene was varied.

Fig. 4a shows the Raman spectrum and SEM image of a sample obtained on copper films at $C_{O2/C2H2}$ = 0.76. Only carbon groups D

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Table 1
Synthesis parameters of carbon nanostructures by the method of oxy-acetylene torch.

Mode	h, mm	t, min				C, O_2/C_2H_2			
No. 1	4	15	30	45	60	0.94			
No. 2	4	5				0.76	0.8	0.84	0.88

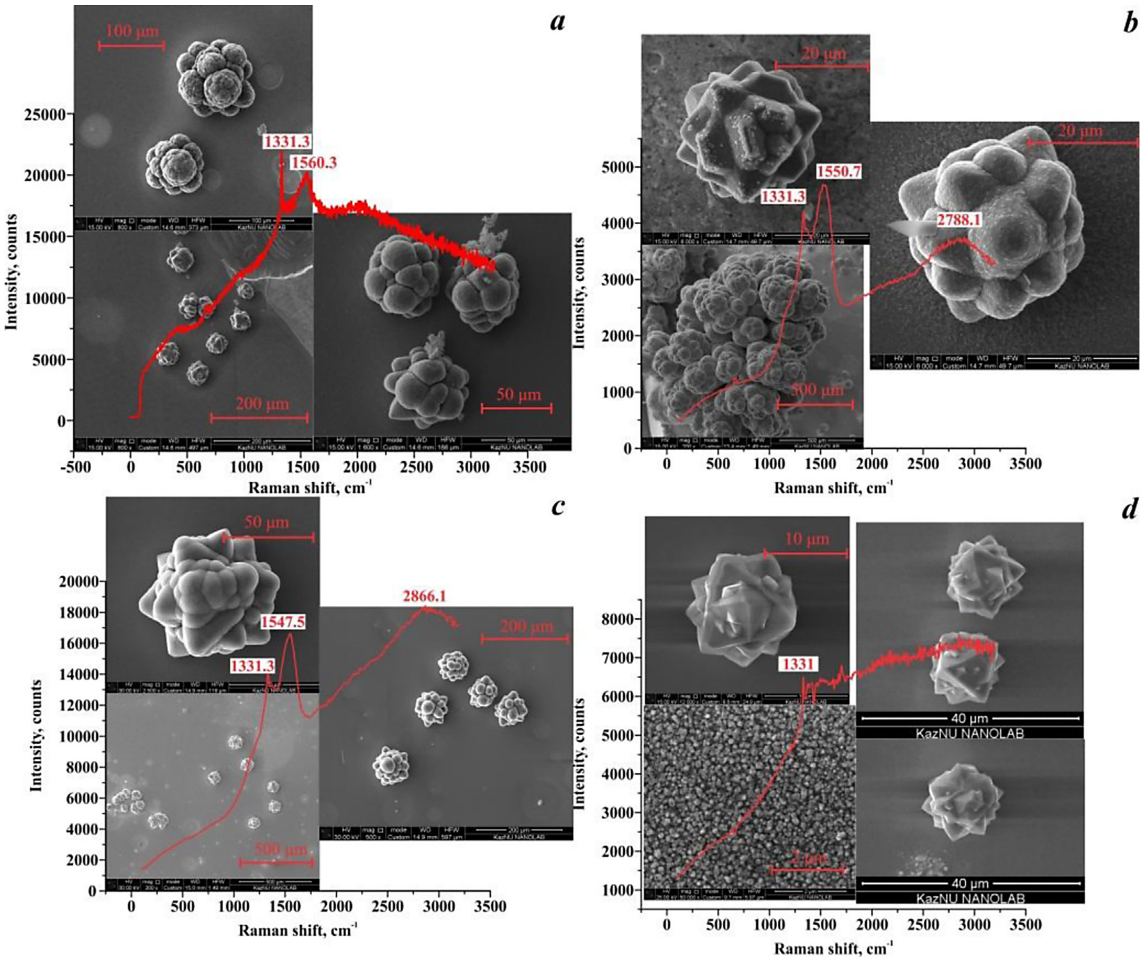

Fig. 3. Raman spectra and SEM images of carbon structures obtained on mode No. 1: a – 15 min, b – 30 min, c – 45 min and d – 60 min.

and G are observed in the sample at 1372.9 and 1594.5 cm^{-1}, respectively. The peaks corresponding to the long range order are not observed in the high-frequency region. SEM images show that the obtained nanostructures have a rough branched surface.

D and G peaks in spectrum 4*b* are located in the region of 1364.1 and 1579.8 cm^{-1}, respectively. In the high frequency region of the spectrum, second order groups D', 2D and D + G, which are located at 2437.6, 2726.7 and 2963.1 cm^{-1}, respectively, are observed. We can also see an additional peak at 3246.8 cm^{-1} which appears due to C–H stretching. The intensity ratio of peaks $I_{2D}/I_G > 2$ that indicates a presence of monolayer graphene in the sample.

Fig. 4c-d shows the Raman spectra and SEM images of the sample obtained on copper films at $C_{O2/C2H2} = 0.84$ and 0.88, respectively. The first spectrum shows the main carbon peaks at 1353.3 and 1594.5 cm^{-1}. The intensity of peak D is higher than that of peak G, which indicates the presence of defects. In the high-frequency region of the spectrum, second-order groups 2D and D + G are located within 2709.3 and 2946.1 cm^{-1}, respectively. According to the given results, one can assume that the obtained structures are carbon nanotubes. The other sample also predominantly shows main carbon peaks at 1360 and 1588 cm^{-1}. In the high-frequency region of the spectrum, second-order groups 2D and D + G are located in the region of 2720 and 2953 cm^{-1}, respectively. Therefore, resulting structures are multilayer carbon nanotubes.

The I_D/I_G ratio was calculated for carbon structures obtained on mode No. 2 to evaluate the crystallinity of the obtained samples and its correlation with synthesis parameters. Low values of I_D/I_G ratio represent high crystallinity degree, being often related to carbon nanostructures with lower content of structural defects [12]. The intensity ratios I_D/I_G of carbon structures obtained on mode No. 2 are presented in Table 2.

As the Table 2 shows, the intensity ratio I_D/I_G of samples obtained at a value of concentrations $C_{O2/C2H2} = 0.8$ and 0.88 are greater than unity, indicating the presence of carbon nanotubes or nanofibers of low structural quality [12,13]. The intensity ratio I_D/I_G of samples obtained at $C_{O2/C2H2} = 0.76$ is 0.72 that corresponds to higher crystallinity degree. The intensity ratio of peaks I_{2D}/I_G is widely used for evaluation of number of layers in graphene structures. $I_{2D}/I_G > 2$ indicates a monolayer graphene [13]. For samples obtained at a value of concentrations

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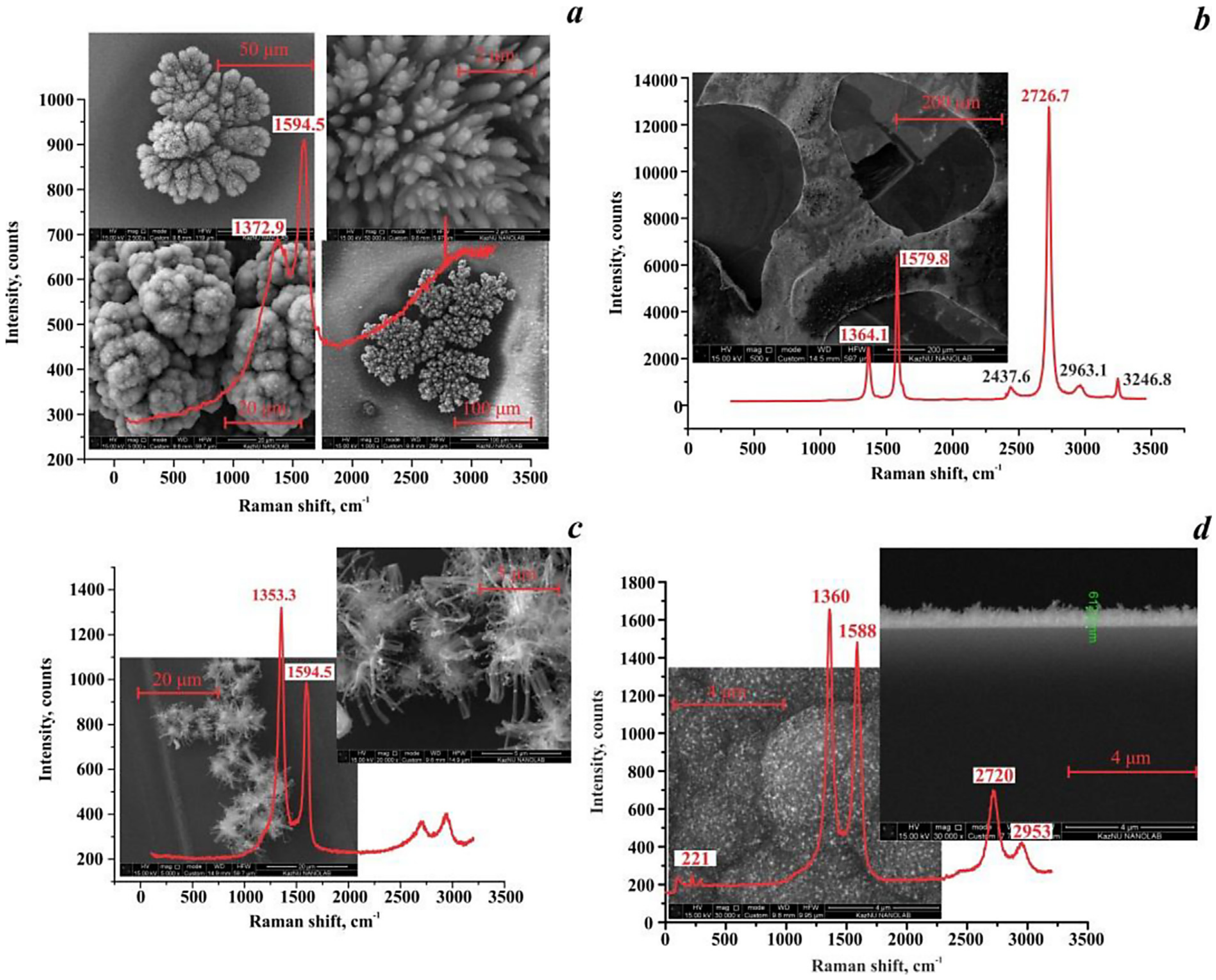

Fig. 4. Raman spectra and SEM images of carbon structures obtained on mode No. 2: a – $C_{O2/C2H2}$ = 0.76, b – $C_{O2/C2H2}$ = 0.8, c – $C_{O2/C2H2}$ = 0.84 and d – $C_{O2/C2H2}$ = 0.88.

Table 2
The intensity ratio I_D/I_G of carbon nanostructures.

№	Experimental conditions	I_D/I_G
1	$C_{O2/C2H2}$ = 0.76	0.72
2	$C_{O2/C2H2}$ = 0.8	1.14
3	$C_{O2/C2H2}$ = 0.84	0.39
4	$C_{O2/C2H2}$ = 0.88	1.43

$C_{O2/C2H2}$ = 0.84, the intensity ratio of peaks I_{2D}/I_G is 2.02 which shows that monolayer graphene was obtained.

4. Conclusions

In the course of the studies experiments on the synthesis of carbon structures by the method of oxy-acetylene torch on copper films were carried out. According to the analysis by Raman spectroscopy and SEM methods, the obtained samples have a different structure and morphology depending on the experimental conditions. As a result of the experiments, monolayer graphene, nano and micro-diamonds with well-defined crystal faces and edges were obtained, as well as carbon structures, which are nanotubes. It is necessary to conduct additional studies using atomic force methods, transmission electron microscopy, and electron diffraction to more detailed analysis of the morphology and structure of the obtained samples. Results of experiments showed that the concentration ratio of oxygen and acetylene and the deposition time rendering an important influence on the structure and morphology of the samples. Thus, the process parameters in which occurs the synthesis of micro- and nano-diamonds have been defined.

The obtained results have a high potential for the development of efficient, low-energy, low-cost technology of synthesis of micro- and nano-diamonds without the use of expensive gas, equipment and the ability to control the structure and properties by macroscopic parameters. These results also can be used for the manufacture of semiconductor materials for active devices, as well as for obtaining hard coatings with good wear resistance.

CRediT authorship contribution statement

Bauyrzhan Zhumadilov: Investigation, Software, Visualization. **Gulmira Partizan:** Data curation, Writing - original draft, Validation. **Botagoz Medyanova:** Formal analysis, Software. **Aidar Kenzhegulov:** Conceptualization, Methodology. **Gulnur Suyundykova:** Software, Validation. **Bakhodir Aliyev:** Supervision, Formal analysis.

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