Synthesis of micro- and nanodiamonds by the method of oxy-acetylene combustion flame

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Abstract. This work presents the results of experiments on synthesis of micro- and nanodiamonds by the method of oxy-acetylene torch on the surface of pre-deposited copper thin films. The influence of the thickness of the buffer copper film and the concentration ratio of oxygen and acetylene on the structure formation of the deposited samples was investigated during performed experiments. Studies by Raman scattering and scanning electron microscopy showed that the synthesis of micro- and nano-diamonds occurs under certain experimental conditions.

1. Introduction

In recent years carbon allotropes, such as nanodiamonds, have shown promising new applications in many fields due to its physical, chemical and surface characteristics. Their high electron mobility, field electron emission and magnetic properties make them important players in carbon based electronics. Their tribological and mechanical properties give rise to harder coatings, which are biocompatible and can provide improved biological prosthesis joints with decreased wear. This biocompatibility allied to their biosensing, optical and nanoprobing functionalities provide drug delivery and cellular labeling capacity. This wide range of novel applications has fostered the active search for new and more efficient synthesis and production methods of carbon allotropes [1]. The method of oxy-acetylene torch refers to the most simple but efficient methods for producing carbon materials, wherein the deposition occurs at atmospheric pressure, i.e. it does not require complex vacuum and electronic equipment. It has various advantages over other methods, such as high synthesis speed and the safety and low cost of the equipment used [2, 3]. Furthermore, conduction of synthesis does not require expensive precursors, including high purity. The results of studies on micro- and nanodiamonds obtained in the flame of oxy-acetylene torch on the surface of copper film, previously deposited on silicon plates by Raman scattering and scanning electron microscopy are presented in this work.

2. Experimental

Preparation and study of substrates

The monocrystalline silicon plates (analogue of brand KDB-20, manufacturer Siegert Wafer GmbH, Germany) \(1 \times 1\) 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 \(\text{NH}_4\text{OH}, \text{H}_2\text{O}_2\) and distilled water at a volume ratio of 1:1:6.5, at a temperature of 20°C for 10 minutes, using sound waves with a frequency of 850 kHz, power 250 Watts. 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 cm³/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 minutes.

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 minutes. SEM studies showed that the thickness of the copper films deposited on silicon wafer for 30 minutes is 437.2 nm, whereas thick layer with thickness of 524.6 nm is observed for deposition time of 60 minutes, regardless of Si orientation.

![Figure 1(a,b) - Cross SEM image of thin copper film on a silicon substrate](image)

**Figure 1(a,b) - Cross SEM image of thin copper film on a silicon substrate: (a) - 30 minutes, (b) - 60 minutes**

### Synthesis of micro- and nanodiamonds

The scheme of technological equipment for synthesis of carbon materials in the flame of oxy-acetylene torch and the procedure of conduction of experiments were described in detail in work [3].

A series of experiments in which the distance from the torch nozzle to the substrate (h = 4 mm) and the tilting angle of the flame front (∝ = 90°) was constant was carried out. The duration of deposition was changed from 15 to 60 minutes, the concentration ratio of oxygen and acetylene (O₂/C₂H₂) was varied from 0.9 to 0.94 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 λ = 473 nm) and Quanta 3D 200i.

The most interesting findings are presented below.

### 3. Results and discussion

Figure 2 shows the Raman spectra and SEM images of structures synthesized on Cu substrates deposited on Si with orientation [111] for 30 minutes. Raman spectra of the samples show peaks characteristic peak of diamond (sp³) in the area of 1335.4 cm⁻¹. The shift from the standard value to the 1334-1342 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 Figure 2α. G peak is observed in the range of 1511.9 and 1537.3 cm⁻¹ for samples 2b and 2c. The additional peaks can be seen in the spectrum of third sample. The peak at 1406.4 cm⁻¹ is a ν3 mode of transpolyacetylene [8]. The group at 1270.4 cm⁻¹ which is a peak in the phonon density of states of diamond can be observed in the case of very small particles [9]. SEM image shows that obtained carbon formations have distinct crystallographic faces. These data are
in good agreement with the results of study by Raman scattering.

**Figure 2(a, b, c).** Raman spectra and SEM images of carbon structures obtained on Cu (30 min) deposited on Si (111) for $h = 4$ mm: (a) - $C_{O_2/C_2H_2} = 0.93$, 30 min, (b) - $C_{O_2/C_2H_2} = 0.94$, 30 min, (c) - $C_{O_2/C_2H_2} = 0.94$, 45 min

Figure 3 presents the Raman spectra and SEM images of carbon structures obtained on Cu films grown on Si (100) for 60 minutes. All spectra show peak at 1331.3 cm$^{-1}$, which is characteristic of the diamond phase. Location of $G$ group shifts to lower frequencies over time. The second order group 2$D$ within 2788.1-2866.1 cm$^{-1}$ can be observed in samples 3b-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 diamond peak intensity (Raman spectra) occurs with an increase in the time of synthesis. This suggests that there is a gradual graphitization of structure.

**Figure 3(a, b, c, d).** Raman spectra and SEM images of carbon structures obtained on Cu (60 min) deposited on Si (100) for $C_{O_2/C_2H_2} = 0.94$, $h = 4$ mm: (a) - 15 min, (b) - 30 min, (c) - 45 min and (d) - 60 min

RS and SEM results show that deposition time of copper film and consequently its thickness mainly effect on the structure formation of diamond crystals. The shift of diamond peak is observed on films deposited for 30 minutes, which is possible due to the presence of stress in the crystals. Whereas, samples synthesized on the copper buffer layer with thickness of 524.6 nm show the peak at 1331.3 cm$^{-1}$. In addition, it can be seen that the growth of diamond crystals has more massive character in the
second case than that of the first.

4. Conclusions
The experiments on synthesis of carbon structures by the method of oxy-acetylene torch on copper films were conducted in the course of studies. According to the performed analysis by RS and SEM some obtained samples have a diamond structure with well-defined crystal faces and edges.

Analysis of the results of the experiments showed that the parameters rendering an important influence on the structure of the samples are:
- The time of deposition of copper film and its thickness;
- The orientation of the 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. Further studies will be directed at determination of the additional process parameters that effect on the structure formation and the search for their optimal combination.

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