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Optical centers and their depth distribution in electron irradiated CVD diamond

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ABSTRACT

Detailed measurements of photoluminescence of commercial CVD diamond irradiated with 1 MeV commercial electron accelerator have been performed. It has been assumed that the depth distribution of radiation-induced defects can be described by contributions of two mechanisms: strong defect production by primary fast electrons and weak secondary irradiation by gamma rays. Thickness of the layer of the strong defect production has been found of 0.7 mm what is about half the theoretically predicted propagation depth of 1 MeV electrons in diamond (1.2 mm). The secondary gamma irradiation penetrates through the whole diamond sample (3.4 mm in the present case). Spectral features of several optical centers formed in as-irradiated CVD diamond and after subsequent annealing at moderate and high temperatures have been discussed. Some of these centers have been ascribed to modified 3H defects. A center with zero-phonon line (ZPL) at 733.2 nm has been ascribed to an intrinsic split-vacancy defect. The radiation-stimulated aggregation of nitrogen has been observed as the formation of H3 defects. It has been shown that the merging of NV defects into H3 defects is not a major pathway of the nitrogen aggregation. It has been confirmed that the temperature stability of NV defects in undamaged diamond lattice exceeds 2000 °C. Destruction of NV centers, frequently seen at temperatures below 2000 °C, is the result of interaction of NV defects with other mobile defects. Recently discovered centers with broad ZPLs at 462.5 and 498.8 nm, which are characteristic of CVD diamond, have been found to be very radiation and temperature stable and immune against any known treatment of diamond. It has been proposed to use detection of these centers as a method of recognition of CVD diamonds.

Prime novelty

Detailed study of depth distribution of defects in CVD diamond irradiated with fast electrons has been performed for the first time.

1. Introduction

Effects of radiation damage of diamond by fast electrons have been studied since many years [1–6]. By now, an extensive data on the defects induced by electron irradiation have been accumulated. In most of these studies, the primary attention has been paid to point radiation defects: their atomic and electronic structure, spectroscopic properties, efficiency of production, and thermal stability. Interaction of radiation defects with impurities, in particular with nitrogen, was studied in many details too.

Although we have a solid understanding in the processes of creation of radiation defects and behavior of these defects in electron irradiated diamonds, an important detail is still missing. It is the distribution of radiation defects through the depth of the electron-irradiated layer. There has been little attempt undertaken to study the damage rate, or production of specific radiation defects as a function of depth for electron irradiation. The most closely related publications in the field are those by Campbell et al. [7,8]. The depth distribution is not of importance in case when diamond sample is thin enough (well below 1 mm) for electrons of energies of 1 MeV and above to penetrate through. In this case the efficiency of radiation damage is believed to be essentially uniform over the sample volume.

However for diamonds of a few millimeters thick, the distribution of radiation damage through the depth cannot be neglected. It is all the more so when the electron energy is in the range of 1 MeV and below. A common case of application of electron irradiation to bulk diamond is the radiation color treatment [9,10]. Frequently 1 MeV irradiation is used. For cut diamonds of size over 0.5 carat, 1 MeV electrons are not enough energetic to penetrate through the whole depth. The effects of non-complete penetration of electron beam through the treated diamond have been reported. One of these effects is so-called "umbrella effect" observed at the culet of electron-irradiated cut diamonds [9].

With the advent of technologies of fast CVD growth of synthetic diamonds [11,12], large diamond samples of a thickness of a few

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millimeters are not uncommon any more in synthetic *gem* diamond industry [13]. Electron irradiation is used for the color modification of these diamonds too. For instance, electron irradiation converts colorless CVD diamonds in very attractive blue stones. Electron irradiation combined with high temperature annealing is a way to suppress brown color of as-grown CVD diamonds and make them near colorless. Electron irradiation followed by annealing at moderate temperatures is a well-known method of conversion of yellowish nitrogen-doped CVD diamonds in bright pink. In order to effectively apply technology of electron irradiation to diamonds of different sizes, one has to have a clear understanding of the defect production over the diamond volume.

In this communication we present a detailed study of radiation defects produced in large commercial CVD diamond subjected to a standard 1 MeV electron irradiation commonly used for color treatment. The emphasis is given to the depth distribution of optically active radiation defects and the defects, the optical efficiency of which is affected by electron irradiation.

2. Experimental

A 3.4 mm thick near colorless CVD diamond purchased from a third party was used in this research. The sample was grown on CVD substrate in ⟨100⟩ crystallographic direction. FTIR absorption measurements did not reveal presence of nitrogen. Thus the concentration of single nitrogen atoms (C-defects) in the sample was below 1 ppm. Initial characterization revealed that after growth this diamond was HPHT annealed. It is known that annealing at high temperature (about 2000 °C) under high pressure (about 50 kbar) is frequently used for production of large commercial CVD diamonds.

Prior to irradiation, the sample was annealed at a temperature of 1900 °C for a few minutes in vacuum in order to stabilize its defect structure. After the annealing, the sample was irradiated perpendicular to its surface with 1 MeV electrons at a dose of 1.5×10^{18} cm^{-2} using irradiation facility of US Diamond Technologies. This dose was chosen as an optimal one. In our previous studies we found that dose in the range of 10^{18} cm^{-2} is high enough to create strong radiation optical centers, but it is still low enough to exclude noticeable formation of radiation defect complexes. Intensity of the electron beam was about 10^{17} cm^{-2} s^{-1}. Temperature of the sample during irradiation did not exceed 150 °C.

After irradiation, the sample was cut along the direction of irradiation in two halves and the cut surfaces were polished mechanically. The polishing was performed carefully and slowly enough to exclude overheating of the sample. Thus we assume that the polishing has not changed the defect structure created by irradiation. The distribution of defects through the sample depth was studied by measuring intensity of the corresponding photoluminescence (PL) centers.

After the sample had been measured in its as-irradiated state, it was subsequently annealed in vacuum at temperatures 1100 °C for 1 h and 1900 °C for 5 min. For annealing we used a home-made all-graphite vacuum furnace with graphite sample container evacuated to a level of 2×10^{-5} mbar. The heating could be ramped up to the target temperature within minutes. Temperature was measured with a W-Re thermocouple directly attached to the container. The calibration of the thermocouple was done against the melting points of pure metals Al, Cu, Au, Si, Pt, and Rh. Error of the temperature measurements did not exceed 10 °C. PL measurements were performed after each step of annealing.

For PL measurements we used confocal Renishaw InVia Raman spectrometers 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). All measurements were performed with the sample submerged in liquid nitrogen [14].

PL intensity was measured relative to the intensity of diamond Raman line. PL intensity measured this way is essentially free from the errors, which may arise from variations in transparency and geometry of reflection. In many cases, PL intensity is discussed in terms of relative concentration of corresponding defects. Justification of this approach is based on the assumption that the position of Fermi level in the studied sample did not change much through the whole experiment. The experimental proof of the stability of Fermi level is the high intensity of NV^0 center (neutral NV defects), which always remained much stronger that the intensity of NV^- center (negatively charged NV defects). Thus

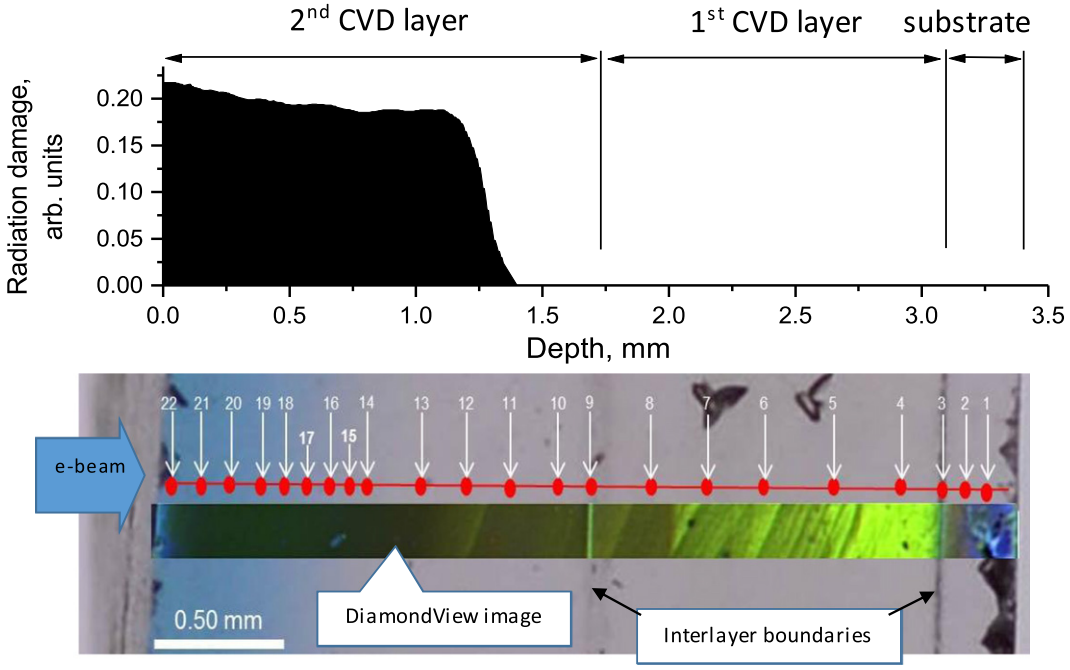

Fig. 1. Photograph of the cross-section of irradiated CVD diamond sample compared with its DiamondView fluorescence image and the theoretical distribution of vacancies for 1 MeV electron irradiation taken from [22]. Interfaces between the substrate layer and the first new CVD layer (point 3) and between two new CVD layers (point 9) are seen as two gray narrow stripes in the photograph and as a dark stripe and a bright green stripe respectively on the fluorescence image. Red points show the spots where PL measurements were performed.