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Photoluminescence studies of 515.8 nm, 533.5 nm and 580 nm centres in electron irradiated type IIa diamond

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ABSTRACT

A series of irradiations has been performed mainly on some very high purity CVD single crystal diamonds but also on some other diamond specimens at various electron doses and dose rates. The electron energies were sufficient to cause atomic displacements creating vacancies and self-interstitials in the irradiated samples. The 515.8 nm, 533.5 nm and 580 nm centres were commonly observed in low temperature photoluminescence examination of electron-irradiated type IIa diamonds. Details of their spectra indicate that they are all related to interstitial complexes.

1. Introduction

Ever since Crookes first irradiated diamond with particles emitted from radium, more and more attention has been directed at the topic of the radiation damage in diamond [1]. Since that pioneering work, various kinds of irradiations such as with neutrons, gamma rays and electrons, have been used as bombarding particles [2]. Electron irradiation has the important property that the electron momentum is insufficient to cause collision cascades of native carbon atoms, instead causing the displacement of individual atoms from their equilibrium sites.

After electron irradiation, a large number of self-interstitial and vacancy-related centres are created in the very pure diamond (type IIa) [3]. The most dominant line observed in low temperature photoluminescence (PL) experiments performed with 488 nm laser excitation is the zero phone line (ZPL) at 741 nm which is associated with the isolated neutral vacancy and known as the GR1 centre. Besides this centre and the commonly observed 3H centre, other optical centres that were commonly observed in electron irradiated type IIa diamond have ZPLs at 515.8 nm, 533.5 nm and 580 nm. It is of particular interest to arrive at information about the atomic structures and charge states of the defects responsible for these latter centres and these issues will be main emphasis of this paper.

2. Experiment

Although this work focuses on very low nitrogen-containing type IIa diamond some related studies were carried on samples of somewhat higher nitrogen-content, on ^{13}C and ^{15}N enriched materials and on boron-doped diamonds. The very high purity single crystals were prepared by chemical vapour deposition (CVD), and the ^{13}C and ^{15}N doped samples were obtained by the high pressure and high temperature (HPHT) method; some low-nitrogen natural diamonds were also studied. The irradiations were performed with a Philips EM430 300 keV transmission electron microscope (TEM) into which a dog-leg had been introduced, enabling the passage of electrons, but blocking ions, thus providing an ion-free electron beam. The TEM was particularly suitable for the irradiation because 300 keV is well above the displacement threshold for carbon in diamond.

After irradiation the samples were transferred to Renishaw micro-Raman spectrometers fitted with Oxford Instruments Microstat liquid helium-cooled stages. PL examination was mainly performed with an argon-ion laser using an excitation wavelength of 488 nm, although a few experiments were carried out using the 325 nm excitation with a He-Cd laser. PL spectra were obtained at chosen points, at equally spaced points along a line across and outside the irradiated region (a "line scan") and at points in a rectangular (x, y) array covering the irradiated region and its periphery (a "map"). All the PL results were obtained with liquid helium cooling down to the temperatures of around 7 K. The resolution of the optical system was degraded by the cryostats to about 4 μm lateral resolution and 6 μm depth resolution. The annealing was carried out in an argon gas flow for 30 minutes, from 350 to 900 °C, in steps of 50 °C.

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3. Results

3.1. Ultra-high purity CVD samples

The centres with ZPLs at 515.8 nm, 533.5 nm and 580.0 nm were found in all the experiments performed on the irradiated very high purity single crystal CVD samples but their relative intensities were found to depend on the conditions of irradiation. One of very high purity single crystal CVD samples was irradiated in three regions at the same dose rate at 300 kV, but with different electron doses (of 2×10^{20}, 10^{20}, 10^{19}, 10^{18} e cm^{-2}). Some typical PL spectra from these regions are shown in Fig. 1. They indicate that after the lowest electron dose (~10^{18} e cm^{-2}) only the 580 nm emission was observed in the range of 500–600 nm of PL spectra. The intensity of the 515.8 nm line increased with increase of electron-dose but the intensities of the 533.5 nm and 580 nm lines first increased and then decreased with increase of dose.

Another very high purity CVD sample was irradiated in four regions with the same dose and at the same voltage (5×10^{19} e cm^{-2} and 300 kV), but at different dose-rates (by changing the diameter of the irradiated region from the 20, 50, 100 and 200 μm). Fig. 2 shows that the faster dose rates lead to considerably weaker 533.5 nm intensity relative to that of the Raman, but a somewhat smaller decrease of the 580 nm intensity relative to Raman intensity. The 515.8 nm intensity increased with increase in the dose rate.

Annealing experiments were performed for fixed times (30 minutes) at 50° intervals and it was found that the 515.8 nm line annealed out by 750 °C, the 533.5 nm line after 800 °C–900 °C and the 580 nm line at 550 °C (see Fig. 3).

A common feature of each of the optical centres investigated here was the existence of high energy local vibrational modes associated with them. It was found that the 515.8 nm centre has a strong, single, high energy local vibrational mode (LVM) at 561.3 nm, that the 533.5 nm centre has a single local mode at 579.3 nm, while the 580 nm centre has several local modes, the most intense being at 639.3 nm and 652.2 nm (see Fig. 4). Two characteristics were used to identify these LVMs. Whenever the relevant ZPL was present the LVM invariably appeared and its intensity ratio to the ZPL was constant. As the ZPL annealed out the LVM intensity decreased at the same rate. Strong evidence for C-atom involvement in each of these optical centres was obtained from parallel studies performed on an electron-irradiated ^{13}C enriched HPHT sample with approximately equal concentrations of ^{12}C and ^{13}C. For the 515.8 nm and 533.5 nm centres it was observed that the energies of the local modes shifted by a factor of approximately $(12/12.5)^{1/2}$ relative to that of a diamond with natural isotope abundance as a consequence of the change in average C-atom mass. The 580 nm emission from this sample was too weak to identify its LVMs from the background of other weak signals.

It has been found previously [4] that high electron doses tend to lead to greater probability of migration out of the irradiated region and therefore we also studied the intensity distributions of the 515.8 nm, 533.5 nm and 580 nm centres in the case of mid and high dose regions (diameter ~100 μm). The results for the 515.8 nm, 533.5 nm, 580 nm and GR1 centres are compared in Fig. 5. From this figure, it is clearly observed that the 515.8 nm and 533.5 nm centre tend to be restricted to the irradiated region itself while the 580 nm centre extends beyond it. At the higher dose, it was found that the 533.5 nm centre was not so strictly limited to the irradiated region.

Some of the irradiated high purity samples were studied with 325 nm laser excitation after first examining them at 488 nm. The focused 325 nm laser beam (approximate FWHM of 3 μm) was stepped across the centre of the irradiated regions. These samples were then re-studied at 488 nm and it was found that several of the centres seen in the first 488 nm experiment had been bleached by 325 nm exposure while others were enhanced as shown in Fig. 6. In particular, the 515.8 nm and 580 nm centres were bleached. There was apparently no change in the intensity of the 533.5 nm centre. If new

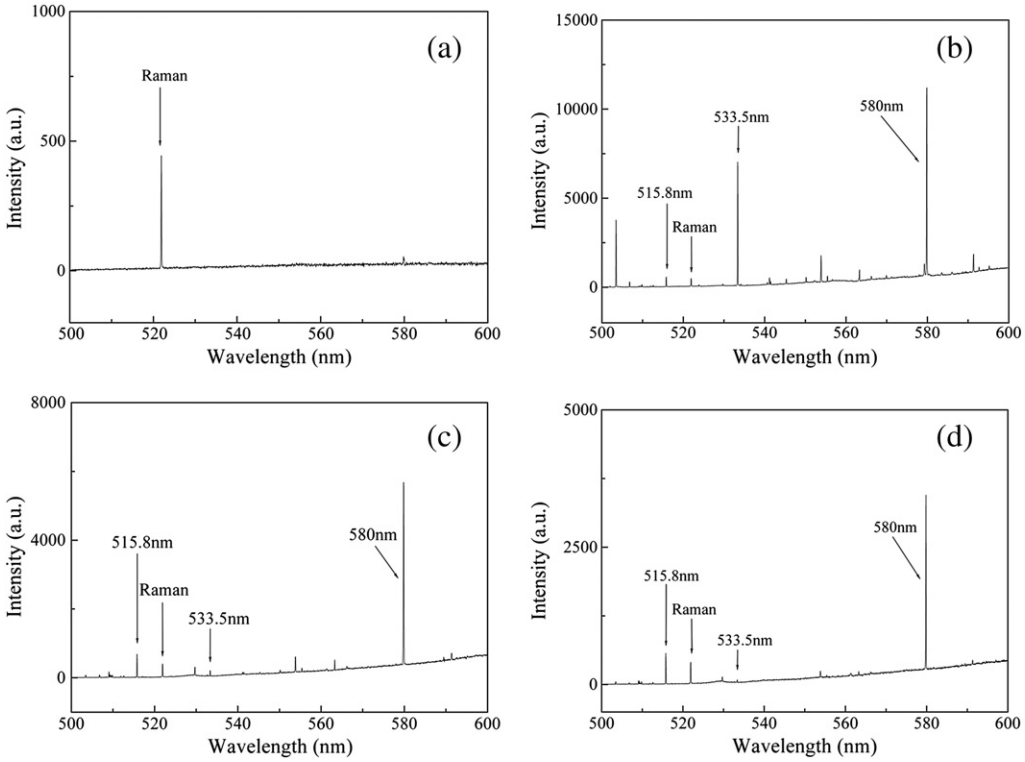

Fig. 1. Typical PL spectra obtained at ~7 K using 488 nm laser excitation of four regions of a slice of very high purity CVD diamond. The doses given to each area were (a) 10^{18} e cm^{-2}, (b) 10^{19} e cm^{-2}, (c) 10^{20} e cm^{-2}, and (d) 2×10^{20} e cm^{-2}.