
PHYSICAL PROPERTIES
OF CRYSTALS

Secondary Radiation in Microdiamonds with NV Centers

V. S. Gorelik^{a,b,*}, S. A. Savinov^a, V. V. Sychev^a, and D. Bi^b

^a Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119991 Russia

^b Bauman Moscow State Technical University, Moscow, 105005 Russia

*e-mail: gorelik@sci.lebedev.ru

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Abstract—The regularities in the secondary radiation (fluorescence and Raman) spectra of single diamond microcrystals have been investigated. The Raman spectrum excited by infrared laser radiation exhibits the fundamental diamond mode with a frequency of 1332 cm^{-1} and a two-phonon band peaking at a frequency of 2615 cm^{-1} . The fluorescence spectra contain zero-phonon lines of NV centers with a pronounced phonon structure.

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INTRODUCTION

Diamond is characterized by several unique properties: chemical stability, mechanical strength, large bandgap energy, record thermal conductivity, and high Debye temperature. The optical properties of diamond crystals, in particular, photoluminescence (PL) spectra, were analyzed in many studies [1–3]. The Raman spectra of diamonds of various types were investigated in [4–13]. A strong peak with a frequency of 1332 cm^{-1} , corresponding to the optical phonon near the Brillouin zone center (with a quasi-momentum close to zero), was found in the Raman spectra of natural diamonds. A work second-order Raman continuum, corresponding to two-phonon scattering processes with participation of phonon pairs from the entire Brillouin zone, including its boundaries, was registered in the Raman spectrum of natural diamonds at a higher excitation intensity [8, 9]. The secondary-radiation spectra of natural diamonds with impurities contain also luminescent bands due to the deexcitation of impurity centers. Photoluminescence was practically absent in pure diamond crystals because of their large bandgap (5 eV), and the samples were colorless.

Centers with nitrogen atoms incorporated into the diamond crystal lattice are most widespread and best studied among several hundreds of observed color centers [1]. The most interesting ones are NV centers, which are formed by a nitrogen atom and a vacancy located nearby along the {111} diagonal of face-centered cubic diamond lattice. The centers exist in two charge states: neutral NV^0 and negatively charged NV^- ; the optical properties of the latter demonstrate a spin-dependent character of PL. The paramagnetism of NV^- center with a possibility of optical recording

and reading of spin state became a basis for studies in the field of quantum technologies [14] (communication channels protected by quantum physics laws, quantum computers, quantum sensors). The studies of the quantum memory on ^{13}C nuclei resulted in a new direction: optically induced hyperpolarizability, which provides a giant increase in sensitivity of the nuclear magnetic resonance and magnetic resonance tomography [15]. The formation of fluorescent labels for protection of industrial products and documents is another promising field of application of microdiamonds.

Commercially available diamond microcrystals with a nitrogen impurity content starting from 100 per mille (type *Ib*) are obtained by high pressure and high temperature (HPHT) synthesis. The issue of applicability of commercially produced microdiamond powders calls for development of techniques for analyzing the optical quality of samples. A possible solution is to combine Raman spectroscopy, which yields information on the crystal matrix quality, and analysis of PL spectra, which provides concentration ratio for NV^0 and NV^- centers.

The purpose of this work is to study the regularities of PL and Raman spectra of HPHT-synthesized single diamond microcrystals. The solution of this problem will facilitate application of commercially available microdiamonds for developments in the field of new quantum and biotechnologies and for protection of the market of industrial products and negotiable papers from counterfeit.

EXPERIMENTAL

The diamond microcrystals under study (Figs. 1a, 1b) were samples of yellow-green color, having a form of

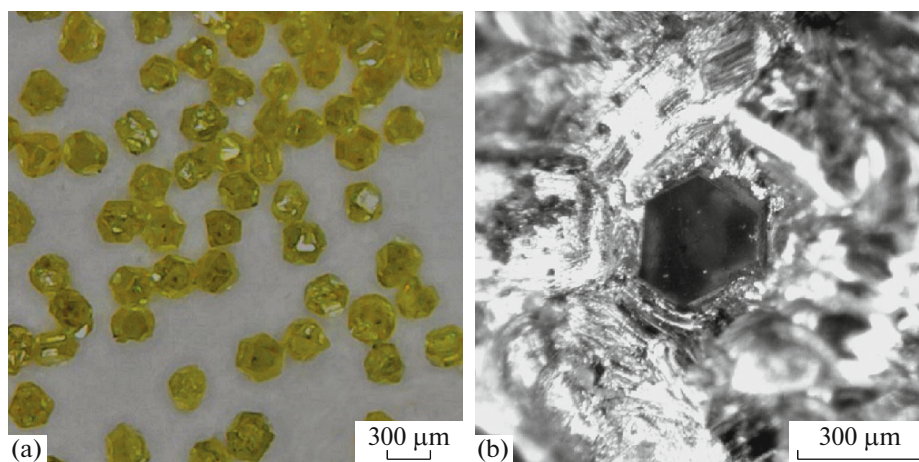


Fig. 1. Artificial diamond microcrystals: (a) the shape of microdiamonds with a size of 250–300 μm and (b) a single microdiamond inserted in an indium substrate.

regular polyhedra of close size ($d = 250\text{--}300\ \mu\text{m}$). The color of the samples is due to the presence of NV impurity centers in them. Similar HPHT-synthesized microcrystals were previously studied by Raman spectroscopy with excitation by infrared laser radiation at a wavelength of $\lambda_0 = 785\ \text{nm}$ [16, 17]. In the present work, the Raman spectra of a single diamond crystal were studied using the infrared excitation method reported in [16, 17]. In addition, we applied a laser with a wavelength $\lambda_0 = 532\ \text{nm}$ to excite secondary

radiation (PL or Raman) spectra. To exclude the contribution of the substrate signal to the analyzed PL spectra, the samples were inserted in a hole filled with indium (Fig. 1b).

The secondary radiation spectra were studied on a setup whose layout is presented in Fig. 2. A cw laser (1) with a lasing wavelength $\lambda_0 = 532\ \text{nm}$ and power 1 mW was used as an excitation source. After band interference filter (3), the laser radiation was reflected from dichroic beamsplitter (4) and focused by microscope objective (5) on sample (6). The PL and Raman scattering radiation, collected by the same objective, passed successively through dichroic filter (4) and notch filter (7) to be focused by lens (8) on the entrance slit of SpectraPro-2300i spectrometer (9) with a cooled light-sensitive CCD array PIXIS-100.

The registration of secondary radiation spectra and their primary processing were performed under control of special computer program WinSpec. The spectral and spatial resolutions of the spectrometer were, respectively, 0.3 nm and $\sim 1\ \mu\text{m}$. The total secondary radiation spectrum of microdiamonds in the range of 550–800 nm was recorded at exposures of about 10 s. The measurements were performed at room temperature.

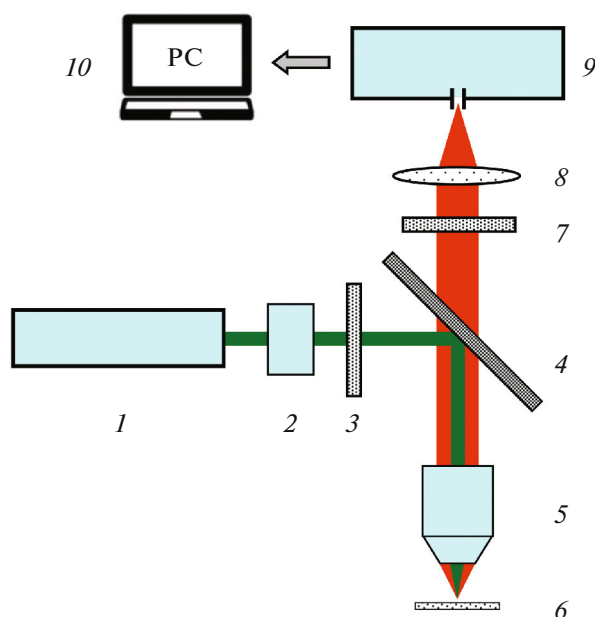


Fig. 2. Schematic of the experimental setup for studying the secondary radiation spectra of microdiamonds: (1) laser, (2) attenuator, (3) band interference filter, (4) dichroic beamsplitter, (5) microscope objective $\times 40$, (6) sample, (7) notch filter, (8) lens, (9) spectrometer, and (10) computer.

RESULTS AND DISCUSSION

The spontaneous Raman spectrum of a diamond microcrystal 300 μm in size, excited at the wavelength $\lambda_0 = 785\ \text{nm}$, is shown in Fig. 3. It contains a strong Raman peak with a frequency of $1332\ \text{cm}^{-1}$. Along with the fundamental peak, there is a two-phonon peak with a frequency shift of $2615\ \text{cm}^{-1}$.

Figure 4 presents the secondary radiation spectra of a single diamond upon excitation at the wavelength $\lambda_0 = 532\ \text{nm}$; the incident radiation intensities are 10^4 and $10^5\ \text{W}/\text{cm}^2$. One can observe intensive PL bands

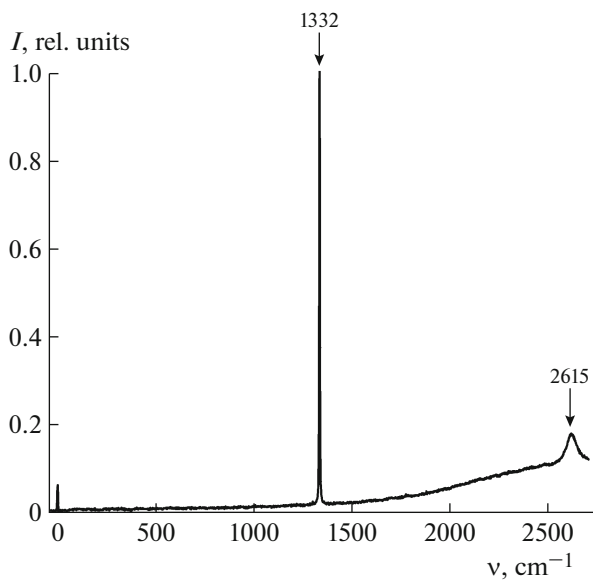


Fig. 3. Normalized Raman spectrum of a 300- μm microdiamond sample (the excitation wavelength is $\lambda_0 = 785 \text{ nm}$).

in addition to the fundamental Raman peak of diamond with a frequency of 1332 cm^{-1} . The PL maxima near 576 and 637 nm are due to PL zero phonon lines (ZPLs) of uncharged (NV^0) and charged (NV^-) centers, respectively. The phonon repetition bands of paramagnetic NV centers extend up to 800 nm. Since the concentration of impurity nitrogen atoms in the diamonds studied exceeds 100 permille, the immediate environment of an NV center contains a sufficiently large number of electrons to form NV^- charged states [18].

When the laser radiation intensity increases from 10^4 to 10^5 W/cm^2 , one observes the well-known effect of photoionization of NV^- centers and their conversion into NV^0 centers [19], which manifests itself in the increase in the magnitude of ZPL peak of NV^0 center (Fig. 4b). In this case, the process is reversible: when the intensity decreases to the initial level, the spectrum recovers its shape.

We did not observe any noticeable changes in the spectra during experiments, both upon mapping a separate sample and upon its replacement by another sample from a given series. This fact indicates a high quality of microcrystals and the absence of inhomogeneities in the spatial distribution of NV centers throughout the sample.

CONCLUSIONS

Based on the measurements performed with a high spatial resolution ($\sim 1 \mu\text{m}$), strong PL peaks (along with the fundamental Raman band with a frequency shift of 1332 cm^{-1}) were found in the secondary radiation spectra of HPHT-synthesized single diamond microcrystals with a size of $d = 250\text{--}300 \mu\text{m}$. These peaks are due to the presence of paramagnetic NV centers in the samples at room temperature, which correspond to zero-phonon impurity excitons in the visible region.

HPHT diamond microcrystals with a high concentration of paramagnetic NV centers are of interest for forming an ordered electron magnetic structure under a dc magnetic field. The presence of a small amount of C^{13} isotopes in the synthesized diamonds is also promising for nuclear spin polarization. The high photosta-

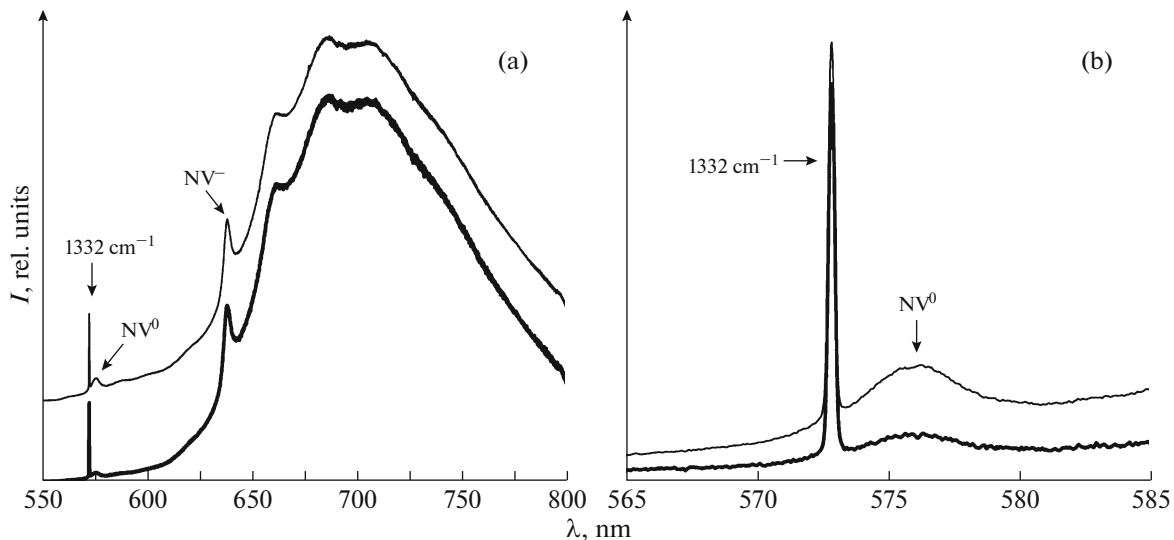


Fig. 4. PL spectra of a 300- μm microdiamond for two laser beam intensities, 10^5 W/cm^2 (thin line) and 10^4 W/cm^2 (bold line), normalized to the Raman signal magnitude: (a) panoramic spectrum and (b) a part of spectrum containing a zero phonon NV^0 line. The excitation wavelength is $\lambda_0 = 532 \text{ nm}$.

bility and biocompatibility of diamond microcrystals open new possibilities of their use in biophysical and quantum applications.

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