Impact of CVD-synthesis parameters and film thickness on growth rate of single-crystal diamond

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Abstract. The widespread use of CVD-reactors of various constructions and the influence of many factors on the formation of energy-saturated reaction zone has led to the fact of significant difference of technological parameters optimal for each reactor even of one brand. An economically important parameter, in addition to the quality of the obtained single-crystal diamond layer, is the growth rate, which depends on many factors: the flow rate and chemical composition of gases, pressure in the reaction chamber, substrate temperature, the shape of the formed plasma cloud, dimensions and shape of molybdenum substrate holders and et al. This work is devoted to the experimental determination of the single-crystal CVD-diamonds growth rate across various synthesis conditions on Ardis 300. In research, we shown the effect of the thickness of the synthesized diamond layer on the rate of formation of subsequent diamond layers, which is associated with a change in the degree of misorientation between the crystallographic plane (100) and direction [100]. Also, this can be associated with an increase in the roughness of the growing surface, leading to an increase in the specific number of active centers thermodynamically favorable for carbon deposition during the formation of the crystal structure of diamond.

1. Introduction

The complexity of the formation of energy-saturated reaction zones of CVD-reactors of various constructions has led to the fact that the technological parameters that are optimal for one reactor may differ in another reactor, even if they are made by the same manufacturer. In this regard, the aspect of the initial optimization of the CVD-synthesis of diamond for a specific growth setup is relevant. In large measure, the stability of the CVD-synthesis also depends on the quality of the initial substrates, which was shown in the works [1-8].

The main factors that affect the growth rate (and, accordingly, the quality of the resulting material) are the flow rate and chemical composition of gases, pressure in the reaction chamber, substrates temperature, substrates characteristics themself and the shape of the reactor [1, 3, 5, 8-14].

The shape of the reactor for growth setups manufacturers can differ significantly, which can significantly affect energy saturation and shape of plasma cloud while maintaining the principle of its formation [15-17]. Most often, manufacturers work on creating of plasma cloud in the form of a ball, compressed along Z-axis.
The dimensions of the plasma cloud depend on the dimensions of the reactor and the parameters of the magnetron. Other parameters are individual for each CVD-setup.

The chemical composition of the gas is selected at the procurement stage in accordance with the requirements of technical specifications. Substrates characteristics must be determined before they are used in the CVD-synthesis process. For this, express certification of diamond substrates can be carried out by Fourier transformed infrared (FTIR) spectroscopy, Raman spectroscopy and spectrophotometry [5, 18-22].

This work is devoted to the study of the influence of CVD synthesis conditions (gas pressure in reactor, microwave power, the quantitative ratio of gases and deposition time) on the growth rate and quality of the obtained single-crystal diamond films.

2. Materials and methods

We used single-crystal CVD-substrates manufactured by Bhapsali Diamond Tools Pvt. Ltd. (India) for CVD-synthesis of diamond single-crystal layers. Substrates roughness was determined using a scanning probe microscope MFP 3D Stand Alone (Asylum Research) using a silicon cantilever at a resonance frequency of 120 kHz and processing the results in the program Gwyddion. Misorientation of plane (100) from direction [100] was determined using diffractometer of high resolution D8 DISCOVER (Bruker).

We used Ardis-300 for deposition of diamond CVD-layers. For this, we used gas phase consisting of methane with a purity of 99.9999% and hydrogen with a purity of 99.99995% in a ratio of 3:97.

The temperature of the diamond substrates was 1100 ºC, the microwave power was varied from 3800 to 4000 W. The gas pressure in the system was varied from 40 to 29.3 kPa.

The calculation of the growth rate of the layers of single-crystal diamond was carried out by measuring the thickness of the deposited layer using a dial indicator with division value of 0.001 mm. The surface morphology study of the obtained diamond single-crystal films was carried out on scanning electron microscope JEOL JSM-IT500.

3. Results and discussion

The roughness of the diamond substrates determined using MFP 3D Stand Alone ranged from 1.0 to 2.5 nm. The misorientation of plane (100) and direction [100] was in the range of angles from 1 to 2°. Analysis of diamond substrates shown that it is possible to use them for the synthesis of high-quality diamond single-crystal layers [6].

The selection of the optimal parameters for studying CVD-diamond growth rate depending on the thickness of the grown layer was carried out in several stages. First of all, we investigated the effect of gas pressure in the reactor on it. Table 1 presents the parameters of CVD-synthesis. The growth process was carried out until a diamond film of 50 μm thickness was formed; gas phase consisted of methane and hydrogen in a ratio of 3:97, the temperature of diamond substrates was 1100 ºC.

**Table 1. Growth parameters.**

|                  | Experiment №1 | Experiment №2 | Experiment №3 | Experiment №4 |
|------------------|---------------|---------------|---------------|---------------|
| Pressure, kPa    | 40.0          | 38.7          | 38.7          | 38.7          |
| Microwave power, W | 4000          | 3800          | 3800          | 3800          |
| Growth time, h   | 5             | 6             | 6             | 7             |
| Film thickness, μm | 50            | 50            | 55            | 50            |
| Growth rate, μm/h | 10            | 8.3           | 9.2           | 7.1           |
Table 1 shows that in these conditions diamond layer growth rate is rather low and ranges from 7 to 10 μm/h. Therefore, we decided to make experiments at reduced gas pressures. The results of growth rate calculating in them are shown in table 2.

**Table 2. Growth parameters at reduced gas pressures.**

| Experiment № | Pressure, kPa | Microwave power, W | Growth time, h | Film thickness, μm | Growth rate, μm/h |
|--------------|--------------|--------------------|----------------|-------------------|------------------|
| №5           | 34.7         | 4000               | 9              | 234               | 26.0             |
| №6           | 34.7         | 4000               | 5              | 135               | 16.4             |
| №7           | 29.3         | 4000               | 5.5            | 42                | 7.6              |

The results of experiments showed that growth rates increased significantly with a decrease of pressure to 34.7 kPa and amounted to 26 μm/h for sample 5 and 27 μm/h for sample 6, respectively. Further reduction of pressure to 29.3 kPa lead to decrease of growth rate to 7.6 μm/h. The growth rate of samples 5 and 6 was sufficiently high, but the quality of their surfaces was very defective [3]. Figure 1 demonstrates the surface of sample 5. Figure 2 shows sample no. 7 with a well surface quality.

![Figure 1. Defective surface of sample 5.](image1)

![Figure 2. Surface of sample 7.](image2)

The CVD-synthesis of diamond of the required geometric size supposes the layer-by-layer growth, therefore, we studied the effect of growth cycle number on CVD-diamond growth rate. We deposited the diamond layer-by-layer over five cycles. The deposition conditions were the same, except that in the first cycle the pressure was 34.7 kPa whereas in all other cycles it was 30.7 kPa (table 3).

**Table 3. Parameters of cyclic growth.**

| Cycle №1 | Cycle №2 | Cycle №3 | Cycle №4 | Cycle №5 |
|----------|----------|----------|----------|----------|
| Pressure, kPa | 34.7     | 30.7     | 30.7     | 30.7     | 30.7     |
| Microwave power, W | 4000     | 4000     | 4000     | 4000     | 4000     |
| Growth time, h | 8.5      | 6.8      | 7.25     | 7.5      | 5.75     |
| Film thickness, μm | 135      | 115      | 150      | 160      | 142      |
| Growth rate, μm/h | 15.9     | 16.9     | 20.7     | 21.3     | 24.7     |
Figure 3 shows the comparison of growth rate in each cycle. It is clearly seen from this bar chart that as the cycle number and, accordingly, the thickness of the deposited diamond layer increased, the growth rate raised up from 15.9 to 24.7 μm/h. In addition, we found that the speed increment between cycles also increases.

![Figure 3. Growth rate dependence on the cycle number.](image)

This trend can be associated with a decrease in the degree of misorientation between the growth plane (100) and the crystallographic direction [100]. This is confirmed by the results of scanning electron microscopy that showed the presence of growth steps on the samples' surface. Figure 4 shows plane (100) surface morphology of the diamond obtained during the experiments.

![Figure 4. The surface of deposited diamond film.](image)

Also, a possible reason for an increase in the growth rate may be an increase in the surface roughness on which the film is depositing. The growth of CVD-layers is a probabilistic process, hence, with an increase in roughness, it becomes more energetically favorable for carbon radicals to settle on the surface of the diamond and complete the growing layer. Therefore, an increase in the growth rate is observed.

4. Conclusion
In this work, we studied the effect of the main parameters of CVD-synthesis on the diamond film growth rate. We noted that the diamond layer grows at different rates depending on the pressure in the reactor and the microwave power.

Also, in work we noticed an increase in the growth rate of a single-crystal diamond layer with an increase in deposited diamond film thickness. The observed trends can be associated with the
perfectioning of the crystallographic plane of diamond substrate (a decrease in the degree of its misorientation), as well as an increase in the specific surface area due to surface roughness increase.

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