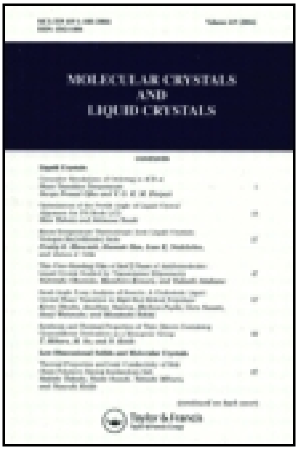

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Spectroscopic Study of Formation of Irradiation Defects in Diamond, Suitable for Persistent Spectral Hole Burning

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SPECTROSCOPIC STUDY OF FORMATION OF IRRADIATION DEFECTS IN DIAMOND, SUITABLE FOR PERSISTENT SPECTRAL HOLE BURNING

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Abstract Neutron irradiation and subsequent thermal annealing have been used to produce diamond-based materials with suitable for high-temperature spectral hole burning properties. From the analysis of the optical spectra of samples subjected to different treatment the optimal conditions for the production of such materials have been deduced.

INTRODUCTION

Diamond, intrinsically transparent in a wide spectral range material can possess a wide variety of optical properties due to different defects and impurities. Understanding of these properties is important for successful application of the material for optical elements, high-pressure anvils or in optoelectronics. For applications one of the problems is finding of materials where persistent spectral hole burning (PSHB) (photobleaching with high spectral selectivity) is feasible not only at cryogenic temperatures but also at ambient conditions. It has been demonstrated that such materials could be prepared on the basis of diamond.[1]

There are many ZPL-s in diamond which have been subjected to spectral hole burning. In 1984 Harley et al.[2] studied the phenomenon in the 415, 496, 637 and 741 nm ZPLs, Yokota et al.[3] have carried out PSHB in the 575 and 637 nm lines in CVD diamond films. We have reported the possibility of PSHB in 649.5, 655, 681, 723, 730.4, 734.1, 774 and 813 nm ZPLs.[4,5,6] In the 649.5 and 655 nm lines holes burnt in at 6 K were registered at temperatures up to 100 and 200 K, respectively. It should also be mentioned that hole burning into 655 nm line can be performed only by pulsed laser and in this case the multiple read-out by means of a continuous-wave laser will not destroy the hole.[6] In the 774 and 813 nm PSHB has been shown to be performable at RT.[1] The spectral lines of neutron-irradiated natural diamonds, where we have performed PSHB are summarized in Table 1.

The aim of the present characterization study is to investigate the process of formation of these defects as it is necessary to create the defects in synthetic diamonds and diamond films either by irradiation and heat treatment, ion implantation or doping during the growth process. Especially interesting for us are the ZPLs at 774 and 813 nm found in the spectra of neutron-irradiated Ia diamond where the inhomogeneous widths of the lines exceed the homogeneous ones at room-temperature (RT) by a factor of 5 and where spectral holes burnt in and registered at RT have been demonstrated. We have carried out spectroscopic measurements to study the properties of the defects and have tentatively ascribed the ZPLs to nitrogen-related defects.[4] Yet, the structure of the defects is not clear.

This paper reports the results of spectroscopic measurements of two natural Ia-type diamond crystals of different origin. The crystal originating from Yakutia was cut and the pieces were subjected to different radiation and heat treatment (referred to as samples Y1 - Y3 thereafter). The other crystal (sample S), originating from Sierra Leone was irradiated as a whole.

TABLE I Spectral hole burning characteristics of the spectral lines in neutron-irradiated diamond.

Peak wavelength of ZPL, nm	Inhomogeneous width, GHz	Width of the narrowest hole observed, GHz	dose of light, hole depth achieved	Comments on PSHB properties (PL-observed in photoluminescence, A-observed in absorption)
649.5	1700	1.7 (at 1.5 K)	250 μJ/mm^2 10% hole at 1.5 K	PL, A; photoproduct at 644 and 651 nm, no crosstalking
655	770	150 (power broadened)	2.8 J/mm^2 80 % hole at 6 K	A; two-step process; hole observable up to 200 K, after cycling 5 K-200K-5K the hole area is reduced to 30 %.
681	970	4.0 (at 1.5 K)	28 mJ/mm^2 10% hole at 1.5 K	PL, A;
712	770			A
723	2000	46 (laser limited)	42 J/mm^2 75 % hole at 6 K	PL, A; PSHB has been performed by cw laser only, pulsed laser causes nonselective reduction of the line
730.4	1350	100 (laser limited)	21 J/mm^2 30% at 6 K	PL;
732	1060	84 (laser limited)	3.6 J/mm^2 30% hole at 6 K	A; strong crosstalking
734.1	560	83 (laser limited)	9 J/mm^2 50% hole at 6 K	PL;
774	3000	5.0 (at 1.5 K)	0.9 J/mm^2 10 %, at 1.5 K	PL; PSHB at RT
813	2500	5.0 (at 1.5 K)	10 J/mm^2 20 % at 1.5 K	PL; PSHB at RT

EXPERIMENTAL

The samples were prepared by irradiating them at controlled temperature with high-energy (>1 MeV) neutrons at different doses: sample S was irradiated up to the dose of 10^{18} n/cm^2, the other crystal was cut into three pieces, the latter were polished ((001) planes) and irradiated up to the doses of 10^{17}, 10^{18}, and 10^{19} n/cm^2 (samples Y1 to Y3 respectively). Subsequent isochronal thermal annealing was carried out in vacuum, at the temperatures of 300, 500, 700, 900, and 1100 °C. After each 30-minute annealing cycle the samples were investigated spectroscopically. Luminescence was analyzed with a 0.8 m double-grating monochromator equipped with a RCA C31034 photomultiplier tube and photon-counting electronics. The samples were cooled down

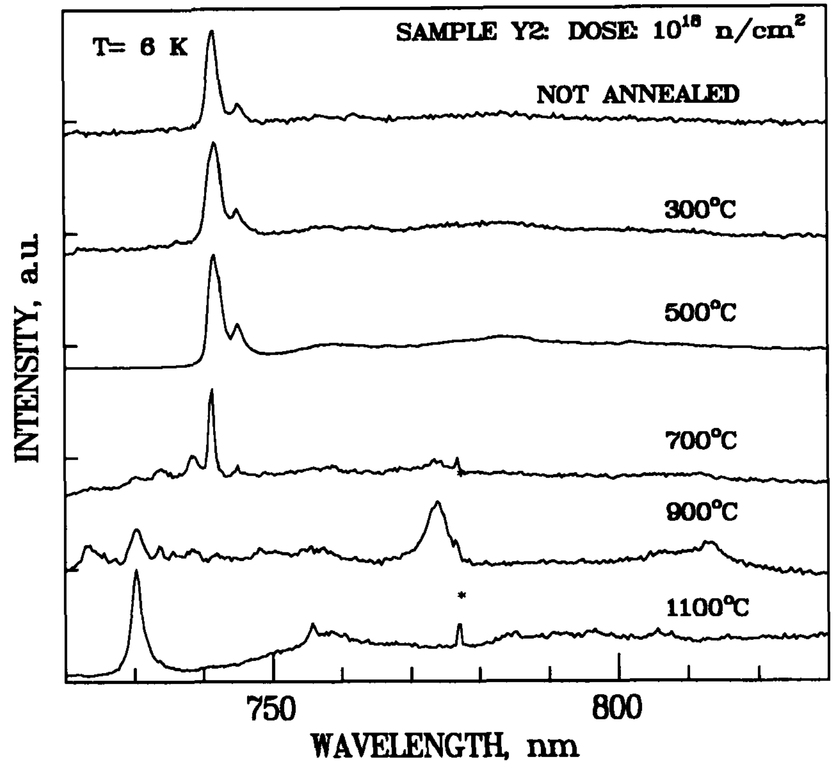

FIGURE 1 The effect of annealing to the photoluminescence spectra of Ia-type neutron- irradiated diamond (sample Y2, dose 10^{18} n/cm^2). Excitation at 704 nm, 40 mW/mm^2. * marks the 1332 cm^{-1} Raman line of diamond.

to 6 K in an optical liquid helium cryostat. An Ar$^+$-ion-laser-pumped cw dye laser was used to excite photoluminescence in the red (700-830 nm) spectral region, otherwise the 488 and 514 nm lines of an Ar$^+$-ion laser and a He-Ne laser were used. All the spectra have been corrected for the spectral response of the detection system.

RESULTS

In the following we shall briefly describe the results of irradiation and heat treatment. Directly after the irradiation all of the crystals turned opaque and their photoluminescence spectra revealed only the vibronic system with a ZPL at 741 nm stemming from single vacancies (GR1). According to our results we can distinguish three annealing stages in the evolution of the spectra of samples Y1, Y2, and Y3.

At the first stage, at annealing temperatures below 500 °C there are no changes in the spectra (figure 1). At the second stage, during annealing at temperatures 500 °C - 900 °C the GR1 line corresponding to single vacancies decreases (figure 1). Simultaneously the vibronic systems with well-known structure and with ZPLs at 496, 503, 575, 594 (the last one in absorption only) and 637 nm appear as can be seen from figure 2, where the photoluminescence spectra of the sample Y1 heated at 900 °C are depicted. We can see that in addition to the above-mentioned lines a number of unidentified ZPLs becomes observable. Peak wavelengths of these lines are 587.6, 612.2, 649.5, 663, 668, 676, 681, 723, 726, 730.4, 734.1, 756, 774, 805.5 and 813 nm. It should be pointed out that measuring the absorption spectra (see fig. 3) revealed ZPLs at 644, 651, 655, 699, 701 712, 774 and 813 nm, which do not exist in photoluminescence signal. Most of these lines have not been mentioned before and none has been identified yet.

In the third stage of annealing, at temperatures higher than 900 °C some of the lines, namely the ones at 587.6, 594, 663, 681, 723, 726, 734.1 774, 813 nm disappear. This can be seen in fig. 4 by comparing curves b, c and d which show the spectra of samples subjected to annealing at 900, 950 and 1100 °C, respectively. The changes in the red spectral region of the Y2 sample can be followed in fig. 1. At this high-temperature annealing another set of lines shows further increase of the intensity, these lines are peaking at 649.5, 676, 730.4, 756 nm (see figure 2). In photoluminescence spectra of sample S (see figure 4, curve a) the H3 (503 nm) and N-V (637 nm) vibronic systems are dominating and additionally only the 774, 805.5, and 813 nm lines are created during annealing.

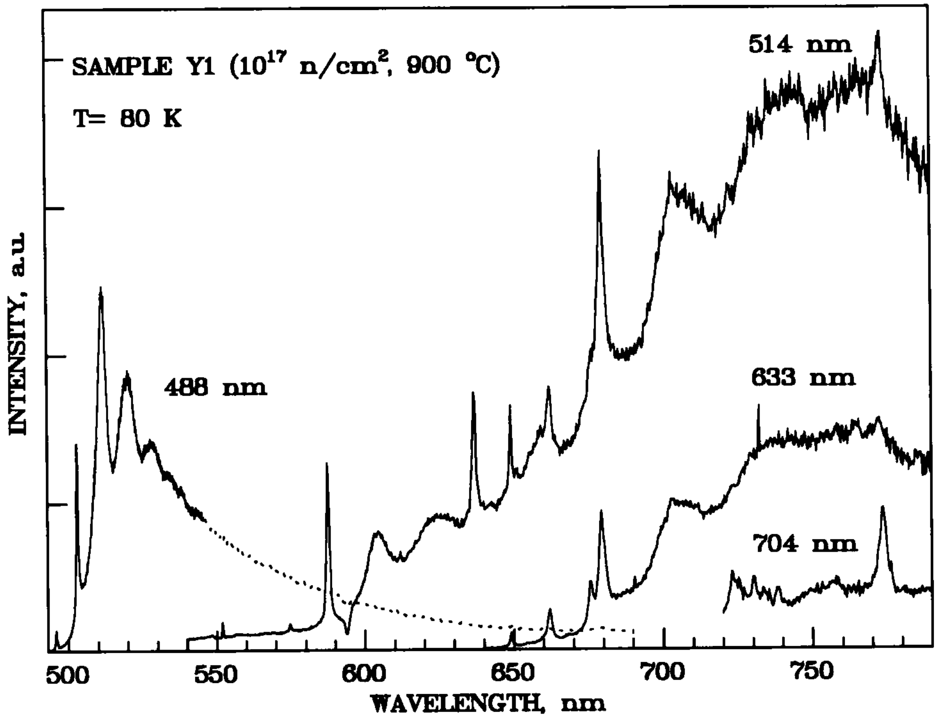

FIGURE 2 Photoluminescence spectra of Ia-type neutron-irradiated diamond (sample Y1) at different excitation wavelength.

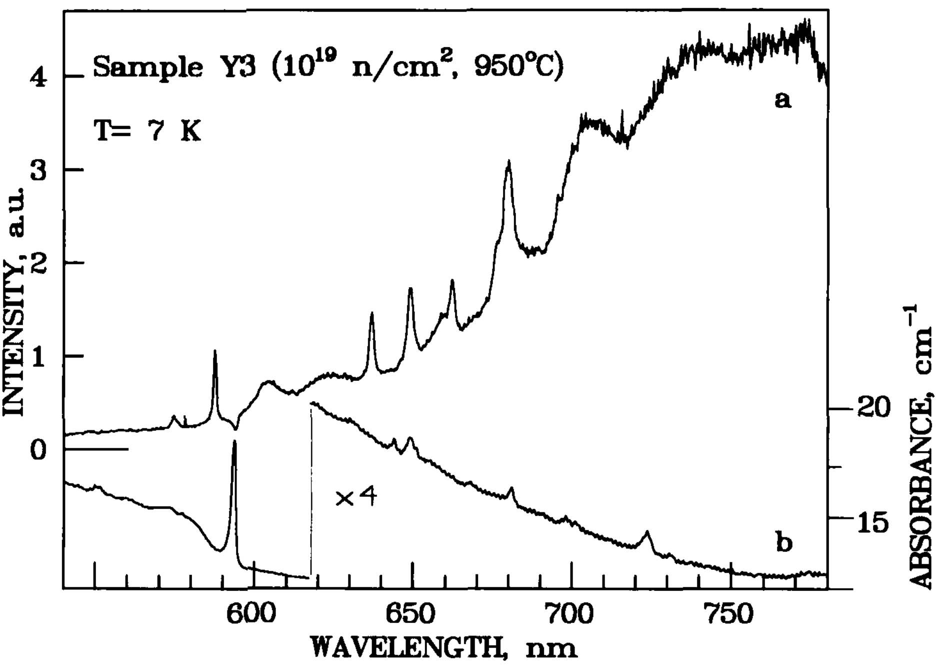

FIGURE 3. Comparison of the photoluminescence (a) and absorption spectra of the sample Y3. Photoluminescence excitation wavelength is 514 nm.

DISCUSSION

Prior to irradiation we measured infrared absorption spectra of the Yakutian samples in order to evaluate the nitrogen content of the sample by using the relations given by Woods et al.[7] As a result we obtained the values of $4 \cdot 10^{19}$ cm^{-3} and $8 \cdot 10^{19}$ cm^{-3} for the amount of nitrogen present in A (pairs of substitutional nitrogen) and B1 (four N atoms) aggregates, respectively. In addition, the samples contain the B2 aggregates (platelets in the (100) planes containing some nitrogen). The visible-range absorption spectra of the samples prior to irradiation were dominated by the N3 system (ZPL at 415 nm) which shows fairly high content of aggregates consisting of three N atoms and a vacancy.

During thermal annealing the irradiation-created vacancies are migrating and trapped mostly by nitrogen-related defects which are pervasive in the sample. According to Davies[8] the activation energy of migration of a single vacancy is 2.3 ±0.2 eV and it starts migrating at temperatures above 500 °C. The decrease of the inhomogeneous width of the GR1 (vacancy) line before it is totally annealed out (see figure 1), can be explained by the influence of two processes: 1) removal of disorder in the lattice during annealing and 2) trapping of the strongly perturbed vacancies which are situated in the vicinity of nitrogen aggregates and contributing to the wings of the GR1 line. Part of the vacancies join to form bivacancies, some are captured by dislocations and impurities. The ones trapped by A and B1 aggregates form H3 and H4

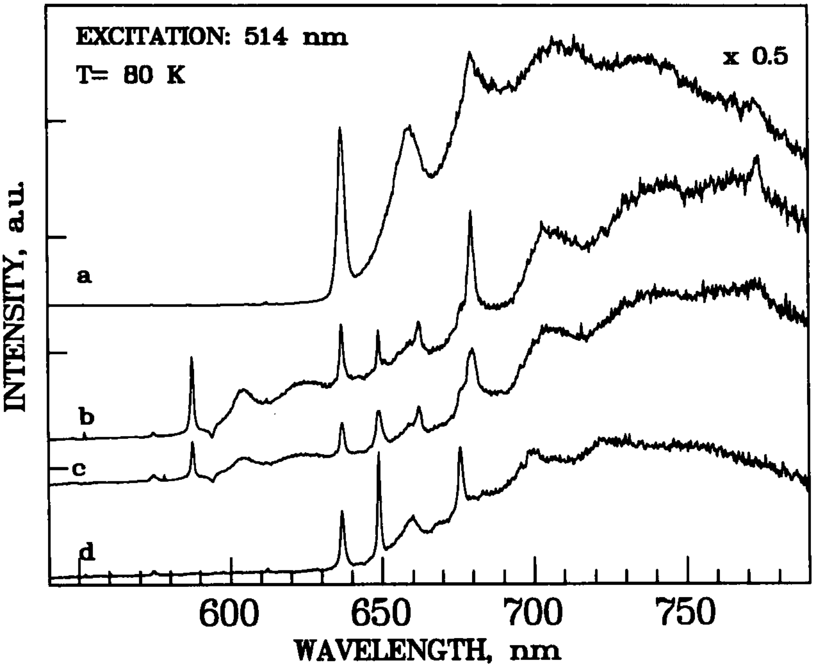

FIGURE 4 Photoluminescence spectra of Ia-type diamonds subjected to various irradiation and heat treatment.
a - sample S, dose 10^{18} n/cm^2, annealed at 900 °C; **b** - sample Y1, 10^{17} n/cm^2, 900 °C; **c** - sample Y3, 10^{19} n/cm^2, 950 °C; **d** - sample Y2, 10^{18} n/cm^2, 1100 °C. Spectra are vertically shifted for clarity.

defects respectively (ZPLs at 503.2 and 496.1 nm). The vacancies are also captured by single nitrogen atoms thus forming the N-V centers (ZPL at 637 nm). All the three vibronic spectra appear in the photoluminescence spectra of samples Y1 - Y3 with the Yakutian origin but in sample S the H4 line is completely absent indicating the absence of the B1 aggregates of nitrogen in this type of crystal. Also, higher intensity of the 637 nm line in the spectra of sample S should be mentioned, showing that the role of single nitrogen atoms is more important in this crystal.

In order to make some generalizations we shall divide the observed spectral lines into three groups: 1) lines that appear during the annealing both in the spectra of samples Y1 - Y3 and sample S (peaking at 774, 805.5, and 813 nm); 2) lines appearing only in samples Y1 - Y3 of Yakutian origin and which are annealed out at temperatures over 900 °C; the growth of these lines correlates with each other during heat treatment (the lines are peaking at 587.6, 663, 681, 723, 726, 734.1 nm); 3) lines also appearing only in the samples Y1 - Y3, but which do not reach their maxima even at the annealing temperature of 1100 °C (peaking at 649.5, 676, 730.4, 756 nm).

The lines in the **first group** are interesting for their PSHB properties and one of our main goals was to find the optimum conditions for the generation of these lines. Taking into account that 1) attempts to create the defects in synthetic Ib-type diamonds and nitrogen-doped CVD diamond films have not yet given any results, 2) the defects were observed in natural Ia type diamond crystals of different origin and of different content of nitrogen aggregates subjected to neutron irradiation and 3) increase of the ZPLs is correlated with the reduction of the number of vacancies, we suggest that these lines belong to defects which consist of a vacancy trapped by a nitrogen-related aggregate. At the temperatures used for annealing in this work no migration of nitrogen atoms occurs as the activation energy of this process is 6.3 eV (5 eV for the vacancy-assisted process) and the activation energy for the aggregates of nitrogen is still higher.[9] Also the other impurities do not migrate at these temperatures. As the only migrating defect is a vacancy and creation of the 774 and 813 nm defects depends on the presence of N aggregates but, at the same time, they do not belong to any of the well-knownvacancy + nitrogen aggregates, it is concluded that either another impurity is included in addition to nitrogen or that the vacancies are trapped by some unknown nitrogenaggregate. As for the conditions of generation of the defects intensity of their ZPLs and their inhomogeneous widths increases with the irradiation dose up to 10^{19} n/cm^2 and the optimum annealing temperature is 900 °C. At higher annealing temperatures the defects are destroyed and at 1100 °C the 774 and 813 nm lines are totally erased from the spectra. It should be mentioned that the H3, H4 and N-V complexes are stable at temperatures up to 1500 °C.

The above-mentioned spectral lines at 774 and 813 nm have not been observed by other investigators, except the study by McCauley et al.[10] where a broad line of unknown origin with maximum at 775 nm was observed in a hot filament CVD diamond film.

The annealing behavior of the **second group of lines** (587.6, 663, 681, 723, 726, 734.1 nm) is quite similar to the behavior of the 774 nm line. They are also created simultaneously with the disappearance of the vacancies and destroyed at temperatures above 900 °C. This leads us to the conclusion that they also consist of a vacancy trapped at some impurity or impurity complex. After annealing at 1100 °C the lines are annealed out completely. Difference from the first group is that none of the lines has been observed in the photoluminescence spectra of sample S. From the absence of the 496 nm ZPL (H4) in the spectrum of the irradiated and annealed sample S we can conclude that no B1 aggregates of nitrogen are present in this sample and the crystal is of type IaA. Following from this the defects giving rise to the lines in the second group must either be related to the B1 nitrogen aggregate or contain another impurity present in samples Y1 - Y3 and absent in sample S.

Two of the ZPLs, the ones at 587.6 and 681 nm exhibit similar phonon sidebands and the dominant electron-phonon interaction is with the 60 meV phonons. The Huang-Rhys factor is estimated to be ≈2 which is quite usual in diamond defects. Phonons with nearly the same energy are also active in the 503 (H3), 637 (N-V), and 737 (Si-containing defect) nm vibronic systems. Our previous studies[6] have shown that the 681 nm ZPL in absorption is fairly temperature sensitive, shifting proportionally to T^4. The luminescence line was shown to consist of two components with a separation of 1 nm. The 587.6 nm line has not been investigated in detail yet.

In this set of spectral lines PSHB has been carried out in the 681, 723, and 730.4 nm lines. Holes in the 681 nm line could be observed at temperatures up to 100 K. A ZPL at 681 nm has been observed earlier[11,12] but it is not clear whether the lines originate from the same defects as in our case. By Nisida et al.[11] the line was observed in an irradiated IaA type diamond and no details were reported, Nazare et al.[12] observed luminescence lifetime of 17 ms which exceeds essentially the lifetime estimated by us (4 ns).

The **third group of lines** behaves differently from the others. As the increase of the lines continues after the vacancies are already recombined or trapped a different mechanism of defect formation must be considered. At the temperature of 1100 °C the intensity of these lines has not reached its maximum yet. None of these ZPLs is present in the spectra of sample S. In absorption the 649.5 and 644 lines have been reported[13] to appear in Ia type diamonds after neutron irradiation, but no details were given nor is the structure of the defects known. PSHB has been carried out by us in the 649.5 nm and 730.4 nm lines. Photoproduct reveals itself at 644 and 651 nm. In this case light-induced defect site distortion caused by the optical excitation of the defect can be proposed as the mechanism of PSHB.

CONCLUSION

As a result of analysis of the optical spectra of Ia-type diamond crystals subjected to different treatment the most favorable annealing conditions for the production of the 774 and 813 nm spectral lines were found. Maximum intensity of the lines in neutron-irradiated crystals was achieved by annealing at 900 °C and the defects are completely destroyed by annealing at 1100 °C. It was concluded that the defects are formed when a single vacancy is trapped by a kind of nitrogen aggregate.

We found that in sample S nitrogen is present in single and paired form and no B-type aggregates were found. As the 774 and 813 nm ZPLs were created in this sample we can conclude that presence of the B1 type of nitrogen aggregates (complexes of 4 N atoms) is not necessary for the creation of these defects.

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