



Spectroscopic studies of yellow nitrogen-doped CVD diamonds



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ABSTRACT

Photoluminescence and absorption properties of commercial brownish yellow nitrogen-doped gem quality CVD diamonds have been characterized using imaging and spectroscopic techniques. The measurements have been performed on the diamonds in as-received state and after treatment with electron irradiation and high temperature (LPHT) annealing. It is found that single nitrogen defects in CVD diamond possess very high temperature stability, the positively charged single nitrogen atoms being exceptionally stable. In the as-received state, the diamonds show the signs of nitrogen aggregation, which are the result of the post-growth HPHT treatment. The treatment with electron irradiation and LPHT annealing has caused further aggregation of neutral nitrogen atoms and suppression (up to complete removal) of brown color. Many optical centers with narrow zero-phonon lines (ZPLs), not reported for natural diamonds, have been found all over the visible and near IR spectral ranges. Most of these centers are tentatively ascribed to Ni-related defects. A strong optical center with broad ZPL at a wavelength of 498.2 nm was excited with 325 nm laser. The effect of resonance Raman scattering on quasi-local vibrations of an optical center with ZPL multiplet at about 488 nm is reported.

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1. Introduction

Synthetic diamond is a common material used for variety of industrial applications. Cutting and grinding tools, surgical scalpels, heat sinks, optical windows and radiation detectors are just a few of them. Natural diamond has been prevalent in the gem industry for a long time. However within the last few years the diamond gem trade has witnessed a drastic surge in production of synthetic gem diamonds. The advent of the massive use of synthetic diamond as gem material is not a matter of discussion any more it is the reality. Today, synthetic gem diamond rivals the best natural stones in quality while offering significantly lower price and promising to become even cheaper as the technology of synthesis improves.

Uncontrolled mixing natural diamonds with their synthetic counterparts in large parcels of meles and replacing larger natural diamonds with their synthetic counterparts with identical gemological parameters becomes frequent fraudulent practice in diamond trade. The reliable identification and recognition of synthetic diamonds and separation them from natural stones is becoming a fast growing concern in diamond gem trade and an urgent task of gemological laboratories. This task, however, is not something to easily implement. Since synthetic diamond is a real diamond, not a simulant, its major physical properties are identical to these of natural diamond. Thus the standard methods of testing, e.g. the methods based on thermal conductivity,

Raman spectroscopy and low resolution spectrometry do not work in this case. Fortunately, some secondary physical properties of synthetic diamonds do differ from those of natural diamonds in subtle details. These differences originate from the different mechanisms of growth of synthetic and natural diamonds and different conditions these diamonds had experienced in their post-growth history. They can be detected using high resolution low temperature optical spectroscopy. Accumulation of the data on specific spectroscopic features of synthetic diamonds is the way to meet the challenge of reliable recognition of synthetic diamonds. Yet, this data, however extensive, can be never comprehensive. The rapidly developing technology of diamond growth constantly involves novel approaches, novel materials and novel post-growth treatments. Thus the diamonds grown by different producers may possess considerably different spectroscopic features. In order to keep up with the variety of synthetic diamonds penetrating into the natural diamond market and to be ready to provide adequate protection of it, gemological laboratories must conduct systematic research on synthetic diamonds and constantly keep eye on the new technologies used for diamond synthesis.

In this communication, we report the result of spectroscopic study of nitrogen-doped CVD-grown diamonds the color of which is modified by low pressure high temperature (LPHT) annealing – a treatment technique which is still novel in diamond gem industry. It is shown that LPHT processing of CVD diamonds may alter some of their spectroscopic features. Most of these features have not been seen reported for natural diamonds and thus can be used for identification of CVD diamonds and the ways treatment they were subjected to.

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2. Experimental

Seven brilliant cut CVD diamonds of yellow color were purchased from a diamond dealer who claimed that the stones were doped with nitrogen for yellow color and, after growth, HPHT annealed in order to reduce the brown color component. The stones were 4.0 to 4.2 mm in diameter and 0.24 to 0.26 ct in mass.

The diamonds were examined using polarizing and fluorescence microscopes Nikon Eclipse Ti-S and DeBeers DiamondView. Their color was graded using standard procedure of the Gemological Institute of America.

Spectroscopic measurements were performed with FTIR, UV–Vis absorption and broad range photoluminescence spectrometers. Thermo Nicolet i550 spectrometer was used for FTIR absorption measurements in the spectral range 400–6000 cm^{-1} with resolution 1 cm^{-1} at room temperature. UV–Vis absorption measurements were performed at liquid nitrogen temperature in a spectral range 300–1000 nm using Avantes Multi channel spectrometer and Avantes Deuterium and Halogen light sources. For the photoluminescence (PL) measurements, a Renishaw InVia Raman confocal spectrometer equipped with He–Cd metal vapor laser (wavelength 324.8 nm), Ar-laser (wavelengths 457.0, 488.0 and 514.5 nm), He–Ne laser (wavelength 632.8 nm) and a laser diode (wavelength 830.0 nm) was used. PL measurements were performed with the samples submerged in liquid nitrogen [1].

Three of the studied diamonds were chosen for further treatment with electron irradiation followed by high temperature annealing (Irr + LPHT treatment). One diamond was annealed at the same conditions without prior irradiation (LPHT treatment). The irradiation was performed with electrons of energy 1 MeV at a dose of $2 \times 10^{18} \text{ cm}^{-2}$ using facilities of US Diamond Technologies (www.usdiamondtechnologies.com). LPHT annealing was performed in hydrogen atmosphere at temperatures 1700 and 1800 °C for 15 min in a graphite furnace described in [2]. The LPHT-processed diamonds were not re-polished after treatment. Thus their visual color might somewhat deviate from that the diamonds would have after re-polishing. However, from our experience, this deviation is minor in most cases.

3. Results and discussion

3.1. Visual examination

The original color of the diamonds in the as-received state was fancy brownish yellow (Fig. 1a). The diamond treated with LPHT annealing at temperature 1800 °C changed its color to fancy yellow (Fig. 1b). The diamonds treated with irradiation followed by LPHT annealing at temperature 1800 °C turned fancy orangey yellow (Fig. 1c). Fluorescence images of these diamonds excited with 360 nm UV light are shown in Fig. 1d, e, f correspondingly. All as-received diamonds revealed bluish green fluorescence. The fluorescence of the diamond treated with sole LPHT annealing became greener. The fluorescence of the diamonds processed with irradiation and LPHT annealing turned almost blue with a faint trace of green and pink colors. DiamondView images of the LPHT-treated diamonds revealed strong greenish yellow fluorescence, the yellow component being stronger after Irr + LPHT treatment (Fig. 1g, h, k).

When viewed in polarized light, all diamonds revealed dense grainy-patchy birefringence patterns, which are very characteristic of CVD-grown diamonds (Fig. 1l, m). The birefringence did not change much after irradiation and/or LPHT annealing. These grainy birefringence patterns, if clearly seen, are a very reliable criterion of recognition of CVD diamonds.

The reduction of the brown color component after LPHT annealing shows that high temperature heating, even performed without stabilizing pressure, is a way to improve color of brown CVD diamond. Brown color of CVD diamonds has a different origin than that of natural brown diamonds, which is vacancy clusters. The brown color causing defects in CVD diamonds have lesser temperature stability and they

can be largely destroyed at relatively low temperatures, e.g. at 1600 °C [3]. In natural diamonds, the brown color component is much more stable and LPHT annealing alone, even when performed at a temperature of 2000 °C, is not effective in its removal (detailed account on LPHT treatment of natural brown diamonds will be published elsewhere).

The changes in the fluorescence color can be well explained by formation and annealing of NV and H3 luminescence centers, which are common contributors to the fluorescence of nitrogen-containing diamonds. Strengthening of the green color component is the result of the increase in intensity of H3 centers. The red-pink color is the manifestation of the formation of NV centers. The yellow-orange component in strong green fluorescence is frequently caused by emission of NV⁰ center.

It is remarkable that none of the diamonds revealed strong red fluorescence of NV centers, neither after sole LPHT annealing, nor after irradiation and subsequent LPHT annealing. Red fluorescence is a very characteristic feature of as-grown commercial CVD diamonds, which always contain dispersed nitrogen (C-defects) in concentrations of at least a fraction of ppm. The more so when the diamonds are doped with nitrogen to a concentration of a few ppm. The absence of the red fluorescence of NV centers in the present case is definitely the result of HPHT and LPHT annealing. Both treatments are effective in aggregation of nitrogen and in destruction of NV defects. Yet, the presence of minor concentration of NV centers can be detected in nitrogen-containing diamonds after any treatment, including HPHT and LPHT heating at extremely high temperatures. Since NV centers are very effective in luminescence, they may produce detectable fluorescence even when in small concentrations.

4. IR absorption

4.1. As-received diamonds

A weak IR absorption due to single nitrogen defects of a comparable intensity at a level of concentration of a few ppm was measured on all diamonds. Thus these diamonds correspond to low nitrogen type Ib (Fig. 2a). Fig. 2b shows the spectral range of one-phonon absorption. It is a complex spectrum, which may somewhat vary from sample to sample. However, the features of C-center (single substitutional nitrogen atoms in neutral charge state) and N⁺-center (single substitutional nitrogen atoms in positive charge state) can be well recognized. The most prominent of them are the sharp lines at 1344 cm^{-1} (C-center) and 1332 cm^{-1} (N⁺ center) [4,5]. These lines were already reported in yellow CVD diamonds in [6,7]. The N⁺ center is a common feature of brown CVD diamonds.

The main absorption band of C-center at 1130 cm^{-1} is unusually weak compared to the 1344 cm^{-1} line. It is in contrast with natural and HPHT-grown synthetic diamonds of type Ib, where the 1130 cm^{-1} band is two to three times stronger than the 1344 cm^{-1} line. Other spectral features identified as components of C-center and N⁺-center are at 1290 cm^{-1} (C), 1245 cm^{-1} (N⁺), 1125 cm^{-1} (C), 1090 cm^{-1} (C), and 1045 cm^{-1} (N⁺). A pronounced band with maximum at 828 cm^{-1} is probably not related to C and N⁺ centers.

Spectra in the lines 1332 and 1344 cm^{-1} are shown in Fig. 2c. Besides these two major lines a minor line at 1353 cm^{-1} is seen too. This line was reported in [8] as a pronounced feature in one-phonon absorption spectra of LPHT-annealed pink CVD diamonds. We did not see this line with the intensity comparable with that of 1332 and 1344 cm^{-1} after any steps of treatment. Thus we assume that the 1353 cm^{-1} line is not a direct result of irradiation and/or LPHT annealing, but a specific feature of a particular CVD growth process and/or HPHT post-growth treatment.

Taking into account the data of [4] on the relationship between the concentration of nitrogen in different charge states and the absorption intensity of peaks 1344 and 1332 cm^{-1} , we can estimate that the studied samples in as-received state had the concentration of neutral

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