

Luminescence excitation spectra in diamond

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Photoluminescence excitation (PLE) spectra, measured at varying temperatures and for different luminescent energies, are applied systematically to the study of defects in *Ia*, *Ib*, *Iib*, and chemical-vapor-deposited (CVD) diamond. It is shown that the green luminescent band in CVD diamond films consists of two distinct components. The first one is attributed to recombination in the amorphous carbon phase. The second component increases with surface hydrogenation in CVD films, but an analogous band remains almost unchanged in *Ib* diamond. This band is ascribed to the donor-acceptor pair recombination. The photoionization threshold for transitions from the valence band to the donor level is determined as 3.25 eV. Based on PLE measurements the broad blue band is assigned to the vibronic band of a dislocation-related center with the ground state position in the range from E_V to $E_V+0.37$ eV. A series of undocumented photoluminescence (PL) lines at 1.81, 1.84, 1.91, 2.02, 2.1, and 2.2 eV is characterized by PL and PLE techniques as belonging to radiative transitions from different excited states to the same ground state of a divacancy-related center. Oscillatory behavior in the PLE spectra from CVD diamond is used to deduce $E_C-2.24$ eV and $E_C-2.05$ eV as the optical ionization thresholds to the conduction band for the divacancy-related and the 1.68 eV centers, respectively.

I. INTRODUCTION

The availability of sensitive optical detectors in the visible range, as well as the possibility of nondestructive study of small samples, have made photo- and cathodoluminescence (PL and CL) two of the major techniques for optical characterization of defects in diamond. One of the prevailing mechanisms of defect luminescence can be outlined as follows. Absorption of light in PL or excitation by an electron beam in CL experiments leads to the population of excited states of a defect. Radiative transitions of the electron back to the electronic and associated vibronic levels of the ground state produce a narrow-line structure, consisting of a sharp zero-phonon line (ZPL) and a vibronic sideband (see, e.g., Figs. 1–3, which are discussed in detail later). The analysis of their spectral shape, which is unique for each optical center, is used for defect identification, provided the structure of the defect is known from independent measurements. Thus, luminescence spectra, while showing the shape and position of the emission bands, do not reveal the origin of the luminescence and the position of the defect levels in the forbidden gap. This information can be obtained from PL excitation (PLE) experiments, which monitor the spectrum of absorption transitions responsible for a certain PL band. Similar results can be deduced from optical absorption spectra, but there the analysis may be complicated by the presence of transitions from different defect centers. The analysis of the high-energy part of PLE spectra has allowed the identification of excited states for several centers in natural and high-pressure high-temperature (HPHT) synthetic diamond. The best known examples are the neutral vacancy (*GR1*) and the vacancy trapped at dinitrogen (*H3*) and trinitrogen (*N3*) centers.¹ Luminescence measurements on diamond films produced by the chemical vapor deposition (CVD) technique show a number of defect centers which are unique for this material, because of the specificity of the synthesis method.² Unfortunately, luminescence from these centers has not yet been characterized by the PLE technique. It, there-

fore, will be a first important topic in this paper.

PLE spectra measured around the interband absorption region in natural diamond^{3–9} revealed a specific oscillatory structure (as shown in Fig. 8, which is discussed later). Such oscillations have also been observed in photoconductivity^{6,7,10} and photoelectron yield¹¹ spectra in diamond and other semiconductors, for both band-to-band^{6,11} and band-to-defect-level^{7,10} transitions. They are explained by phonon-assisted modulation of the carrier lifetime when a carrier is excited to the valence or conduction band^{6,7} (VB or CB): if the excited state of a defect in the forbidden gap lies close to the VB or CB edge, there is enhanced probability of transition of a photoexcited carrier from the band to this state by cascade emission of phonons, without thermalization of the carrier to the bottom of the band. This probability has maxima when the energy to dissipate is a multiple of the phonon energy, which leads to the appearance of maxima in PLE and corresponding minima in photoconductivity excitation spectra.^{6,7} It has been shown^{3–6,8,9} that in some *Ia* diamonds the oscillations in PLE spectra, measured for the broad blue luminescence band, may extend to the sub-band

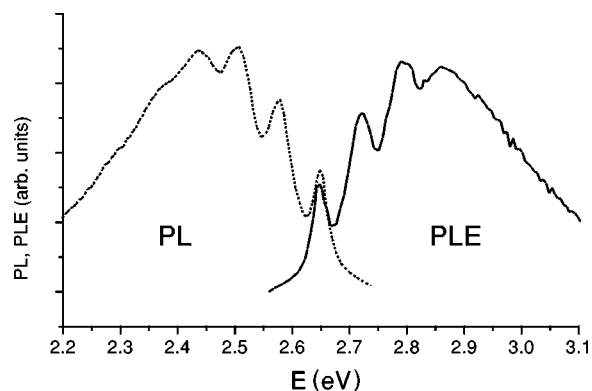


FIG. 1. PL and PLE spectra measured at 77 K in a CVD film. PL was excited at 2.9 eV and PLE was measured for 2.4 eV emission.

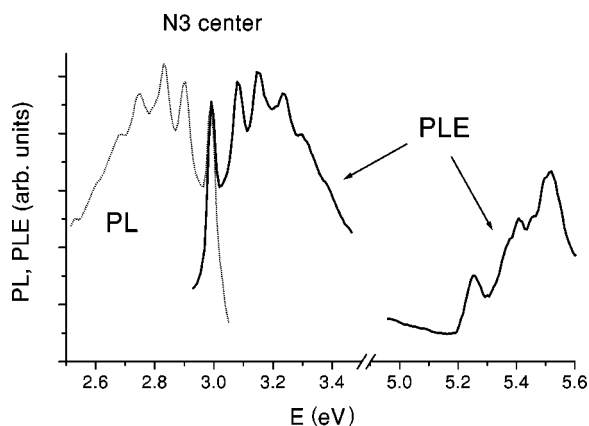


FIG. 2. PL and PLE spectra measured at 77 K for Ia diamond. PL was excited at 3.4 eV and PLE was measured for 2.8 eV emission.

gap region (5.2–5.5 eV). This subclass of Ia diamond was called intermediate,^{3–5,8,9} but this classification was not widely accepted later and we will call it just Ia diamond. The same sub-band gap oscillations were observed also in absorption^{5,8,12} and emission,¹² and attributed to the so-called N9 center.^{1,9,12} The mechanism of excitation transfer from the N9 to the emitting centers has remained uncertain. In the PLE studies^{3–6,8,9} mentioned, PL emission energy was selected by a broadband filter (with a 1–1.5 eV bandpass), and no control of PLE was performed: different PL bands could (and possibly did, as will be shown later) contribute to the total PLE spectrum. The shape of sub-band gap PLE spectra was found to be very different in Ib, Ia, IIa, and IIb diamond,^{3–5,8,9} which could not be satisfactorily explained. No further work on PLE oscillations has been reported after those studies, and the open questions, although important for the understanding of the mechanism of PL excitation in diamond, have remained unanswered. Consequently, we will also focus on this issue in our study of luminescence excitation.

Along with narrow peaks, luminescence measurements on diamond also reveal broad bands, having no narrow-line structure, not even at low temperatures and in the best-quality unstressed samples.^{1,13,14} The most widely known are the green and blue bands,^{1,13,14} centered at about 2.3 eV and

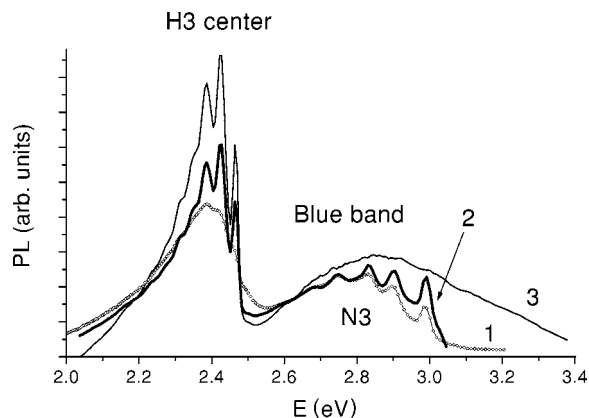


FIG. 3. PL spectra from Ia diamond excited at 3.4 eV at 300 K (curve 1) and 77 K (curve 2), and at 5.5 eV at 77 K (curve 3).

2.8 eV. The ubiquity of these bands in all kinds of diamond determines the importance of their interpretation. Nevertheless, in spite of a large number of elaborate reports, no satisfactorily argued model exists at the moment. Dean¹⁴ proposed a unified donor-acceptor (D-A) recombination model for all broad bands in diamond. However, further experimental work^{15–17} showed that the blue band emission originates at dislocations and does not involve a D-A pair; no alternative emission mechanism has been proposed. In natural and CVD diamond the blue band is dominant in defect-free crystalline sectors.^{1,13} Moreover, no obvious correlation of the blue band intensity with any impurity doping has been reported thus far, suggesting that this band is probably related to structural defects. The observed increase in the blue band intensity with boron doping¹⁷ could be due to the increase in dislocation content due to the doping.¹⁷ The broad green band, on the other hand, is believed to be boron related, since a series of reports^{1,13,14,17–19} shows that its intensity increases with boron doping. However, there still exist contradictions in the reports on the green band luminescence, contradictions that cannot be explained by the specificity of the samples studied or by experimental errors. The green band is observed in samples grown in boron-free reactors, showing no detectable amount of boron. For example, the broad green band was observed²⁰ in good-quality CVD films with concentration of boron and nitrogen atoms less than 10 ppb. The original measurements on natural diamond show an activation energy of about 0.3 eV for the intensity of the green band,¹⁴ while, in contrast, almost no temperature dependency was observed for the green band in undoped and boron-doped CVD films.^{18,21} Spatially resolved CL measurements show that the green band emission in samples containing structural imperfections and grain boundaries either can be localized at these imperfections¹⁹ or can be homogeneously distributed over the sample.¹⁷ A series of papers by Hayashi *et al.*²² shows that the green band is hydrogen related. In these investigations the CL from the broad green band could be repeatedly enhanced and quenched by cycled treatments of the surface of CVD films by oxygen and hydrogen plasma, while by changing the penetration depth of the exciting electron beam it was proved that the emission indeed originates from the surface layers. Reports by Bergman *et al.*²¹ show that the intensity of the green band in boron-free CVD films correlates linearly with the integrated intensity of amorphous carbon (*a*-C) related Raman peaks. At the same time, it was found that the intensity of another band, namely, the broad red band, excited at 2.41 eV, also correlates with increase in the *a*-C component.²³

An obvious conclusion from the above collection of disparate results is that further clarifications on the origin and nature of the broad PL bands are needed. For this reason, we include in the present work a characterization of the broad green and blue emission bands in natural and synthetic diamond by means of PL and PLE techniques. An attempt is made to reveal the structure and origin of these bands, and to explain some of the discrepancies in the reports on the broadband green luminescence.

II. EXPERIMENTAL DETAILS

Undoped and nitrogen-doped unoriented polycrystalline diamond films were grown on Si substrates in an ASTeX

PDS-17 microwave plasma reactor at the Institute for Materials Research, Diepenbeek, Belgium.²⁴ By the same technique, $\langle 100 \rangle$ -oriented undoped and unoriented boron-doped polycrystalline films were grown in separate reactors at the University of Wuppertal, Germany. The Si substrates were removed by chemical etching after the film deposition. *Ib* HPHT synthetic and *Iib* natural diamond samples were $2 \times 2 \times 0.5$ mm³ polished, homogeneous blocks obtained from Drukker International. *Ia* natural diamond was an unshaped stone of about 1 mm in diameter. Raman and transmittance measurements confirmed its homogeneity and undetectable content of foreign inclusions.

Confocal micro-Raman spectroscopy was utilized to monitor the *a*-C content and the intensity of PL in one measurement, and to establish a spatial correlation between PL and structural defects in CVD films. Measurements were performed at 300 K, using the 2.71 eV (457.9 nm) or 2.41 eV (514.5 nm) line from an Ar⁺ laser focused to a 2 μ m diameter spot. Quasi-steady-state PL and PLE experiments were performed in the range 77–300 K with a spectral resolution about 20 meV, using the following excitation light sources: a 150 W Xe lamp with a double monochromator, a 200 W Hg lamp with interference filter and a single monochromator, an Ar⁺ laser (one of the emission lines in the range 2.41–3.53 eV selected by a prism), and a nitrogen laser, providing 3 ns 0.3 mJ pulses at 3.68 eV. In PLE experiments, the intensity of PL at fixed wavelength, selected by a monochromator, was measured as a function of excitation photon energy. The whole PL spectrum was then measured at different PLE energies in order to check for the presence of underlying PL bands. Contribution of stray light to the PLE spectra was carefully inspected and, if present, taken into account. Optical absorption measurements showed the insignificance of self-absorption of luminescence in any of the samples studied. In polarization experiments PL signals I_{\parallel} and I_{\perp} were detected at polarizations parallel and perpendicular to the polarization of the exciting laser beam. The value $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ was used as a measure of the degree of polarization. Unoriented polycrystalline films show strong light scattering, leading to the total depolarization ($P = 0$) of PL due to multiple reflections at the grain boundaries. In order to reduce the scattering, highly textured oriented films with large grains have been used, with the excitation beam focused almost fully within one grain. Polarization response of the detection system was measured independently and taken into account.

III. RESULTS AND DISCUSSION

A. PL excitation

Figure 1 shows a typical example of PL and PLE spectra from a defect center. PL was excited at 2.9 eV, PLE was measured for 2.4 eV PL, and the same excitation curves were observed for other PL energies within the range 2.2–2.65 eV. The spectra were recorded at 77 K for a CVD film, in which this center dominates the PL. Almost perfect mirrorlike symmetry relative to a ZPL at 2.65 eV is seen between the PL and PLE spectra, which is typical for internal excitation of a defect center with a weak Jahn-Teller interaction. The relative broadness of the spectral lines, in comparison to monocrystalline diamond, is due to local strain and inhomogeneity typical for CVD diamond.²

The 2.65 eV optical center shown in Fig. 1 was, under appropriate excitation (2.71 eV), observed in most CVD films studied. However, most energies in the range 3–5.5 eV effectively excited other PL bands as well, which then masked the 2.65 eV center. This could be the reason for the absence of reports on this center in the literature. In fact, the presence of this center can be seen in the CL spectra²⁵ from CVD films upon careful analysis. Annealing at 1400°C in 10^{-8} Torr for 2 h results in a slight increase in the PL from the 2.65 eV center, showing that it is probably unrelated to the so-called *TR12* center with a ZPL at 2.64 eV, which is observed in irradiated natural diamond,^{1,26} because the latter center anneals out^{1,26} at 900°C. We observe an increase in intensity of the 2.65 eV system with nitrogen doping. Further studies by independent techniques are required to reveal the microscopic nature of this center.

Figure 2 presents PL and PLE spectra measured at 77 K for the *N3* center (ZPL at 2.99 eV) in *Ia* diamond. PL was excited at 3.4 eV and PLE was measured for 2.8 eV emission. As in Fig. 1, a mirrorlike symmetry is seen in the range 2.5–3.5 eV between PL and PLE. In the range 5.2–5.6 eV the PLE spectrum shows oscillatory structure, which is discussed further below. Such a PLE spectrum has already been reported and attributed to the *N3* center by Nahum and Halperin.⁸ In Fig. 3 PL spectra from the same sample are presented, when excited with 3.4 eV photons at 300 K (curve 1) and 77 K (curve 2), and with 5.5 eV photons at 77 K (curve 3). They reveal that excitation by 3.4 eV photons (or others in the range 3.3–4.9 eV) produces PL from the *N3* and *H3* centers, while the band-to-band excitation at 5.5 eV generates a broad blue band centered at 2.8 eV along with the *H3* center and with negligible contribution of the *N3* center. Similar PL spectra were reported by Dean and Male,³ but not analyzed in conjunction with the PLE results. They demonstrate that the high-energy part of the PLE spectrum in Fig. 2 belongs to the broad blue band, but not to the *N3* center, as assumed by Nahum and Halperin.⁸ Indeed, the *N3* center is weak in CL,¹³ and therefore should not show the PLE rise in the intrinsic absorption range. Figure 3 also shows that, while the structure of the *H3* center significantly sharpens when temperature decreases from 300 K to 77 K, the line shape of the *N3* center remains almost unchanged. These differences can be explained by the difference in the local phonon mode densities for these centers.²⁷ Figure 4 shows PL spectra for the same sample, under 2.41 eV excitation at 300 K and 77 K. While the excitation in the range 2.54–5.5 eV did not reveal any PL centers, except *N3* and *H3*, the 1.945 eV and 2.156 eV centers, attributed to the negative and neutral charge states of nitrogen-vacancy centers²⁸ ($[N-V]^{-}$ and $[N-V]^0$), appear under 2.41 eV excitation, demonstrating the importance of the choice of excitation energy for the observation of PL from a certain center. Figure 4 also reveals that 2.41 eV excitation at 300 K can effectively produce PL from the *H3* center with a ZPL at 2.463 eV without significant shift in the position of the vibronic band maximum. Such anti-Stokes PL can be excited via transitions from the upper vibronic levels of the ground state to the lowest level of the excited state; of course, the decrease in temperature quenches these transitions due to the depopulation of the higher vibronic states.

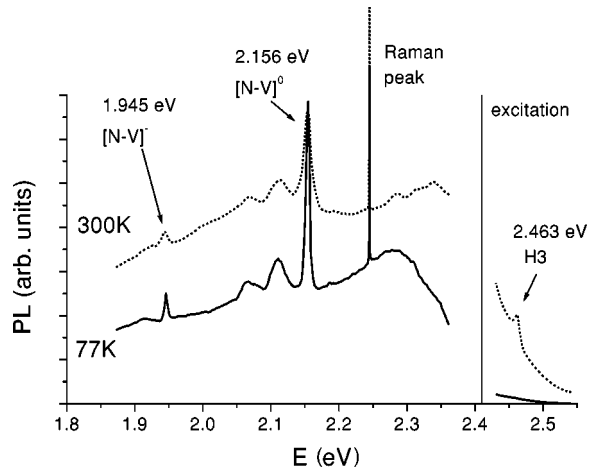


FIG. 4. PL spectra for Ia diamond under 2.41 eV excitation at 300 K and 77 K.

B. Broad green bands

Figure 5 presents PLE (curves 1,2) and PL (curves I,II) spectra measured at 77 K for the broad green band in an undoped CVD film. Also shown are PLE (curve 3) and PL (curve II) spectra for Ib synthetic diamond. PLE spectra were measured for the 2.3 eV emission. No difference in the shape of PLE spectra was observed for different emission energies within the PL band. The PLE spectrum for the CVD film (curve 1) shows two components: a symmetric band centered at 2.95 eV and a steplike feature with a threshold at 3.25 eV. The relative intensities of these components were temperature and sample dependent. The second PLE component disappeared after annealing of a sample at 400°C for 30 min in 10^{-5} Torr or after ultrasonic rinsing in acetone, to leave the spectrum shown by curve 2. The original PLE spectrum could then be restored by exposing the sample to a humid atmosphere for about a day. Electrical measurements performed during such treatment showed a strong increase in the electrical resistance after vacuum annealing (10^3 – 10^6 times, depending on the sample) followed by a gradual relaxation of resistance to its original value.²⁹ The alteration of

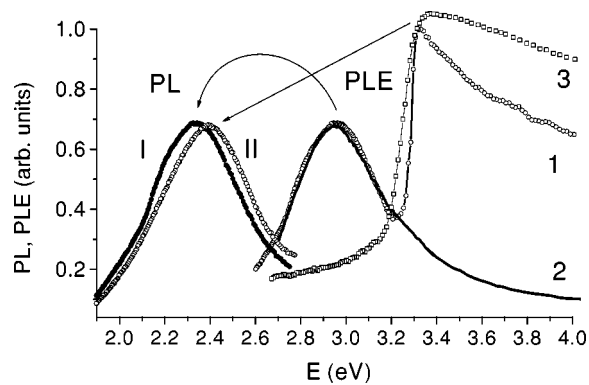


FIG. 5. PL and PLE spectra measured at 77 K for the broad green band in an undoped CVD film and in Ib diamond. Curves 1,2: PLE spectra for 2.3 eV emission from a CVD film before and after annealing (400°C, 10^{-5} Torr, 30 min). Curve 3: PLE spectrum for 2.3 eV emission from a Ib diamond. Curves I, II: PL spectra excited at any energy in the range 2.7–3.1 eV in CVD film (curve I) and in the range 3.3–4.9 eV in CVD film or Ib diamond (curve II).

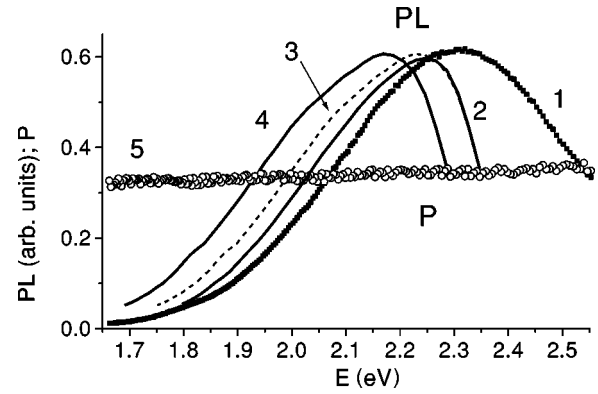


FIG. 6. Curves 1–4 show PL spectra measured at 300 K for the CVD film used in Fig. 5, under 2.71 eV (1), 2.6 eV (2), 2.54 eV (3), and 2.41 eV (4) excitation. PL spectra are normalized to peak intensity. PL spectra of polarization P measured under 2.71 eV (same for 2.41, 2.54, and 2.6 eV) excitation.

the PLE spectral shape and electrical resistance could be repeated for at least 10 cycles. The PLE spectrum for the green band in synthetic Ib diamond (curve 3) shows only the step-like threshold at 3.2 eV, very similar to the one in the CVD film. No significant changes in the spectrum of curve 3 could be induced by annealing or acetone treatment. Luminescence spectra excited at any photon energy in the ranges 2.7–3.1 eV and 3.3–4.9 eV are presented by curves I and II, respectively. These spectra have an almost identical shape and only a slight difference in the peak position (2.34 eV for curve I and 2.39 eV for curve II). Photoluminescence spectra for CVD and Ib diamond were indistinguishable under excitation in the range 3.3–4.9 eV, and are both shown by curve II. Because of the different behavior with respect to the surface treatment and different excitation energies, the two green bands, shown by curves I and II and hereafter called bands I and II, could be easily separated and studied independently. These bands reveal different temperature dependencies: the band I shows only a factor of 2 increase with the decrease in temperature from 300 K to 77 K, while the intensity of band II strongly increases when the sample is cooled, showing an activation energy of 0.3 eV. Moreover, these bands show different spatial distributions: the intensity of the band I was up to 10 times higher at the grain boundaries, while the band II PL was homogeneously distributed over the sample surface. Micro-Raman measurements at 2.71 eV performed on different samples show that the intensity of the band I, normalized to the integrated diamond Raman peak, linearly increases with the a -C content, which was monitored by the ratio of integrated nondiamond carbon peaks to the integrated diamond line, in agreement with the results of Bergman *et al.*²¹ Step-by-step decrease in the excitation photon energy of the Ar⁺ laser in the range 2.71–2.41 eV leads to the gradual redshift in the position of the maximum of the band I, as seen from Fig. 6. Curve 5 of Fig. 6 shows the spectral dependency of the degree of PL polarization P , measured under 2.71 eV excitation. Rotation of a sample with respect to the direction of laser polarization did not result in a variation of PL intensity, showing that polarization of luminescence is induced by the exciting laser beam but not by the symmetry of the PL center. Essentially the same spectral dependencies of P were observed under any excitation in the

range 2.71–2.41 eV. Similarities in PL polarization spectra and the gradualness of PL changes with excitation energy suggest that the change in the shape of the PL spectrum is due to the shift in the position of the maximum of the green band I, but not due to the appearance of another band. This suggestion is confirmed by the same weak temperature dependencies of PL excited at 2.71 eV and 2.41 eV and by the results of further micro-Raman measurements performed at 2.41 eV. They showed the same spatial behavior and similar correlations of the PL intensity with *a*-C content for 2.41 eV and 2.71 eV excitation.

The observed correlations of the amplitude and spatial distribution of the green band I with the *a*-C related defects agree with the assignment of this band to the *a*-C carbon phase.²¹ Remarkable is the Gaussian-like shape of the PL and PLE spectra from this band, along with their mirrorlike symmetry. Similar PL and PLE spectra were observed in brown diamond and were shown to originate from the vibronic band of a defect center with a specific shape of local phonon mode density.³⁰ If one assumes a similar vibronic origin for the green band I, the ZPL position should be approximately in the middle between the PL and PLE peaks, i.e., at 2.65 eV. However, the fact that this band can be effectively excited at 2.41 eV then leads to a contradiction. Indeed, if one accepts the possibility of anti-Stokes PL excitation, as for the *H3* center (see Fig. 4), then the decrease in temperature should lead to a strong decrease in PL intensity due to depopulation of the vibronic states. On the contrary, experiment shows a slight increase in intensity of the PL excited at 2.41 eV with decrease in temperature.

Another possible mechanism for the green band I emission is radiative recombination in the tail states of *a*-C clusters.³¹ This process shows a similar temperature dependency of the PL and similar spectral dependencies of PL emission, excitation, and degree of polarization^{31,32} as the ones shown in Figs. 5 and 6. It should therefore be considered as the most likely origin of the green band I. A shift of PL peak with excitation energy, analogous to the one presented in Fig. 6, is also typical^{31,32} for *a*-C. Nevertheless, an increase in the green band intensity in CVD films with boron doping has also been reported.¹⁸ However, as the temperature dependency for this band is strikingly similar to the one for the *a*-C related band observed in reports of Bergman *et al.*²¹ and in the present work, a possible joint increase in the *a*-C and boron content should be considered as a reason for the increase in the intensity of the green band with boron doping. In spite of the above, there remains some uncertainty in the *a*-C recombination model for the green band I: Since it is known that the peak position of PL from *a*-C depends on the structure of the *a*-C clusters,³³ it is quite surprising that CVD films with a very different *a*-C content show the same position of the green band I maximum.

For the green band II, the shape of the PLE spectrum, with a sharp threshold followed by a slow decrease in absorption toward the higher energies, is characteristic for electronic transitions from the valence or conduction band to some defect level.³⁴ The increasing effects of surface recombination with increase in photon energy may also contribute to the high-energy decrease in excitation probability.³⁵ Results of the present work as well as other studies on the effect of surface treatment on the green band luminescence²² show

that the green band II in CVD films originates from a surface region with low-resistive *p*-type conductivity. Therefore, the PLE threshold at 3.25 eV can be attributed to electron transitions from the VB to a defect level, which should then participate in the emission process. The most logical model for this process is a D-A pair recombination. Increase in intensity of excitation (nitrogen laser) light in the range 10^6 – 10^8 W/cm² leads to a blueshift of the green band II peak position. This fact is in agreement with the proposed model. It implies saturation of the PL from the distantly spaced pairs, having slower relaxation than the closely spaced pairs, with increasing excitation.¹⁴ The 3.25 eV threshold is also present in the PLE spectrum for *Ib* diamond (Fig. 5, curve 3), where the dominant defect is a single substitutional nitrogen donor¹ (the so-called *P1* center). However, not a single feature around 3.25 eV was seen in either optical transmission or photoconductivity measured on the same sample. This seems to exclude the *P1* center as a candidate for the donor in the D-A pair and suggests that the donor is some other center, which could be masked by the *P1* center.

In order to explain the increase of the green band II intensity in polycrystalline CVD films with surface hydrogenation we propose the following tentative model. Before the hydrogenation the Fermi level is situated above the acceptor level energy. In this case the acceptor is occupied and D-A recombination is suppressed. Hydrogenation leads to a shift in the Fermi level position down to the valence band edge,^{22,29} which increases the number of unoccupied acceptors able to participate in the D-A recombination. This mechanism probably is not active in monocrystalline *Ib* diamond, where the surface activity with respect to hydrogenation is much lower than in CVD films, and the Fermi level is probably pinned by a dominating *P1* center. In order to explain the increase in the green band in diamond crystals with increasing boron content,^{13,14} boron should be considered as the acceptor in the D-A pair recombination responsible for the green band II. This hypothesis roughly agrees with the observed activation energy of 0.3 eV for the temperature dependency of the green band II PL (Ref. 14): in the case of D-A recombination with boron as the acceptor, a decrease in temperature should lead to an increase in PL, with activation energy close to the boron ionization energy [0.37 eV (Ref. 1)], because more boron acceptors become unoccupied and can participate in the D-A pair recombination.

C. Oscillatory PLE and the broad blue band

PL and PLE spectra for the broad blue band in an undoped CVD diamond film, measured at 77 K, are presented in Fig. 7. PL was excited at 3.4 eV and PLE was measured at 2.8 eV. The same shape of PLE spectra was observed for other PL energies in the range 2.5–3 eV. Similar results were obtained for boron-doped CVD films and *Iib* diamond. No spectrum in this range could be recorded for the blue band in *Ib* and *Ia* diamond because of the strong background due to the green band II and the *N3* center. The intensity of the blue band increased with temperature decrease showing an activation energy of 0.3 eV. Since the position, shape, and temperature dependencies of the broad blue band were the same in our *Ia*, *Ib*, *Iib*, and CVD diamond, we further assume

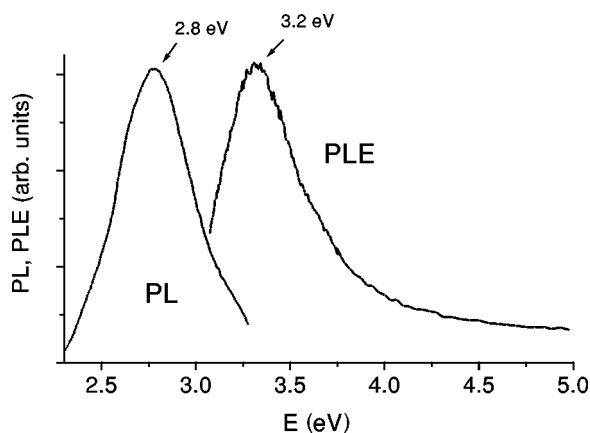


FIG. 7. PL and PLE spectra for the broad blue band in undoped CVD diamond film, measured at 77 K. Similar results were obtained for boron-doped CVD films and *I**II*** diamond. PL was excited at 3.4 eV and PLE was measured at 2.8 eV. The same shape of PLE spectra was observed for other PL energies in the range 2.5–3 eV.

the same origin of this band in the different samples. Blue band PLE spectra from *I**b***, *I**II***, and *I**a*** diamond are shown in Fig. 8. The spectrum for *I**b*** diamond at 300 K (curve 1) shows a threshold at about 5.15 eV, which can be assigned to transitions of electrons from the boron acceptor level with activation energy 0.37 eV to the CB followed by their capture by the defects responsible for the blue band PL (or blue band center). This threshold is not seen at 77 K (curve 2), while a rise at 5.47 eV appears, along with oscillations in the range 5.5–5.9 eV. Similar temperature variations in PLE spectra were reported by Dean and Male⁴ and interpreted in terms of increasing population of the boron level by holes with temperature decrease, which leads to a decrease in electron transitions from this level to the CB, unraveling the band-to-band absorption threshold. PLE oscillations in the range 5.5–5.9 eV were explained by transitions of electrons from the CB to an excited state of the blue band center with emission of a number of phonons.^{6,7} It is important that these transitions occur without thermalization of electrons to the CB bottom, suggesting that electrons in the CB should be generated near the defect site. The PLE spectrum for *I**b*** diamond (curve 3) shows a threshold at 4.6 eV at 300 K and 77 K with no high-energy oscillations. The threshold at this energy was observed in optical absorption in the same sample and can be ascribed to an optical transition involving the single substitutional nitrogen (*P1*) center.^{1,36} For both band-to-band and boron acceptor excitation, it is the electron, that is essential for blue band generation. Therefore, the 4.6 eV threshold can be ascribed to the transitions from a nitrogen-related level to the conduction rather than the valence band. The absence of PLE oscillations in *I**b*** and *I**II*** diamond at 300 K can be explained as follows. As assigned on the basis of the PLE spectrum in Fig. 8, in diamond of these types electrons are excited from boron- or nitrogen-related defect levels to the CB. In order to result in blue band emission, they should move to the PL center via the CB, where they quickly thermalize to the bottom of the CB and, therefore, will not emit a number of phonons while being captured by the blue band centers.

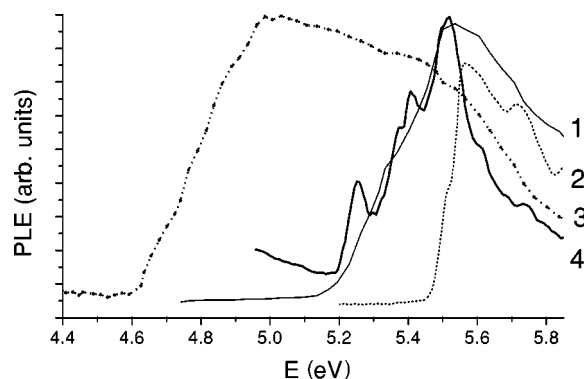


FIG. 8. Ultraviolet PLE spectra measured for the broad blue band in different kinds of diamond at different temperatures. Curves 1,2: *I**b*** diamond at 300 K and 77 K; curve 3: *I**b*** diamond at 77 K, same for 300 K; Curve 4: *I**a*** diamond at 300 K.

The PLE spectrum for *I**a*** diamond (curve 4), along with the discussed oscillations in the range 5.5–5.8 eV, shows peaks at 5.26, 5.36, and 5.39 eV. In some samples these peaks, named the *N9* center, may be seen in absorption^{5,8,12} and their mirror replica, inverted with respect to the 5.26 eV line, can be observed in emission.¹² A correlation between the strength of these peaks and the concentration of nitrogen in an aggregated form was observed^{1,12} and the model of an exciton trapped into a nitrogen-related center was proposed for the *N9* center. This model explained the weak temperature dependency of the intensity and line shape of the *N9* lines, but did not reveal the mechanism of the blue band excitation via absorption at the *N9* center. There is no correlation between the intensity of the blue band PL and *N9* absorption and PLE peaks, suggesting that the *N9* center is not another excited or charged state of the blue band center. Moreover, the *N9* center shows a well-defined narrow-line structure in both absorption^{5,8,12} and emission,¹² while the blue band PL and PLE spectra are structureless (see Fig. 7). We suggest that the blue band in *I**a*** diamond is excited by an exciton trapped at the *N9* center via a resonant tunneling interaction between excited states of the *N9* and blue band centers. The presence of an excited state of the blue band center lying close to the CB bottom follows from the interpretation of PLE oscillations in the intrinsic absorption range.^{6,7} Defect pairs including the *N9* and blue band centers should exist for such exciton tunneling. The ratio of amplitudes of *N9* peaks and PLE peaks in the range 5.5–6 eV shows a weak temperature dependency,^{3,4} excluding the possibility of an alternative mechanism of excitation transfer via thermal ionization of the *N9* exciton.

The PL and PLE spectra shown in Fig. 7 are very similar to the corresponding spectra for the green band I in Fig. 5 and therefore the same two major mechanisms, namely, recombination between two defect levels (or two bands) due to different centers and intercenter transitions from the excited to the ground state, will be considered. It is worthwhile to note that unlike the blue band, the green band I did not show any thresholds or PLE oscillations in the range 5–6 eV. The blue band is observed in the best-quality monocrystalline diamond and therefore the *a*-C model, proposed for the green band I, is hardly applicable in this case. The mirror symmetry between PL and PLE spectra for the blue band

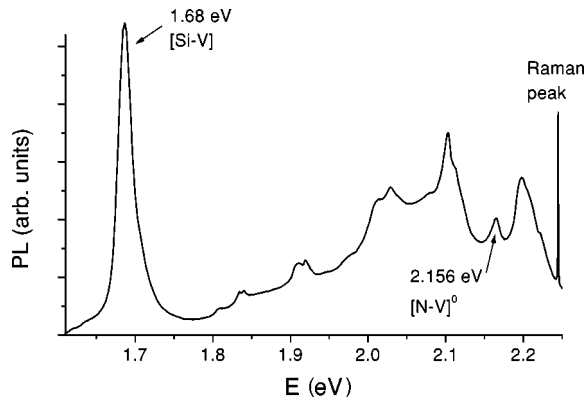


FIG. 9. Room-temperature PL spectrum for undoped CVD film under 2.41 eV excitation.

with no sharp asymmetric thresholds suggests that excitation light is absorbed by the blue band center, with no conduction or valence band involved. These spectra are observed in boron-doped CVD films and IIb diamond, where the Fermi level position is $E_V + 0.37$ eV. For internal excitation of the blue band center its ground state should then be occupied by electrons and therefore the energies of the ground and excited states of this center should be lower than $E_V + 0.37$ eV and $E_V + 0.37 + 2.8$ eV, respectively. In the two-center (e.g., D-A) recombination model a threshold around the energy $E_V + 3.15$ eV should be seen in the blue band PLE spectra for boron-doped diamond, which is not observed (see Fig. 7). Therefore, we suggest that the blue band corresponds to the vibronic sideband of a dislocation-related¹⁵⁻¹⁷ center with a ZPL around 3.0 eV, as deduced from Fig. 7. The integral intensity of the vibronic band is temperature independent as far as vibronic properties are concerned,²⁷ therefore the temperature dependency of the blue band is probably determined by nonradiative processes. The absence of a narrow-line structure for vibronic bands in PL and PLE spectra was already observed in brown diamond³⁰ and can be attributed to high local stress around the dislocation.

D. PLE oscillations in CVD diamond

The room-temperature PL spectrum for a CVD film under 2.41 eV excitation is shown in Fig. 9. The sharp peak at 2.24 eV is a diamond Raman line. Peaks at 1.68 and 2.156 eV, attributed to the [Si-V] and [N-V]⁰ centers,²⁸ along with bands centered at 1.81, 1.84, 1.91, 2.02, 2.1, and 2.2 eV, are seen. Most of the latter peaks are split doublets. The splitting energy was different in different samples and different parts of the same sample, and probably is induced, or at least affected, by local strain. Measurements on different samples, annealed at different temperatures, show that the peaks at 1.81, 1.84, 1.91, 2.02, 2.1, and 2.2 eV belong to the same defect center, unrelated to the 2.156 eV and 1.68 eV ones. At the same time, a good correlation was found between the intensity of these PL peaks and the electron spin resonance (ESR) signal, which was interpreted as originating from a $S=1$ center. ESR and PL signals from this center (hereafter called the $S=1$ center) decrease with nitrogen doping and increase with annealing at 1400°C in 10^{-8} Torr for 2 h. Preliminary analysis of the ESR hyperfine structure and the

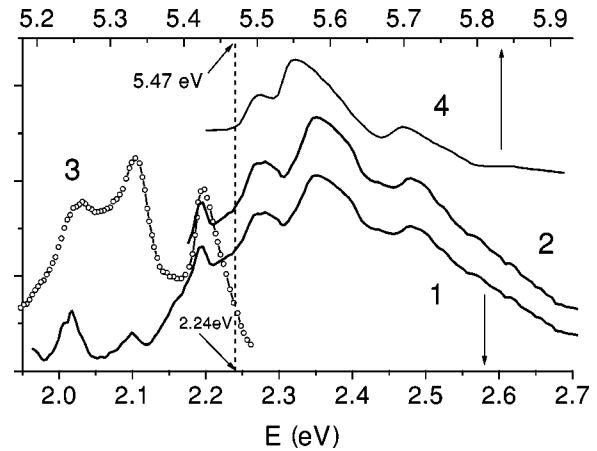


FIG. 10. Optical properties of the “ $S=1$ ” center at 77 K in the CVD film used for Fig. 9. Curve 1: PLE spectrum, measured at 1.91 eV (same for 1.84 and 1.81 eV); curve 2: PLE spectrum, measured at 2.02 eV (same for 2.1 eV) for the same sample; curve 3: luminescence spectrum; curve 4: PLE spectrum of the broad blue band in natural diamond in the range of intrinsic absorption (note the different x axis) taken from data of Dean and Male (Ref. 3).

annealing behavior suggest a divacancy, stabilized by an impurity atom, as a model of this center. A detailed joint analysis of the ESR and PL data will be published in a separate paper.

PLE spectra for the $S=1$ center in the CVD film used for Fig. 9, measured at 77 K, are presented by curves 1 and 2 in Fig. 10. Curve 3 shows the PL spectrum for the same sample. Curve 1 was measured at 1.91 eV, but the same shape of PLE spectra was observed for the 1.84 and 1.81 eV PL. PLE spectra measured at 2.02 and 2.1 eV (curve 2) were indistinguishable within experimental resolution. The width and position of the PLE peaks at 2.02, 2.1, and 2.2 eV (curves 1,2) are very similar to those present in the PL spectrum (curve 3). This suggests that the 1.91, 1.84, and 1.81 eV lines can be excited via absorption of excitation by any of the 2.02, 2.1, or 2.2 eV bands and that 2.02 and 2.1 eV emission can be excited via the 2.2 eV band. Similar behavior was observed in the PLE spectrum from the neutral vacancy in diamond¹ (the $GR1-8$ system). Analogous to the $GR1-8$ system, the whole set of PL lines due to the $S=1$ center can be attributed to the transitions from different excited states to the same ground state of this center.

The PLE spectrum from the 1.68 eV center in the CVD film used for Figs. 9 and 10, measured at 77 K in the range 1.8–2.6 eV, is presented by curve 1 in Fig. 11. Also shown are luminescence (curve 2) and absorption (curve 3) spectra for this center. In the range 1.8–1.9 eV the PLE spectrum shows several small peaks whose positions correlate with those of the vibronic features of the 1.68 eV center, which are seen in absorption (curve 3) and probably correspond to PLE via electron-phonon vibronic transitions. These transitions are also present in PL emission (curve 2).

Both the 1.68 eV and $S=1$ centers show a PLE oscillatory structure in the range 2–2.5 eV. These oscillations are very similar to the ones shown by curves 4 in Figs. 10 and 11, which represent a PLE spectrum from the broad blue band in natural diamond in the range of intrinsic absorption (note the different x axis) taken from the data of Dean and

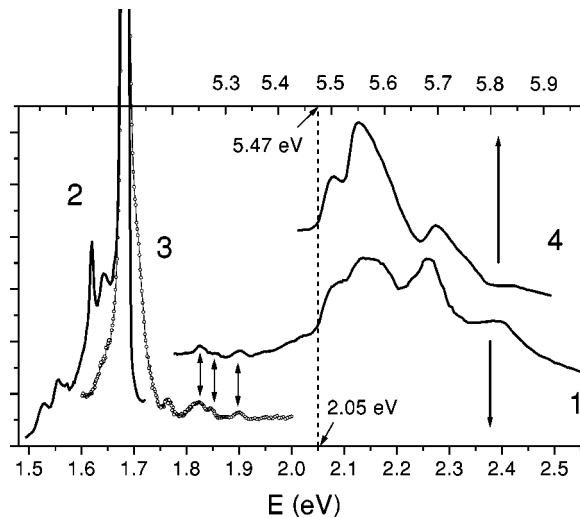


FIG. 11. Optical properties of the 1.68 eV system at 77 K in the CVD film used for Figs. 9 and 10. Curve 1: PLE spectrum; curves 2 and 3: luminescence and absorption spectra of the 1.68 eV system; curve 4: PLE spectrum of the broad blue band in natural diamond in the range of intrinsic absorption (note the different x axis) taken from data of Dean and Male (Ref. 3).

Male.³ The oscillations in the PLE spectra for the 1.68 eV and $S=1$ centers occur at energies much lower than the band gap of diamond, and therefore can be attributed to transitions from the ground state of some defect center to the CB. It would be possible for the electron in the CB to be generated from some dominant defect center and then captured by excited states of the 1.68 eV and $S=1$ centers. However, in this case the same position and shape of PLE oscillations should be seen for both centers, which is not observed: As seen in Figs. 10 and 11, PLE spectra for the 1.68 eV and $S=1$ centers measured in the same sample are distinctly different. We therefore suggest that the electrons captured by the excited states of the 1.68 eV or $S=1$ centers may have been originally generated from the ground states of the same centers. Some kind of localization should then take place: the generated electron should have a relatively high probability to be captured by the center before it moves away along the CB.

The oscillatory structure allows us to make a proposal for the position of the 1.68 eV and $S=1$ centers in the diamond band gap. By aligning, as in Figs. 10 and 11, the PLE spectrum shown by curve 4 with its characteristic threshold at 5.47 eV, corresponding to the energy of the indirect band gap of diamond, with a corresponding threshold on curve 1, we then obtain differences of 2.05 eV and 2.24 eV between the CB bottom and the ground state of the 1.68 eV and $S=1$ centers, respectively.

Finally, ultraviolet PLE spectra, measured at 300 K in CVD diamond, for the 1.68 eV center in different samples (curves 1,2) and for the blue band (curve 3) are shown in Fig. 12. The shape of the PLE threshold at 5.47 eV was sample dependent as seen from curves 1 and 2. Similar behavior was observed in natural diamond^{4,8} and ascribed to different surface quality, whose effect on the PLE spectral shape increases with decrease in absorption length in the intrinsic absorption range. The surface of CVD films is much more disordered than that of monocrystalline diamond, and that

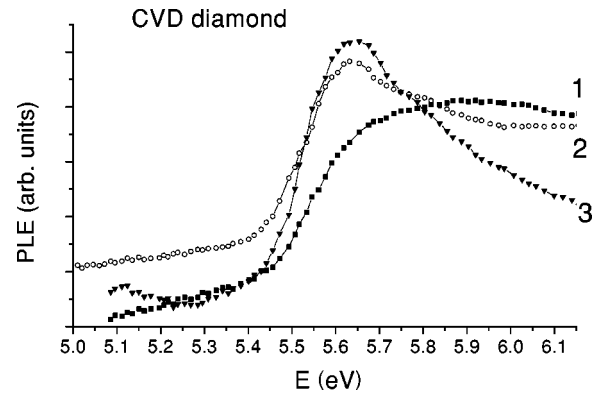


FIG. 12. Ultraviolet PLE spectra, measured at 300 K in CVD diamond, for the 1.68 eV center in two different samples (curves 1,2) and for the blue band (curve 3).

probably explains the absence in Fig. 12 of PLE oscillations in the range 5.5–6 eV. No PLE peaks due to the N_9 center were observed in any of our CVD films either, which can be explained by the general absence of aggregated nitrogen in CVD diamond.⁷

IV. SUMMARY AND CONCLUSIONS

Results of photoluminescence excitation measurements were shown to contribute significantly to the modeling of luminescent centers in Ia , Ib , IIf , and CVD diamond. The green band in CVD diamond films was found to consist of two distinct components. The first one is attributed to recombination in the amorphous carbon phase. The second component, which also corresponds to the green band of Ib diamond, increases with surface hydrogenation in CVD films, but not in Ib diamond. On the basis of excitation and temperature dependencies of PL the second band is ascribed to a donor-acceptor pair recombination. The photoionization threshold for transitions from the valence band to the donor level is determined as 3.25 eV. Again based on PLE measurements, the broad blue band is assigned to the vibronic band of a dislocation-related center with the ground state position between E_V and $E_V+0.37$ eV. A series of undocumented PL lines at 1.81, 1.84, 1.91, 2.02, 2.1, and 2.2 eV is characterized by PL and PLE techniques and assigned to radiative transitions from different excited states to the same ground state of a divacancy-related center. Oscillatory behavior in PLE spectra from natural and CVD diamond is observed. It has been utilized to deduce the optical ionization thresholds to the conduction band for the vacancy-related and 1.68 eV centers as $E_C-2.24$ eV and $E_C-2.05$ eV. Especially with respect to positioning of luminescence centers within the diamond band gap, the excitation spectra are of great value.

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