

The characterisation of point defects in diamond by luminescence spectroscopy

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Abstract

Luminescence spectroscopy is a vitally important technique for characterising the defects present in diamond. In this paper the two major methods for generating the emission — photoluminescence and cathodoluminescence — are considered, and the defects responsible for the most significant luminescence bands are discussed in detail. Problems with the donor–acceptor pair model, conventionally used to interpret the broad blue and green emission bands in cathodoluminescence, are outlined, and the fundamental differences between photoluminescence and cathodoluminescence are presented. The paper concludes with a cathodoluminescence study of diamond grown by the combustion flame technique. Not only does this material exhibit intrinsic edge emission, but there is evidence of bound-exciton recombination at a currently unknown donor or acceptor centre.

1. Introduction

More than 100 of the optical centres that have been documented for diamond give rise to luminescence. Some of these centres are present in the as-grown diamonds, whether of natural origin, or produced by high-pressure synthesis or chemical vapour deposition (CVD); additional centres may be produced by radiation damage or ion implantation. The spectral range covered by the luminescence bands extends from around 230 nm (5.3 eV) associated with the “edge emission” [1] in the ultraviolet to around 1000 nm (1.2 eV) for the “H2” vibronic band [2] in the near-infrared. Most of the known optical centres are listed either by Davies [3] or in a forthcoming review by Clark *et al.* [4]. In the present paper the major photoluminescence and cathodoluminescence spectra will be considered, and the information that can be derived from these spectra will be discussed in detail.

The luminescence from diamond has been studied extensively for more than 40 years. Much of the early work was carried out using ultraviolet radiation [5] or X-rays [6] to excite the luminescence. The use of a focused electron beam (of typical energy 50 keV) to stimulate luminescence in diamond was pioneered at King's College London in the late 1950s using first a converted electron microscope [7] and later, custom-built cathodoluminescence equipment. Today scanning electron microscopes with a cathodoluminescence facility are available in a number of laboratories, and lasers are frequently used to generate photoluminescence.

2. Defects in diamond

Before discussing the luminescence bands, we need to examine the defects that are present in diamond. The perfect diamond crystal absorbs strongly at energies above 5.5 eV (wavelengths less than 225 nm) corresponding to the indirect energy gap, and has weak vibrational absorption in the two- and three-phonon combination bands between about 4000 and 1500 cm^{-1} (2.5 to 6.7 μm). No other absorption bands are present in such a specimen, and the only luminescence process possible is intrinsic “edge emission,” following the generation of electron-hole pairs (see Section 4.1). No crystal, of course, is perfect and the deviation from perfection results in the optical systems so common in diamond. The defects may be chemical or structural, or a combination of both, and are briefly considered below.

2.1. Nitrogen

Nitrogen is by far the most common impurity in diamond, occurring in concentrations up to about 0.25% in some natural stones. A recent description of nitrogen in diamond has been given by Woods [8], and some of the essential points are briefly reiterated here. In type Ia diamond the majority of the nitrogen is present in either the A form (a nearest-neighbour pair of substitutional nitrogen atoms) or the B form (four nitrogen atoms on substitutional sites symmetrically surrounding a vacancy). In type Ib diamond the nitrogen is present on isolated substitutional sites. Very few natural diamonds are of this type, but all commercial synthetic diamonds are type Ib, containing around 200 ppm of

nitrogen. (In this article the description “synthetic diamond” will be reserved for diamonds grown by high-pressure synthesis). The different forms, and concentrations, of nitrogen may be determined from the impurity-activated one-phonon absorption, most of which lies between 1350 and 800 cm^{-1} (7.5 to 12.5 μm). Nitrogen is also the dominant impurity in type IIa diamonds, although it is present in too low a concentration to be detected by infrared absorption. It is also difficult to measure the one-phonon absorption for thin films of CVD diamond, but the evidence to be discussed below shows that any nitrogen present in this material is predominantly in the isolated substitutional form.

The isolated nitrogen and the A nitrogen both have donor-like properties with ionisation energies around 1.7 and 4.0 eV respectively [9], but there is no evidence that the B nitrogen behaves as a donor.

2.2. Boron

When boron is the major impurity in diamond the material is semiconducting. The properties of semiconducting (type IIb) diamond have been reviewed by Collins and Lightowers [9], and discussed again more recently in the context of electronic and optoelectronic devices [10]. Natural type IIb diamond is rare, and typically has an uncompensated boron concentration of $5 \times 10^{16} \text{cm}^{-3}$. Semiconducting synthetic or CVD diamond may readily be made by doping with boron (and excluding nitrogen), and much higher acceptor concentrations can be obtained than in natural diamond.

2.3. Nickel

Synthetic diamonds grown using nickel or a nickel alloy as the solvent-catalyst, contain a number of optical centres which are absent if other transition metals are used [11]. In the present article we shall be particularly concerned with the 484 nm and 1.40 eV luminescence systems.

2.4. Silicon

Silicon appears to be incorporated in some CVD diamond to form a vibronic absorption–luminescence band with a zero-phonon line at 1.681 eV [12–14]. This defect has not been observed in as-grown natural or synthetic diamond, but it can be introduced by ion implantation [12–14] (see Section 2.6). The association of this optical centre with Si is based on the pioneering ion implantation measurements of Vavilov *et al.* [12].

2.5. Radiation damage products

When diamond is subjected to radiation damage by, for example, high-energy electrons or fast neutrons, some of the carbon atoms are displaced into interstitial positions, leaving a vacancy. For annealing temperatures above about 550 °C the vacancy becomes mobile, and

can be trapped at other defects in the crystal. This gives rise to a number of optical centres, many of which have absorption and luminescence bands in the visible spectral region. Centres that are formed at lower annealing temperatures are presumed to involve the interstitial.

2.6. Ion implantation

Most of the luminescence centres produced by irradiation with high-energy electrons or fast neutrons are also generated by ion implantation. However, some ions (*e.g.* Ni, Zn, Ag, Ti and Si) produce, in addition, unique luminescence bands [12].

2.7. Dislocations

Optical centres may form in the vicinity of slip lines, stacking faults and growth planes. In some cases the optical centres are the same as those produced by radiation damage and annealing [15], and can be understood simply in terms of the trapping of vacancies and interstitials. In other cases the slip lines, or extended defects such as platelets (discussed in ref. 8), appear to be “decorated” and give rise to characteristic emission bands [16].

3. Excitation of luminescence

With the exception of the edge emission and “band A” luminescence to be discussed below in Sections 4.1 and 4.2, all of the different luminescence bands are associated with vibronic centres. These centres have their ground and excited energy levels situated somewhere in the forbidden energy gap between the valence band and the conduction band (Fig. 1(a)). The absorption process produces a sharp zero-phonon line and a band at higher energy (shorter wavelength) as shown in Fig. 1(b); in luminescence a sharp zero-phonon line and a band at lower energy are observed (Fig. 1(c)).

3.1. Photoluminescence

The photoluminescence process is the simplest to visualise. (We shall assume here that the photons used for excitation have an energy less than the bandgap of diamond, so that no electron-hole pairs are produced.) The optical centre is excited using a wavelength lying in the absorption band (see Fig. 1(b)); after a short time the centre relaxes to the ground state, emitting light in the luminescence sideband. Many of the absorption bands in natural diamond extend into the ultraviolet spectral region, and excitation with a mercury “black lamp” (365 nm) produces blue, green, yellow or red luminescence in suitable specimens.

If the diamond contains a large number of centres that emit visible light they will all be excited to some extent using ultraviolet illumination. However, within

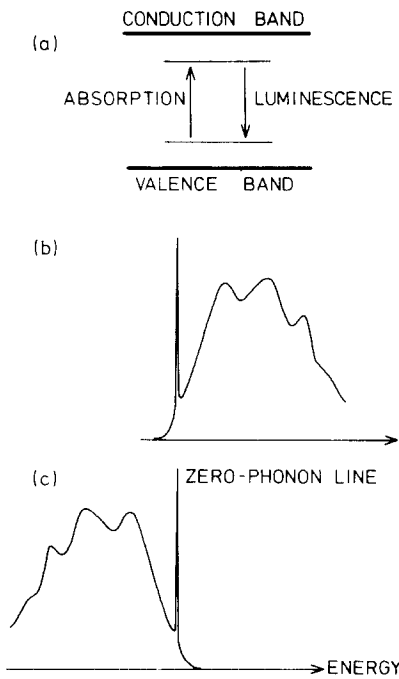


Fig. 1. (a) Simplified energy level scheme for a vibronic centre, and representative (b) absorption and (c) luminescence spectra.

certain limitations, the longer wavelength bands can be excited *selectively*. Suppose we have two optical centres 1 and 2 with *absorption* spectra as shown in Fig. 2. Excitation at wavelength A will excite both centres and luminescence will be observed from each; excitation at wavelength B, however, will only excite system 2. If in a diamond the concentration of centre 2 is very much less than that of centre 1, then if both systems are excited the luminescence from centre 2 will be completely obscured by that from centre 1. By adjusting the exciting wavelength the luminescence from centre 2 can be preferentially excited, and its spectrum may be studied.

It is clear that, in order to produce strong luminescence, an appreciable fraction of the exciting radiation must be absorbed; therefore a sufficient concentration

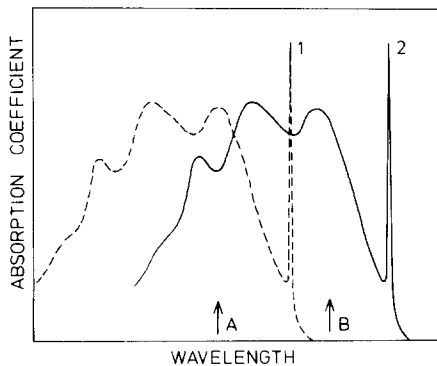


Fig. 2. Representative absorption spectra of two optical centres 1 and 2. Photoexcitation at wavelength A excites both centres, but at wavelength B excites only centre 2.

of the relevant optical centre must be present to produce that absorption. However, weak luminescence does not necessarily mean that the concentration of corresponding defects is low. As the A nitrogen concentration in a diamond is increased the luminescence from the H3 and N3 centres (see below) is quenched because of a non-radiative transfer of energy to the A nitrogen [17]. As we shall see, most of the optical centres in diamond involve nitrogen, and so the photoluminescence may be weak both at very low and at very high nitrogen concentrations.

When a laser is used to excite photoluminescence, the Raman scattered line is also present in the spectrum. Since the photoluminescence and Raman scattering intensities depend upon the volume of the crystal excited, as well as the intensity of the exciting light, the ratio of the photoluminescence intensity to the first-order Raman scattering intensity measured in the same spectrum provides a useful semi-quantitative technique for comparing the emission spectra from different samples and after various treatments [18].

3.2. Cathodoluminescence

Electron-beam excitation is simply a very convenient method of producing a high concentration of electron-hole pairs. The generation rate of a typical 50 kV beam, at a current density of 0.01 A/cm², is about 2×10^{23} electron-hole pairs per cm³ per second in a region of the diamond about 9–18 μm below the surface. Cathodoluminescence is a “near-surface” technique; the emitting region at V kilovolts is located $(0.007-0.014) \times V^{1.825}$ μm below the surface [19]. Electrons and holes may recombine in a variety of different ways. In very pure diamonds the electron and hole recombine directly to give the free-exciton “edge emission” (see Section 4.1); in diamonds containing both nitrogen and boron, the broad “band A” emission (see Section 4.2) has been identified as donor-acceptor pair recombination [20], and problems with this model are discussed later. In addition, many (but not all) vibronic centres may capture an exciton and subsequently de-excite producing luminescence. The luminescence decay time of many optical centres in diamond is very short (typically 10–50 ns) and so even very small concentrations of such defects can produce bright cathodoluminescence. By way of illustration, if we assume that 10% of the electron-hole pairs at the above generation rate recombine by capture of a luminescence centre with a decay time of 20 ns, the concentration of centres required is only 3×10^{14} cm⁻³. This is quite different to the situation with photoluminescence where, if the defect concentration is small, the amount of exciting light absorbed is small and the luminescence is weak.

In many diamonds non-radiative traps are present, and, in addition, the same comments about quenching

of the luminescence by A nitrogen apply as for photoluminescence. In general, therefore, the brightest cathodoluminescence is obtained from relatively pure diamonds.

Electron-hole pairs may also be produced in diamond by the absorption of electromagnetic radiation with energy greater than the band-gap of 5.5 eV [5]. Laboratory sources of continuous radiation in this wavelength region (a deuterium arc, for example) are rather feeble, and lasers such as the ArF excimer laser at 193 nm can only be operated in the pulsed mode at a low repetition frequency. Very little spectroscopic work has therefore been carried out using these methods of excitation. However, Robins *et al.* [21] have recently obtained luminescence and luminescence-excitation spectra from a gem-quality natural diamond and a number of CVD diamond films using a xenon flash lamp and a pulsed laser at 215 nm (obtained by frequency-doubling a dye laser pumped by a nitrogen laser). As expected, the luminescence spectra were similar to those obtained using electron-beam excitation, but with a lower signal-to-noise ratio.

4. Luminescence spectra

After dealing with edge emission (Section 4.1) and band A emission (Section 4.2) the major luminescence spectra associated with vibronic bands are discussed below in order of increasing wavelength. Spectra are shown for those optical centres that occur in CVD or synthetic diamond; for spectra that occur only in natural diamond the original references should be consulted. In most cases, both in this paper and in the literature, the spectra shown have not been corrected for the wavelength-dependent response of the measuring systems, so detailed comparisons of spectral shapes are not always possible. The zero-phonon lines of all the optical centres in diamond are much sharper at 77 K than at room temperature [3], and in only a few cases is any further sharpening observed on cooling to 4.2 K. It is important to realise that the *energy* of the zero-phonon line also changes with temperature, and the standard values are tabulated at 77 K [3, 4].

4.1. Edge emission

Intrinsic edge emission may only be observed in the cathodoluminescence spectra from diamonds that are relatively free from defects [5]. A typical spectrum is shown in Fig. 3(a) for a synthetic diamond containing very low concentrations of nitrogen and boron. Diamond is an indirect gap semiconductor with its valence band maxima at wavevector $k=0$ and its conduction band minima at $k=k_{\min}=0.76$ of the $\langle 001 \rangle$ zone boundary [5, 22]. The peaks labelled A, B and C are due to the

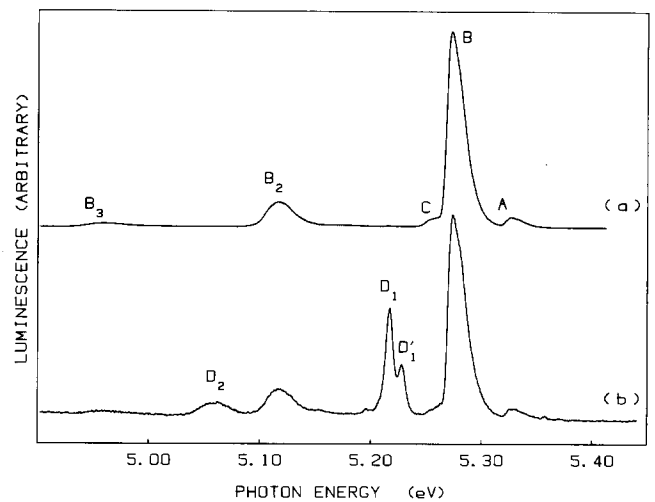


Fig. 3. Edge emission from (a) a very pure synthetic diamond and (b) a natural semiconducting diamond, recorded with the specimens at 77 K. Features A, B and C, and the replicas B₂ and B₃, are produced by the recombination of free excitons; features D₁ and D'₁, and the replica D₂, are due to the recombination of excitons bound to the boron acceptor centre.

recombination of a free exciton with the emission of momentum-conserving phonons of wavevector $\pm k_{\min}$, having energies of 87 ± 2 meV (transverse acoustic), 141 ± 1 meV (transverse optic) and 163 ± 1 meV (longitudinal optic), respectively. The low energy threshold of each peak occurs at an energy given by

$$h\nu = E_g - E_x - \hbar\omega \quad (1)$$

where E_g is the energy gap (5.49 eV at 77 K), E_x is the exciton binding energy and $\hbar\omega$ is the energy of the corresponding phonon (\hbar being planck's constant). Features B₂ and B₃ are further free-exciton processes involving a transverse optic (TO) phonon of $\pm k_{\min}$ together with one or two $k=0$ optic phonons respectively.

Figure 3(b) shows the edge emission from a natural type IIb diamond. Here, in addition to the free-exciton peaks described above, we see features D₁ and D'₁ which are associated with the recombination of excitons bound to the boron acceptor. The very weak zero-phonon lines D₀ and D'₀ (not visible in Fig. 3(b)) occur at energies $E(D_0) = E_{gx} - E_{4x}$ and $E(D'_0) = E'_{gx} - E'_{4x}$ where E_{gx} and E'_{gx} are the energies of the excitons associated with the upper and lower valence bands and E_{4x} and E'_{4x} are the binding energies of the upper and lower valence band excitons to the neutral acceptors. The peaks D₁ and D'₁ are TO phonon replicas of D₀ and D'₀, and a further replica D₂ is clearly visible.

The intensity of the bound-exciton peaks, relative to that of the free-exciton features, gives an indication of the uncompensated boron concentration in the region of the diamond examined. For the diamond shown in Fig. 3(b) this is about $5 \times 10^{16} \text{ cm}^{-3}$, as determined from Hall-effect measurements [23].

Collins *et al.* [24] first detected intrinsic edge emission in single particles of CVD diamond grown by the microwave technique, showing that this material can be grown with very low defect concentrations. Those authors were, however, unable to find any edge emission in polycrystalline films grown by the same method. Kawarada *et al.* [25, 26] have subsequently observed intrinsic edge emission in single particles of their CVD material, and also bound-exciton recombination from boron-doped polycrystalline samples. Weak intrinsic free-exciton luminescence has also been observed from polycrystalline films by Partlow *et al.* [27], and from single particles by Robins *et al.* [28]. We shall return to this topic at the end of this paper.

Kawarada *et al.* [25, 26] make the interesting observation that the edge emission is produced only in the $\{100\}$ growth sectors of the CVD particles, a result that has been confirmed by Robins *et al.* [28]. Nitrogen and boron are taken up less readily in the $\{100\}$ growth sectors than in the $\{111\}$ growth sectors of synthetic diamonds [29], and other defects such as Ni are present exclusively in the $\{111\}$ sectors [11]. The observation of edge emission from only the $\{100\}$ regions of CVD particles shows that for this material, also, the $\{100\}$ regions have a lower defect concentration.

4.2. Band A

Band A is the most commonly observed cathodoluminescence emission from diamond. Figure 4 shows typical spectra observed from natural type Ia and IIb diamonds, and from a synthetic type IIb diamond. The emission from the latter is green, whilst that from the natural diamonds is two different shades of blue. Dean [20] suggested that the spectra could be interpreted in terms of donor-acceptor pair recombination. If a donor centre and acceptor centre are in close proximity, the extra electron on the donor occupies the hole on the acceptor. When electron-hole pairs are generated in the sample the donor captures an electron, the acceptor

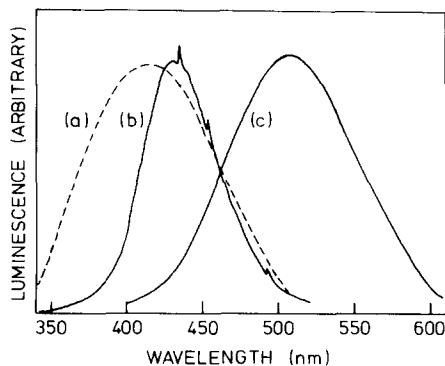


Fig. 4. Band A cathodoluminescence from (a) a natural type Ia diamond, (b) a natural type IIb diamond and (c) a synthetic type IIb diamond, recorded with the specimens at 77 K.

captures a hole and then this electron and hole recombine releasing energy E (in eV) given by

$$E = E_g - (E_A + E_D) + e/(4\pi\epsilon r) - A/r^6 \quad (2)$$

where E_g is the energy gap, E_A and E_D are the acceptor and donor ionisation energies, ϵ is the permittivity, r is the separation of the donor and acceptor, and A is a constant. Dean argued that random strain in the diamond would broaden the discrete lines expected from eqn. (2) into a band and that in natural diamond, close-separation pairs predominate, resulting in blue luminescence, whilst in synthetic diamonds the pairs are more diffuse and the emission occurs in the green.

When Dean proposed this model it was believed that there was only one possible donor with an ionisation energy of 4 eV, and indeed the low energy limit (as $r \rightarrow \infty$ in eqn. (1)) of the band A emission in synthetic diamond seemed consistent with this. However, we now believe that the donor ionisation energy in synthetic diamond is about 1.7 eV which should result in a donor-acceptor pair band in the ultraviolet region [9]. Such a band is not observed; furthermore the model does not account for the differences between natural type Ia and type IIa diamonds evident in Fig. 4.

More recent data on synthetic and CVD diamond cast further doubt on the above model; as stated above, it was proposed [20] that the much longer growth time of natural diamond (compared with synthetic diamond) favoured close separation pairs. However, blue cathodoluminescence is observed from the small $\{110\}$ growth sectors of synthetic diamond in which the nitrogen content is low [30]. What is more, green and blue luminescence are observed from CVD diamond films grown under identical conditions, apart from accidental boron contamination in the case of green luminescence [31].

Boron is incorporated most readily in the $\{111\}$ growth sectors of synthetic diamond [29] and in lightly doped crystals the residual nitrogen in the $\{100\}$ sectors may still be the major impurity. As shown in Fig. 5, although the boron-rich regions exhibit the green luminescence formerly believed to be characteristic of synthetic diamond [20] a very broad blue luminescence band is observed from the $\{100\}$ growth region.

In natural type IIb diamond [32], and in undoped CVD diamond films [33], the blue luminescence clearly originates from dislocations, and it has been assumed, on the basis of Dean's model, that these dislocations are decorated with donor-acceptor pairs [32]. This conclusion may not be valid, however. Finally we note in this section that for faceted CVD particles both the blue and the green luminescence are much stronger from the $\{100\}$ faces than from the $\{111\}$ faces [31]. More recent work suggests the situation may be more complex than this [28].

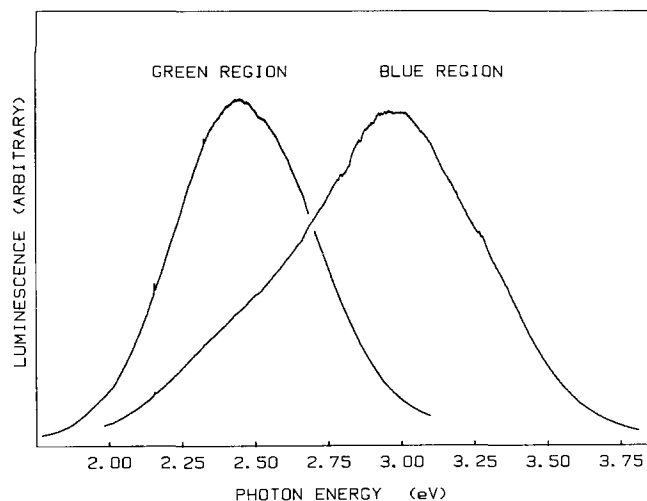


Fig. 5. Band A cathodoluminescence from two different regions of a boron-doped synthetic diamond. The green luminescence originates from a {111} growth sector containing a high boron concentration, and the blue emission comes from a {100} growth region in which the impurity concentration is much lower.

At present there is no theory which accounts adequately for all of the phenomena described, and it is probably better to use the description “band A”, rather than “donor–acceptor pair recombination”. The blue band A in natural diamond is weaker at room temperature than at 77 K, and is almost completely quenched if the diamond is heated to 150 °C [5, 34]. No detailed studies have been carried out on the temperature dependences of the emission from synthetic or CVD diamond.

4.3. The N9 system

The N9 vibronic band occurs naturally in diamonds containing nitrogen in the B aggregate form, and the intensity of the absorption band correlates approximately with the concentration of nitrogen in the B form [35, 36]. The energy of the zero-phonon transition — at about 5.26 eV (236 nm) — is the highest observed in diamond. Some diamonds in which the N9 absorption is observed exhibit the band in cathodoluminescence [1]. The zero-phonon region is made up of three closely spaced lines at 5.252, 5.262 and 5.277 eV; the relative intensities of these components change with temperature in the luminescence spectrum, but not the absorption spectrum, showing that the splitting is in the excited state [1].

4.4. The 5RL system

The 5RL system is observed in absorption and cathodoluminescence in relatively pure diamonds following primary radiation damage [37], and in cathodoluminescence only in type Ib diamonds (in which the intense absorption due to the nitrogen makes it impossible to detect any absorption that may be present) [38]. Figure 6 shows a cathodoluminescence spectrum recorded for a

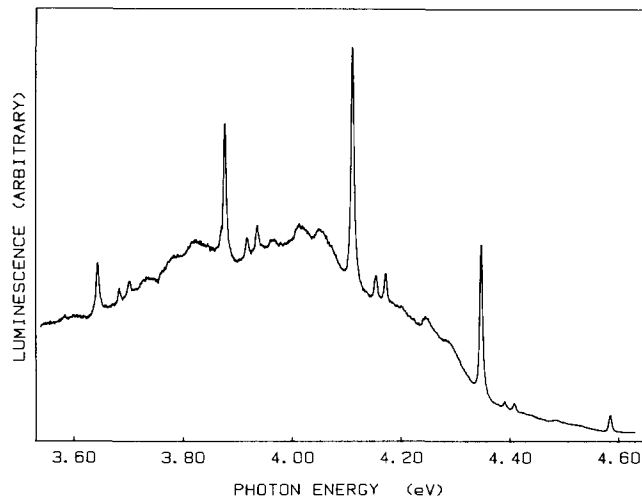


Fig. 6. The 5RL system observed in the cathodoluminescence spectrum from a single crystal of CVD diamond grown by the microwave process, following radiation damage and annealing at 800 °C. The specimen, about 100 μm across, was held at 77 K.

single particle of CVD diamond, following radiation damage and annealing at 800 °C. The system is interesting because the purely electronic zero-phonon transition at 4.582 eV (270.5 nm) couples to local-mode phonons with energies well above those of the lattice phonons, producing the sharp lines evident in Fig. 6.

Even in very pure diamonds the intensity of the absorption spectrum increases approximately linearly with the irradiation dose [37]; furthermore the energies of the local-mode phonons are lower by a factor close to $(12/13)^{1/2}$ in diamonds grown using ^{13}C . On the basis of this evidence, Collins *et al.* [38] have proposed that the centre involves the carbon interstitial. This is a significant result, because the 5RL system is sometimes seen in the cathodoluminescence spectra from as-grown CVD diamond films, particularly those grown using high methane concentrations [39]. These growth conditions introduce in the film disorder similar to that produced by radiation damage, but because of the random strain present the sharp lines in the 5RL spectrum are considerably broader [39] than those shown in Fig. 6.

4.5. The 3.188 eV system

The 3.188 eV (388.8 nm) system is observed in the cathodoluminescence spectra of most diamonds following radiation damage and annealing [40]. Figure 7 shows this emission band for a single particle of CVD diamond, following radiation damage and annealing at 400 °C. Many *as-grown* films of CVD diamond exhibit some 3.188 eV luminescence, and in the study by Collins *et al.* [39] it was much stronger in the relatively poor quality specimens grown at high methane concentrations. Again, because of the random strain, the fea-

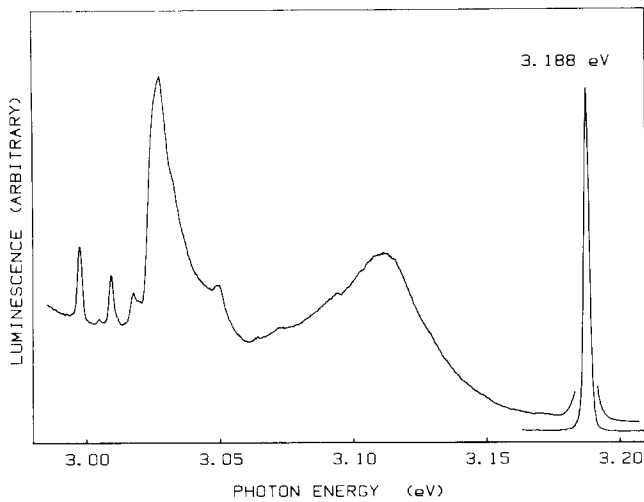


Fig. 7. The 3.188 eV system observed in the cathodoluminescence spectrum from a single crystal of CVD diamond grown by the microwave process, following radiation damage and annealing at 400 °C. The specimen, about 100 μm across, was held at 77 K.

tures were not as well defined as in Fig. 7. Isotope substitution studies [40] have shown that the 3.188 eV centre involves a carbon interstitial and a single nitrogen atom. Observation of this system in the spectra from CVD diamond, either as-grown, or following radiation damage, provides unmistakable evidence that the material contains some nitrogen. In single particles of nitrogen-doped CVD diamond that have been irradiated and annealed at 900 °C, the 3.188 eV emission originates principally from the $\{111\}$ growth sectors [26].

4.6. The N3 system

The N3 system, with a zero-phonon line at 415.2 nm (2.985 eV), is one of the most studied vibronic bands in natural diamond and is responsible for the blue emission observed in samples excited by a mercury “black lamp”. The N3 centre is believed to be three nearest-neighbour nitrogen atoms on a $\langle 111 \rangle$ plane “bonded” to a common vacancy [41]. The intensity of the N3 absorption band is approximately correlated with the intensity of the “platelet” peak at 1365 cm^{-1} ($7.3\ \mu\text{m}$), but there is no correlation with the concentration of A or B nitrogen [8, 36]. It is believed that the conditions that favour the growth of platelets also result in the production of N3 centres [36].

High concentrations of A nitrogen quench the luminescence [17], so that many diamonds that have a substantial N3 absorption may nevertheless exhibit no blue luminescence. In cathodoluminescence some type IIa diamonds and many type IaB diamonds (those type Ia diamonds containing mostly B nitrogen) show an N3 luminescence band superimposed on the blue band A emission. Many samples of CVD diamond exhibit a sharp line close to 2.985 eV in the cathodoluminescence

spectrum (an example will be shown later in Fig. 15), but the shape of the vibronic band is unlike that of the N3 system. (The conclusion by Collins *et al.* [13] that this peak is due to the N3 centre was based on erroneous data.)

4.7. The H3 and H4 systems

The H3 and H4 systems with zero-phonon lines at 2.463 and 2.499 eV (503.2 and 496.0 nm) are produced in type Ia diamond by radiation damage followed by annealing at temperatures above about 550 °C [42]. Davies and Summersgill [35] have shown that the H3 and H4 centres are due to a vacancy trapped at the A form and the B form of nitrogen, respectively. In diamonds with relatively low concentrations of A nitrogen (so that there is no quenching of the luminescence) these centres produce bright green luminescence when the diamonds are illuminated with long wave ultraviolet (365 nm). The H3 centre occurs naturally in some diamonds, but naturally-occurring H4 centres are extremely rare [44].

Both centres exhibit strong cathodoluminescence which can be much brighter than the blue band A in the same diamond. There is a sharp line at 537.8 nm (2.305 eV) superimposed on the H3 band, and correlated in intensity with it, which is absent from the photoluminescence spectrum; the reason for this is not known.

As shown in Fig. 8, many synthetic diamonds exhibit intense H3 cathodoluminescence from the $\{100\}$ faces only, and Dodge [44] has put forward a model to explain how small concentrations of H3 centres can be grown-in during synthesis. This model also accounts for the polarisation of the luminescence from polished sections of synthetic diamond. The concentration of H3 centres is too small to detect any photoluminescence

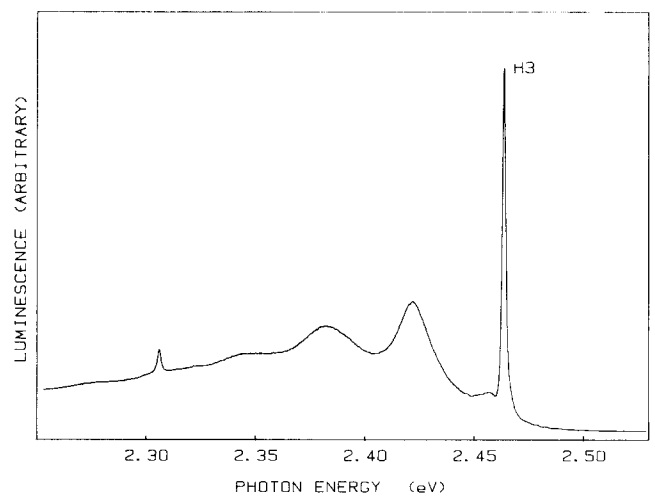


Fig. 8. The H3 system observed in cathodoluminescence from a $\{100\}$ growth sector of a synthetic diamond containing about 200 ppm of nitrogen. The spectrum was measured with the diamond at 77 K.

with a gemmological long wavelength (365 nm) lamp [45], but H3 emission from synthetic diamond is readily observed using laser excitation at 488 nm [44].

Collins *et al.* [13] were able to detect a trace of H3 cathodoluminescence from a single particle of CVD diamond, following radiation damage and annealing, showing that small concentrations of A nitrogen can be present in this material.

4.8. The 484 nm system

When cooled to 77 K, synthetic diamonds grown using a nickel-based solvent-catalyst emit an intense green cathodoluminescence from the {111} faces, particularly in specimens with a low nitrogen concentration [11]. The emission band shown in Fig. 9 has a complex zero-phonon multiplet at 2.56 eV (484 nm). The system can also be observed using photoluminescence, but only if the exciting wavelength is shorter than 400 nm; unlike most vibronic bands, there does not appear to be any absorption immediately to the short-wavelength side of the zero-phonon line [46]. For both photoluminescence and cathodoluminescence the emission is quenched as the temperature is increased above about 200 K [46].

4.9. The 2.721 eV system

Some as-mined gem-quality diamonds, colour-graded as "brown" exhibit a bright yellow luminescence when excited with 365 nm ultraviolet radiation [47]. This is produced by a vibronic band with a zero-phonon line at 2.721 eV (455.5 nm) and a maximum near 2.3 eV (540 nm). Such diamonds invariably have a featureless absorption band with a maximum near 2.6 eV (477 nm) and excitation of the diamond with light lying in this

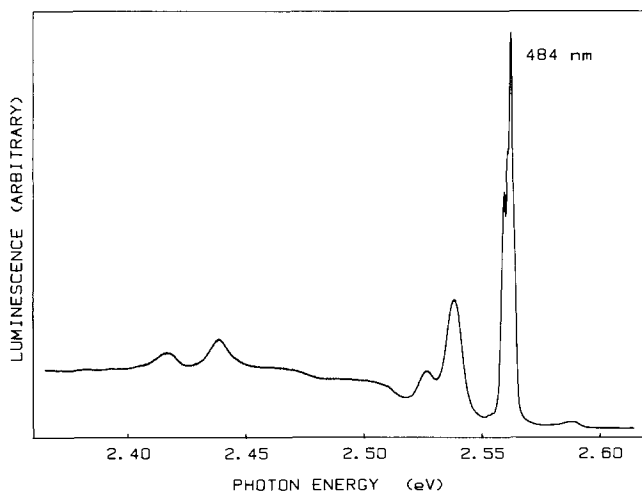


Fig. 9. The 484 nm system observed in cathodoluminescence from a {111} face of a synthetic diamond grown using a nickel-iron solvent-catalyst. The spectrum was measured with the diamond at 77 K, and the fine structure in the zero-phonon multiplet is just evident at this temperature.

band (using, for example the 488 nm line from an Ar ion laser) produces red luminescence [47] in a broad band with a maximum near 1.8 eV (690 nm). The nature of the defects giving rise to these luminescence bands is not known.

In cathodoluminescence both the yellow and the red bands are excited, together with blue band A and a multitude of zero-phonon lines [48]. Under certain excitation conditions the emission therefore appears almost white.

4.10. The 2.526 eV centre

Slip lines in natural diamonds, particularly those containing predominantly B nitrogen, frequently display bright yellow cathodoluminescence that is linearly polarised, with the *E* vector lying in the direction of the slip line [16]. At 77 K this can be the major emission in some diamonds, but the luminescence is much weaker at room temperature [16].

4.11. The 575 nm system

Following radiation damage and annealing, most diamonds exhibit some cathodoluminescence in a system with a zero-phonon line at 574.9 nm (2.156 eV). The emission is strongest in type Ib diamonds which generate an intense pink or orange luminescence. Plastic deformation of type Ib diamond also produces this emission system [49], and it is frequently observed in as-grown CVD diamond [39]. In nitrogen-doped thermal-CVD diamond, and some material produced by the oxy-acetylene flame technique, the 575 nm system is the most intense in cathodoluminescence spectra. An example of this will be shown later in Fig. 16. Collins and Lawson [50] have reviewed the information available on the 575 nm optical centre, and conclude that it is comprised of a single nitrogen atom and a vacancy. In single particles of nitrogen-doped CVD diamond that have been irradiated and annealed at 900 °C, the 2.156 eV emission originates mainly from the {111} growth sectors [26].

The 575 nm system is readily observed in photoluminescence, and is responsible for the pink emission observed from some natural diamonds with long-wave ultraviolet illumination. This band is also prominent in the photoluminescence spectra from CVD diamond excited using an Ar⁺ laser [51]. The zero-phonon line responds relatively rapidly to stress, and the width of the line can be used to estimate the random stress present in a given sample. Collins and Robertson [52] proposed that the stress *S* (in GPa) can be estimated from the linewidth *W* (in meV) using the expression $S = W/10$ (this is equivalent to $S = w/2.7$ where *w* is the linewidth in nm).

4.12. The 1.945 eV system

The dominant absorption band produced by radiation damage of type Ib diamond, followed by annealing at

800 °C, has a zero-phonon line at 1.945 eV (637.2 nm). The 1.945 eV centre has been shown to be a vacancy trapped at a single substitutional nitrogen atom [53]. This is one of the major centres in diamond which may be observed in photoluminescence, but does not exhibit cathodoluminescence (another is the H2 centre [2] — see Section 4.16); the reasons for this are not understood. A typical photoluminescence spectrum is shown in Fig. 10.

The 1.945 eV system has been observed in photoluminescence spectra from as-grown CVD diamond produced by the oxy-acetylene flame technique [51, 54], again indicating that this material contains significant concentrations of nitrogen. As with the 575 nm centre, the width of the 1.945 eV zero-phonon line may also be used to estimate the random stress in a given sample [18] using (with the notation from Section 4.11) $S = W/10$ or $S = w/3.3$.

4.13. The 1.681 eV system

The 1.681 eV system is often seen in as-grown CVD diamond, and has been studied in luminescence by a number of workers [12–14, 27, 51, 55–57]. The zero-phonon line is sometimes just detectable in absorption [13]. The proximity of the zero-phonon line to that of the GRI system (q.v.) has led to some groups wrongly identifying the optical centre responsible for the emission as the neutral vacancy. However, Vavilov *et al.* [12] reported producing this centre in natural diamond by implantation with Si atoms, and that result has recently been reconfirmed [13, 14]. It is now generally agreed that this emission band, which may be observed in photoluminescence and cathodoluminescence spectra from CVD diamond, is due to the incorporation of silicon during growth.

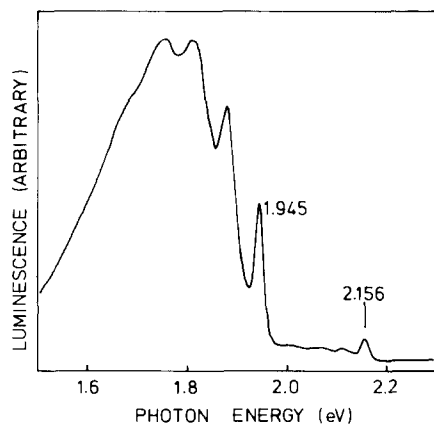


Fig. 10. Photoluminescence spectrum excited at 488 nm of a diamond film grown by DC-plasma deposition, recorded with the specimen at 77 K. The spectrum consists predominantly of the 1.945 eV system with a little emission in the 2.156 eV system. The diagram is based on Fig. 5.24 of ref. 67.

4.14. The GRI system

The GRI band with a zero-phonon line at 1.673 eV is produced in all types of diamond by all types of radiation damage. Most studies have been carried out in absorption, and a number of pieces of evidence have established that the optical centre involved is the neutral vacancy [58, 59]. Excitation with a laser or an electron beam produces relatively weak luminescence. In natural type IIb diamonds the zero-phonon line is very sharp in photoluminescence, but in cathodoluminescence additional structure is present, the origin of which is not understood [60, 61]. In Fig. 11 the GRI and 1.681 eV cathodoluminescence spectra are compared. A type IIb diamond has been used for this work, and the structured zero-phonon line is clearly visible. We note that in addition to the energy difference between the two zero-phonon lines the vibronic bands have a quite different shape, so that there should be no confusion about which optical system is being detected, even with a low resolution monochromator.

4.15. The 1.40 eV system

Synthetic diamonds grown using a nickel-based solvent-catalyst generally exhibit cathodoluminescence in a vibronic band with a zero-phonon doublet at 1.40 eV [11]. A typical spectrum is shown in Fig. 12, and for some diamonds this emission can be particularly intense. The 1.40 eV centres are segregated exclusively in the {111} growth sectors, and the luminescence from a polished section of diamond is strongly polarised [62].

For specimens with a low nitrogen concentration there is appreciable absorption associated with the 1.40 eV centre, and photoluminescence may then be generated

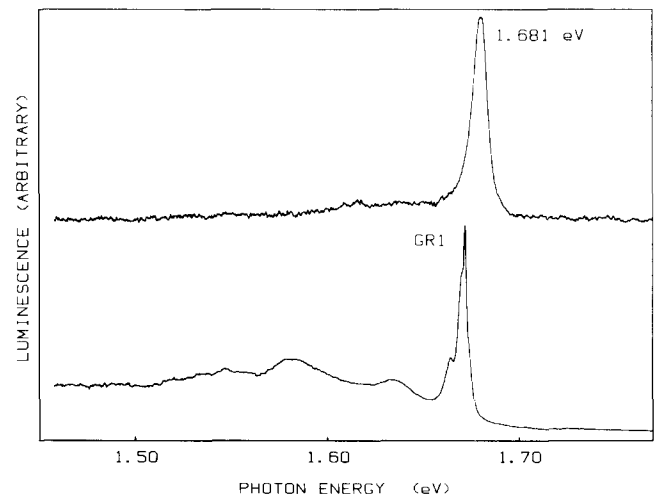


Fig. 11. Comparison between the cathodoluminescence spectrum of a polycrystalline film containing 1.681 eV centres (top spectrum) with that for a natural type IIb diamond containing GRI centres as a result of radiation damage (lower spectrum). The spectra were recorded with the specimens at 77 K, and it can be seen that the vibronic bands on the low-energy sides of the zero-phonon lines are quite different.

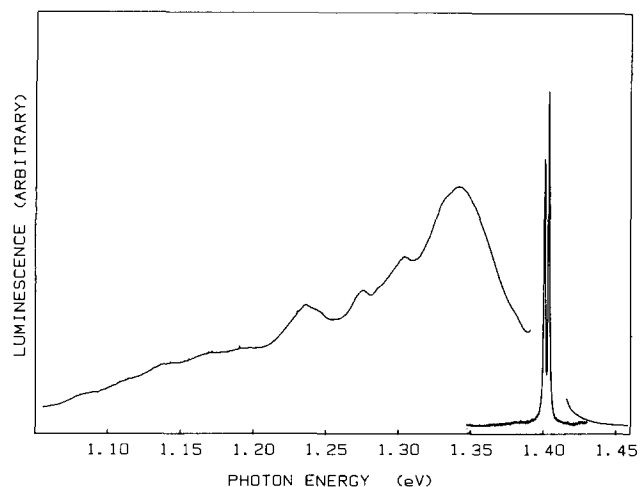


Fig. 12. The 1.40 eV system observed in cathodoluminescence from a {111} growth sector of a synthetic diamond grown using a nickel-iron solvent-catalyst. The spectrum was measured with the diamond at 77 K.

efficiently by pumping with a Krypton ion laser [63]. At low temperatures (approx ~ 10 K) the two components of the zero-phonon doublet become extremely narrow in suitable samples, and it is possible to see structure associated with the 5 stable isotopes of nickel [63].

4.16. The H2 system

The H2 vibronic band with a zero-phonon line at 1.267 eV is produced in synthetic type Ib diamond by intense radiation damage, followed by prolonged annealing at around 1700 °C [64]. This annealing leads to a partial aggregation of the nitrogen, producing some A-nitrogen, but leaving sufficient isolated nitrogen that the Fermi energy is shifted well towards the conduction band. Mita *et al.* [64] have proposed that the H2 centre is a negative charge state of the H3 centre (*i.e.* a vacancy trapped at an A-aggregate, but with the centre in a negative charge state because of the position of the Fermi level).

Lawson and co-workers have shown that the symmetries of the H2 and H3 centres are the same, and that the shift rates of the split components of the zero-phonon lines under uniaxial compression are similar for the two centres [2]. These findings give considerable support to the model proposed by Mita *et al.*, but thus far the ESR signal expected to be produced by the H3 centre in a negative charge state has not been detected [65]. The photoluminescence spectrum of the H2 centre, excited by a Kr⁺ laser, is shown in Fig. 13, and this is the longest wavelength emission currently known in diamond. As remarked earlier (Section 4.12), no H2 cathodoluminescence can be produced.

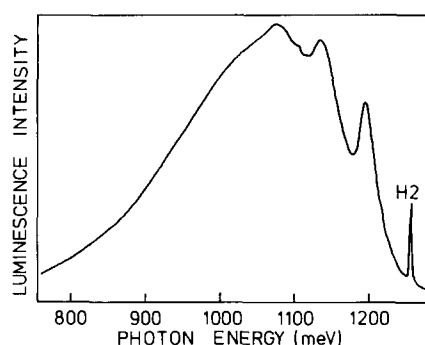


Fig. 13. The H2 system recorded in photoluminescence from a synthetic diamond that has been subjected to intense radiation damage and prolonged annealing at 1700 °C. The diamond was at 77 K and excited with the red lines from a Kr ion laser. The absorption band is quite strong in the diamond used for this spectrum, and the zero-phonon line in luminescence may therefore be attenuated by self-absorption.

5. Recent studies of CVD diamond

In this paper we have reviewed the major optical centres in diamond that give rise to photoluminescence or cathodoluminescence, and currently accepted models for these centres have been discussed, where they have been established. Measurements on CVD diamond have detected a number of further sharp emission lines of unknown origin [39], and many other luminescence systems have been documented [3, 4] but either occur very rarely, or make only a minor contribution to the total emission.

Research on conventional diamond over a period of years, and still ongoing, has enabled a number of important conclusions to be reached from luminescence studies of CVD diamond. We have discussed some of these findings in Section 4, and in this section we refer to recent Raman scattering work, and new cathodoluminescence studies of CVD diamond grown by the combustion flame technique.

5.1. Raman scattering

Raman scattering is frequently used to assess the quality of CVD diamond. A sharp first-order line at 1332.5 cm^{-1} , and the absence of broad structure around 1550 cm^{-1} (produced by sp^2 -bonded carbon) is indicative of high-quality material.

The laser radiation, of course, also excites any luminescence centres that may be present, and useful information can often be extracted from the spectrum, even though the measurement is generally carried out with the specimen at room temperature. As an example we show in Fig. 14 the Raman spectrum measured by Grot *et al.* [66] on a 180 μm thick homoepitaxial layer of boron-doped CVD diamond. Knowing the laser wavelength it is easy to calculate that the two sharp features in the spectrum are the 575 nm and 1.945 eV zero-phonon

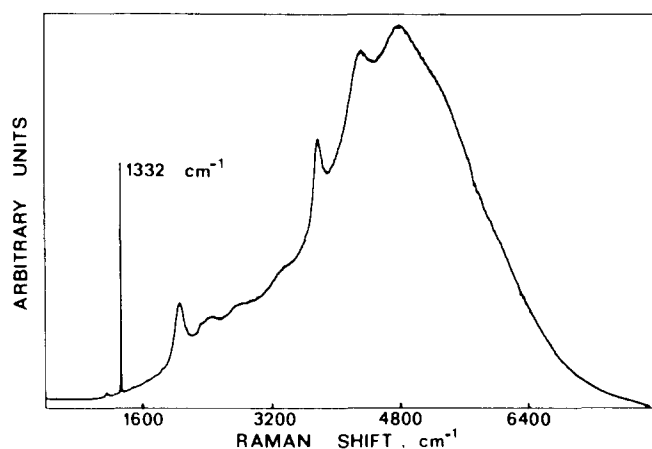


Fig. 14. Raman scattering and luminescence spectrum produced from a boron-doped homoepitaxial diamond film at room-temperature, on excitation with the 514.5 nm line from an Ar ion laser. (Spectrum from Grot *et al.* [66]). The moderately sharp peaks at apparent Raman shifts of around 2040 and 3740 cm^{-1} are the 575 nm and 1.945 eV zero-phonon lines, respectively, and the luminescence is mainly due to the 1.945 eV vibronic band.

lines. This shows that, although the film was doped with boron, certain areas contain nitrogen, and some disorder, resulting in the formation of these two nitrogen-vacancy centres.

5.2. Diamond grown by combustion flame

The author has recently examined the cathodoluminescence spectra from a specimen of diamond film grown by the oxy-acetylene film technique. At the centre of the film the luminescence was blue, and the emission became progressively pinker, and then orange, as the electron beam was traversed towards the outside edge of the specimen (which was about 8 mm in diameter).

The spectrum from the central region is shown in Fig. 15, and we note that this is comprised principally of the blue band A emission (see Section 4.2) together with a number of sharp lines, many of which are characteristic of CVD diamond. One of these, at 2.985 eV, is at the same energy as the well-known N3 zero-phonon line in natural diamond (see Section 4.6), but appears unrelated to it. Also in Fig. 15 we see a weak, sharp line at 2.156 eV (575 nm), showing that, even at the centre of the film, some nitrogen is present.

Figure 16 shows the luminescence from the pink-emitting region of the film, and we see that this is now dominated by the 2.156 eV system. This suggests that the nitrogen concentration is significantly higher in this part of the specimen. We note also that the width of the zero-phonon line is significantly greater than that observed from the blue-emitting region. This indicates that the random strain in this area of the sample is higher, probably because of the higher defect concentration. Because these films are grown in the ambient

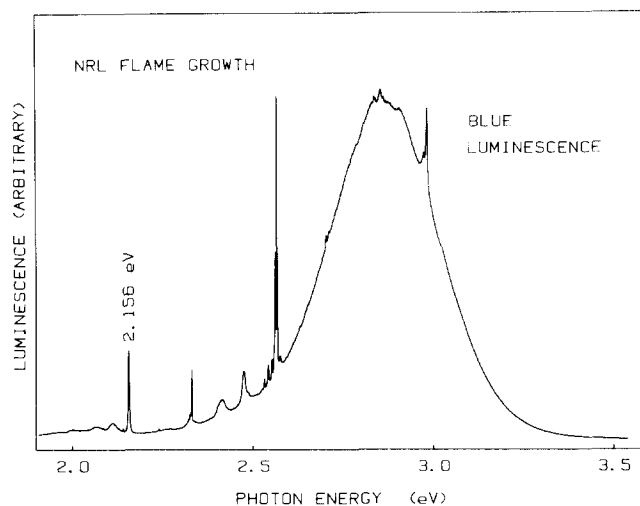


Fig. 15. Cathodoluminescence spectrum from the blue-emitting region of a CVD diamond film produced by the combustion flame technique, recorded with the sample at 77 K. The luminescence is mainly blue band A, with a number of sharp lines characteristic of CVD diamond and a weak 2.156 eV (575 nm) line due to nitrogen.

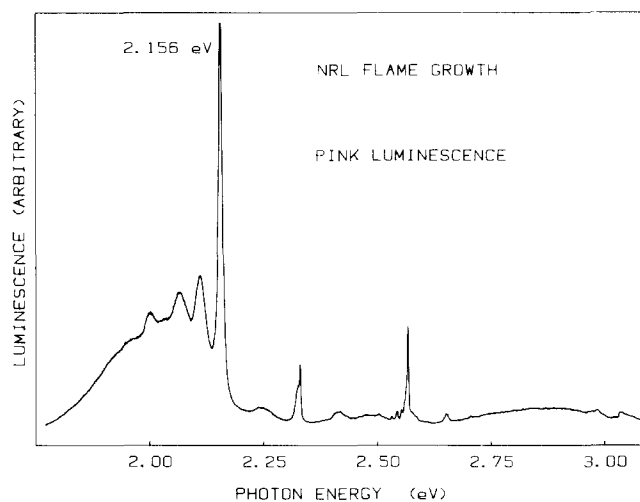


Fig. 16. Cathodoluminescence spectrum from the pink-emitting region of a CVD diamond film produced by the combustion flame technique, recorded with the sample at 77 K. The luminescence is mainly in the 2.156 eV system.

atmosphere it is not surprising that more nitrogen-related defects are found near the periphery of the film. Similar conclusions have been reached from photoluminescence studies [51].

Finally we return again to the blue-emitting region which also shows unmistakable evidence of edge-emission. The cathodoluminescence spectrum is shown in the upper diagram of Fig. 17, and may be compared with the lower spectrum of the edge emission from a natural type IIb diamond (also shown earlier in Fig. 3(b)). The free-exciton peaks A, B and C, together with the phonon replica B_2 , are clearly visible in the upper spectrum, but there is no evidence in that spectrum for

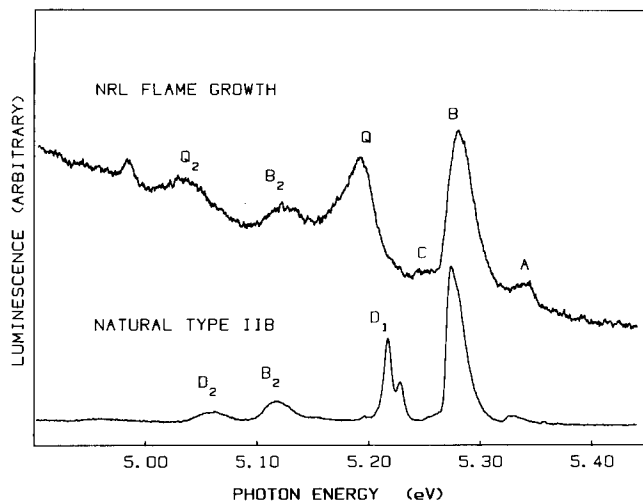


Fig. 17. Edge emission from the blue-emitting region of a CVD diamond film produced by the combustion flame technique (upper spectrum) compared with the edge emission from a natural type IIB diamond (lower spectrum). Both spectra were obtained with the specimens cooled to 77 K. The D peaks produced by bound-exciton recombination at the boron acceptor are absent from the top spectrum, but the Q features may be produced by bound-exciton recombination at an unknown donor or acceptor.

the bound-exciton peaks D which are associated with boron in semiconducting diamond. However, we do detect a previously unreported feature labelled Q which, like the D_1 peaks in the lower spectrum has a phonon replica Q_2 . It is tantalising to ask the question, "Is it possible that the Q features are produced by the decay of bound excitons at an unknown acceptor or donor centre?"

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