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NOVEL NITROGEN-HYDROGEN DEFECTS IN CVD DIAMOND

A. M. Zaitsev[1, 2], K. Moe[2], W. Wang[2]

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[1] College of Staten Island, CUNY, NY 10314, USA
[2] Gemological Institute of America, New York, NY 10030, USA
Corresponding author: A. M. Zaitsev (Alexander.Zaitsev@csi.cuny.edu)

Nitrogen-doped CVD diamond treated with electron irradiation and subsequent annealing at temperatures from 860 to 1900 °C was studied using FTIR absorption. It was found that nitrogen impurity produces many novel optical centers active in infrared spectral range. The most prominent of them are ascribed to nitrogen-hydrogen complexes. These centers produce absorption lines at 2827, 2874, 2906, 2949, 2990, 3031, 3107, 3123 and 3310 cm^{-1}. Two characteristic absorptions at wavenumbers 1293 cm^{-1} and 1341 cm^{-1} were tentatively ascribed to a modified form of nitrogen A-aggregates. A conclusion has been made that in nitrogen-doped CVD diamonds nitrogen atoms may form nitrogen-hydrogen clusters, which are can be considered as modified A-defects.

Key words: CVD diamond; HPHT-grown synthetic diamond; nitrogen-hydrogen clusters; irradiated with electrons; high temperature annealing; FTIR spectroscopy; IR absorption.

INTRODUCTION

Nitrogen is a principal impurity in diamond [1, 2]. Like no other impurity, nitrogen influences all physical properties of diamond of any origin and type [2–5]. Nitrogen in diamond is one of the most studied impurity in solids. Quite extensive research on behavior of nitrogen in synthetic diamonds grown at high pressure (HPHT synthetic diamonds) has been conducted. In contrast, little is known about nitrogen in CVD-grown synthetic diamond. It is usually believed that behavior of nitrogen in CVD diamond is not much different from that in natural and/or HPHT-grown diamonds. However, some experimental facts suggest that nitrogen in CVD diamonds may behave differently. The most striking difference is the efficiency of doping during growth. It is difficult to introduce high concentration of optically active nitrogen into CVD diamond during growth [6]. Also, in CVD diamond, it is difficult to achieve substantial aggregation of C-defects (single substitutional nitrogen atoms) into A- and B-aggregates. In CVD diamond, nitrogen may produce numerous specific optical centers [7, 8, 9], which have not been reported in spectra taken from natural and HPHT-grown synthetic diamonds. The present communication presents further information on optical centers active in IR absorption in nitrogen-doped CVD diamond.

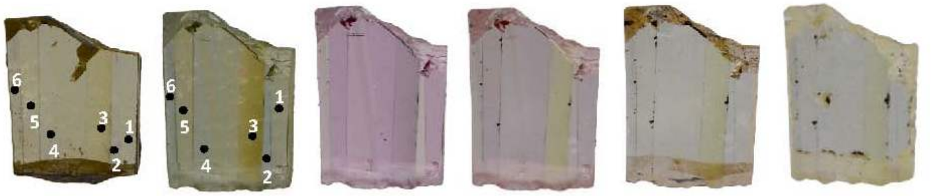
EXPERIMENTAL

The primary specimen used in this research was a 4 mm thick piece of nitrogen-doped yellow color CVD diamond commercially used for production of yellow and pink color gem diamonds. The specimen was cut in plane perpendicular to the growth surface (cross-sectional cut) in two sample plates of a thickness of 0.5 mm each. The samples revealed multilayered structure typical of commercial CVD diamonds. Five growth layers with very different intensity of yellow color were identified (Fig. 1). On each layer a spot was chosen for IR absorption measurements. These spots labeled from 1 to 6 are shown in Fig. 1. The spot 3 is on the layer with the most intense yellow color (layer 3). Since strength of yellow color directly relates to the concentration of nitrogen, layer 3 is discussed below as the high nitrogen layer. Layer 2 is the most colorless one and therefore we assume it contains the least concentration of nitrogen.

One of the samples was irradiated with electrons of energy 1 MeV to a dose of 3×10^{18} cm^{-2}. 1 MeV electrons penetrate 0.5 mm thick diamond through [10], so we assume that the distribution of radiation-induced defects over the sample volume is essentially uniform. After irradiation, the sample was annealed in four steps: at temperature 860°C for 30 minutes in vacuum, at temperature 1580°C for 30 min in vacuum, at temperature 1870°C for 3 minutes in vacuum, and at temperature of 1900°C in hydrogen at a pressure of 500 mbar for 20 minutes. For annealing, we used a commercially available graphite furnace HTT10 produced by Part Beam Sys MEO, Ltd [11].

Absorption measurements were performed at room temperature in a spectral range 650-4000 cm^{-1} in the regime of diffuse reflectance FTIR spectroscopy. Thermo Scientific Nicolet iS50 spectrometer was used for collecting spectra from the whole samples. Thermo

Scientific Nicolet iN10 FTIR Microscope equipped with motorized stage and 50×50 micron aperture was used for local measurements in spots shown in Fig. 1.



(*a*) as-received (*b*) as-irradiated (*c*) 860°C (*d*) 1580°C (*e*) 1870°C (*f*) 1900°C in H_2

Figure 1. – Optical images of two adjacent samples cut from yellow CVD diamond: sample 5254-1 (*a*) and sample 5254-2 (*b*). Location of spots chosen for the measurements are shown with black circles. Sample 5254-1 was kept and measured in the as-received state (*a*). Sample 5254-2 was irradiated (*b*) and subsequently annealed at temperatures as shown in (*c-f*)

VISUAL IMAGING

Visual images of samples reveal that intensity of yellow color considerably varies from layer to layer (Fig. 1). The yellow color is particularly strong in layer 3. Intensity of yellow color is not uniform through the growth layers. It may increase as the layer grows and it may also concentrate within stripes, which do not follow the orientation of the growing surface. After irradiation, low nitrogen layers turned bluish. The blue color is especially pronounced in the low nitrogen layer 2. In contrast, high nitrogen areas acquire some brownish component and become more distinctive.

After annealing at temperature 860°C, the irradiated sample turned pink (Fig. 1, c). The pink color was especially bright in the layers with moderate nitrogen concentration. The low nitrogen layer 2 showed negligible component of pink color. The high nitrogen layer 3 turned brown-pink. Annealing at temperature 1580 °C reduced pink color considerably. In the low nitrogen layer 2, pink color disappeared completely. High nitrogen layer 3 practically returned to its original yellow color. After high temperature annealing at temperatures 1870 and 1900 °C, the whole sample became significantly lighter and obvious yellow color retained only in the high nitrogen layer 3.

IR ABSORPTION

IR absorption measured on the sample in as-received state is shown in (Fig. 2, *a*). It reveals the presence of single nitrogen atoms (C-defects) represented by the component 1344 cm^{-1} of a broad line at 1342 cm^{-1} and a band at 1120 cm^{-1}. N^+ defects (positively charged nitrogen atoms) represented by a narrow line at 1332 cm^{-1} are detected too. The 1342 cm^{-1} line can be resolved in two components at 1341 and 1344 cm^{-1} (Fig. 3, *a*). There is also a band at wavenumber 1293 cm^{-1}. All these features were reported in nitrogen-doped CVD diamonds of pink color [7, 8]. No obvious presence of A-defects (band at 1282 cm^{-1}) and B-defects (band at 1175 cm^{-1}) could be detected.

The band 1293 cm^{-1} and the line 1341 cm^{-1} have not been reported in spectra of natural and HPHT-grown synthetic diamonds and as such they are probably unique of CVD diamonds. They are not detected in spectra of CVD diamonds with little nitrogen content but always present in spectra of nitrogen-doped CVD diamonds. The both absorptions are not seen in spectra of as-grown nitrogen-doped CVD diamonds, but they are generated by heating at high temperatures. For instance, they are absorption features of commercial yellow and pink CVD diamonds, which are nitrogen-doped and which are always treated at high temperature (usually HPHT treatment) with the aim of removal of their initial brown color. The line 1341 cm^{-1} and the band 1293 cm^{-1} reveal correlation in intensity (Fig. 4, *a*).

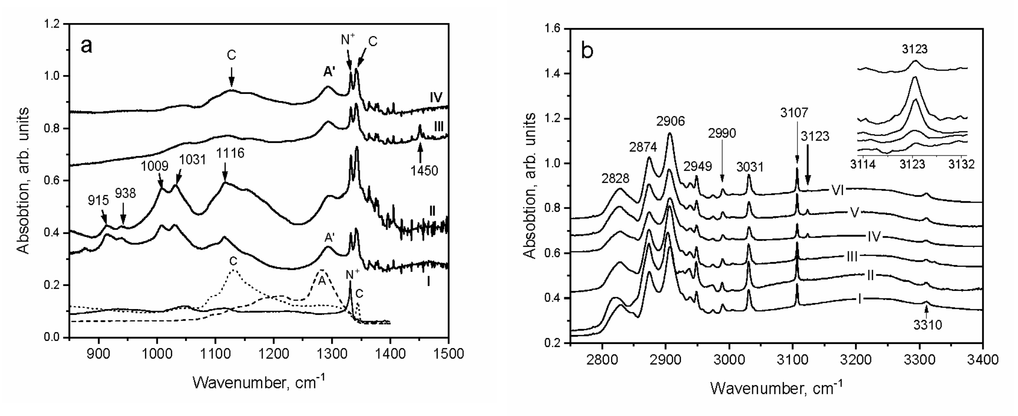


Figure 2. – (*a*) IR absorption spectra taken from the whole sample: (I) - as-received; (II) - after electron irradiation; (III) - after annealing at 860°C; (IV) - after annealing at 1900 °C. Absorption spectra of nitrogen A, C and N^{+} defects are shown with narrow lines at the bottom of the graph. (*b*) Absorption spectra in the range of absorption of hydrogen-related defects collected from as-received sample (I), after irradiation (II) and after annealing at temperatures 860°C (III), 1580°C (IV), 1870°C (V) and 1900°C (VI). Insert shows evolution of 3123 cm^{-1} center

This correlation suggests that they belong to closely related defects if not to one and the same defect. We tentatively ascribe the band 1293 cm^{-1} and the line 1341 cm^{-1} to a modified form of A-defects (A'-defects) and speculate that this modification results in spectral shift of the 1282 cm^{-1} band to 1293 cm^{-1} and strongly stimulates the 1341 cm^{-1} feature, which otherwise is negligible in spectra of regular A-defects.

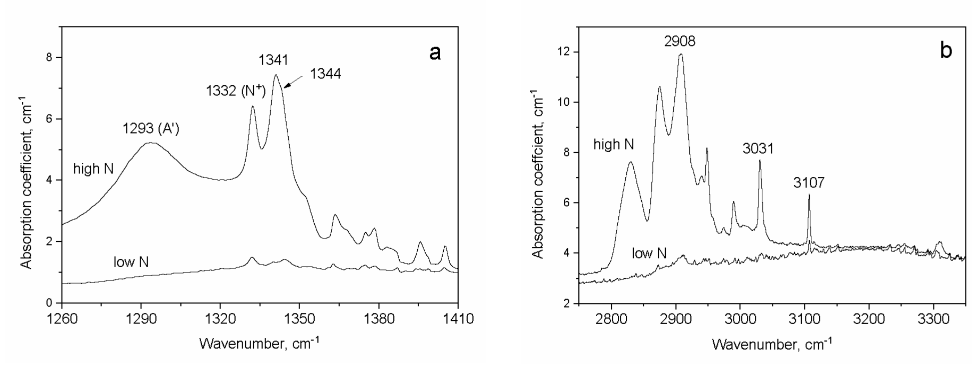


Figure 3. – Absorption spectra of nitrogen-related defects in one-phonon spectral range (*a*) and hydrogen-related defects (*b*) measured in high nitrogen layer and low nitrogen layer. Intensities of spectra are adjusted to equal intensity of intrinsic absorption at wavenumber 2020 cm^{-1}

Assuming that the origin of this modification is unique of CVD diamond, we suggest that this could be the presence of hydrogen and formation of stable complexes of A-defects and hydrogen.

After irradiation, IR absorption does not change noticeably. After annealing at temperature 860°C, the main change is disappearance of the features in the range 850–1150 cm^{-1}. The remaining spectrum is composed of three absorptions due to C-, A'- and N^{+}-defects. A narrow line at 1450 cm^{-1} is the center H1a, which relates to a defect containing interstitial nitrogen atoms [12]. H1a absorption disappears after annealing at temperatures 1580°C and above. Further annealing at higher temperatures has not changed IR absorption spectra significantly.

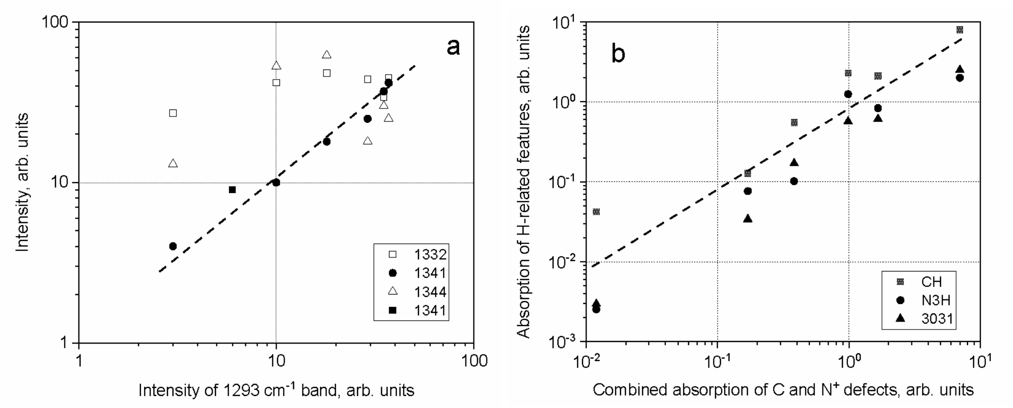


Figure 4. – (*a*) Intensities of 1332, 1341 and 1344 cm^{-1} lines versus intensity of 1293 cm^{-1} band. Full square is the result obtained on a random commercial yellow CVD. (*b*) Intensity of hydrogen related absorptions versus integrated absorption intensity of isolated nitrogen atoms (C- and N^{+}-centers): (squares) – band 2906 cm^{-1}; (circles) – center 3107 cm^{-1}; (triangles) – center 3031 cm^{-1}

In the spectral range of absorption of hydrogen-related defects, the spectra are dominated by three narrow bands with maxima at 2827, 2874 and 2906 cm^{-1} (Fig. 2, *b*; 3,*b*). There are several narrow lines, the most prominent of which are lines at 2949, 2990, 3031 and 3107 cm^{-1}. These absorptions are attributed to C-H vibrational modes of different defects containing hydrogen. The most intense feature at 2906 cm^{-1} is ascribed to C–H vibrations sp^{3} CH configuration [13, 14]. The 3107 cm^{-1} line is ascribed to N_3V-H defect. The lines 2827, 2874 and 2906 cm^{-1} are very thermally stable and survive a 10-hour annealing at temperature 2200 °C. In contrast, the lines 2949, 2990 and 3031 cm^{-1} anneal out completely after long-time annealing at 2200 °C.

Of the hydrogen-related absorptions, only the centers 3107 cm^{-1} and 3123 cm^{-1} have been unambiguously attributed to defects containing both hydrogen and nitrogen. However, in our samples, intensity of most of the hydrogen-related absorption features well correlate with absorption intensity of nitrogen defects (Fig. 4, *b*). This result suggests that these centers, commonly attributed to hydrogen-related defects, may relate to defects containing hydrogen and nitrogen.

CONCLUSION

Nitrogen impurity produces many optical centers in IR absorption spectra of CVD diamond. The most prominent of them are nitrogen-hydrogen centers with absorption lines at

2827, 2874, 2906, 2949, 2990, 3031, 3107, 3123 and 3310 cm^{-1}. High temperature annealing produces two characteristic absorptions: a band at wavenumber 1293 cm^{-1} and a line at 1341 cm^{-1}. These features are unique of CVD diamond. Tentatively, they are ascribed to nitrogen A-aggregates modified by interaction with hydrogen. Electron-irradiated nitrogen-doped CVD diamond reveals the brightest pink color after annealing at temperatures about 1000°C. High temperature annealing at temperatures over 1800°C destroys the radiation-induced pink color completely.

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ПРОЦЕССЫ КЛАСТЕРООБРАЗОВАНИЯ ФОСФОРА И БОРА В КРЕМНИИ

О. И. Величко

Белорусский государственный университет информатики радиоэлектроники,
ул. П. Бровки, 6, 220013 Минск, Беларусь,
e-mail: velichkomail@gmail.com

Проведено моделирование процессов кластерообразоваиия атомов фосфора и бора при термической диффузии в кристаллическом кремнии. Сравнение с экспери-