Three-dimensional mapping of the optical centers in the bulk of natural diamond by photoluminescent spectroscopy

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Abstract. Optically active defects in natural diamonds form specific spectral bands in the optical absorption and luminescence spectra and are called optical centers. Optical centers in the visible spectral range and their corresponding defects are called color centers. Spectral absorption and luminescence bands usually occupy several tens of nanometers in the spectral range and often have a complex structure. This spectral structure is unique to each optical center. The stationary broadband UV-MIR characterization of the set of optically active defects in the bulk of natural diamond with a widely varying concentration of impurities was carried out in this work. Comparison of the initial and modified impurity-defect structures of near-surface diamond layers was carried out by the method of cathodoluminescence and cathodoluminescence topography.

1. Introduction

The main distinctive property of diamond crystals of different natural origin is the chemical composition and concentration of nitrogen and nitrogen-vacancy defects. Nitrogen and nitrogen-vacancy defects, as well as other active impurity defects, form specific spectral bands in the optical absorption and luminescence spectra, called optical centers [1]. If the optical center is located in the visible spectral range, then the corresponding defect is called the diamond color center. As a rule, optical centers occupy several tens of nm in the spectral range and often have a complex structure [2]. The presence and structure of spectral bands and luminescence can be used to identify, characterize and classify the color center.

Over the years, many methods have been developed for mapping both natural and synthetic diamonds. However, the most informative methods of gemological analysis of diamonds are optical methods, such as birefringence [3], Raman spectroscopy [4], IR spectroscopy [5], optical absorption [6], and the most sensitive of all the above mentioned methods – photoluminescence (PL) [7]. The classical luminescence method is based on the forced removal of electrons from a stable state to an "excited" state. The relaxation of an "excited" electron proceeds with the release of energy, the spectral range of which mostly corresponds to visible radiation. The process of electron excitation occurs under the influence of various radiation sources (UV lamp, X-ray tube, electron gun, etc.), including those in the visible spectral frequency range such as lasers [8]. Depending on the wavelength of the pumping radiation (visible or IR range), the nature of the radiation (continuous or pulsed), power, energy etc., the PL spectrum will undergo certain changes due to the quantum energy.

If the output of laser acting as a pumping source is a diverging beam, then focusing of radiation in the sample under study is required. Regardless of the focusing methods used, the PL process will occur only in the region of maximum energy concentration or, in other words, in the radiation waist, as well
as in the nearby region in the longitudinal direction of laser radiation propagation. The transverse dimensions of the waist directly depend on the methods of focusing, while the longitudinal dimensions also depend on the energy parameters of the laser radiation. By moving the waist in accordance with the available degrees of freedom inside the diamond, one can obtain information about the presence of impurities and structural defects with reference to spatial coordinates.

The physics of the PL has many aspects, including the very process (path) of returning an electron to the ground state (directly or through intermediate quantum states), the rate of return, which depends on the impurity-defect structure of the diamond, external conditions, etc. All these points will be taken into account during the experimental part of this study, but will not be considered in detail. It should only be noted that to obtain narrower spectral lines of the luminescence spectrum, the object of study is subjected to the cooling.

2. Experimental studies of the method

In this work, an experimental testing of the method of multidimensional PL in the volume of natural diamond with reference to spatial coordinates was carried out in order to map optical centers. The experimental setup is shown in figure 1.

![Figure 1. Scheme for recording PL and three-dimensional mapping of the distribution of optical centers.](image)

A diode-pumped femtosecond laser was used as a monochromatic source of ultrashort pulses for exciting photoluminescence. It generates radiation at two harmonics: \( \lambda_1 = 1050 \text{ nm} \) and \( \lambda_2 = 525 \text{ nm} \), respectively. Ultrashort pulses with a duration of \( \sim 150 \text{ fs} \), with a repetition rate of \( 80 \text{ MHz} \) were focused in natural diamond using a microscope objective with a numerical aperture \( NA = 0.25 \). It forms a waist of \( \sim 4.4 \mu\text{m} \) in the transverse direction along the \( 1/e^2 \) level. PL radiation was transferred from the bulk of natural diamond to the slit of the spectrometer via a UV quartz microscope objective with a numerical aperture \( NA = 0.2 \), mounted perpendicular to the axis of propagation of laser radiation. The photoluminescence analysis was performed using an ASP-150F broadband spectrometer.

The scheme of the experiment was organized so that the front focal planes of the objectives for focusing the radiation and observation were static and conjugated into one region. A cubic natural diamond with geometric dimensions along each coordinate equal to \( 2 \text{ mm} \) was used as a sample for the research. The diamond was fixed on a motorized platform with five degrees of freedom, including three translators of linear displacements for each spatial coordinate, respectively. During the experiment, the PL spectrum was recorded at 10 different points of the diamond. Figure 2 shows the normalized amplitudes of the PL spectrum at these points. From the figure 2 it can be seen that due to the different optical absorption coefficient caused by the presence of impurities of different concentrations, the
intensity of the spectral lines is not constant. However, the nature of the spectrum itself does not change from point to point, which allow us to speak of the absence of defects of various types.

![Figure 2. Normalized PL spectrum for different points in the bulk of the diamond.](image)

The diamond was scanned in a plane perpendicular to the propagation axis of laser ultrashort pulses and the observation axis. Such restrictions were imposed in order to exclude the influence of different phase shifts (different optical path inside the bulk of the diamond) during the propagation of the PL spectrum. This eliminates the influence of the refractive index of the diamond when measuring at different points.

Figure 3 shows the cross sections of the maxima of the amplitude of PL spectrum for each point in the bulk of the diamond. The step between the measurement points is ~ 200 µm. It can be seen from the figure 3 that the amplitude of the spectrum changes by more than a factor of 2 at some points. It can be concluded that in this region with size of about ~500 µm, there is a local change in optical absorption. In addition to the global maximum of the PL spectrum, several local maxima from the general spectrum were also analyzed. Figure 3 shows that the pattern of the functions remains unchanged for the selected wavelengths.

![Figure 3. Cross sections of the maxima of the amplitude of PL spectrum for different points of study in bulk of the diamond.](image)
3. Discussion
Despite the advances in the above methods [2–7], other imaging techniques have evolved over the decades, such as interferometric microscopy [9] and digital holography [10, 11]. In particular, digital holography techniques, due to their unique advantages and capabilities of digital recording and digital reconstruction, have made significant progress over the past two decades and have become the benchmark for quantitative phase measurements and microscopy [12]. In this regard, it is possible that the above-mentioned alternative methods will be used at the next stages of diamond mapping.

4. Conclusion
Optical methods are the most effective for identifying and characterization of the natural, synthetic and processed diamonds. Photoluminescence can be used as a powerful tool for mapping of an entire crystal. It is possible only to reveal the features of the internal structure of the crystal, but also to produce its full value characterization. Ultrashort pulses, which can be tuned not only in wavelength, but also in duration and energy in the waist region, in addition to revealing the inner structure of the crystal can allow to fully characterize it. The discovered effect opens up possibilities for detailed studies and theoretical structural modeling of local and quasi-local modes of known diamond color centers, which determine the violation of coherence, relaxation, and spin-orbit interaction for their excited states, which are of interest for quantum optics, quantum computing and nanophotonics, as well as optical technology. Invisible luminescent volumetric marking of large natural and artificial diamonds for the purpose of their industrial tracking (tracing).

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