Certification of diamond HPHT-plates for their use as substrates for CVD-synthesis

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Abstract. Incoming control of substrates and gases is very important part of technological chain. The properties of diamond layer on substrates with different misorientation angles may differ considerably, therefore, determining the deviation of diamond growth plane (100) from the direction [100] is important. Also, in order to select diamond substrates that are most suitable for synthesis of pure quality crystal, it is required to determine the content of impurities in them and the roughness of their surface. In this research, HPHT-plates of one lot were examined using Fourier transform infrared spectrometry, high-resolution diffractometry and scanning probe microscopy in order to classify them according to the studied parameters. Further the classified diamond substrates were used to synthesize diamond layers. Ardis 300 was used for deposition of monocrystalline diamond; synthesis was carried out from a methane-hydrogen plasma with 3% methane at a temperature of 1100 °C, a pressure of 26.7 kPa and a power of 3800 W. The studies have shown that certification of diamond HPHT-plates allows to select substrates for the synthesis of pure quality monocrystalline diamonds.

1. Introduction
The characteristics and origin of raw materials plays an important role role in the deposition of single-crystal diamonds (SCD) from gas phase (CVD). The surface defects and coarse roughness of substrates can lead to the deposition of discontinuous single-crystal layers (SCL), as well as to the formation of polycrystalline particles [1-4]. The orientation of the substrate surface affects the probability of deposition of SCL and its growth rate [5-7]. The content of impurities in the initial substrates (first of all – nitrogen, which is one of the most common impurity in diamond) can also strongly affect the growth process of CVD-diamond: rate and probability of growth in certain directions, stresses inside the obtained crystals and homogeneity of their properties [8].

Definition of the surface roughness of diamond substrates can be carried out using various techniques, however, the most accurate and reliable is scanning probe microscopy, which makes it possible to determine the roughness of the nanometer range.

The determination of the orientation of crystals is carried out by methods of X-ray structural analysis using various scientific instruments. In the synthesis of diamond from the gas phase, not only the orientation of the crystal is important, but also its deviation from the required direction; therefore, high-resolution X-
ray diffractometry was used in this research. This method allows to orient the crystal in space and the available software of the device makes it possible to determine with high accuracy the angle of misorientation of the plane (100) from the direction [100] [9-11]. The level of this deviation is fundamentally important for the growth of pure-quality SCD, since a large misorientation provokes the growth of polycrystalline diamonds consisting of columnar crystallites, the growth direction and size of which depends on the composition of the gas phase and on the growth conditions [12, 13].

Analysis of the impurity compound of substrates can be defined by various spectroscopic and mass-spectrometric methods, as well as by the special capabilities of electron microscopy [14-19]. Fourier transform infrared spectroscopy (FTIR) allows obtaining quantitative data on the impurity composition of diamonds most quickly and with high reliability [20-24].

2. Materials and methods

In this research, we carried out certification of 20 synthetic HPHT-plates of SCD with dimensions of 5.0x5.0x1.0 mm. The following techniques were used to assess the quality of the substrates:

- deviation of the plane (100) of the substrates from the [100] direction was estimated using high-resolution X-ray diffractometry on a D8 DISCOVER diffractometer (Bruker);
- surface roughness was estimated by measurements on a scanning probe microscope MFP 3D Stand Alone (Asylum Research) using a silicon cantilever at a resonance frequency of 120 kHz using the Gwyddion software (version 2.51);
- qualitative and quantitative analysis of the nitrogen content in the substrates was carried out using Fourier transformed infrared spectroscopy;
- surface of the diamond after synthesis was examined on scanning electron microscope Jeol JSM-6700F (Center for Collective Use "Materials Science and Metallurgy" NUST “MISIS”).

The methodology for calculating the nitrogen content in diamond is based on special mathematical processing of the infrared spectra of diamond crystals and is discussed in detail in the article [5].

Ardis 300 was used for the deposition of SCL from the methane-hydrogen plasma (3% methane with a purity of 99.9999%, 97 % hydrogen with a purity of 99.9995%). The substrate temperature was 1100 °C, the pressure was 26.7 kPa, and the microwave power was 3800 W.

3. Results and discussion

In this work, we determined the qualitative and quantitative characteristics of diamond HPHT-substrates separately and assessed the spread of values within a one lot. Figure 1 shows the appearance of the investigated diamond plates.

![Figure 1. Single-crystal diamond HPHT-substrates.](image)

The misorientation angle of the substrate plane was calculated using high-resolution X-ray diffractometry. The calculation model makes it possible to minimize mechanical hardware errors, including inaccuracies in positioning and displacement, and to determine the optimal parameters for the location of
the sample relative to the incoming radiation for the correct study of the perfection of the crystal structure. As a result of the investigations, it was determined that substrates of one lot have a small spread in the misorientation angle of the (100) plane from the [100] direction, which is less than 1°.

Scanning probe microscopy showed that the roughness of separate sections of the substrates in a lot with an area of 5x5 μm² is satisfactory and quite stable. For example, for different parts of the substrate № 9 it ranges from 1.37 to 2.18 nm (figure 2), which is optimal for synthesis. The rest of the substrates in this lot have a similar roughness, which ranges from 0.7 to 2.5 nm.

![Figure 2. Images of the surface of the substrate № 9, obtained by the scanning probe microscope.](image)

The determination of the substrates composition was carried out by FTIR-spectroscopy. The base for defect concentration in diamonds determining from absorption spectra in the IR-range are based on the fact that the shape of absorption bands induced by basic defects is stable, which has been established experimentally. The spectra showed that nitrogen is the main impurity in these substrates. In the result of nitrogen content calculation, 20 plates from one lot were divided into three groups. The first group includes substrates with nitrogen content up to 100 ppm, the second - 110-150 ppm, and the third - more than 160 ppm. The spectra of each type of substrate are shown in figure 3. Table 1 presents data on their distribution in the batch.
Figure 3. IR-spectra of diamond plates.

Table 1. Nitrogen content in SCD.

| Sample number | Nitrogen content, \(10^{19}\)at/cm\(^3\) | Sample number | Nitrogen content, \(10^{19}\)at/cm\(^3\) |
|---------------|------------------------------------------|---------------|------------------------------------------|
| №1            | 150                                      | №11           | 80                                       |
| №2            | 125                                      | №12           | 140                                      |
| №3            | 130                                      | №13           | 170                                      |
| №4            | 140                                      | №14           | 80                                       |
| №5            | 160                                      | №15           | 120                                      |
| №6            | 90                                       | №16           | 110                                      |
| №7            | 170                                      | №17           | 130                                      |
| №8            | 200                                      | №18           | 130                                      |
| №9            | 70                                       | №19           | 160                                      |
| №10           | 90                                       | №20           | 200                                      |

All IR-spectra show a clear diamond peak in the range of 1500-2700 cm\(^{-1}\); in the range of 2750-3300 cm\(^{-1}\) there are peaks of C-H vibrations. In the range 600–1400 cm\(^{-1}\), we observed peaks which refer to nitrogen centers, whose integral concentration was calculated by the method [5]. The main form of nitrogen entry into these samples is B1 (1180 cm\(^{-1}\)) – a complex consisting of 4 nitrogen atoms and vacancy. No other impurities were observed in the investigated substrates.

As a result of the studies, it was revealed that these substrates have similar qualitative characteristics in terms of roughness and orientation but differ in their nitrogen content. The synthesis of SCD was carried out on substrates № 9, № 5 and № 8, assigned to groups 1, 2 and 3, respectively. We observed no fundamental difference in the growth rate and surface quality of single-crystal CVD-films obtained on
substrates with different nitrogen content. Figure 4 shows a sample obtained using substrate № 9. A single-crystal diamond layer of 1020 μm thick was applied to it by the CVD-method.

![Image of diamond CVD-layer on substrate № 9.](image)

Investigations of samples using scanning electron microscope have shown that polycrystalline diamond is formed along the perimeter of the substrate; growth waves caused by the high growth rate of the diamond layer are visible on the diamond surface. The diamond layers obtained on substrates № 5 and № 8 had a similar morphology of the growing surface.

4. Conclusion
In this work, we have comprehensively investigated and certified a lot of diamond substrates, consisting of 20 single-crystal HPHT-plates. To certify the substrates with the aim of using them later for CVD-synthesis of pure-quality SCD, the methods of FTIR spectroscopy (determination of impurities and their concentration), high-resolution X-ray diffractometry (determination of the deviation of the orientation of the plane (100) from the direction [100]) and scanning probe microscopy (determination of the surface roughness of substrates) were used.

It was found that the substrates of the investigated lot have the same qualitative characteristics, the main difference being the nitrogen content, one of the main impurities of HPHT-diamonds. The substrates of this lot were conditionally divided into three groups according to nitrogen concentration. CVD-synthesis of SCD was carried out on substrates of each group. We observed no fundamental differences in growth process, as well as in the morphology of obtained SCL.

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