Fourier-transform infrared spectroscopy for analysis of diamond materials of different origin

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Abstract. The study of impurity composition of diamond materials is an important element of their classification for use in various fields of science and technology. Many physical (thermal and electrical conductivity, optical purity), mechanical (hardness and strength) and aesthetic (color grade and clarity) properties of diamond depend on the presence of impurities in their structure; therefore, it is important to quickly and reliably determine each impurity in diamond. In this work, the method of FTIR spectroscopy is proposed as an express method for determining the impurity composition of diamonds. We examined three types of diamond materials: single crystal natural diamonds (before and after heat treatment), single crystal synthetic HPHT-diamonds and synthetic polycrystalline diamond CVD-films. We have established that the used technique allows to determine impurities in single crystals of natural and synthetic origin reliably and effectively, while the study of polycrystalline thin films is best performed using spectrophotometry.

1. Introduction

From the standpoint of solid-state physics, diamond as well as germanium and silicon is a wide-gap semiconductor; therefore, optical processes in it are determined by impurities and defects in its crystal structure [1]. In addition, impurities also affect the thermophysical, mechanical and other properties of diamonds [2-6]. The set of impurities and defects in diamonds is wide-ranging and very diverse. About 300 optically active centers were found in diamonds, including about 20 varieties of nitrogen defects and about 10 types of intrinsic defects. These centers correspond to more than 2000 bands in the absorption spectra, luminescence and cathodoluminescence spectra [7-10]. Impurities and defects in diamond belong to deep centers, and their optical activity is usually caused by intracenter transitions.

The main impurity in diamond is nitrogen [7-8], the concentration of which can reach up to 0.2 at.%. Nitrogen atoms enter the diamond structure due to their capture during crystal formation. Depending on the temperature and time conditions, nitrogen atoms can form various defects: A, B1, C, B2 and N3, which
differ in structure [11]. These defects are optically active, that is, they are noticeable in the absorption and luminescence spectra [12].

Nitrogen has a significant effect on the electrical and thermal properties of diamonds; also, it can give crystals a color ranging from light yellow to dark yellow and even brown. In addition, researches on the synthesis of diamond from the gas phase (CVD), which are actively developing at the moment, show an increase in the growth rate of the diamond layer with an increase in the nitrogen concentration in the gas phase [13]. In this case, the nitrogen content in deposited layers increases too; this affects the quality of the material obtained [14]. Hence, it is important to control its amount and form of entering in diamond structure.

The impurity composition of diamonds can be analyzed using various spectroscopic and mass-spectrometric methods. The most useful and informative, as well as non-destructive and requiring no complicated and lengthy sample preparation [15], is Fourier-transform infrared spectroscopy (FTIR). An advantage of this method is also the ability to obtain quantitative results based on the experimentally established fact of the stability of the shape of absorption bands induced by main defects.

In this paper, we will review the aspects of studying the impurity composition of various diamond materials by FTIR-spectroscopy.

2. Materials and methods
In this work, we examined three types of diamond materials:

- single crystal natural diamonds: initial – M1; heat treated – M2; heat treatment was carried out at 1500 °C in vacuum for 15 min;
- single crystal synthetic HPHT-diamonds – HPHT;
- synthetic polycrystalline diamond CVD-plates: plate 1 and plate 2.

Samples were studied using Fourier-transform infrared spectroscopy (IR-spectrometer Thermo Scientific Nicolet 6700), Raman spectroscopy (Raman spectrometer Renishaw inVia Raman Microscope, Raman confocal microscope Thermo DXR), spectrophotometry (Cary 400 UV-Vis Spectrophotometer).

The nitrogen concentration in studied single crystals was calculated from the IR spectra in accordance with the formula [15]:

\[ N = 160.49 \cdot 10^{18} \cdot \left( \frac{S_N}{S_0} \right)^{0.9919} \]

where \( N \) – nitrogen content, at/cm\(^3\);
\( S_N \) – peak area in the range of 950–1450 cm\(^{-1}\) (nitrogen defects);
\( S_0 \) – peak area in the range of 1500–2700 cm\(^{-1}\) (diamond).

3. Results and discussion
Figure 1 shows infrared (IR) spectra of diamond materials studied in this work.
Figure 1. IR-spectra of studied materials.

All spectra demonstrate a clear diamond peak in the range of 1500-2700 cm\(^{-1}\). The spectra of single crystals also exhibit peaks of C-H vibrations in the range of 2750-3300 cm\(^{-1}\). According to the method [15], we determined nitrogen concentrations in them, the calculation results are shown in Table 1.

| Sample | Nitrogen content, \(10^{19}\) at/cm\(^3\) |
|--------|-----------------------------------|
| M1     | 12.2                              |
| M2     | 9.6                               |
| HPHT   | 1.2                               |

The data of FTIR-spectroscopy show that nitrogen enters the examined natural single-crystal diamond mainly in the form of defect A (two substituting nitrogen atoms), which corresponds to the peak at 1280 cm\(^{-1}\), that is the most intense. A less intense peak at 1180 cm\(^{-1}\) corresponds to defect B1 (4 substituting nitrogen atoms and a vacancy). Nitrogen enters the studied HPHT-crystals mainly in the form of the B1 defect, as evidenced by the high intensity of the 1180 cm\(^{-1}\) peak. Also, in all single crystals studied in this work, there was a peak at 1363 cm\(^{-1}\). This band of FTIR-spectrum corresponds to the B2 defect in diamond, which is supposedly interstitial carbon atoms in the \{100\} planes [16, 17]. Figures 2 and 3 show Raman spectra in different wavelength ranges for samples of natural diamond M1 and M2.
The study of natural single-crystal diamonds revealed changes in the crystal lattice and in the content of impurities after heat treatment. The difference in the IR-spectra of samples M1 and M2 was identified in the hydrogen line ($3106.64 \text{ cm}^{-1}$ for M1 and $3109.96 \text{ cm}^{-1}$ for M2) and its intensity, as well as in the intensity of nitrogen lines; this, apparently, indicates the effect of heat treatment on the diamond structure. To clarify
the effect of heat treatment on the structure of diamond material, we carried out the study of natural single crystals by the method of Raman spectroscopy.

The position of the diamond line for both samples is completely the same. As a result of the analysis, it was concluded that the diamond line for the heat-treated sample M2 is narrower: it is 7.5 cm\(^{-1}\), while for M1 it is 10.5 cm\(^{-1}\). Obtained result indicates an increase of structural perfection of natural diamond as a result of heat treatment. This effect arises as a result of a decrease in stresses and the number of defects in single-crystal diamond due to the process of high-temperature annealing; at the same time partial graphitization of the diamond occurs. As a result of annealing, the structure of defect-impurity centres changes, which detect itself in the observed IR-spectra.

In the analysis of diamond polycrystalline CVD-films by FTIR spectroscopy, strong interference is observed due to the small thickness of the samples (figure 1). Therefore, the study of the impurity composition of polycrystalline thin films using this method is difficult. To achieve it in such films, the spectrophotometry method is more suitable. Results of this experiment are shown in figure 4.

![Figure 4. Results of spectrophotometry for diamond polycrystalline CVD-films.](image)

As a result of the analysis by spectrophotometry, a small difference in the films thickness was revealed, which is evident from the difference in the arrangement of spectral lines. C-center defects (single nitrogen atoms) were beyond the limits of detection; that indicates about their very small number in the samples and high quality of the analyzed material.

4. Conclusion
In this work, we established that the method of Fourier-transformed infrared spectroscopy can quickly and reliably identify impurities in single-crystal diamonds of different origin. Difficulties associated with interference due to the small thickness of the samples arise during the study of diamond CVD-films by this method. Therefore, it is better to determine the presence of impurities in them using spectrophotometry.

The assessment of changes in single-crystal diamond structure after thermal treatment by the method of FTIR spectroscopy can be carried out only circumstantially; to obtain more accurate qualitative and quantitative results, the Raman spectroscopy method is recommended.
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