equations and finding on their basis the functional relationship between the physical characteristics of the crystal and the field strengths is a very difficult task.

One of the options for constructing the achievement of such a goal may be to use the formalism of statistical physics and fluid theory. By the way, we note that the use of the theory of integral, and, in particular, Fourier, transformations in statistical physics and fluid theory allows us to talk about an analogy between the phenomena described in them with the processes of wave field formation in Fourier optics and apply a number of results , for example, in computer optics [7].

CONCLUSION

Thanks to the advent of lasers, the theory of the interaction of radiation with substances received a certain impetus to development. For some types of lasers and substances, mathematical models of these processes have been developed. The literature contains the development of a mathematical model and an algorithm for calculating the temperature distribution in complex multilayer systems under the influence of laser radiation. These models are based on the finite-difference method and take into account the anisotropy of the optical and thermal parameters of the structure of materials. Typically, the model is two-dimensional and non-stationary and allows you to simulate the interaction of various types of laser with substances.

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THE LUMINESCENCE CENTER WITH ZPL AT 468 nm IN CVD DIAMONDS

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It is shown that the luminescence center with zero-phonon line at 468 nm commonly seen in spectra of CVD-grown diamonds is associated with the vacancy clusters. Based on the results of the measurements performed on several samples doped with nitrogen we could make an assumption that the defects responsible for the 468 nm center are complexes

of nitrogen, hydrogen and vacancies in negative charge state. These complexes are located at the walls of vacancy clusters. Taking into account high luminescence efficiency of the 468 nm center, we anticipate that this center could be used for detection of trace concentrations of vacancy clusters in CVD diamonds.

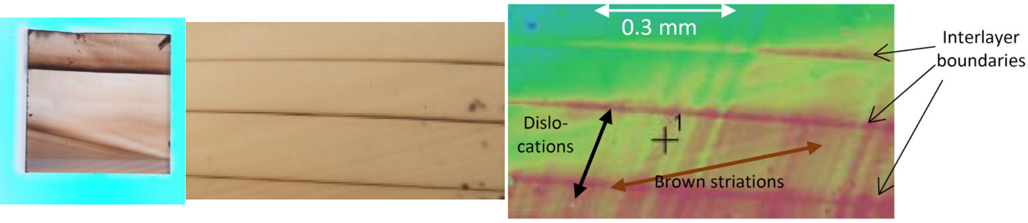
Key words: CVD-grown diamonds; the vacancy clusters; the luminescence; strong electron-phonon interaction; complexes of nitrogen; hydrogen and vacancies.

INTRODUCTION

Brown is a common color of as-grown CVD diamonds. It is especially intense in diamonds grown at high growth rate and when nitrogen is added to the growth gas. Vacancy clusters are thought be the defects responsible for the brown color in natural and CVD diamonds [1–3]. This unwanted coloration has always been a matter of concern. Thus, the methods of the reduction (eventually elimination) of brown color as well as the evaluation of the brown color intensity are the subjects of attention of researchers and technologists dealing with CVD diamonds. Intensity of brown color can be measured using optical absorption. However, due to the limited sensitivity of commercial optical absorption spectrometers, more sensitive methods of the detection of traces of brown coloration have to be developed. Below, we show that the luminescence center with zero-phonon line (ZPL) at 467.7 nm at liquid nitrogen temperature (468 nm center), which is common for CVD diamonds [4], is closely related to the brown color and this center can be used as a very sensitive indicator of the presence of vacancy clusters.

EXPERIMENTAL

Single crystal CVD diamonds of brown color grown in GIA CVD Diamond Lab using PLASSYS150 2.45 GHz microwave plasma reactor were studied. The diamonds were grown in hydrogen plasma with addition of 5 % of methane. Some samples were grown with addition of nitrogen at concentrations from 10 to 200 ppm. The diamonds were grown as blocks in several layers to a total thickness from 3 to 4 mm. The as-grown blocks were cross-sectionally cut in sample plates. Optical image of one of the samples is shown in Fig. 1, *a*.



a ***b*** ***c***

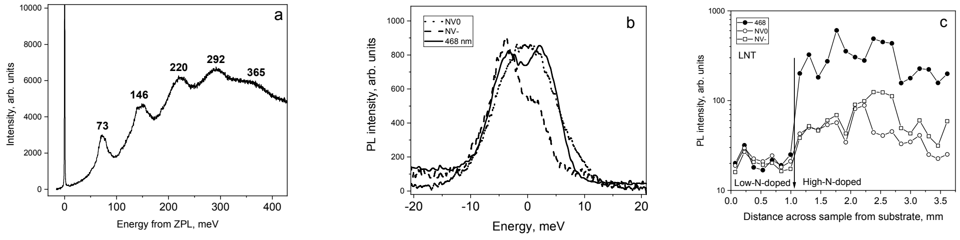
Figure 1. – (*a*) Optical image of CVD diamond sample showing typical distribution of brown color. (*b*) Optical image of an area with brown striations and boundaries between growth layers. (*c*) Distribution of luminescence intensity of 468 nm center over the area shown in (*b*). In (*c*), red color corresponds to high luminescence intensity, while green color shows areas of low luminescence intensity

Distribution of brown color is highly non-homogeneous forming linear striations and diffused areas (Fig. 1, *a*). The luminescence imaging reveals that the intensity of the 468 nm center follows the brown striation pattern (brown arrow) simultaneously forming other striations along direction close to the perpendicular with respect to the growth surface (black arrow) (Fig. 1, *b*, *c*). Thus, the 468 nm center luminescence is the most intense at the intersections of these two types of striations. These other striations look very similar to the bundles of dislocations formed in CVD diamonds grown on (100)-oriented substrates [5–7].

Comparative studies of the intensity distributions of 468 nm center and NV centers revealed their strong correlation, the closest correlation being with NV$^-$ center (ZPL at 637 nm). This correlation suggests that 468 nm center probably relates to nitrogen-containing defects in negative charge state. The electron-phonon spectrum of the 468 nm center is shown in Fig. 2, *a*. The strong electron-phonon interaction in 468 nm center is determined primarily by quasilocal vibration of energy 73 meV [4]. The spectral positions of the electron-phonon bands in its spectrum are precisely equidistant suggesting weak interaction with lattice phonons. Relatively high energy of the quasilocal vibrations is suggestive of the involvement of light atoms, e.g. hydrogen.

ZPL of 468 nm center considerably broadens and even splits in diamonds with intense brown color suggesting that the defects responsible for 468 nm center are "soft", contain vacancy and are located in highly stressed crystal lattice (Fig. 2, *b*). The two-component splitting pattern is similar to that of NV$^-$ center.

In nitrogen-doped samples, the intensity of 468 nm center follows the intensity of NV centers (Fig. 2, *c*). However, in the highly-doped layers, the 468 nm center is over-proportionally stronger than NV centers. This may suggest that the intensity of the 468 nm center is a product of three parameters: the total nitrogen concentration, the concentration of nitrogen donors and the concentration of vacancy clusters.

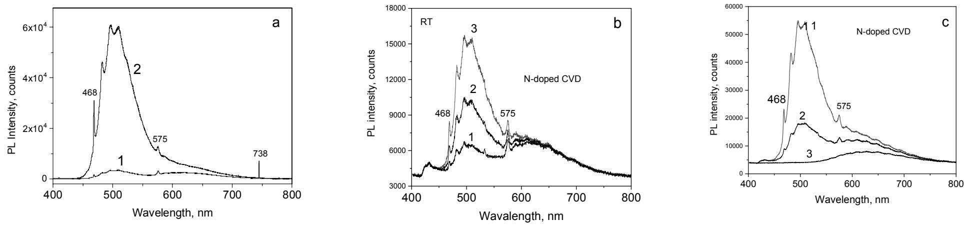


a ***b*** ***c***

Figure 2. – (*a*) Spectral structure of the electron-phonon band of the 468 nm center. (*b*) Distortion of ZPLs of 468 nm, NV^0 and NV$^-$ centers in dark brown CVD diamond. (*c*) Luminescence intensities of NV^0, NV$^-$ and 468 nm centers measured across N-doped CVD sample. Vertical arrow shows the boundary between low-doped and high doped layers. All measurements at liquid nitrogen temperature

Peculiarities of 468 nm center are its presence in actually any CVD diamonds including visually colorless (Fig. 3, *a*), the strong stimulation of its intensity by UV irradiation in nitrogen-doped diamonds (Fig. 3, *b*), and the complete quenching by relatively low temperatures (Fig. 3, *c*).

The thermo- and photo-chromic behavior of the 468 nm center resembles that reported for the brown color absorption, NVH center and the concentration of neutral and positively charged nitrogen. This suggests that the 468 nm center is directly involved in the process of the charge transfer between the vacancy clusters and nitrogen donors.



a ***b*** ***c***

Figure 3. – Dependence of luminescence intensity of 468 nm center on (*a*) intensity of brown color: *1* - near colorless, *2* - dark brown (measurements at room temperature); (*b*) time of exposure to UV irradiation, *1* – 2 s, *2* – 7 s, *3* – 162 s (measurements at room temperature); (*c*) measurement temperature, *1* – 20°C, 2 – 50 °C, *3* – 200 °C. All measurements with excitation at wavelength 360 nm

Natural brown diamonds have a number of ZPLs at wavelengths close to 468 nm. However, none of them has been identified as the 468 nm center seen in CVD diamonds. This suggests that there is a substantial distinction between the vacancy clusters in natural and CVD diamonds. We assume that the culprit is the hydrogen, which fills vacancy clusters in CVD diamond during growth. In natural diamonds, vacancy clusters are essentially hydrogen-free. Thus, the involvement of hydrogen in atomic structure of the defects responsible for 468 nm center is possible.

Optical absorption of the 468 nm center is not detected even in dark brown samples. Small concentration might seem to be an obvious explanation. However, strong luminescence of the 468 nm center in these diamonds is a contradicting fact. The recharging of the defects from negative to neutral charge state during intracenter photoexcitation could be an alternative explanation.

The available experimental data allow us to assume that the defects responsible for the 468 nm luminescence center of brown CVD diamonds are nitrogen-vacancy-hydrogen complexes residing at vacancy clusters. When in negative charge state, these defects produce 468 nm luminescence center.

CONCLUSION

The vacancy clusters responsible for brown color of CVD diamonds are luminescence active. We assume that this activity is the result of formation in the vicinity of vacancy clusters, or even may be at their surface, the nitrogen-vacancy-hydrogen complexes which produce optical center with ZPL at 468 nm. Since nitrogen and hydrogen are impurities in any CVD diamond, the 468 nm center always appears once vacancy clusters are formed. From our experience, the 468 nm center is detected in luminescence spectra of practically any as-grown CVD diamond. High luminescence efficiency of the 468 nm center suggests that it can be used as a very sensitive indicator of the presence brown color.

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ПАРАМАГНИТНЫЕ СВОЙСТВА HPHT АЛМАЗОВ ПОСЛЕ ОБЛУЧЕНИЯ УСКОРЕННЫМИ ЭЛЕКТРОНАМИ И ОТЖИГА

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Изучено влияние облучения ускоренными электронами с энергией 6 МэВ и последующего отжига на парамагнитные свойства пластинок алмаза, вырезанных из кристаллов, синтезированных методом HPHT в системах Fe-Ni–C. Установлено, что для всех исследованных образцов наблюдается рост интенсивности сигнала С-дефекта уже при флюенсе $1{,}5 \cdot 10^{17}$ эл/см^2, а также сигналов, ответственных за наличие примесного никеля. Спектры ЭПР облученных электронами пластинок алмаза после вакуумного отжига вернулись к исходным значениям.

Ключевые слова: HPHT алмазы; ЭПР; электронное облучение; вакуумный отжиг.

PARAMAGNETIC PROPERTIES OF HPHT DIAMONDS AFTER IRRADIATION WITH ACCELERATED ELECTRONS AND ANNEALING

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The effect of the fluence of accelerated electrons with an energy of 6 MeV on the paramagnetic properties of diamond crystals synthesized by the HPHT method in the Fe – Ni – C was studied. It was found that for diamonds, a sharp increase in the intensity of the signal from the C-defect was observed at a fluence of $1.5 \cdot 10^{17}$ el/cm^2, as well as a change in the saturation power for the central signal component.

Key words: HPHT diamonds; ESR; accelerated electrons; vacuum annealing.