Silicon substrate surface modification with nanodiamonds for CVD-synthesis of polycrystalline diamond

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Abstract. The use of polycrystalline diamond films is promising in photonics and electronics, as well as in other fields of science and technology. At present, it is limited by the complexity of obtaining high-quality films of required size, associated with the cracks formation at the film periphery caused by thermal stresses. Also, one of the key points is to increase films growth rate without sacrificing of their continuity and high quality. Substrate surface preparation makes possible to increase the initial rate of film formation and to form a continuous layer of diamond film on its surface. This work presents the results of polycrystalline films synthesis and the selection of optimal deposition regime. These results make possible to obtain high-quality polycrystalline diamond films of a larger area, which will significantly expand scope of their application.

1. Introduction

High quality single-crystal and polycrystalline diamond films can be obtained using synthesis from the gas phase (CVD). At the same time, precise control of synthesis parameters (temperature, pressure, flow rate and purity of used gases) gives the possibility to obtain films with the required structure and, respectively, required properties with high repeatability [1-4].

CVD-synthesis of polycrystalline diamond films can be realized using substrates of various materials. The quality of the receiving films directly depends on the used substrate properties; in order to avoid the cracks formation along the plate periphery and discontinuities of the depositing film, the substrate must have a number of special properties [4]. Silicon substrates are the most used due to the specific properties of silicon: high heat resistance and thermal conductivity, a low coefficient of thermal expansion and a high probability of diamond nucleation on its surface [5-8].

An increase in the number of nucleation centers is a promising direction for increasing the continuity of the deposited film and for the possibility of obtaining diamond films with the required grain size and, respectively, properties. Special substrates pretreatment, including seeding with nanodiamonds, can be used to increase the number of nucleation centers [9-13]. At the present time, there are different variations for modifying of silicon substrate surface with nanodispersed diamonds. This work presents one of the variants of seeding a silicon substrate with nanodiamonds for the synthesis of continuous polycrystalline diamond
CVD-films. Diamond films obtained on such substrates can be used as electrodes, in microelectronics and in other fields of technology [14-20].

2. Materials and methods

In this work, polycrystalline diamond CVD-films were deposited on silicon substrates with diameter of 62.5 mm and orientation (111). We used diamond nanopowder manufactured by the company “Diamond Center” (St. Petersburg, Russia) as centers of nucleation. The study of the quality of nanodiamonds and their dimensional characteristics was carried out using transmission electron microscope JEOL JEM 2100F.

The selection of the dispersing medium was carried out using analyzer Malvern Zetasizer Nano ZS and was based on the study of colloidal solutions stability (tests of particles zeta potential) and on the measuring the average size of their agglomerates.

We used the unique scientific equipment for dispersion and control of dispersion of our system – the hardware and software complex for analysis and production of nanodispersed systems by chemical methods and the unique research stand for high-intensity cavitation effects (UNIS VKV, NUST “MISIS”, Moscow, Russia).

We used Ardis 300 to deposit a polycrystalline diamond film of optimal quality. The gas phase consisted of methane with a purity of 99.5% and hydrogen with a purity of 99.9999%; the microwave power was maintained at 3800 W, the pressure in the system was 8.7 kPa, the substrate temperature was 900 °C.

3. Results and discussion

3.1 Preparation of nanodiamond suspension

Figure 1 shows an image of diamond nanoparticles and electron diffraction pattern of the selected area that was taken with transmission electron microscope JEM JEOL 2100F.

![Figure 1. Photo of diamond nanoparticles (a) and their electron diffraction pattern (b).](image)

Statistical processing of a series of images showed that nanoparticles have an average size of 4-6 nm; the rings on the electron diffraction pattern are sharp, which indicates their crystal structure corresponding
to diamond. The absence of rings blurring shows that nanodiamonds consist of crystalline particles that do not have X-ray amorphous films or particles on their surface.

We studied following substances as a dispersing medium for nanodiamond deposition on silicon substrate:

- double-distilled water obtained using a Merck Millipore Direct Q8 UV;
- heptane;
- ethyl alcohol 95%.

Experiments using the Zetasizer Nano showed that the best dispersion was achieved in ethyl alcohol media. This is confirmed by measuring the zeta potential of a colloidal solution of nanodiamond in each medium. Zeta-potential was minus 34.8 V for the double-distilled water with nanodiamonds, minus 44.1 V – for heptane, minus 43.8 V – for ethanol. Taking into account the proximity of values of the zeta potentials of diamond nanopowder colloidal solutions in heptane and ethyl alcohol, as well as the higher cost of heptane in comparison with ethyl alcohol, in this work we decided to use as a dispersing medium ethyl alcohol.

Figure 2 demonstrates a typical bar graph of nanodiamond agglomerates size distribution in ethanol after using UNIS VKV.

![Figure 2](image)

Figure 2. Bar graph of nanodiamond agglomerates size distribution in ethanol after special treatment.

The average size of agglomerates is about 20 nm. This was connected with strong bonds between individual particles due to the peculiarities of the diamond nanopowder obtaining process, with the formation of double electrical layer in ethanol, and with the tendency of nanoparticles to compensate their high surface energy by reducing the specific surface area.

The activation of nanodiamonds surface and its modification (functionalization) was carried out using the unique research stand for high-intensity cavitation effects (UNIS VKV) in NUST “MISIS” (Moscow, Russia). For this we loaded the optimal amount of nanodiamond powder (0.002 g) into the UNIS VKV reactor and then added ethanol up to 0.1 l. Then the installation was turned on for 4 min with ultrasonic power of 500 W.

To control the dispersion of the system we used the hardware and software complex for analysis and production of nanodispersed systems by chemical methods.
3.2 Substrate preparation
In this work, we used silicon wafers with a diameter of 62.5 mm as substrates for the deposition of diamond polycrystalline CVD-films. One of these substrates is shown in figure 3.
To create homogeneous seeding for the subsequent operation of forming crystallization centers, the plate must be polished to a roughness of less than 1 μm. Figure 4 shows a silicon wafer after polishing.

3.3 Formation of crystallization centers
To form crystallization centers, we applied the colloidal solution to a silicon substrate immediately after preparation using a pipette and then rubbed for 30 s with a lint-free tissue. Then we left samples for natural drying in a ventilation hood until they were completely dry. After which samples were ready for depositing of diamond CVD-layer.

3.4 Polycrystalline diamond synthesis on silicon wafers
In this study, we used Ardis 300 to deposit polycrystalline diamond films of optimal quality. The gas phase consisted of methane with a purity of 99.5% and hydrogen with a purity of 99.9999%; the microwave power was maintained at 3800 W, the pressure in the system was 8.7 kPa, the substrate temperature was 900 °C.
By varying the flow of gases, we experimentally chose their optimal value to obtain high-quality films:

- hydrogen – 591 cm³/min;
- methane – 9 cm³/min.

Based on the flow values, we calculated the percentage of methane in the plasma which was 1.5%. The percentage of hydrogen, respectively, was 98.5 %. In the research, we obtained polycrystalline diamond layers on silicon substrates; films thickness was 20 μm (figure 5).
3.5 Silicon substrate etching
Etching is used to separate the obtained polycrystalline diamond film from the silicon substrate. In order to reduce gas formation in the process of etching, it is advisable to use a solution of ammonium fluoride with hydrofluoric acid.

After etching was completed, we washed separated films in distilled water twice. After that, the resulting films are dried; also, they can be subjected to further operations, for example, annealing in air at 540 °C to remove the graphite-like phase and clarify obtained polycrystalline diamond films.

4. Conclusion
In this work, we optimized polycrystalline diamond film deposition process. We obtained the parameters at which a high-quality polycrystalline diamond film grows:

- Power of microwave radiation from the magnetron: 3.8 kW.
- Methane content in plasma: 1.5%, hydrogen: 98.5%.
- Total gas pressure in the reactor: 8.7 kPa.

The developed technology of polycrystalline diamond film deposition makes possible to synthesize experimental samples of CVD diamond polycrystalline wafers for use in high power lasers.

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