



# Optical properties of CVD single crystal diamonds before and after different post-growth treatments

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## ABSTRACT

Single crystal diamonds grown by chemical vapor deposition (CVD) before and after different post-growth treatments were studied using optical spectroscopy. The most pronounced changes in color were observed after irradiation with subsequent annealing at 800 °C whereas a weakening of gray tint took place after the high-pressure high-temperature annealing. Low-pressure high-temperature annealing in microwave plasmas of different composition and by electric arc discharge did not produce a noticeable effect on the diamond properties. Signals from nitrogen-vacancy complexes were detected in the absorption and luminescence spectra of CVD diamonds, but the pink tint in the irradiated and annealed diamonds is due to Si–V complexes, not N–V. The peaks at 150 and 262 K associated with boron were observed in thermoluminescence (TL) curve of original CVD diamonds. Combined irradiation and annealing allowed us to create deep traps of charge carriers responsible for TL peaks in the 430 to 470 K range, which made CVD diamonds promising for TL dosimetry.

## 1. Introduction

Gem-quality diamonds grown by chemical vapor deposition (CVD), which produces tabular crystals that are colorless or evenly colored, are of more recent manufacture. Development of CVD technique from the moment of its origin to the present day is described in [1]. CVD growth technique has progressed significantly in recent years with improvements in crystal size and quality. The outlooks of application of CVD diamonds in a new generation of electronic devices stimulated the mass production of these diamonds as well as study of their properties. In particular, gemological and luminescence/absorption properties of CVD diamonds produced by their leading manufacturers were described in [2–4]. However, in spite of the impressive amount of scientific publications and abundance of other information, there are few data on the optically active defects in CVD diamonds and the opportunity of controlled changes of their properties under different post-growth treatments. This information is very important for applications and our study covers this gap partially.

Interest to diamond thermoluminescence (TL) is caused by their potential applicability in the dosimetry of UV and ionizing radiations. Solid state TL dosimetry is one of the most wide-spread, reliable and simple techniques of dosimetry control. Typical materials for TL

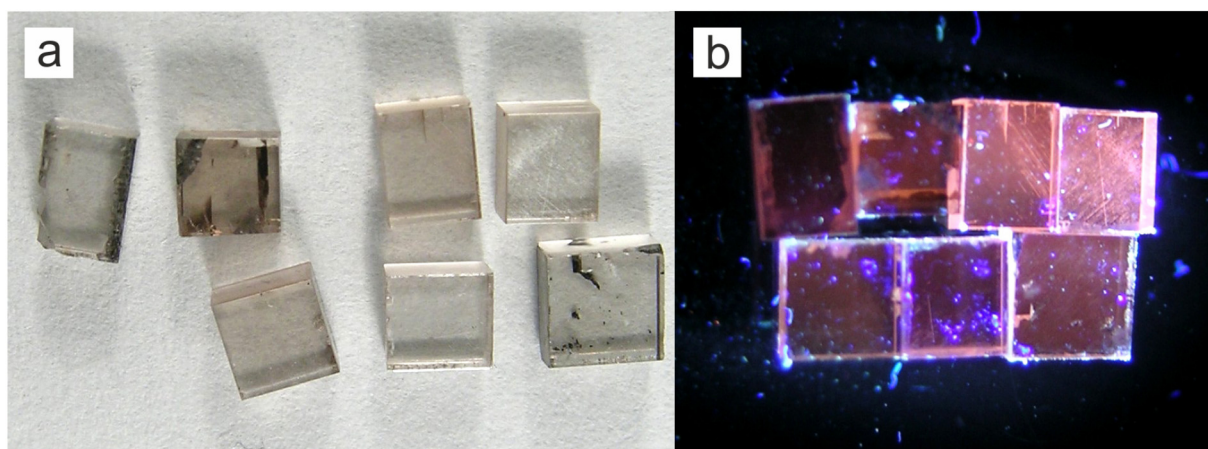
dosimeters are LiF, B<sub>2</sub>Mg<sub>3</sub>O<sub>6</sub> and Al<sub>2</sub>O<sub>3</sub>. Diamond is attractive for dosimetry because of its tissue-equivalence, radiation stability and chemical inertness. Diamonds of different types, namely natural and synthetic high-pressure high-temperature (HPHT) diamonds with different nitrogen concentrations and state, were compared in [5]. Diamonds for TL dosimetry would have high-temperature peaks well above room temperature in order the corresponding deep traps of charge carriers keep the light sum for a long time. Many authors studied polycrystalline diamond films where the dominant TL peak is near 500 K [6–9], but the information about single crystal CVD diamonds is absent. In this paper we studied TL of the CVD single crystals and suggested a way to produce high-temperature TL peaks applicable in TL dosimetry.

## 2. Experimental

### 2.1. Samples

The growth was carried out in a heated mixture of hydrocarbon gas (such as methane, CH<sub>4</sub>) and hydrogen. The major impurity found in the resulting diamond crystals is hydrogen unless some other type of atom (such as B, N or Si) is introduced into the gas mixture. Within the vacuum chamber, activation of the gas by an energy source (typically a

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**Fig. 1.** Appearance (a) and photoluminescence at UV 365 nm excitation (b) for seven CVD diamonds of grayish-brown color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

microwave plasma) breaks apart the gas molecules to release carbon atoms. These gas atoms are drawn down toward the cooler substrate that consists of natural or synthetic diamond.

Using optical spectroscopy, we studied 21 rectangular pieces of single crystal CVD diamond. These samples were 0.5 mm thick plates with approximately  $3 \times 3$  mm<sup>2</sup> polished opposite faces. The plates were grayish-brown of varying color intensity (Fig. 1a). They demonstrate violet to orange photoluminescence (PL) typical of CVD diamonds [4]: main components of these spectra are 467.5 and 575.0 nm vibronic systems. The appearance and PL patterns for seven of these plates are shown in Fig. 1a, b, respectively. Some crystals contain black inclusions, supposedly of graphite.

## 2.2. Optical spectroscopy

To record absorption spectra in the mid-IR spectral region we used an Infracum FT-801 IR-Fourier transform spectrometer. Transmission spectra in the UV–visible–near IR range were obtained on a Shimadzu UV-2501 PC spectrometer. IR absorption spectra were measured at temperature of 300 K, whereas absorption spectra in the UV–visible–near IR region and PL spectra were recorded at 80 K with a sample located inside an optical vacuum cryostat. Photoluminescence spectra were recorded at 80 K with a SDL1 luminescence spectrometer. PL spectra were obtained by excitation in the 365 nm line from a 100 W mercury lamp isolated by a UFS6 filter from a set of colored glass, as well as in the 527 nm line (the 2nd harmonic of a diode-pumped Nd:YLF laser). The curves of thermoluminescence (TL) were measured when diamond was heated at the rate of 20°/min after UV 365 nm excitation at 80 K. An optical cryostat with four silica windows was used for low-temperature absorption and luminescence measurements.

## 2.3. Post-growth treatment of CVD diamonds

All 21 samples of CVD diamonds were divided into three groups, each consisting of 7 samples. Samples of each group were treated in a specific way: The description of the type of treatment is given in Table 1.

CVD diamonds of one group (7 samples) were at first irradiated with 3 MeV fast electrons (dose  $5 \times 10^{18}$  cm<sup>-2</sup>) with further annealing during 2 h at 800 °C in vacuum (A1 treatment in Table 1). Irradiation with 3 MeV fast electrons was carried out at 300 K on a linear electron accelerator in the Institute of Catalysis SB RAS. Seven diamond samples were mounted on a water-cooled finger. The electron beam diameter was 15 mm, samples were located at a distance of 200 mm from the accelerator output window. The rate of dose accumulation was  $10^{18}$  electrons/cm<sup>2</sup> × h. Then these samples were annealed

**Table 1**

Description of CVD samples and the treatments.

CVD samples	NN	Treatment parameters
7 plates of CVD diamond with $\sim 3 \times 3$ mm <sup>2</sup> opposite polished faces, 0.5 mm thick	A1	3 MeV irradiation with subsequent annealing at 800° C during 2 hours
	A2	Further annealing at 800° C during 24h
7 plates of CVD diamond with $\sim 3 \times 3$ mm <sup>2</sup> opposite polished faces, 0.5 mm thick	B	HPHT annealing during 10 min at 7 GPa and temperature in the 2200 to 2300°C range
	7 plates of CVD diamond with $\sim 3 \times 3$ mm <sup>2</sup> opposite polished faces, 0.5 mm thick	C1
C2		7 plates of CVD diamond with $\sim 3 \times 3$ mm <sup>2</sup> opposite polished faces, 0.5 mm thick
C3		“Thermal shock” treatment in Ar plasma of flow-through arc plasmatron: 5 to 7 repeating cycles each 20 sec long with 10 to 15 sec gap between the cycles. Total: several min at temperature of about 2200 °C

additionally during 24 h at 800 °C (A2 treatment). The samples were placed into a silica ampoule and the latter was evacuated. Annealing was carried out in an ohmic furnace. Absorption and PL spectra as well as the TL curve were recorded before the treatment and after A1 and A2 treatments.

Seven other CVD samples were annealed at high pressure and high temperature (HPHT) during 10 min at 7 GPa and temperature 2200–2300 °C (B treatment in Table 1). To produce the HPHT treatment B, we used a pressless multi-anvil high-pressure set-up of the split-sphere type with the hydraulic drive BARS-2000 developed at the Institute of Geology and Mineralogy SB RAS [10–14].

The remaining 7 samples were annealed three times in different set-ups in sequence (treatments C1 + C2 + C3). The first annealing C1 was carried out for 30 min at 1700 °C in a microwave Ar–H plasma of 1 Torr pressure (low-pressure high-temperature annealing, LPHT). The second treatment C2 was annealing during 2 min. in AC arc discharge in He atmosphere of 25 Torr at a temperature of about 2200 °C. The third treatment C3 was annealing during several minutes at a temperature of about 2200 °C in Ar plasma of flow arc plasmatron.

New types of post-growth treatments such as annealing in plasma and in the electric arc were carried out in the home-made experimental set-ups described below.

The set-up for the LPHT annealing C1 was a microwave plasma reactor. We took a silica tube 450 mm long and 30 mm in diameter, which was evacuated to  $10^{-2}$  Torr. Then this volume was filled with the Ar–hydrogen mixture to 1 Torr pressure. The silica tube went through a metallic hood in which a microwave field was created using a standard magnetron of 750 W power. Plasma arose in the working part of the silica tube 60 mm long. Ar is used to facilitate the ignition of hydrogen plasma. The temperature of diamond in the plasma was determined using a pyrometer and varied in the 850 to 1700 °C range. In

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