

Investigation of Microdiamonds Obtained by the Oxygen-Acetylene Torch Method

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Abstract

The results of experiments on the synthesis of micro- and nano-diamonds by an oxy-acetylene torch on the surface of the pre-deposited copper thin films are presented in this article. The influence of thickness of a buffer copper film and the ratio of the concentrations of oxygen and acetylene on the structure of the deposited samples has been studied in the course of the conducted experiments. The studies by Raman scattering and scanning electron microscopy showed that the synthesis of micro- and nano-diamonds occurs under certain experimental conditions. From the results of the analysis of the obtained samples by the methods of Raman scattering and scanning electron microscopy, it was determined that the deposition time of the copper films and consequently its thickness mainly influence on the structure formation of diamond crystals. On copper films grown for 30 min, the Raman scattering method showed a shift of the diamond peak from the standard (1332 cm^{-1}) to the low-frequency band (1331.3 cm^{-1}), which may occur after the presence of stress in the crystals. The results of the investigation showed that with increasing of synthesis time take place smoothing of the facets of crystallites (scanning electron microscopy) and decrease in intensity of the diamond peaks (Raman scattering method).

1. Introduction

In recent years, nanodiamonds are used in many scientific and technical areas due to unique set of physical, chemical and tribological properties. The high mobility of electrons, the field electron emission and magnetic properties allow to use them in electronics. Excellent tribological and mechanical properties of nanodiamonds formed the basis for the synthesis of hard coatings to create a wide variety of abrasive materials. Nanodiamond coatings are biocompatible material with human tissue and can provide improved adhesion and low wear of prosthesis. This wide range of possibilities of technological applications contributed to active search for new, more efficient and cost-effective methods for the synthesis and manufacture of diamond and diamond-like materials [1].

At present, some basic methods for the synthesis of nano- and microdiamonds, such as various kinds of physical and chemical vapor deposition (methods of crystallization from hydrogen-hydrocarbon mixtures activated by high-frequency and microwave discharges, DC plasma, thermally using an incandescent filament of refractory metal) are developed [1, 2]. In addition, the applied physical techniques: shock wave or detonation synthesis, crystallization at high pressures and temperatures, the method of magnetron sputtering are used [3, 4]. The simplest but efficient methods for producing carbon materials refers method 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

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cost of the equipment [5, 6]. Furthermore, expensive precursors as well as high purity are not required for the synthesis.

This paper presents the results of studies of 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 and scanning electron microscopy.

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 [100] and [111] 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, wash-out 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 $6\text{ cm}^3/\text{min}$ and it was controlled by the gas flow controller MCV-500SCCM. Experiments were conducted at a constant voltage on the anode target (740 V), the plasma current of 35 mA. The time of experiments was 30 and 60 min.

The obtained samples were investigated by scanning electron microscopy (SEM) in the National nanotechnological laboratory of open type using a microscope Quanta 3D 200i.

Figure 1 shows a cross-sectional SEM image of a thin copper film on the silicon substrate grown for 30 and 60 min. SEM studies showed that the thickness of the copper films deposited on silicon wafer for 30 min is 437.2 nm, whereas thick layer with thickness of 524.6 nm is observed for deposition time of 60 min, regardless of Si orientation.

2.2. Synthesis of micro- and nanodiamonds

Figure 2 presents the scheme of technological equipment for synthesis of carbon materials in the flame of oxy-acetylene torch.

The construction of equipment allows to change the tilting angle of the torch nozzle to the substrate

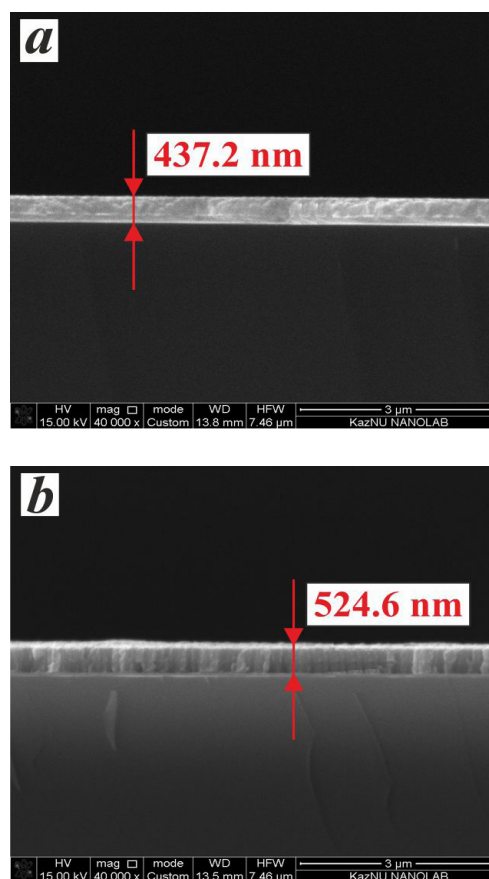


Fig. 1. Cross SEM image of thin copper film on a silicon substrate: a – 30 min, b – 60 min.

in the range from 0° to 90° and vertical distance between them. The ratio of concentrations $\text{C}_2\text{H}_2:\text{O}_2$ 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.

A series of experiments in which the distance from the torch nozzle to the substrate ($h = 4\text{ mm}$) and the tilting angle of the flame front ($\alpha = 90^\circ$) was constant was carried out. The duration of deposition was changed from 15 to 60 min, the concentration ratio of oxygen and acetylene ($\text{O}_2/\text{C}_2\text{H}_2$) was varied from 0.85 to 0.95 in 0.01 increments.

The obtained samples were studied by SEM and Raman scattering (RS). Investigation of the samples was carried out in the National nanotechnological laboratory of open type using spectrometer NT-MDT NTegra Spectra (laser wavelength $\lambda = 473\text{ nm}$) and Quanta 3D 200i. The most interesting findings are presented below.

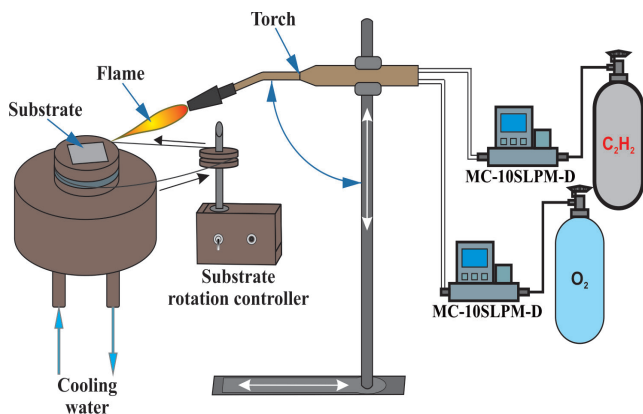


Fig. 2. The scheme of technological equipment.

3. Results and discussion

Figure 3 shows the Raman spectra and SEM images of structures synthesized on Cu substrates deposited on Si with orientation [111] for 30 min.

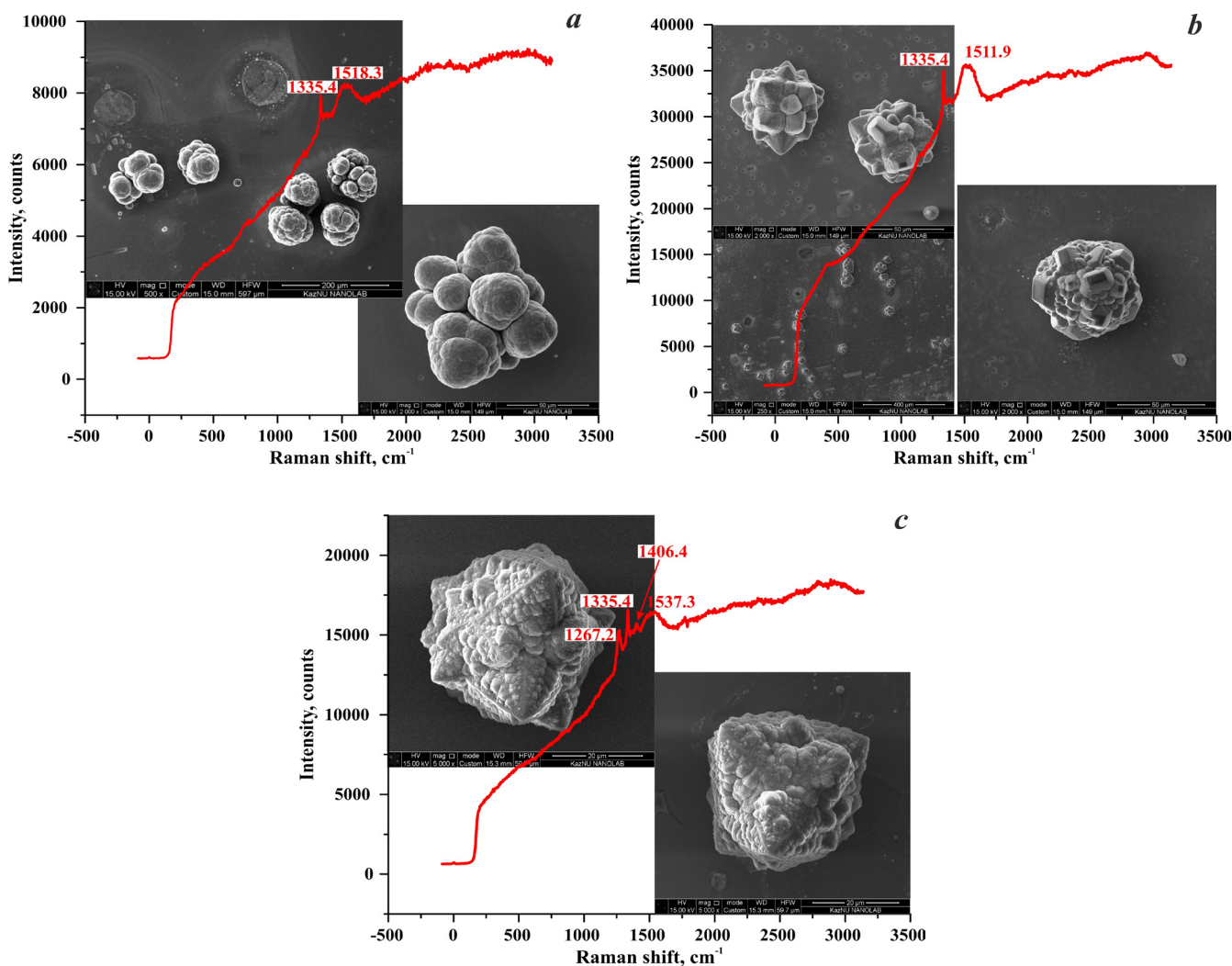


Fig. 3. Raman spectra and SEM images of carbon structures obtained on Cu (30 min) deposited on Si (111) for $h = 4$ mm: a – $\text{CO}_2/\text{C}_2\text{H}_2 = 0.93$, 30 min, b – $\text{CO}_2/\text{C}_2\text{H}_2 = 0.94$, 30 min, c – $\text{CO}_2/\text{C}_2\text{H}_2 = 0.94$, 45 min.

Raman spectra of the samples show characteristic peak of diamond (sp^3) in the area of 1335.4 cm^{-1} . The shift from the standard value to the $1334\text{--}1342 \text{ cm}^{-1}$ may take place due to a compressive biaxial stress which occurs because of mismatch of thermal coefficient of expansion between the silicon substrate and the diamond film [7]. A peak corresponding to G group is at 1518.3 cm^{-1} in Fig. 3a. G peak is observed in the range of 1511.9 and 1537.3 cm^{-1} for samples 3b and 3c. The additional peaks can be seen in the spectrum of third sample. The peak at 1406.4 cm^{-1} is a ν_3 mode of transpolyacetylene [8]. The group at 1270.4 cm^{-1} which corresponds to the phonon density of states of diamond can be observed in the case of very small particles [9]. 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 Raman scattering

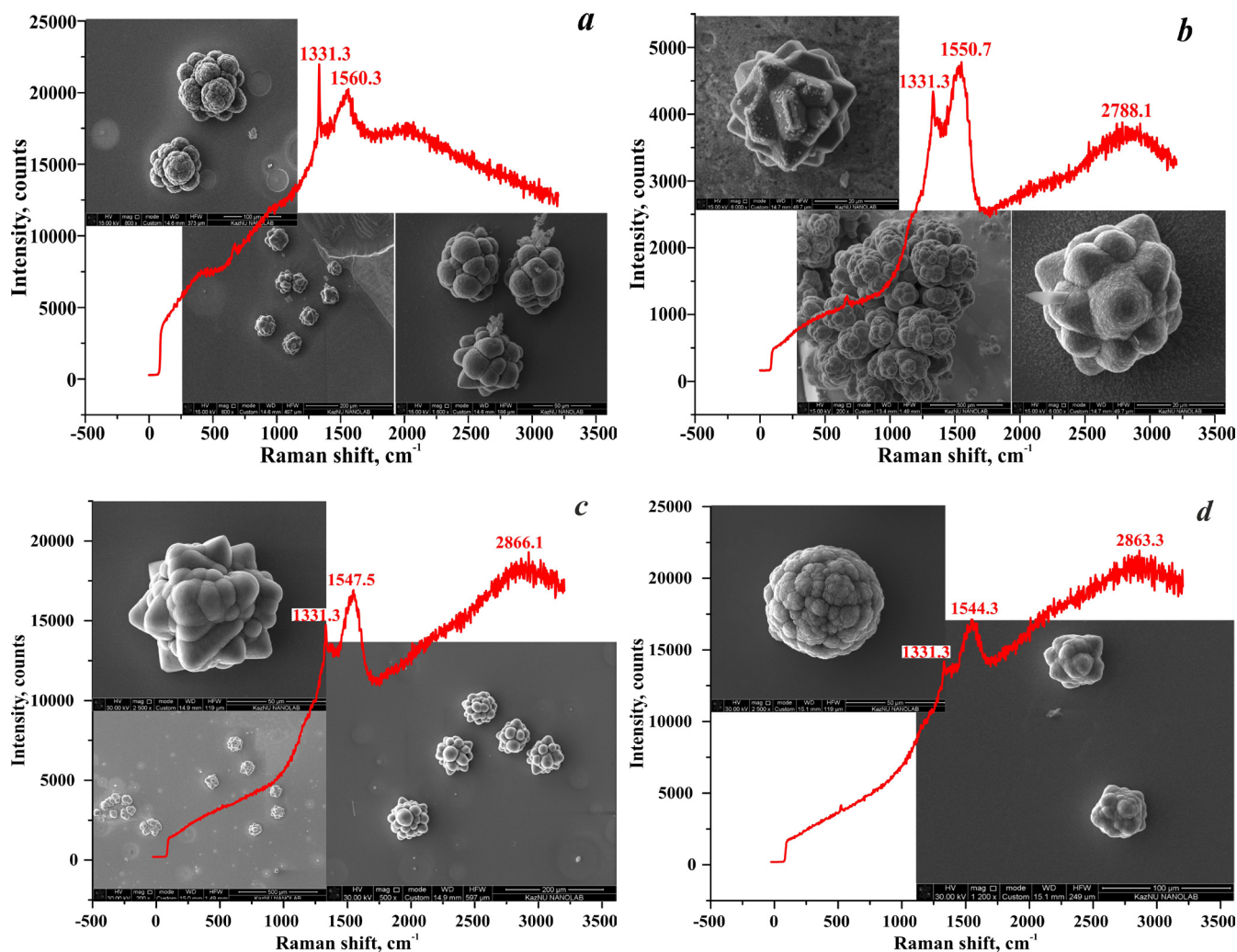


Fig. 4. Raman spectra and SEM images of carbon structures obtained on Cu (60 min) deposited on Si (100) for $\text{CO}_2/\text{C}_2\text{H}_2 = 0.94$, $h = 4$ mm: a – 15 min, b – 30 min, c – 45 min and d – 60 min

Figure 4 shows the Raman spectra and SEM images of carbon structures obtained on Cu films grown on Si (100) for 60 min. All spectra showed peak at 1331.3 cm^{-1} , which is characteristic of the diamond phase. Location of G group shifted to lower frequencies over time. The second order group 2D can be noticed within $2788.1\text{--}2866.1\text{ cm}^{-1}$ in samples 4b-d. The presence of diamond microcrystals is confirmed by SEM images. It is obvious that the smoothing of the crystallite faces (SEM images) and a reduction of the intensity of the diamond peak (Raman spectra) occur with an increase in the time of synthesis. This suggests that gradual graphitization of the structure takes place.

The results of investigations by RS and SEM show that the time of deposition of copper film and consequently its thickness mainly influence on the structure formation of diamond crystals. The shift of diamond peak is observed for films deposited for 30 min which may occur due to the presence

of stress in the crystals. Whereas, the samples synthesized on the copper buffer layer with the thickness of 524.6 nm show the peak at 1331.3 cm^{-1} . In addition, it can be seen that in the second case the growth of diamond crystals is more massive, than the first.

Conclusions

In the course of the studies experiments on 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 the obtained samples have a diamond structure with well-defined crystal faces and edges. Analysis of the results of experiments showed that the parameters rendering an important influence on the structure and morphology of the samples are:

- The time of deposition of copper film and its thickness, respectively;

- The orientation of silicon substrate;
- The concentration ratio of oxygen and acetylene.

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.

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