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The influence of methane concentration during chemical vapor deposition of diamond on the formation of needle-like crystallites with nitrogen vacancy centers

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A comparative study of the photoluminescent and cathodoluminescent characteristics of color centers in diamond needle-like crystallites was conducted. The diamond needles were extracted from polycrystalline films deposited from a direct current discharge-activated gas mixture of methane and hydrogen. During the growth of the diamond films, the methane concentration in the gas mixture was varied from 0.5 % to 3.5 %. The study revealed a significant influence of the methane concentration on the concentration and charge state of nitrogen-vacancy (NV) centers formed within the diamond needles. It was found that while the total concentration of NV centers decreases with increasing methane content, the relative fractions of the negatively charged (NV^-) and neutral (NV^0) centers exhibit a non-monotonic dependence. A local maximum in the concentration of NV^- centers and the minimum for NV^0 centers were observed at a methane concentration of 1.5 %. The results obtained can be used to optimize the luminescent characteristics of diamond needles for practical use in quantum optical devices.

Keywords: diamond needles, microscopy, luminescence, NV centers, chemical vapor deposition.

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Diamond materials have unique physical and chemical properties and form a promising basis for the development of new devices in quantum information science [1,2], magnetometry [3], and sensorics [4]. The practical implementation of these technologies, in particular those involving color centers, require the synthesis of diamond structures with specified geometric characteristics (including filamentary or needle-like structures) and an acceptable degree of imperfection. The most widespread methods to the formation of single-crystal diamond needle-like structures are those based on the processing of bulk crystals (see, e.g., [5,6]). Despite their effectiveness, these methods are characterized by a significant technological complexity and high production costs, which stimulates the search for alternative strategies for synthesis of diamond materials with specified structural and morphological parameters. One promising alternative is chemical vapor deposition, which provides an opportunity to obtain pyramidal and needle-like diamond crystallites with a high degree of structural perfection [7].

Potential approaches to the formation of various color centers (SiV, NV, GeV) in needle-like diamond structures were considered in [8] . Among the various types of diamond crystal lattice defects with promising applications in quantum optical devices, nitrogen-vacancy (NV) centers, which are one of the best-studied point defects with stable luminescent properties, attract special attention. NV centers exist in two optically active charge states: neutral (NV^0) and negative (NV^-). Different ratios of these states are needed in different operating conditions.

Despite the critical importance of the charge state of luminescent centers in the development of quantum-optical nanosensors, the problem of their controlled formation during the synthesis of diamond structures remains unsolved. In the present study, we investigate the dependence of concentration and luminescent characteristics of NV centers on the methane concentration during chemical vapor deposition.

The examined textured diamond polycrystalline films were synthesized by carbon deposition from a DC discharge-activated methane-hydrogen gas mixture using the setup discussed in detail in [9]. The reaction chamber has two cylindrical electrodes 100 mm in diameter. Their flat end surfaces were positioned horizontally and parallel to each other with an interelectrode gap of 50 mm. The upper electrode (cathode) was connected to the negative pole of a DC source, and the lower electrode (anode), which serves as a substrate holder, was grounded. Substrates 20×20 mm in size were made from standard silicon wafers. The substrate temperature was 900 °C. The other parameters of the deposition process were as follows: interelectrode voltage, 900 V; current, 7 A; pressure in the chamber, 9.5 kPa.

It should be noted that small amounts of impurities (nitrogen included) enter the reaction chamber in the process of deposition due to imperfect sealing of the reactor

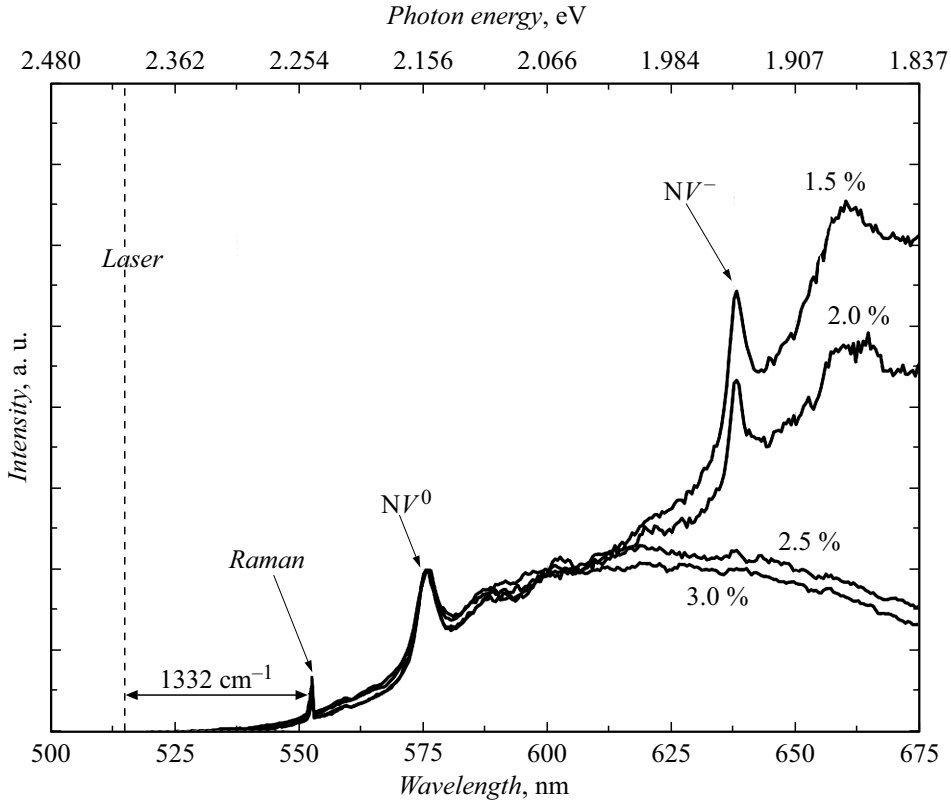

Figure 1. Photoluminescence spectra of diamond needles synthesized at different concentrations of methane in the gas mixture: 1.5, 2.0, 2.5, and 3.0 %. The laser radiation wavelength is 514.5 nm. The laser radiation power on the sample surface is 217 μW (the exposure time is 4 min).

or gas supply lines and due to the presence of impurities in the gases used (hydrogen and methane). The removal of such uncontrolled impurities requires significant and costly technical effort. It was noted in most studies that such impurities induce the formation of nitrogen-related luminescent centers in diamond with a certain concentration level, which is taken as a minimum.

Selective oxidation of the synthesized films was carried out in air using a PT-1.3-20 tubular furnace. The temperature regime and duration of the oxidation process were optimized in accordance with the data of our previous study [10] and were set to 630 °C and 50 h, respectively. Following oxidation, a white powdery material consisting predominantly of pyramidal diamond single crystals was left on the substrate surface.

Structural and morphological analysis of the synthesized samples was performed using LEO 1550 Zeiss (electron energy, 5 keV) and JEOL JSM-7001F scanning electron microscopes (SEM) and a GATAN MonoCL3 attachment designed to record cathodoluminescence (CL). Raman optical spectroscopic studies were also carried out using Jobin Yvon U1000 (laser excitation wavelength, 514.5 nm) and RENISHAW inVia (laser wavelengths, 514 and 785 nm) spectrometers. These spectrometers also provided the opportunity to study the photoluminescent (PL) characteristics of the synthesized samples (confocal studies included). CL and PL measurements were performed at room temperature.

A series of carbon films with the methane content varying within the 0.5−3.5 % range were synthesized in order to study the influence of methane concentration in the gas phase on the formation processes of nitrogen-vacancy centers in diamond needles. The PL spectra of point defects in single-crystal diamond are characterized by a relatively narrow band of zero-phonon luminescence (ZPL) and an accompanying set of phonon repetitions localized in the long-wavelength region of the spectrum. Figure 1 shows the typical PL spectra of diamond needles synthesized at different methane concentrations. All these spectra are normalized to the intensity of the 575 nm peak corresponding to ZPL of an NV^0 center. ZPL of NV^0 centers at a wavelength of 575 nm and NV^- at 637 nm and bands associated with phonon-associated energy levels were identified in all the recorded spectra. In addition, the spectra also contain a Raman signal, which is manifested as a narrow peak near 552 nm corresponding to the optical phonon mode of diamond [11].

Having analyzed the PL spectra, we found a pronounced dependence of the ratio of charge states of NV centers on the concentration of methane during the chemical vapor deposition process. As the methane concentration increases from 0.5 to 1.5 %, the intensity of the ZPL line of NV^-

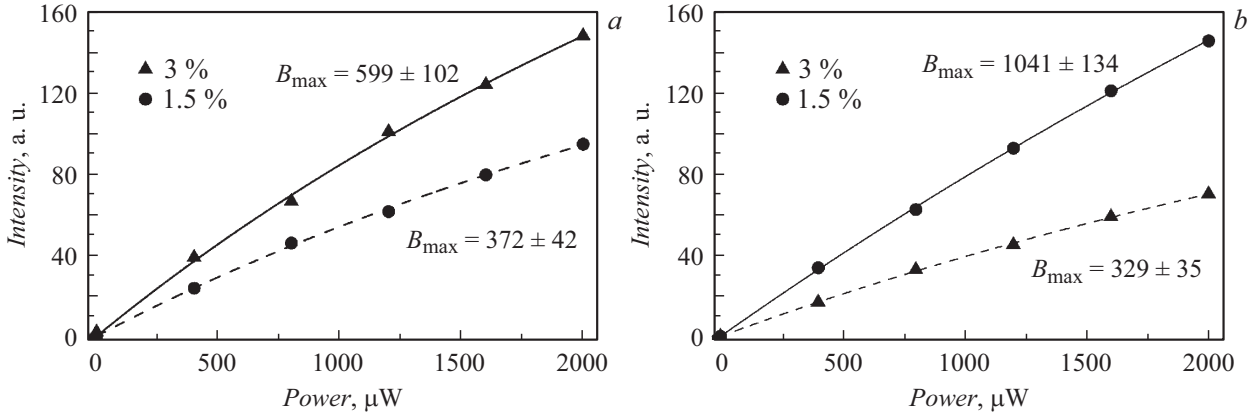

Figure 2. Characteristic dependences of the luminescence intensity on the laser radiation power for NV^0 (*a*) and NV^- centers (*b*) in diamond needles for the samples obtained at methane concentrations of 1.5 and 3 % during synthesis. Experimental data for the samples with 3 % and 1.5 % of methane are denoted by triangles and circles, respectively. Solid and dashed curves represent the results of approximation by function $B(P) = B_{max}P/(A + P)$, where variable P is the laser radiation power and A and B_{max} are the approximation parameters.

grows monotonically, reaching a maximum value at a concentration of 1.5 %. A further increase in methane concentration to 3.5 % leads to a reduction in intensity of the NV^- ZPL line. It is fair to assume that the intensity of the NV^- ZPL line is proportional to the concentration of centers of this type. An approach similar to that detailed in [12] may be used to determine the relative ratios of NV^0 and NV^- concentrations. It is taken into account that each radiative recombination event following optical excitation is characterized by a certain time interval, which is unique to a particular type of center. This results in luminescence saturation: when the threshold power of optical excitation acting on a fixed ensemble of centers is exceeded, a further increase in pump intensity does not translate into an increase in luminescence intensity [13].

To obtain relative estimates of the concentration of N*V* centers, PL of diamond needles synthesized at methane concentrations of 1.5 and 3 % was measured with the power of excitation laser radiation varying within the range of $0.7-2000\,\mu$W. The obtained dependences of luminescence intensity on excitation power are presented in Fig. 2. The experimental dependences are approximated by an analytical function $B(P) = B_{max}P/(A + P)$, where variable P is the laser radiation power and A and B_{max} are the approximation parameters. The corresponding saturation levels B_{max} are shown in Fig. 2 for different types of centers in diamond needles obtained at methane concentrations of 1.5 and 3 %.

Saturation intensities B_{max} presented in Fig. 2 are proportional to the concentrations of the corresponding N*V* centers. Thus, the data presented in Fig. 2 reveal that a reduction in methane concentration from 3 to 1.5 % during synthesis leads to contradirectional changes in the concentrations of centers of different types: the concentration of neutral NV^0 centers decreases (the B_{max} value drops from 599 to 372 a.u.), while the concentration of negatively charged NV^- centers grows (the B_{max} value increases from 329 to 1041 a.u.).

CL of needle-like diamond crystallite samples was also examined in order to investigate the influence of variations of methane concentration during deposition on the integral efficiency of formation of N*V* centers. It is known that the signal from negatively charged NV^- centers in CL spectra is lacking or suppressed strongly as a result of their conversion to neutral state NV^0 under the influence of an electron beam [14,15]. Thus, the CL intensity should correspond to the total concentration of N*V* centers irrespective of their charge state.

Diamond needles were synthesized with dynamic adjustment of the gas mixture composition in order to visualize the influence of methane concentration on the formation of N*V* centers. Deposition proceeded under a methane concentration of 3.0 % for 48 h, and then the concentration was reduced to 1.5 %. Figure 3 shows the SEM image and the distribution of CL intensity recorded in the spectral range of luminescence of NV^0 centers (in a 2-nm-wide band with its center at 575 nm) for a diamond needle synthesized with dynamic adjustment of the composition of the gas mixture. The CL intensity distribution map (Fig. 3, *b*) reveals a clear interface between the needle parts that were formed at methane concentrations of 3.0 and 1.5 %. A lower methane concentration resulted in a significant increase in CL intensity and the concentration of N*V* centers. The experimentally discovered dependences of the number of NV^0 and NV^- centers and the absolute values of concentration determined earlier [12] suggest a qualitative conclusion regarding the nature of changes in their concentration. These changes are shown schematically in Fig. 4 and include the assumption that the sum of partial concentrations of NV^0 and NV^- is equal to the integral concentration of N*V* centers, which decreases monotonically as the methane concentration increases from 0.5 to 3.5 %. A methane concentration in the gas mixture of 1.5 % in the

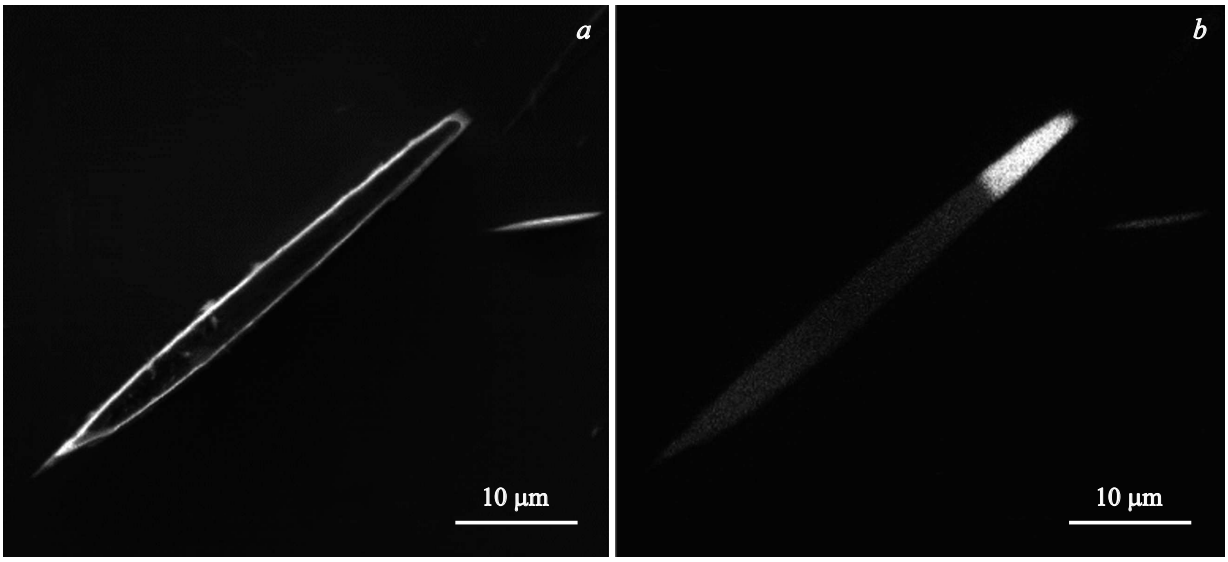

Figure 3. Diamond needle obtained by varying the methane concentration in the gas medium during synthesis from 3.0 to 1.5 %. *a* — SEM image; *b* — cathodoluminescence map for a wavelength of 575 nm (near the ZPL of NV^0 centers). The brightness of the needle is proportional to the intensity of recorded radiation.

process of diamond formation corresponds to the maximum relative fraction of NV^- centers with a fairly low value of the concentration of NV^0 centers. The specified methane content is optimal, e. g., for the synthesis of diamond films and needles for magnetometers, the operation of which involves the use of single isolated NV^- centers [16].

The obtained data are consistent with recent studies [17,18] indicating that a reduction in concentration of NV centers may be induced by carbon diffusion, which leads to vacancy recombination. The intensity of such diffusion and recombination increases with increasing concentration of methane in the gas medium.

Thus, a comparative analysis of PL and CL of diamond needles obtained with different methane concentrations in the gas mixture during deposition is indicative of a general monotonic reduction in concentration of such (NV) centers with an increase in methane concentration from 0.5 to 3.5 %.

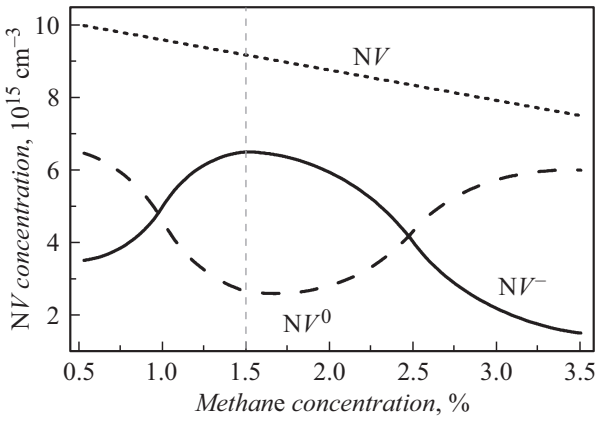

Figure 4. Dependence of partial concentrations of neutral (NV^0) and negatively charged (NV^-) centers in diamond needles on the concentration of methane in the gas medium during synthesis.

The partial concentrations of NV^- and NV^0 centers vary non-monotonically in such a way that a concentration of methane in the gas mixture of 1.5 % corresponds to the maximum relative fraction of NV^- centers at a sufficiently low value of concentration of NV^0 centers. The obtained results may be used to optimize the production processes of diamond materials intended for application in various devices.

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Conflict of interest

The authors declare that they have no conflict of interest.

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