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Change of Cathodoluminescence Spectra of Dimonds Irradiated by Electron Beam

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Abstract—Here we investigate the changes in the cathodoluminescence spectra of HPHT diamonds irradiated by electron beam at the room temperature (298 K) and liquid nitrogen temperature (77K). The temperature of diamond samples was varied from 80 to 300 K. The RADAN-220-IMA3-150E accelerator was used as a source of electrons (120 keV). For temperature control we used platinum thermo-resistor. All experiments were conducted in the vacuum chamber (10^{-2} Pa). Optical spectra of diamonds cathodoluminescence were recorded ever ~ 30 K and then compared with each other.

Keywords—HPHT, diamond, defects in diamond, N-V centers, cathodoluminescence.

I. INTRODUCTION

It is known, that nitrogen-vacancy (NV) centers in diamond are adjective single-photon emitters, with applications in quantum technologies. Two charge states are known for N-V centers: $N-V^0$ and $N-V^-$, with the latter being mostly studied due to its long electron spin coherence time. NV centers in diamond are promising elements for quantum

optical systems since they are single-photon emitters with high photostability, quantum yield and brightness, even at room temperature [1-3]. Typically, synthetically prepared diamonds with NV centers contain both $N-V^0$ and $N-V^-$ states. Therefore, control of NV centers state in diamond is an important scientific problem.

The technologies of diamond synthesis by the high-pressure high-temperature (HPHT) and chemical vapor deposition (CVD) methods are constantly improving. The HPHT method is used for obtaining bulk diamond samples with sizes up to $20\text{ mm} \times 17\text{ mm} \times 11\text{ mm}$ [4]. The CVD method is used for obtaining diamond wafers up to 120 mm in diameter and 3 mm in thickness [5]. Both of these synthesis processes make it possible to create various types of vacancies in the volume of diamonds. Thus, they are approaching research aimed at studying various kinds of vacancies.

The main goal of our work was to investigate the changes in the optical spectra of different specimens of diamonds cathodoluminescence and find a specimen with

The work was carried out as part of the state task of the Ministry of Education and Science of Russia (# 0721-2020-0048).

cathodoluminescence at the edge of fundamental absorption. We used five diamond samples, which were synthesized by the high pressure and high temperature method (HPHT). For those samples we measured optical cathodoluminescence spectra in the range of 200–1100 nm.

II. EXPERIMENTAL SETUP

The cathodoluminescence of HPHT (high pressure, high temperature) diamond plates was studied using the vacuum electron beam system of RADAN-220 [6] and vacuum electron tube. Operating vacuum in the chamber was 10^{-2} Torr and estimated by the forevacuum pump. During the experiments the surface of the diamond specimens was exposed to electron beam (120 keV). The cathodoluminescence was measured by the optical spectrometers in the range of 200 – 1100 nm (Ocean Optics HR 2000+ES) and 200 – 300 nm (Ocean Optics HR 4000). The temperature of specimens was controlled by the platinum thermo-resistor Heraeus Pt 1000 C420, the resistance of which was measured by the multimeter Mustech MY63, and which was placed near the specimens in the operating chamber.

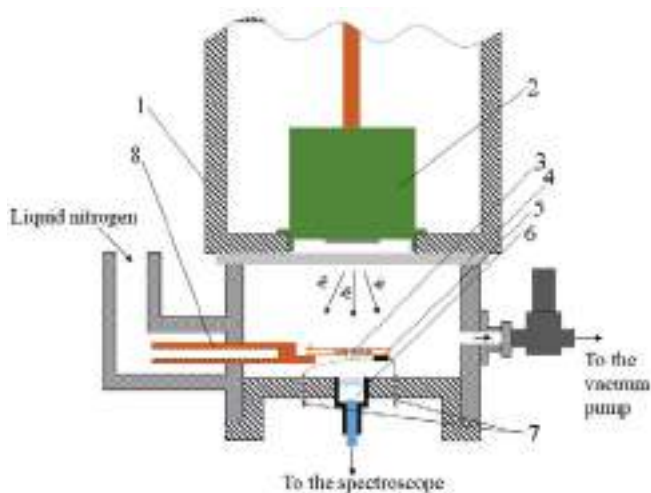


Fig. 1. Vacuum electron beam system for studying the cathodoluminescence of diamonds: 1 – RADAN-220 body, 2 – vacuum electron tube, 3 – diamond specimens holder, 4 – 10 micron aluminium foil, 5 – thermistor, 6 – optical collimator with a fiber, 7 – contact pins, 8 – copper “finger”, filled by liquid nitrogen for specimens chilling.

Fig. 1 shows the experimental system for studying the cathodoluminescence of diamond specimens. All diamonds in the experiment were made by the HPHT technology, had a plate-like shape and were 200- μ m in thickness. The specimens were paced into the holder between two copper plates with a hole in the center. A chilling system in the experimental chamber – copper “finger” with a hole inside was connected to the specimen’s holder and filled by liquid nitrogen (Fig. 1 (8)). To control the temperature of specimens, a thermo-resistor was used, which was placed behind the holder to prevent damaging from electron beam. Cathodoluminescence of diamond specimens were collected by the optical collimator to the fiber and measured by optical spectrometers.

All our experiments were carried out in forevacuum to prevent misting of specimens by water vapor and other chemicals contained in the environmental atmosphere.

Five HPHT diamond specimens were characterized by optical spectroscopy. Four of them, marked as C29, C30, C31, C32, were made with nitrogen-vacancy centers (NV-centers) and the last one with Ni-defects. Cathodoluminescence of specimens C29, C30, C31, C32 was investigated by using a survey spectrometer HR 2000 in the range of 200–1100 nm. And cathodoluminescence of the C12 specimen was studied by HR 2000 and HR 4000 (200–300 nm range) spectrometers.

III. RESULTS

Figs. 2 and 3 show the comparison of cathodoluminescence spectra of C29, C30, C31 and C32 diamonds at the room temperature (298 K) and at the temperature of liquid nitrogen.

A wide band is observed with a maximum at 650 nm with a zero-phonon line at $\lambda = 575$ nm. It is seen that the behavior of all curves at the shortwave region of spectra similar – constriction of the N-V⁰ spectrum band (near 575 nm, Fig. 2). For specimens C29 and C31 it is observed that intensity of N-V⁰ center after chilling specimens to liquid nitrogen temperature sharp increases. We also observed strongly marked phonon repetition of N-V⁰ center (picks near 585, 600, 630 nm).

At the same time for C32 specimen (Fig. 3) completely different behavior of cathodoluminescence spectra is observed both at the room temperature and liquid nitrogen temperature – strong increasing of intensity at the longwave region of spectra and absence of N-V⁰ pick. We also observe a wide band with a maximum at 495 nm for the specimen at the room temperature and the maximum at 580 nm. Both of this spectra have a feebly marked zero-phonon line at $\lambda = 455$ nm. This could be due to the presence of some other defects in the volume of the diamond, the intensity of which is higher than the intensity of nitrogen vacancies. This gives us an opportunity for further detailed study of such behavior of the cathodoluminescence spectra.

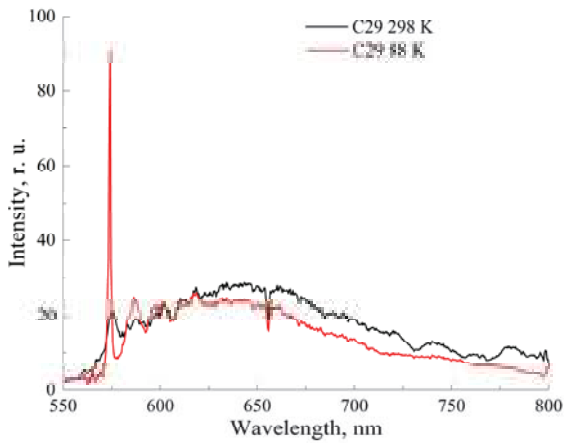
Let us look closer to the temperature dependence of cathodoluminescence intensity. Diamond specimen C31 was chosen for the study because of its highest intensity at the room and liquid nitrogen temperature in comparison with other specimens.

Fig. 4 shows the temperature dependence of cathodoluminescence of C31 specimen. It is seen that the intensity of the N-V⁰ center pick slightly increases with decreasing the temperature of the specimen.

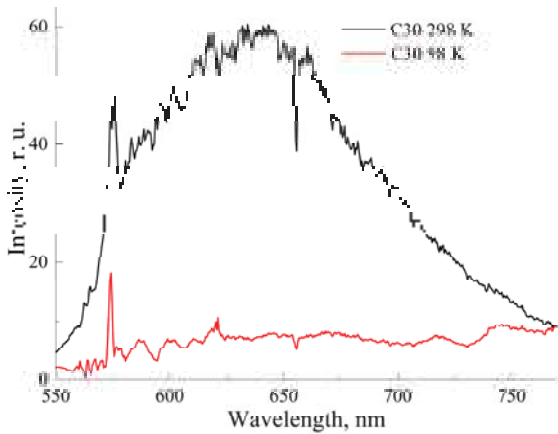
For example, the intensity of the zero-phonon line (N-V⁰ center) at the temperature 81 K is 3 times higher than at the room temperature. The dependence of the maximum of this line has exponential nature.

The general intensity level of the phonon wing also decreases with decreasing the temperature of the specimen.

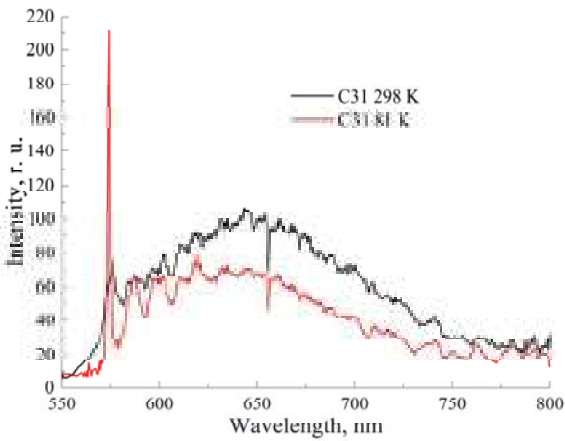
Both of this processes correlate with the theory that an increase in temperature leads to a weakening of the zero-phonon line and “transfer” of energy to the phonon wing (the total intensity is practically independent of temperature) [7].



(a)



(b)



(c)

Fig. 2. Comparison of cathodoluminescence spectra of C29 (a), C30 (b) and C31 (c) specimens at the room and liquid nitrogen temperature.

In addition, there is an increase in the intensity of phonon repetitions with decreasing the specimen temperature, as well as their more pronounced and clear character – for example the difference between the black and brown curves in Fig. 4.

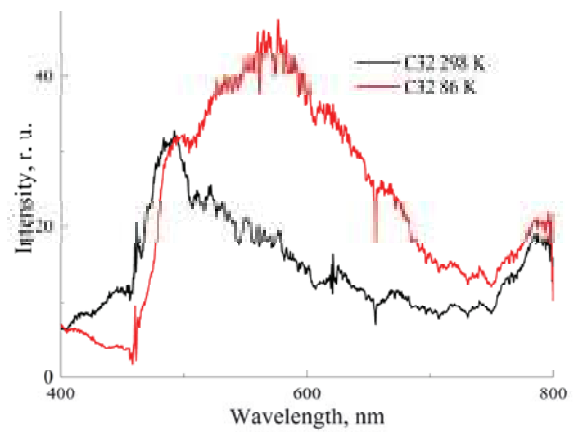


Fig. 3. Comparison of cathodoluminescence spectrum of C32 specimen at the room and liquid nitrogen temperature.

All of the above samples have cathodoluminescence only in the visible region of the spectrum. An interesting situation is when a diamond sample has luminescence in the ultraviolet region. Such a sample could help in the creation of a cathodoluminescent source of ultraviolet radiation. Since various mercury lamps, which are excellent sources of UV radiation, are rejected all over the world, there is a public demand to find new such sources.

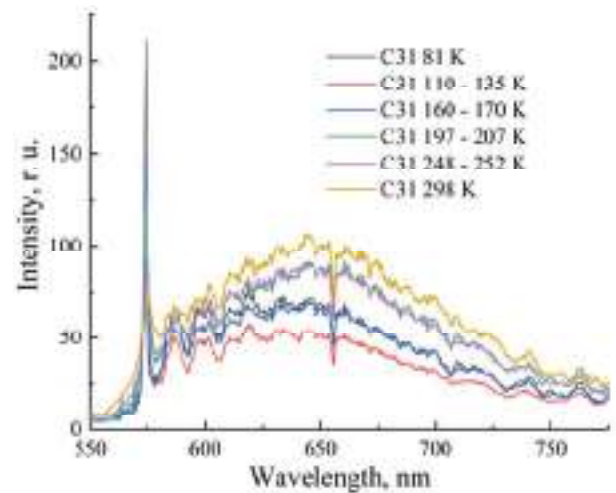


Fig. 4. Temperature dependence of cathodoluminescence intensity of C31 specimen from 81 K to 298 K.

It is known from the literature that near the edge of fundamental absorption, the luminescence of diamond is associated with the recombination of excitons [8-10]. Free excitons in diamond recombine to generate phonons. The dominant is the line of recombination of free excitons (line at 235.2 nm). In addition, in the UV spectral region, one can observe the recombination of excitons on defects. Boron [11], dislocations, and nitrogen complexes can be such defects.

Fig. 5 shows the temperature dependence of C12 cathodoluminescence in UV region of spectrum.

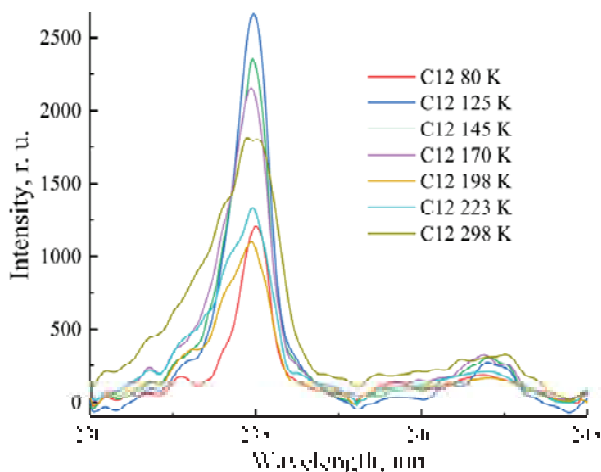


Fig. 5. Temperature dependence of cathodoluminescence intensity of C12 specimen in the UV region from 80 K to 298 K.

HPHT single crystal C12 excited by electron beam shows a free exciton (FE) radiative recombination band with a peak near 235.2 nm. It is observed that FE band restricted with decreasing the specimen temperature. The intensity of this line increases with decreasing temperature, as predicted in our previous work [12]. However, the dependence of the 235 nm line intensity on the sample temperature has a maximum at 125 K.

Another interesting result was obtained with cathodoluminescence of the C12 sample in the visible region of the spectrum.

Fig. 6 shows the temperature dependence of cathodoluminescence of C12 specimen in the visible (“green”) spectrum region. A wide band is observed with a maximum at 485 nm, which corresponds to Ni-defect in the diamond.

A decrease in the luminescence intensity was observed with decreasing the sample temperature, as well as the full «freezing» of the cathodoluminescence radiation at the temperature below 224 K. The background from cathodoluminescence in the visible region of the spectrum “illuminated” the rest of the luminescence of the sample (including in the UV region).

The cooling of the sample led not only to an increase in the cathodoluminescence intensity of diamond at the edge of fundamental absorption (Fig. 5, 235.2 nm), but also to the elimination of more intense luminescence in the visible region.

Such a sample looks like a real contender for creating a UV cathodoluminescent radiation source and requires further study.

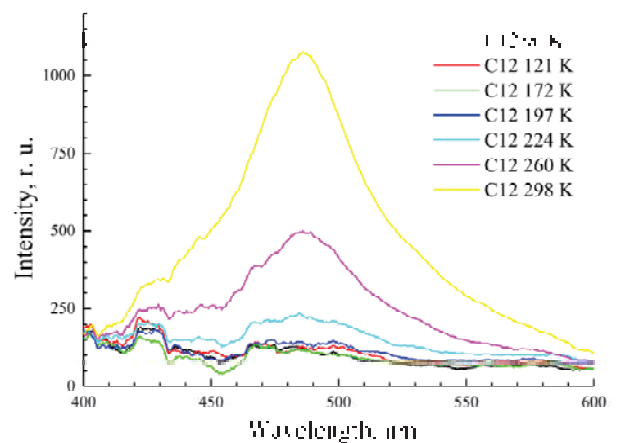


Fig. 6. Temperature dependence of cathodoluminescence intensity of C12 specimen in the visible region from 90 K to 298 K.

IV. CONCLUSION

In our work we investigated the optical cathodoluminescence (in the range of 200 – 1100 nm) of five HPHT synthesized diamond samples at the temperature range of 80 – 300 K.

Specimens C29, C30, C31 showed an increase in the intensity of the phononless line at a wavelength of 575 nm with decreasing the specimen temperature.

Cathodoluminescence of C32 specimen has a different character than for C29-C30 specimens, which requires further investigation.

Single crystal C12 synthesized by the HPHT method exhibited a strong free excitons radiative recombination band at 235.2 nm and “freezing” of cathodoluminescence in the range 400 - 600 nm with decreasing temperature.

Based on the experimental data obtained, it can be concluded that the C12 sample can be a good candidate for the role of a source of cathodoluminescence of UV radiation.

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