

USE OF OPTICAL SPECTROSCOPY METHODS TO DETERMINE THE SOLUBILITY LIMIT FOR NITROGEN IN DIAMOND SINGLE CRYSTALS SYNTHESIZED BY CHEMICAL VAPOR DEPOSITION

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We have studied the upper limits for incorporation of nitrogen and formation of arrays of nitrogen–vacancy (NV) color centers in optical-quality single-crystalline diamond synthesized by chemical vapor deposition (CVD). The CVD diamond samples were grown in a microwave plasma in methane–hydrogen mixtures with high content (200–2000 ppm) of the nitrogen dopant in the gas mixture, and were analyzed using Raman and photoluminescence spectroscopy. From the UV absorption spectra, we established that the solubility limit for substitutional nitrogen in the studied material is close to $2 \cdot 10^{18} \text{ cm}^{-3}$ (under typical synthesis conditions), which lets us in particular form arrays of NV center with similar concentrations by means of irradiation and annealing.

Keywords: luminescence, diamond, impurity center, synthesis by chemical vapor deposition, nitrogen–vacancy center.

Introduction. The growing interest in recent years in studying luminescent and spin properties of color centers in diamond based on an impurity nitrogen atom, forming a complex with vacancies in the diamond lattice (NV centers), is due to their promise for application in various modern technologies ranging from quantum information technologies [1–3] to biomedical technologies [4, 5]. Efficient and stable photoluminescence (PL) is observed for two charge states of NV centers: neutral (NV^0) with an electronic transition not involving a phonon at $\lambda = 575 \text{ nm}$, and negatively charged (NV^-) with a transition at 637 nm.

Scanning confocal luminescent microscopy is widely used today for targeted manipulation of emitting centers in diamond [6]. This method limits the planar resolution of individual emitters to the $1 \mu\text{m}^{-2}$ level. However, development of modern optical microscopy methods such as near-field scanning optical microscopy (NSOM) and stimulated emission depletion microscopy (STED), permits achievement of resolution limits on the order of 10 nm, i.e., lets us completely resolve arrays of point light sources of density up to $10,000 \mu\text{m}^{-2}$. Note that the 2014 Nobel Prize in Chemistry was awarded just for development of super-resolution STED microscopy [7]. Optimal methods for creating such close-packed arrays of NV centers and their effect on the optical and spin properties of the NV centers have not yet been systematically studied. A necessary condition for achieving high concentrations of NV centers is to increase the nitrogen impurity content in the diamond as much as possible, preferably in the form of paramagnetic substitutional nitrogen (N_s), which is converted to NV by creating vacancies by bombardment with high-energy particles, followed by annealing [8]. Thus when synthetic diamond single crystals grown under high pressures (HPHT diamond) and containing 100–200 ppm single paramagnetic nitrogen (in diamond, 1 ppm = $1.78 \cdot 10^{17} \text{ cm}^{-3}$) are bombarded by protons, the conversion efficiency for converting N_s to NV^- is ~10% [9].

Close-packed NV arrays are usually obtained by implantation of nitrogen into diamond. However, synthesis of diamond by vapor phase deposition (the CVD method) is more promising for these purposes, where nitrogen is introduced into the crystal or film during their growth. In contrast to implanted nitrogen, which inevitably creates structural defects in the

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diamond lattice in the vicinity of the nitrogen, the nitrogen atom in CVD diamond can be found in a defect-free environment. Furthermore, in CVD diamond with low content of paramagnetic defects ($<10^{13} \text{ cm}^{-3}$), the dephasing time for the electron spin of the NV^- centers reaches record high values for diamond in a few milliseconds at room temperature [10]. Recently [11] it was reported that there is preferential formation of NV centers in two directions of $\langle 111 \rangle$ crystallographic axes instead of the four possible directions for CVD synthesis of single-crystalline diamond in the $\langle 110 \rangle$ direction. The preferred orientation of the NV centers is quite important, for example, for creating ultrasensitive magnetometers and temperature sensors with high planar resolution that are based on large arrays of NV centers in thin diamond films [12].

An effect from adding nitrogen N_2 to the growth gas mixture (usually CH_4/H_2) on the growth rate of diamond films has been observed for a rather long time, while the efficiency of incorporation of nitrogen from the gas into the diamond lattice, or its solubility in diamond, has been mentioned in only a few publications. The nature of the several-fold increase in the diamond growth rate from nitrogen-containing mixtures is still under debate. For low nitrogen concentrations C_{N_2} in the gas (usually $<100\text{--}200 \text{ ppm}$), the growth rate increases as C_{N_2} increases [13, 14]. In [15, 16], it was established that in single crystals of CVD diamond, the amount of substitutional nitrogen, monitored by either EPR [15] or secondary-ion mass spectrometry (SIMS) [16], also increases with an increase in C_{N_2} in the range $0\text{--}200 \text{ ppm}$. For high nitrogen concentrations in the gas mixture, we see saturation of the growth rate [17] and at the same time saturation in the content of nitrogen incorporated into the diamond, as established using SIMS [14]. Recent calculations using density functional theory have observed an important effect specifically from the nitrogen atom incorporated in a substitutional position (rather than adsorbed on the growth surface) on the rate of deposition of single-crystalline diamond [18]. Thus saturation in the growth rate of the crystal can be used as an indicator of saturation of the nitrogen impurity in diamond. However, the absolute concentration of the incorporated nitrogen in CVD diamond in the saturation regime may depend on the synthesis conditions.

In this paper, we have used optical spectroscopy methods to study the upper limits for creating nitrogen centers in single-crystalline CVD diamond when it is grown in the region of high ($\geq 200 \text{ ppm}$) N_2 concentrations in the gas, under conditions when high structural perfection is preserved, as is necessary to achieve high photoluminescence efficiency for the NV centers.

The Experiment. In order to determine the dependence of the growth rate of single-crystalline layers of diamond on the nitrogen concentration in the gas mixture $\text{CH}_4(4\%)/\text{H}_2$, we synthesized five samples with addition of N_2 in the amounts of 0, 20, 200, 1000, and 2000 ppm. We studied the optical properties of three samples obtained for the highest nitrogen concentrations in the mixture: 200 ppm (sample *A*), 1000 ppm (*B*), and 2000 ppm (*C*). All the samples were grown in a microwave plasma chemical reactor (iPlas GmbH, Germany; frequency 2.45 GHz). The substrates for epitaxial growth were commercially available polished plates of CVD diamond (Element Six) of size $2 \times 2 \times 0.5 \text{ mm}$, with nitrogen impurity content $<1 \text{ ppm}$ and (001) crystallographic orientation of the growth face. The general gas flow rate in the experiments was $500 \text{ cm}^3/\text{minute}$; pressure in the chamber, 200 mbar; microwave power 3.8 kW; substrate temperature, $800\text{--}850^\circ\text{C}$.

The samples obtained were studied using optical microscopy, UV absorption spectroscopy, and confocal luminescent spectroscopy. The optical Raman and photoluminescence spectra were recorded on a LabRam-800 spectrometer with excitation by the emission from a semiconductor laser at $\lambda = 473 \text{ nm}$, while the UV/visible absorption spectra were recorded on a Specord 400M double-beam spectrophotometer. The basic characteristics of the samples (in the nitrogen-doped layer of CVD diamond) and the concentrations of nitrogen and NV centers in them are given in Table 1.

Results and Discussion. Figure 1 shows a typical surface relief for sample *C*, obtained using an optical microscope. The surface has a wavy structure with terraces, which is typical for fast epitaxial growth of diamond [17]. The dependence of the growth rate for the diamond layer on the concentration of nitrogen introduced into the chamber is shown in Fig. 2. For undoped diamond, the growth rate is $6 \mu\text{m}/\text{h}$. Adding N_2 in amounts up to $\approx 200 \text{ ppm}$ promotes an up to four-fold increase in the growth rate, which upon further enrichment of the mixture with nitrogen, goes to a plateau at the $24 \pm 4 \mu\text{m}/\text{h}$ level.

The UV absorption spectra of the samples were recorded in the range $200\text{--}400 \text{ nm}$ at room temperature. The concentration of nitrogen incorporated into the sample was determined from the intensity of the absorption line at 270 nm (Fig. 3), proportional to the amount of single substitutional nitrogen atoms N_s . The procedure for identifying the 270 nm line on a background of broadband absorption is described in detail in [19]. In sample *A*, the concentration of incorporated nitrogen is $\approx 8.5 \text{ ppm}$; in sample *B*, 8 ppm ; in sample *C*, 9.5 ppm (Table 1); in the undoped sample, $< 0.5 \text{ ppm}$; and in the substrate from the Element Six company, 0.09 ppm . Absorption due to impurity nitrogen in the substrate is taken into account in determining the nitrogen concentration in the CVD layer. Thus when the nitrogen content in the gas mixture is varied within the range $200\text{--}2000 \text{ ppm}$, the concentration of substitutional nitrogen in the diamond varies insignificantly (within 15%), which means that nitrogen solubility close to the saturation is achieved in the single-crystalline CVD diamond at a

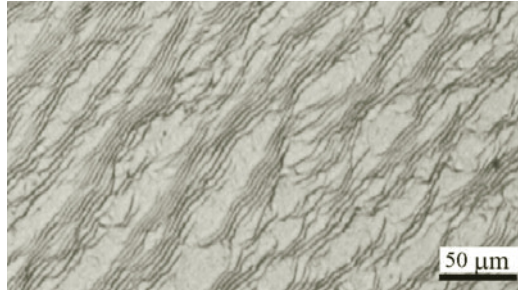


Fig. 1. Image of the surface of sample *C* under an optical microscope.

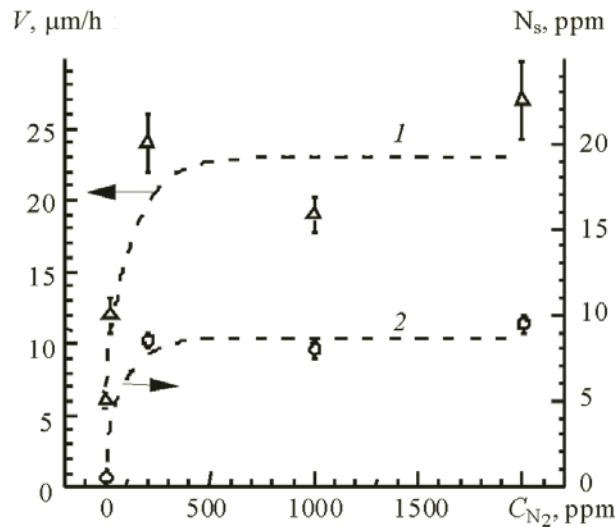


Fig. 2. Growth rate of diamond (*1*) and concentration of N_s centers (*2*) vs. nitrogen content in the gas; the point corresponding to a nitrogen concentration <100 ppb in diamond grown without addition of nitrogen to the gas mixture is taken from [17].

level of ~ 10 ppm, or $\approx 2 \cdot 10^{18} \text{ cm}^{-3}$. This conclusion is possibly limited to the region of substrate temperatures used and (100) orientations of their faces. In this work, the solubility limit for nitrogen was determined for single crystals of CVD diamond of high optical quality, which is confirmed by their visual transparency and the narrowness of the diamond peak in the Raman spectra. In single crystals of CVD diamonds obtained at significantly faster growth rates ($>100 \mu\text{m/h}$) and containing impurity of a graphite-like phase, the concentration of incorporated nitrogen may be as high as ~ 100 ppm [20, 21].

The quality of the synthesized diamond and the efficiency of formation of NV centers as the nitrogen concentration varies in the gas mixture were studied using confocal Raman and photoluminescence spectroscopy at room temperature. For all the samples, in the Raman spectrum we observe a narrow diamond line at a frequency of 1332.5 cm^{-1} (width 2.5 cm^{-1}) and no line for amorphous carbon at 1500 cm^{-1} or graphite at 1580 cm^{-1} . For comparison, for the same measurement conditions we determined the width of the Raman line at half-maximum for type IIa natural diamond, also equal to 2.5 cm^{-1} , which indicates that the synthesized diamond samples were of high quality. Taking into account the laser linewidth (1.4 cm^{-1}), the true Raman linewidth for the studied diamond films is 1.6 cm^{-1} [22].

The measurements of the photoluminescence spectra were made at 10 points in the center of the samples. The spread in the intensities of the photoluminescence lines for an individual sample is not more than 15% of the average value for each type of center. The luminescence spectra, averaged over 10 points, are shown in Fig. 4. The spectra are normalized to the intensity of the Raman line for diamond, proportional to the volume of the sample from which the photoluminescence is detected. The 504 nm line belongs to the Raman spectrum of diamond. In all the spectra, we observe three groups of bands associated with NV^0 and NV^- centers and also with the H3 (N_2V) center, which is a complex consisting of two substitutional

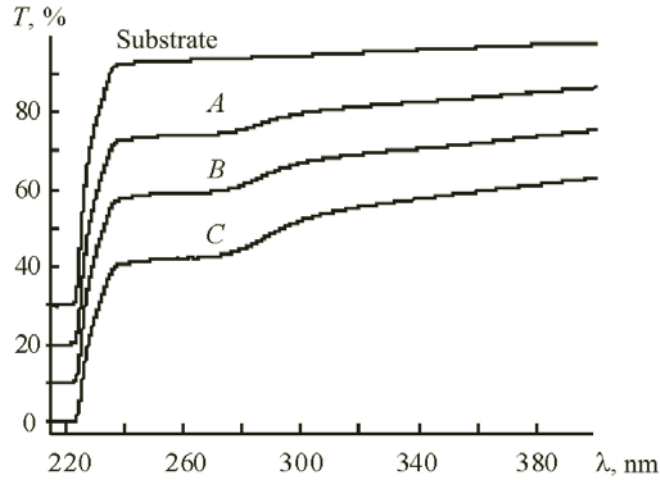


Fig. 3. UV absorption spectra for the studied samples; the concentration of N_s was determined from the integrated intensity of the absorption line at 270 nm. For clarity, the spectra are spaced 10% apart along the vertical.

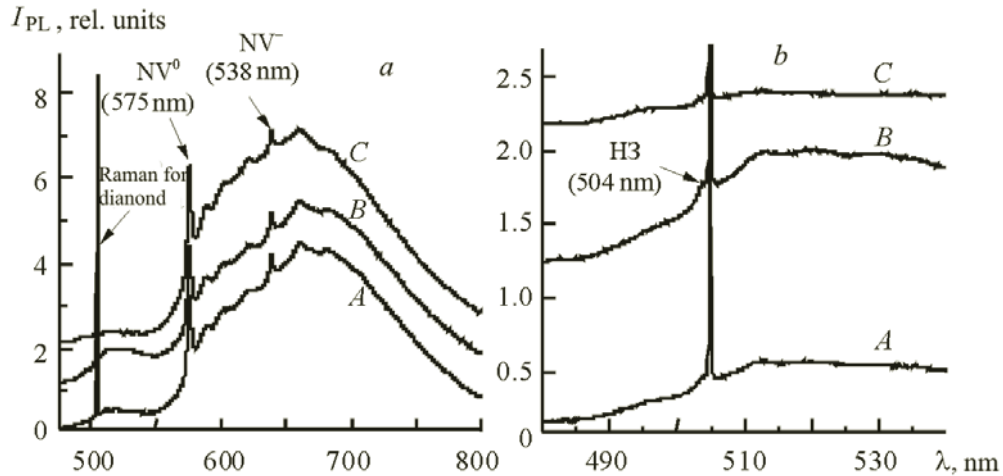


Fig. 4. Photoluminescence spectra of samples *A*, *B*, *C* in the ranges 480–800 nm (a) and 480–540 nm (b). For clarity, the spectra are spaced 1 relative unit apart along the vertical.

nitrogen atoms plus a vacancy between them. The source of the bands in the 550–630 nm range are NV^0 centers with main phononless band (PLB) at $\lambda = 575$ nm, and the source of the bands in the 630–800 nm range are NV^- centers with phononless band at 638 nm (Fig. 4a). The group of lines for the H3 center (N2V) with a phononless band at 504 nm is located in the 480–540 nm range (Fig. 4b).

A comparative evaluation of the relative concentrations of NV centers in different CVD diamond samples can be carried out using the photoluminescence intensity of these centers, provided that the interaction between NV centers and between NV centers and other defects in diamond are the same [23]. We assume that this condition is met for our samples, since the dominant defect is substitutional nitrogen and its concentration remains practically unchanged from sample to sample. Then we can hypothesize that the integrated photoluminescence intensities we measured are proportional to the total concentration of NV^0 and NV^- centers in the range 550–800 nm, and are proportional to the concentration of H3 centers in the range 480–540 nm (Table 1). As we see, the relative total concentration of NV centers, like the N_s concentration, varies insignificantly in the studied samples (~15%); the concentration of the H3 centers shows less stable behavior, varying from sample to sample by more than a factor of two. Thus our results indicate that with saturation relative to the growth rate of the diamond, saturation is also achieved relative to the number of N_s and NV centers formed in the diamond.

TABLE 1. Basic Characteristics of Studied Samples

| Sample | Thickness, μm | Nitrogen content in mixture, ppm | Nitrogen content in sample, ppm | Width of diamond Raman line, cm^{-1} | Luminescence intensity for H3 centers, rel. units | Luminescence intensity for NV^0+NV^- centers, rel. units |
|--------|--------------------------|----------------------------------|---------------------------------|---|---|--|
| A | 60 | 200 | 8.5 | 2.5(1.6)* | 32 | 690 |
| B | 80 | 1000 | 8 | 2.5(1.6) | 53 | 790 |
| C | 50 | 2000 | 9.5 | 2.5(1.6) | 25 | 700 |

*After taking into account the width of the laser line on which Raman scattering was excited.

In [11] it is shown that the ratio of the concentrations of NV/N_s in diamond single crystals synthesized in a microwave plasma is rather stable over a broad range of concentrations for the dopant nitrogen, and is $\sim 1/300$ for the $\langle 100 \rangle$ growth direction of the crystal. From this proportion and the concentrations of N_s determined from the absorption spectra, we obtain an estimate of the concentrations of NV centers for saturation of the diamond relative to nitrogen equal to ~ 30 ppb, i.e., saturation relative to the concentration of NV centers in deposited and unirradiated diamond layers is achieved at the $5 \cdot 10^3 \mu\text{m}^{-3}$ level.

Single substitutional nitrogen in diamond can be converted to the NV form when a sufficient number of vacancies are created in it, with conversion efficiency $\sim 10\%$ [9]. In this case, for the studied samples we can achieve concentrations of NV centers equal to $\sim 10^5 \mu\text{m}^{-3}$, and for a thin film (10 nm) of CVD diamond, we obtain a quasi-two-dimensional array of NV centers with concentration $10^3 \mu\text{m}^{-2}$. Finally, this estimate is not universal, and depends on the CVD process conditions. Thus in our experiments, the substrate temperature is $\sim 800^\circ\text{C}$. In [13], it is shown that the maximum efficiency of NV center formation is achieved just at this temperature, and falls off as the substrate temperature increases. A change in the crystallographic direction of the plane of the substrate from $\langle 100 \rangle$ to $\langle 110 \rangle$ leads to a three-fold increase in the efficiency of incorporation of nitrogen into the substrate [11].

Conclusions. We have established that when single-crystalline diamond is doped with nitrogen during its synthesis in a microwave plasma in CH_4/H_2 mixtures, saturation relative to dissolution of nitrogen in the diamond is achieved for concentrations of the incorporated nitrogen equal to ~ 10 ppm, which corresponds to the highest attainable concentration of close-packed arrays of NV centers in single crystals of CVD diamond with high structural quality, at a $10^5 \mu\text{m}^{-3}$ level. We have confirmed that as the content of nitrogen introduced into the reactor increases, the growth rate of the diamond layer first increases and then reaches saturation, which is accompanied by saturation in the concentration of both the impurity substitutional nitrogen and the NV centers within the volume of the diamond.

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