Donor-acceptor pair recombination in synthetic type-IIb semiconducting diamond

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Steady-state- and time-resolved-photoluminescence (PL) and cathodoluminescence (CL) studies have been carried out on several synthetic type-IIb boron-doped semiconducting diamond samples. The behavior of the 1.84-eV red donor-acceptor pair band is compared directly with that of the well-known green band-A emission near 2.3 eV. Time-dependent CL studies show conclusively that the green band is also a donor-acceptor pair emission, thus confirming at least a part of the model introduced by Dean 30 years ago. Time-dependent PL measurements also indicate that the green and red emissions are in direct competition, thus suggesting a model in which pair emission occurs from two different donors to the neutral boron acceptor.

I. INTRODUCTION

The current interest in the properties of semiconducting diamond is motivated by the potential for producing electronic devices from this material that are unaffected by high temperature or by other adverse environmental conditions. Consequently, there has also been a renewed interest in investigating the transport and related optical properties of this system. While any real device will undoubtedly be fabricated from epitaxially grown layers, the optical characterization of these layers has relied heavily upon the wealth of information that exists from studies of bulk natural and synthetic, high-temperature high-pressure (HPHT) grown diamonds.

An essential ingredient to any device fabrication has always been the understanding and control of electrically active impurities and defects. In diamond these are often related to nitrogen donors, boron acceptors, and vacancies. While boron acts as a shallow acceptor with a binding energy of 0.37 eV,[1] nitrogen can incorporate in several forms, ranging from an isolated substitutional impurity to larger aggregates.[2] Substitutional nitrogen forms a donor with a binding energy of ≈ 1.7 eV, while nitrogen A aggregates (nearest-neighbor substitutional nitrogen pairs) act as deep donors with ≈ 4-eV binding energy.[2] In type-IIb semiconducting diamond the study of the optical properties associated with these defects has a rather long history. Nevertheless, many important aspects of the transport and optical properties associated with these centers are still not well understood. For example, it was thought almost three decades ago that the detailed nature of the dominant radiative recombination in type-IIb material had already been determined. This

emission, which was referred to as band A, appeared as a strong green luminescence band centered near 2.3 eV in synthetic samples and as an intense blue emission peak centered near 2.8 eV in natural samples. A careful and exhaustive study by Dean[3] concluded that these were both due to the same donor-acceptor pair (DAP) recombination process, the pairs being closer together (and thus emitting at a higher energy) in natural samples as compared to the synthetic material. This was understood as resulting from the fact that synthetic samples were grown at a much faster rate than the natural crystals, which were formed on geological time scales. The donors and acceptors responsible for this emission were determined to be nitrogen and aluminum (this was later shown to be boron[1]).

While Dean's model stood for many years, it has recently come into serious question. It was shown several years ago that the boron acceptor is incorporated preferentially in the {111} growth sectors of diamond,[4] and that in lightly doped crystals residual nitrogen is the major impurity in the {100} sectors. However, it is recently demonstrated[5] that the green band-A emission can be excited from the {111} growth sector of a synthetic diamond containing a high boron concentration, and that the blue band-A peak originates from a {100} growth region in which the impurity concentration is much lower. These observations are clearly inconsistent with Dean's model. It has also been observed that in natural type-IIb diamond[6] and in undoped diamond films grown by chemical vapor deposition (CVD),[7] the blue emission is clearly associated with dislocations. A recent cathodoluminescence (CL) study of boron-doped CVD diamond films carried out by Ruan, Kobashi, and Choyke[8] also conclud-

ed that the blue band is not of DAP origin and is not related to the incorporation of boron. In addition, these authors determined that the green band-*A* emission was clearly related to the presence of boron, and concluded that the blue band was probably associated with dislocations. Ruan, Kobashi, and Choyke also noted that since the two bands have been determined to have different origins, the term band *A* is misleading, and should no longer be used. In what follows we will refer to these luminescence bands as either green or blue, or by their spectral positions at ≈ 2.3 or ≈ 2.8 eV, respectively.

Recently, we have reported the observation of a new red photoluminescence (PL) band centered near 1.84 eV in synthetic, *p*-type semiconducting type-IIb diamond.[9] This band was observed to exhibit many of the dependences upon excitation intensity and time that are the hallmarks of classic DAP recombination. It was concluded that this band was due to DAP emission associated with boron acceptors, and probably nitrogen-related donors, as the band intensity decreased in samples with lower nitrogen content. When exciting this band with near-UV radiation, it was found to be always present with, and often dominated by, the green emission band near 2.3 eV. The red band could be isolated by excitation at longer wavelengths (514 and 532 nm) that were ineffective in producing any green band emission. In this work we will show that there is, in fact, an intimate connection between the red and green bands; that both bands are due to DAP recombination involving the same shallow boron acceptor and different donors. This result also confirms part of the model proposed by Dean 30 years ago.

II. EXPERIMENT

Three related sets of luminescence measurements were carried out on several synthetic, *p*-type semiconducting IIb diamond samples. First, steady-state (cw) PL measurements were made on two samples exhibiting both the red and green bands, the samples differing predominantly in their nitrogen contents. The PL spectra of these samples were studied as a function of laser power and excitation wavelength. These samples were also studied by time-resolved PL measurements. The time-resolved PL spectra and PL decays were investigated as a function of both the emission and excitation wavelengths. While these measurements contributed to determining the relationship between the red and green emission bands, cw and time-resolved CL measurements were also carried out on a second set of type-IIb samples in order to probe the nature of the green band itself. The PL and CL measurements were carried out independently, and are being presented together in this work, as the results of the two measurements complement each other and allow us to conduct a more complete analysis than could have been done independently. A consequence of this is that the PL and CL measurements were made on different, albeit similar sample sets.

A. Samples

The PL measurements were carried out on two synthetic type-IIb samples, SYNTH #1 and SYNTH #2, which were grown at De Beers Diamond Research Laboratory using Ni-Fe and Fe-Al, respectively, as solvent-catalyst. Boron doping was achieved by adding a small quantity of iron boride to the growth capsule. Since Al is a well-known nitrogen getter, SYNTH #2 is expected to have a lower nitrogen concentration. On examining SYNTH #1 under an optical microscope, we can see a region that is still yellow (nitrogen is the major impurity), while most of the stone is blue. The SYNTH #2 sample has a fairly high boron concentration, and appears dark blue to the naked eye. The time-resolved CL measurements were carried out on two diamonds, D1002 and sample 23, which were grown at the General Electric Research Laboratory, and which had concentrations of nitrogen and boron impurities similar to those of SYNTH #2.

B. PL and time-resolved PL measurements

Steady-state PL spectra were obtained with the samples placed in a continuous-flow liquid-helium cryostat, the temperature being kept constant at 6 K. The samples were excited with the UV output of a He-Cd laser or an argon-ion laser (325 or 351 nm, respectively) or from the visible argon laser emissions between 458 and 514 nm. The PL emission was analyzed by a 0.85-m double-grating spectrometer, and detected by a GaAs photomultiplier employing a UV-transmitting window and operating in the photon-counting mode.

Time-resolved PL spectra were obtained at 10 K in a continuous-flow helium cryostat. Excitation was from a Q-switched Nd:YAG (yttrium aluminum garnet) laser operating at 10 or 20 Hz, and putting out 10-nsec pulses which were either frequency doubled or tripled, resulting in either 532- or 355-nm radiation, respectively. The PL emission was analyzed by a 0.28-m double monochromator and detected by a GaAs photomultiplier with a few-nsec response. The resultant wave forms were digitized and stored in a transient digitizer (Tektronix 7912 AD).

C. Time-resolved CL measurements

The cathodoluminescence equipment operated at 45 kV with beam currents of typically 10 μA. The electron beam was focused to a spot about 300 μm in diameter onto the diamond, which was mounted on a liquid-nitrogen-cooled cold finger. By applying a voltage pulse to a pair of parallel plates in the electron flight tube, the electron beam could be deflected on or off the sample in about 1 nsec. The luminescence from the sample was focused onto the entrance slit of a Spex 1500 monochromator. The photomultiplier used (ITT type 4027) differed from a conventional tube in having a fine mesh grid structure immediately behind the photocathode. By applying a small bias potential to this gate electrode, the photomultiplier could be turned on or off, depending on the polarity of the bias. For time-resolved spectroscopy the photomultiplier was pulsed on for a short time by a

Tektronix type-111 pulse generator which was triggered by the pulse generator deflecting the electron beam. The time interval between the excitation of the sample and the switching on of the photomultiplier could be varied, enabling spectra to be recorded at different delays.

III. RESULTS

A. Luminescence spectra

Luminescence spectra for all three bands (red, green, and blue) are shown in Fig. 1 for a variety of excitation conditions. The time-resolved CL spectra of sample D1002 using a 10-nsec-wide excitation pulse and a 2-nsec gate width are shown for gate delays ranging from 0 to 15 nsec in Fig. 1(a). The blue emission band near 2.8 eV decays in several nanoseconds, while the green band is considerably slower. There is no apparent shift of the peak of the latter with gate delay on the nanosecond time scale. The cw PL spectrum in Fig. 1(b), excited at 325 nm in sample SYNTH #1 (higher nitrogen concentration) is dominated by an intense green band and a weaker red band component. The sharp structure on the high-energy edge of the spectrum, with a zero-phonon line at 2.56 eV, is due to a set of vibronic bands related to Ni centers introduced during growth.[10] At longer excitation wavelengths the excitation threshold of the green band (in the blue portion of the spectrum) becomes evident: At 351-nm excitation the red band can dominate, while at 514-nm excitation, shown in Fig. 1(c), the green band has disappeared altogether. The sharp zero-phonon line at 2.156 eV is due to the well-known 575-nm nitrogen-vacancy center.

In sample SYNTH #2 the red band is clearly observed,[11] but is much weaker than the green band. This behavior is in part thought to be due to the fact that[9] the red band may involve a nitrogen-related donor, which is at a much lower concentration in SYNTH #2 than in SYNTH #1.

B. Time-resolved photoluminescence

The luminescence properties of the red emission band were reported in Ref. 9, and are summarized here because of the intimate connection that we will show to exist between the two emissions. The log-log plot in Fig. 2 of red band PL intensity versus time (see Ref. 9), resulting from 532-nm pulsed excitation, reflects a rapid decay for times earlier than 200 nsec, and a much slower nonexponential decay at later times. The slow decay was observed[9] to follow the dependence determined by Thomas, Hopfield, and Augustyniak[12] (THA) for DAP recombination. The fast component is unrelated to the DAP band, and appears to be a competing process that can be either radiative or nonradiative. This is confirmed in Fig. 3, where the 532-nm excited red band decay is superimposed for several emission wavelengths across the PL band. While the fast component is essentially identical for all of the decays, the slow component exhibits faster decays for the shorter emission wavelengths, as expected for a DAP emission.

In Fig. 4 the decay of the red emission at 650 nm for sample SYNTH #1 is compared for excitation at 532 nm, where no green band luminescence is excited, to excitation at 355 nm, where both red and green bands are ob-
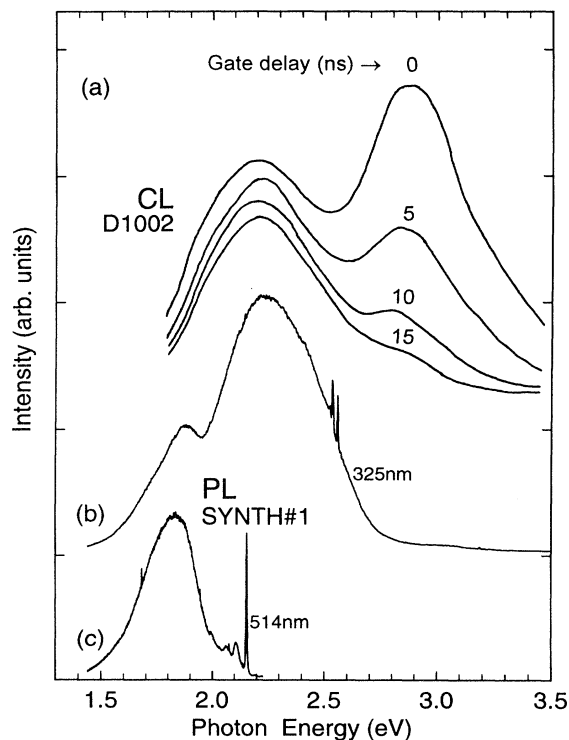

FIG. 1. (a) Time-resolved CL spectra of band A from synthetic sample D1002 at 77 K as a function of gate delay between 0 and 15 nsec. The excitation time was 10 nsec at a pulse repetition frequency of 50 kHz and a gate pulse width of 2 nsec, (b) CW PL spectrum of sample SYNTH #1 at 6 K, excited at 325 nm, (c) CW PL spectrum at 6 K of the same sample excited at 514 nm.
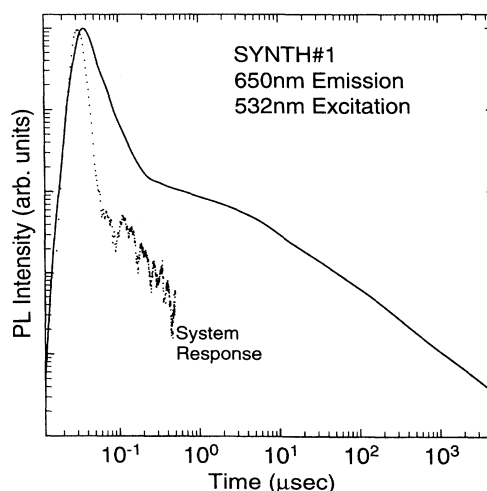

FIG. 2. Log-log plot of PL intensity of the red emission band vs time for sample SYNTH #1 at 10 K for 650-nm emission and 532-nm pulsed excitation.
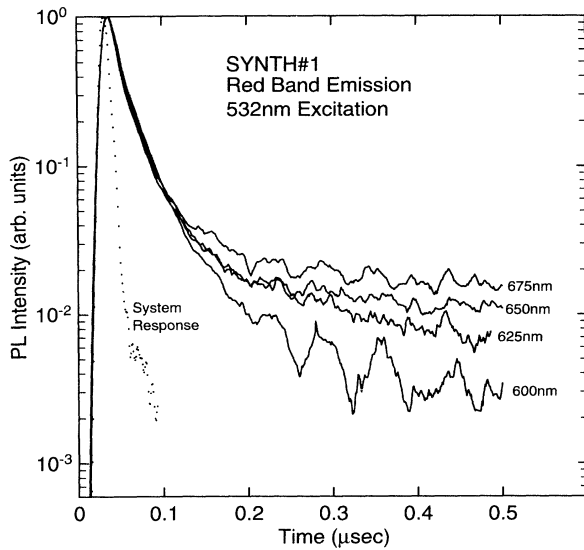
FIG. 3. PL decay of the red emission band as a function of the emission wavelength. At times later than ≈ 100 nsec after the excitation pulse the longer wavelength emissions decay more slowly, as expected for DAP emission. The response at earlier times is independent of the luminescence wavelength, indicating an independent process that competes with the DAP emission.

served. Both decays are compared to that of the green band itself, observed from sample SYNTH #2, where competition from the red band is minimal. It is clear from the figure that the fast decay component of the red band, reflecting competing processes, has become much faster with 355-nm excitation. Since this occurs in concert with the appearance of the green band at the shorter excitation wavelength, it suggests the possibility that the green band itself is competing *directly* with the red band.

If this assertion is correct, then the total decay rate of the fast component of the red band excited at 355 nm should be equal to the sum of the decay rate of the fast component of the red band excited at 532 nm and the decay rate of the fast component of the green band. That is,

$$1/\tau_{\text{red}}(355 \text{ nm}) = 1/\tau_{\text{red}}(532 \text{ nm}) + 1/\tau_{\text{grn}}(355 \text{ nm}) \; ,$$

$$(1)$$

where $\tau_j(\lambda)$ is the measured exponential decay of band j (red or green) excited at wavelength λ. To the extent that these rapid decay components are exponential, this sum may be effected by taking the product of the green band decay with the 532-nm-excited red band decay, as the exponents simply add. This product is shown as the dashed line in Fig. 4, and is seen to reproduce the 355-nm-excited red band decay very well for about a factor of 40 in intensity decay, up to the point where the nonexponential nature of the decays begins to dominate. Hence the green
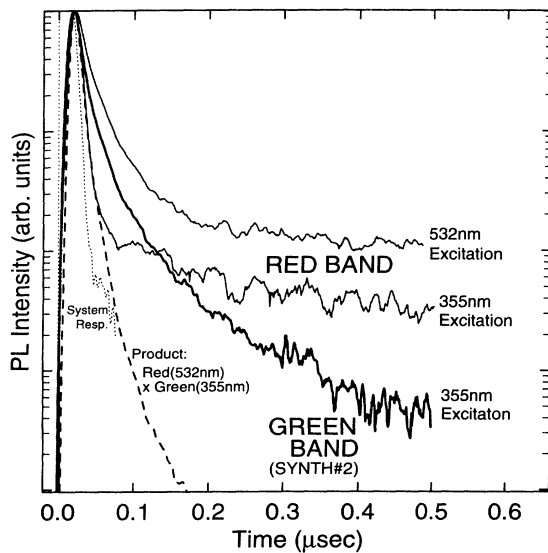

FIG. 4. The 650-nm DAP decay from sample SYNTH #1 is compared for excitation at 532 and 355 nm, and both are compared to the decay of the green band in sample SYNTH #2 (negligible competition from the weak red band). The fact that these decays follow Eq. (1) is shown graphically by plotting the product (represented by the dashed line) of the red band decay at 532-nm excitation and the green band decay excited at 355 nm. This is seen to reproduce the 355-nm excited red band decay very well, as discussed in the text.
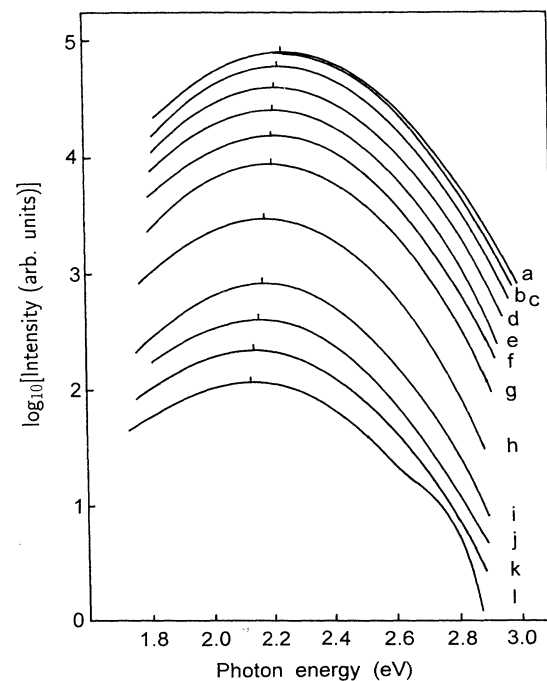

FIG. 5. Time-resolved 77-K CL spectra of the green band for synthetic diamond sample D1002. Curves *a* through *l* correspond to gate delays between 200 nsec and 20 msec. The full range of pulse generator parameters used to obtain these spectra is listed in Table I.

TABLE I. Parameters used for the time-resolved spectra in Fig. 5.

Curve	Delay (μsec)	Excitation time (μsec)	Pulse repetition frequency (Hz)	Gate pulse width (μsec)
a	0.2	20	10 000	2
b	0.7	20	10 000	2
c	2.7	20	10 000	2
d	7.7	20	10 000	2
e	17.7	20	10 000	2
f	37.7	20	10 000	2
g	87.7	20	10 000	2
h	380.0	100	100	200
i	1880.0	100	100	200
j	5000.0	2000	10	10 000
k	10 000.0	2000	10	10 000
l	20 000.0	2000	10	10 000

band decay rate accounts very well for the difference in the red band decay rates for 355- and 532-nm excitation. This suggests quite clearly that both emissions are in direct competition.

C. Time-resolved cathodoluminescence

Time-resolved CL spectra of the green band emission were obtained at 77 K with gate delays ranging from 200
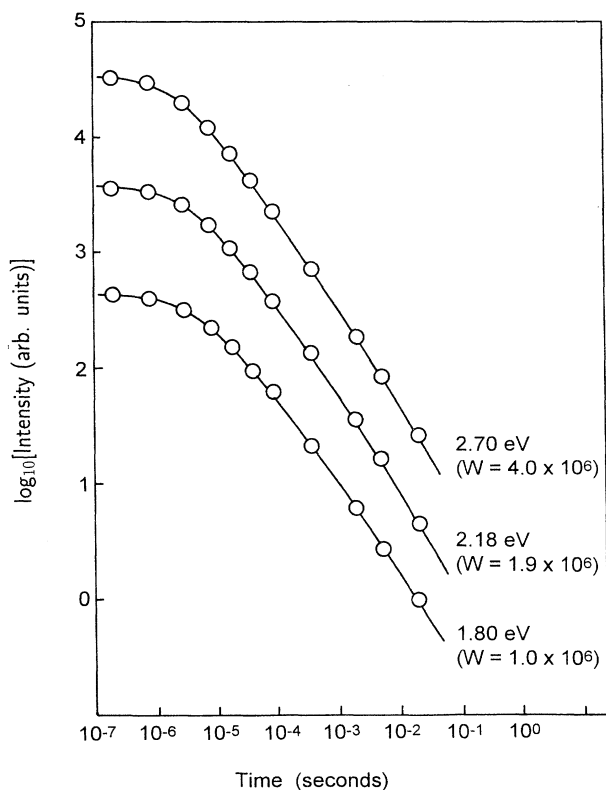

FIG. 6. Log-log plot of CL intensity vs gate delay determined from the data in Fig. 5 for three representative emission energies across the luminescence band, for sample D1002. The open circles are the experimentally determined points, while the solid lines are calculated using Eq. (4) with $nR_0^3 = 5 \times 10^{-5}$. The fitting parameters W for each curve are indicated in the diagram.

nsec to 20 msec. Typical examples are shown in Fig. 5 in a semilog plot for diamond D1002; similar data were obtained for sample 23. The length of the excitation pulse, the repetition rate, and the gate width were adjusted at the longer delays. These parameters are indicated in Table I for each spectrum. In Fig. 5 a vertical bar marks the peak of each spectrum. The peak is observed to shift to lower energy by about 100 meV over the time ranges shown. This behavior of the green emission is very suggestive of DAP recombination, where closer pairs, corresponding to higher emission energies, recombine faster than the more distant, lower-energy pairs. Plotting the intensities as a function of time at three representative energies across the band (1.8, 2.18, and 2.7 eV) results in the very nonexponential CL decays shown by the open circles in the log-log plots of Fig. 6. The solid lines through the data points are theoretical fits derived as explained in Sec. IV. The relative vertical positions of the three decay curves are not relevant: they are merely drawn on the same axes for compactness. These data suggest a DAP origin for the green band.

IV. DISCUSSION

A. Green band CL emission

The theory of the time decay of the fluorescence due to DAP recombination, where one particle has a much smaller ionization energy than the other, has been worked out by Thomas and co-workers,[13,14] and they have shown that the intensity of luminescence at a time t after the excitation is given by the expression

$$I(t) = \left\{ 4\pi n \int_0^\infty W(r) \exp[-W(r)t] r^2 dr \right\}$$
$$\times \exp \left\{ 4\pi n \int_0^\infty \{\exp[-W(r)t]-1\} r^2 dr \right\}. \quad (2)$$

$W(r)$ is the transition probability for a pair of separation r, and n is the concentration of the majority species, in the present case boron. In their original paper, Thomas

and co-workers determined $I(t)$ by numerical integration of (2). Subsequently, Onsager and Stewart[15] obtained analytic approximations to (2) for the two cases $Wt \leq 0.1$ and $Wt \geq 3$, these being

$$I(t)/I(0) = W 8\pi n R_0^3 \{ 1 - Wt(1/8 + 8\pi n R_0^3) \} , \qquad (3)$$

and

$$I(t)/I(0) = \frac{\{[\ln(Wt)+\gamma]^2+\pi^2/6\}}{2Wt} \exp \left\{ \frac{-4\pi n R_0^3}{3} \{ [\ln(Wt)+\gamma]^3 + [\ln(Wt)+\gamma]\pi^2/2 + 2\zeta(3) \} \right\} , \qquad (4)$$

respectively, where γ is Eulers constant, $\zeta(3)$ is the zeta function of argument (3), and R_0 is one-half of the Bohr radius. As we are proposing that the green band is due to distant pairs, i.e., not nearest-neighbor pairs (e.g., note the continuous shift of the band with time in Fig. 5), and we are considering relatively long delays after excitation, Eq. (4) applies.

The relevant parameters for fitting the experimental data to Eq. (4) are W and nR_0^3. On a log-log plot of intensity versus time, such as Fig. 6, the effect of changing W is to shift the decay curve rigidly along the log-time axis, while decreasing nR_0^3 decreases the overall rate of decay. However, the fit becomes insensitive to this parameter for very small values: for nR_0^3 less than about 5×10^{-8}, the calculated curves become independent of nR_0^3.

The solid lines in Fig. 6 represent the results of such a fit to the experimental data for sample D1002. As may be seen, very good fits to all three curves are obtained by using a value for nR_0^3 of 5×10^{-5}, and values for W of 4×10^6 sec^{-1} for the 2.7-eV decay, 1.9×10^6 sec^{-1} for the 2.18-eV decay, and 1×10^6 sec^{-1} for the 1.88-eV decay. Similarly, very good fits are also obtained for sample 23, with $nR_0^3 = 1 \times 10^{-4}$, and for the 1.8-, 2.18-, and 2.7-eV decays W corresponds to 4.0×10^5, 6.3×10^5, and 1.3×10^6 sec^{-1}, respectively. The fact that the form of the decay curves is exactly that predicted theoretically by the above DAP theory makes the evidence for the green band-A emission being due to DAP recombination virtually conclusive, thus verifying at least part of the original model of Dean.[3] However, it is as well to check that the values of nR_0^3 and W required to fit the above decays are realistic. Certainly the variation of W with emission energy is sensible, the transition probability decreasing with decreasing emission energy. However, nR_0^3 poses something of a problem, because the shapes of the theoretical curves become insensitive to nR_0^3 below $nR_0^3 = 1 \times 10^{-4}$. A second problem is that of assigning an appropriate value to R_0. Thomas, Gershenzon, and Trumbore[14] made the assumption that the shallow acceptor in GaP was hydrogenic, and let R_0 equal one half of the Bohr radius of the acceptor. Since the shallow boron acceptor in diamond acts as though it was hydrogenic, we arrive by a similar path at a value of $R_0 \approx 1.7 \times 10^{-8}$ cm. Using this estimate, the values for nR_0^3 obtained from the experimental curves above suggest values for n of around 10^{19} cm^{-3}. Since the typical boron concentration (bulk) is in the range[16] of 10^{17} to $\geq 10^{19}$ cm^{-3}, and in view of the difficulties described, this is felt to be reasonable agreement.

B. The origin of the red and green bands

From the experimental data presented in Sec. III and the discussion above, we can make two general conclusions: the green emission band is of donor-acceptor pair origin, and it competes directly with the red DAP band. Since these materials are boron doped, and since boron is the only identified shallow acceptor in diamond, the most logical conclusion that can be made is that the red and green emission bands correspond to DAP transitions between two different neutral donors and the neutral boron acceptor.

This picture is consistent with the conclusion reached by Ruan, Kobashi, and Choyke,[8] that the green emission band in type-IIb, boron-doped samples grown by CVD is due to boron-related centers. While there may be some question as to whether the green emission bands in CVD and synthetic samples are of the same origin, it should be noted that the green band observed in Ref. 8 and that described in this work both occur with the same peak energy, ≈ 2.3 eV, and bandwidth, ≈ 0.6 eV, exhibit the same structureless, bell-shaped line shape, and occur only in boron-doped samples. This suggests that the green emission bands are of the same origin in samples grown by either technique. From the present work, we conclude that this origin is neutral donor-to-neutral boron acceptor transitions. This is discussed in more detail below.

The identification of the donor involved in the DAP transition has been conspicuously absent from any of the discussion thus far. In the case of the red emission band, the PL intensity was correlated with the nitrogen content, suggesting a nitrogen donor-to-boron acceptor transition.[9] In fact, since nitrogen is by far the predominant donor in diamond, it is usually assumed that the donors are due to nitrogen, either as a single substitutional impurity ($E_D \approx 1.7$ eV) or as an A aggregate ($E_D \approx 4$ eV). However, for DAP transitions, these assumptions must be consistent with the observed emission energies. The emission energy for a DAP transition between pairs of separation r is given by the well-known relation[14]

$$h\nu(r) = E_g - (E_D + E_A) + e^2/\epsilon r - \frac{e^2}{\epsilon}(a^5/r^6) , \qquad (5)$$

where $h\nu$ is the emission energy, E_g, E_D, and E_A are the band gap, donor, and acceptor binding energies, respectively, e is the electronic charge, ϵ is the static dielectric constant, and a is the effective van der Waals coefficient for the interaction between a neutral donor and a neutral acceptor. The last term is significant only for very close pairs, and is neglected when dealing with distant pair

bands. The binding energy of the donor is often estimated, assuming that E_A is known, from the low-energy limit of the DAP spectrum, E_{min}, determined from the limit of Eq. (5) for infinitely separated pairs,

$$E_{min} = E_g - (E_D + E_A) . \tag{6}$$

In Ref. 9, E_{min} for the red emission band was estimated to be ≈ 1.5 eV, leading to a donor binding energy (assuming a boron acceptor) of $E_A \approx 3.6$ eV, which is near the binding energy of nitrogen A aggregates.[16] Analogous DAP emission involving single substitutional nitrogen donors would occur in the UV (≈ 365 nm), and is not observed. Applying this procedure to the green emission band, we estimate that $E_{min} \approx 1.8 - 1.9$ eV, resulting in an estimated donor binding energy of $E_D \approx 3.2 - 3.3$ eV. This would suggest that the two DAP bands involve similar but distinct deep donors.

Not long after Dean's original proposal of a DAP origin for band A, Bezrukov et al.[17] also suggested that the green band was of DAP origin, and attempted to apply Eq. (6) to the asymmetric, long-wavelength tail of the green band spectrum. They found $E_{min} \approx 1.5$ eV and $E_D \approx 3.6$ eV, which are identical to the same parameters for the red emission band. Indeed, an inspection of the data of Berzukov et al. reveals evidence of an additional band centered near ≈ 1.9 eV, of which the authors were unaware, contributing to the low-energy tail of the spectrum. This example emphasizes one of the main difficulties in applying Eq. (6) to broad emission bands, and in particular to those that are not well understood or well characterized.

It is also important to consider the manner in which the DAP recombination is excited. While this is obvious for CL measurements, it becomes a nontrivial matter in PL experiments involving optical excitation well below the band gap. For example, it was observed that while the red emission band was efficiently excited with 514- (2.41 eV) or 532-nm (2.34 eV) light, this excitation was unable to produce any emission from the green band, even though there are many available distant pair emissions below these energies. Since all of the samples studied were p type due to boron doping, at cryogenic temperatures the Fermi level is fixed near the boron acceptor level, 0.37 eV above the valence band. This means that before optical excitation, all donors are ionized, and since boron is the shallowest known acceptor in diamond, and in much greater numbers than others acceptors, all other acceptors are neutral. The boron acceptors are partially compensated (ionized) by the donors and partially neutral. In order to create DAP emission, the donors must be photoneutralized. Given the initial conditions, below-gap excitation can only excite electrons into the donor levels from either the valence band or the ionized boron acceptors. This situation is depicted schematically in Fig. 7(a). The charge states of the impurities indicated in the figure correspond to conditions before optical excitation. From the figure, it is clear that in order to excite DAP emission in this case we must have either

$$h\nu_{exc} \geq E_{min} \quad \text{(acceptor-to-donor excitation)} \tag{7}$$

or

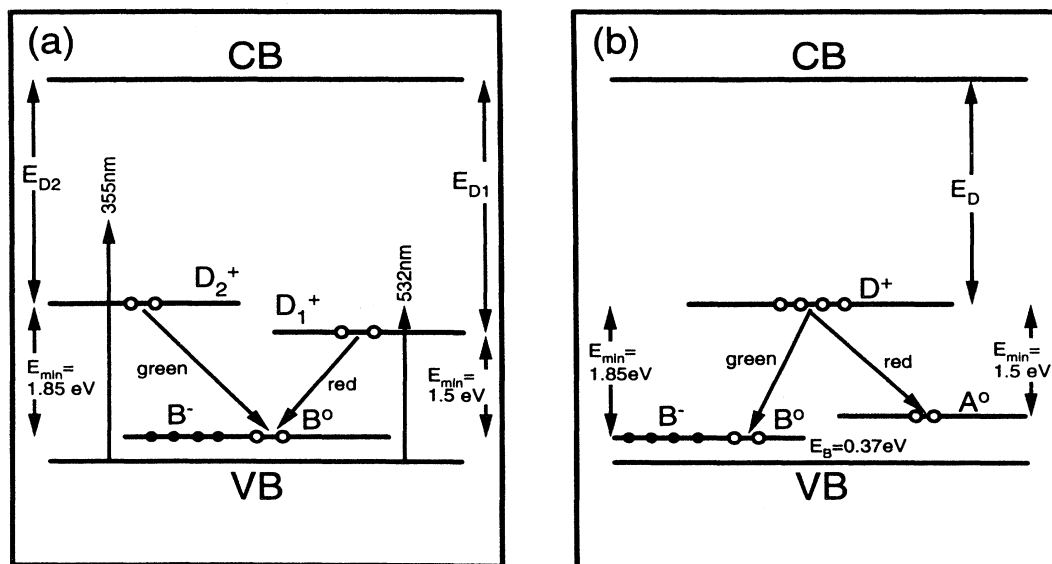$$h\nu_{exc} \geq E_{min} + E_A \quad \text{(valence-band-to-donor excitation)} . \tag{8}$$

FIG. 7. A schematic energy-level diagram depicting the two possible excitation and recombination models for the red and green band emissions in p-type IIb boron-doped semiconducting diamond. The closed and open circles represent filled and empty electron levels, as determined by the p-type doping of the material. The impurity charge states indicated reflect conditions before optical excitation. In (a) the red and green DAP bands involve different neutral deep donors, but compete for the same neutral boron acceptors. In (b) these bands are considered to result from transitions from the same neutral donor to different neutral acceptors, the most shallow being boron. The experimental data tend to favor (a).

For the green band, we are not able to excite emission for $E_{\min} \leq h\nu \leq (E_{\min} + E_A)$ (i.e., $1.8-1.9$ eV $\leq h\nu \leq 2.2-2.3$ eV), as noted by the absence of green band emission with 532-nm (2.34 eV) excitation. This would suggest that the dominant excitation process results from transitions between the valence band and the ionized donors. Below-gap excitation of DAP recombination by this type of process has been observed in III-V compounds and recently in SiC.[18]

The above discussion favoring valence-band-to-donor excitation does not take into account the possible effects of lattice relaxation. However, the donor binding energies were estimated above to be in the 3–4 eV range, while the boron acceptor is relatively shallow, $E_A = 0.37$ eV. This is a situation analogous to DAP emission in oxygen-doped GaP ($E_g = 2.34$ eV) from, e.g., Zn-O pairs, where the Zn acceptor is shallow ($E_A = 64$ meV) and the O donor is very deep ($E_D = 895$ meV). In that case the deep donor is strongly coupled to the lattice. As a result, there is a large lattice relaxation following photoexcitation of the donor, which leads to a significant broadening of the pair band and a shift of the peak to lower energies.[19] This shift in the peak energy is related to the vibronic coupling, as might be described by a configuration coordinate diagram. In such a case the zero-phonon emissions are difficult to observe, and can only be seen under conditions of very low excitation or very long-time delays in time-resolved measurements, when the broadening of the zero-phonon lines is minimized.[20] Equation (5) still holds for the zero-phonon emissions,[19] which will be positioned (even if not observed) on the high-energy side of the peak emission energy.

Because of the very deep donor binding energies, the possibility of strong lattice coupling in the case of the boron-related DAP bands in diamond must also be considered. While a detailed study of the extent to which lattice relaxation is important in this instance is beyond the scope of the present work, some general observations can be made. In the case of strong lattice coupling, the values determined for $E_{\min}$ will have been underestimated, typically by up to a few tenths of an eV. This will tend to reduce the inferred donor binding energy and consequently to position the donor level further above the valence band than originally determined. While both red and green bands could be susceptible to lattice relaxation effects, the very large width of the green band, ≈ 0.6 eV (as compared to ≈ 0.25 eV for the red band), indicates that lattice relaxation effects are a distinct possibility for the green emission. The result of large lattice relaxation for the green band would be to shift the inferred position of the donor level closer to the conduction band. This would be more consistent with the absence of green band emission with 514- or 532-nm valence-band-to-donor excitation, as $(E_{\min} + E_A)$ might be expected to increase from 2.2–2.3 to $\approx 2.5-2.6$ eV. However, the inferred threshold for acceptor-to-donor excitation would also be expected to increase. Under conditions of very strong lattice coupling, the threshold for this process could also become consistent with the absence of green band emission with 514- or 532-nm excitation, and cannot be ruled out. Until a complete study of lattice relaxation is car-

ried out for this band, we will be unable to determine which of these two processes is dominant. We are currently carrying out measurements of PL excitation spectroscopy and of thermal linewidth broadening in order to better understand the details of the excitation process.

We have concluded from the experimental observation of direct competition between the red and green band emissions that both DAP bands are competing for the same neutral acceptors (boron) and involve two different donors. It is necessary to point out why we have eliminated the possibility that this competition could occur for a single donor and involve two different acceptors. This situation is depicted in Fig. 7(b). Since boron is the shallowest known acceptor in diamond, it will give the highest DAP emission energies for a given donor, and should be associated with the higher-energy band, i.e., the green band. This would also be consistent with the results of Ruan, Kobashi, and Choyke,[8] where the green band was associated directly with boron. The red band would have to be associated with a deeper acceptor. As before, as a result of the doping conditions, there are neutral acceptors available for DAP recombination, but no neutral donors. These must still be excited optically by transitions from the valence band or from ionized boron acceptors. Therefore, the same excitation conditions (i.e., creating neutral donors) are necessary to excite either DAP band, since both bands share the same donor. Once neutral donors are photoexcited, both DAP bands will be observed by parallel (competing) transitions to the appropriate acceptors. Consequently, there should not be a range of excitation energy where only the red band can be excited. This result is contrary to experiment, so we must conclude that the two bands compete for the same acceptor. We identify this acceptor as boron because (i) all of the samples studied were boron doped, so that boron is the dominant acceptor; and (ii) the green emission band has been positively identified as being due to boron in Ref. 8. Since the two emission bands compete for the same acceptor, this would imply that the red band is also due to boron, as suggested in Ref. 9.

V. SUMMARY

Boron-doped, p-type semiconducting IIb diamond samples have been studied by steady-state and time-resolved PL and CL measurements. The CL time-dependent measurements on the green emission band centered near 2.3 eV are found to be in excellent agreement with theoretical models for donor-acceptor pair recombination, thus making a very strong case for assigning this band as a DAP emission. As this band has already been associated with boron doping in CVD material, and, since the samples studied were all boron doped, the green band is associated with a deep-donor-to-boron-acceptor transition.

Time-resolved PL measurements determined that the green band competes directly with the red DAP band centered near 1.84 eV. Consideration of the p-type doping led to the conclusion that the two emission bands were competing for the same neutral acceptor, namely boron. Because of the p-type doping, the excitation of

the DAP PL emission with $h\nu_{\text{exc}} \ll E_g$ was determined to be constrained to transitions from either the ionized boron acceptors or from the valence band to the ionized donors.

While the validity of Dean's original model for DAP recombination from band-A emission in diamond is presently under serious question, the results of the present work confirm his determination of a DAP origin for the 2.3-eV green emission. However, it is becoming increasingly clear that the blue band-A emission at 2.8 eV is not simply a manifestation of the green emission in natural samples, with DAP separations that are closer in the natural samples than those found in synthetic materials.

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