Diamond Luminescence

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Abstract

Luminescence spectroscopy is an established tool to investigate natural, high pressure synthesized, and chemical vapour deposited (CVD) diamond. The spectral range extends from 5.3 eV in the ultraviolet to approximately 1.2 eV in the near-infrared. More than 100 optical centres have been observed.

Since the early 1930's, semiconducting diamond for electronic devices has been of interest to science. The large bandgap (5.5 eV), low dielectric constant (5.7), and high thermal conductivity (about 5 times larger then that of Ag), as well as the superior charge-carrier transport properties, such as electron and hole mobility (μ^-: 2200 cm^2/Vs, μ^+: 1600 cm^2/Vs), lead to applications in active and passive electronics.

At the beginning of the 1980's, the first successful experiments of diamond films synthesis by low pressure chemical vapour deposition method were presented. Cathodoluminescence (CL) and photoluminescence (PL) are important techniques for characterising the defects present in CVD films and natural diamond.

In this presentation, the most significant luminescence bands, the defects and the problems with the models used to interpret the bands are discussed.

Key Words: Diamond, luminescence, cathodoluminescence, photoluminescence, defects.

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Introduction

The luminescence from diamond has been studied for more than 50 years and is an established tool to investigate natural, high-pressure synthesized, and chemical vapour deposited (CVD) diamond. The spectral range covered by the luminescence band extends from 5.3 eV (230 nm) in the ultraviolet (associated with the "edge emission" (Dean et al., 1965) corresponding to the indirect energy gap to around 1.2 eV (1000 nm) in the near-infrared ("H2" vibronic band; Lawson et al., 1990). More than 100 of the optical centres that have been documented for diamond give rise to luminescence. Most of them are listed by Clark et al. (1992). Before discussing the luminescence bands, we determine the defects that are present in diamond. These defects may be chemical or structural or a combination of both.

Diamonds are generally classified into four main types: Ia, Ib, IIa, and IIb. Nitrogen is by far the most common impurity (up to 0.5% in natural type Ia diamonds), with many forms from isolated substitution via simple aggregates to platelets. Type Ia and Ib diamonds contain dissolved nitrogen. In Ia diamond (majority of natural diamonds), the majority of the nitrogen is not electron paramagnetic resonance (EPR) active and is present in platelet form: A form, a pair of adjacent substitutional nitrogen atoms (Davies, 1976, 1979b); B form, four substitutional nitrogen atoms situated tetrahedrally about a vacancy. In Ib diamonds (majority of synthetic diamonds and very rare $\approx 0.1\%$ in nature), the nitrogen is EPR active and present on isolated substitutional sites. Both Ib and the A form of diamond have donor-like properties. Types IIa (very rare in nature) and IIb (extremely rare in nature) diamonds do not contain appreciable nitrogen. Type IIb diamonds are semiconducting if boron is the major impurity (270 ppm in specifically doped synthetic diamond). The properties of semiconducting diamonds and ion implanted diamonds have been discussed by Prinz (1992).

All CVD-diamond films grown on Si substrates have a strong peak at 1.681 eV (737.4 nm) in their Cl spectra. This defect has not been observed in natural diamond. The association of this optical centre with Si is

based on the pioneering ion implantation measurements of Vavilov *et al.* (1981) in epitaxial diamond films. Later on Si ion implanted natural diamond, this peak is attributed to a silicon centre (Zaitsev *et al.*, 1981; Collins *et al.*, 1990a) which is stable up to an annealing temperature of 1625K (Ruan *et al.*, 1991).

Synthetic diamond grown by high-pressure synthesis using nickel or a nickel alloy as solvent-catalyst emits an intense green luminescence from the <111> faces, particularly in specimens with low nitrogen concentration (Collins *et al.*, 1990b). Wakatsuki *et al.* (1991) measured the concentrations of nickel in different growth sectors and found that the concentration in the sectors is several 10 ppm, and in the <001> and <113> sectors, below the limits of detection of 0.5 ppm. The emission shows a zero-phonon doublet at 1.40 eV (885 nm) and a zero-phonon multiplet at 2.56 eV (484 nm). Both bands may also be detected in cathodoluminescence (CL) from natural diamonds which have been implanted with Ni^+ ions (Gippius *et al.*, 1983). The 1.40 eV luminescence from a polished section of diamond, believed to be due to a Ni^+ ion which has relaxed on a <111> axis from the Td substitutional site (Nazare *et al.*, 1991), is strongly polarised (Collins, 1989).

In the visible region, many absorption and luminescence bands are produced by electron and neutron irradiation. Some of the carbon atoms are displaced into interstitial positions and the vacancies become mobile for high annealing temperatures (Woods, 1984). While the centres that are formed at low temperatures are presumed to involve the interstitial, the vacancies that are formed at high temperatures may be trapped by other defects in the crystal. Investigations by replacing nitrogen-14 isotopes by nitrogen-15 in synthetic diamonds (Woods and Collins, 1982; Collins *et al.*, 1987; Collins and Woods, 1987) and changing carbon-12 to carbon-13 (Collins *et al.*, 1988) gave further knowledge about several of the radiation induced centres.

As diamond has a wide energy gap (5.5 eV), the CL technique has proved to be very useful in the characterisation of this material. The electron beam promotes simultaneously a wide variety of intrinsic and extrinsic processes. Cathodoluminescence spectroscopy, due to the high electron energies, is therefore generally less selective than photoluminescence (PL) spectroscopy, where the energies of the incident photons are normally less than the band gap. The generation rate of a 50 kV beam at a current density of 0.01 A/cm^2 is about $2 \cdot 10^{23}$ electron-hole pairs per cm^3 per second (Davies, 1979a). A change in the energy of the electron beam used to excite Cl can be exploited to provide useful information. The penetration depth is comparable with GaAs (Kanaya and Okayama, 1972) and is illustrated in Figure 1.
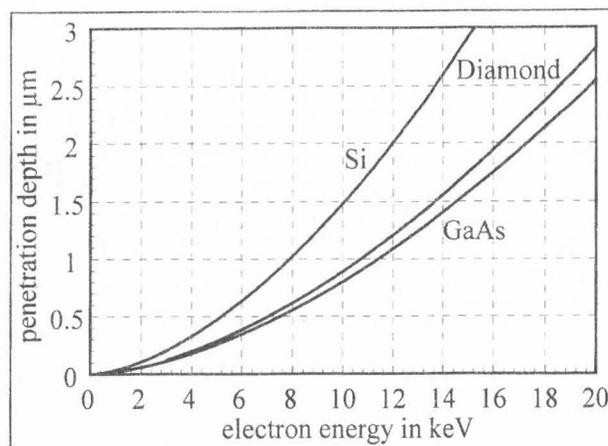

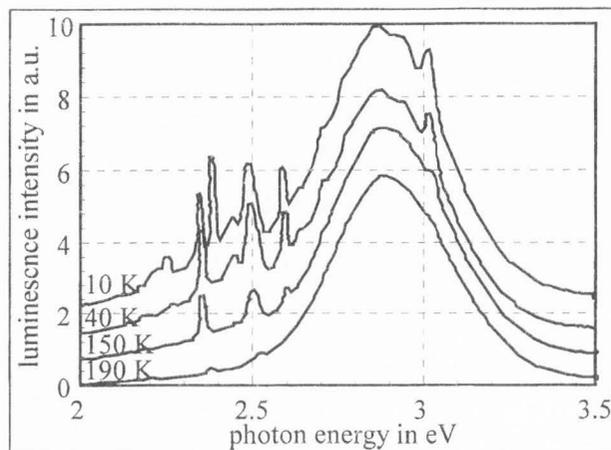**Figure 1.** Penetration depth of diamond compared to other semiconductors.

Figure 2. Temperature dependence of Cl from CVD diamond (Khong and Collins, 1993).

Luminescence Spectra

The major luminescence spectra associated with vibronic bands, edge emission, and "band A" emission are discussed below. The values for the intrinsic and extrinsic CL as listed in the following, are valid for 77K. Temperature dependence of CL from CVD diamond has been examined by Khong and Collins (1993). The spectra show a characteristic group of emission lines on the long wave length tail of the blue band A, together with another line near the peak of this band (see Fig. 2). The intensities of these lines decrease as the temperature is increased from 120K to 200K, and the band A intensity increases in this temperature interval. The zero-phonon lines of all the optical centres in diamond are much sharper at 77K than at room temperature, and in only a few cases is any further sharpening observed on cooling to 4.2K.
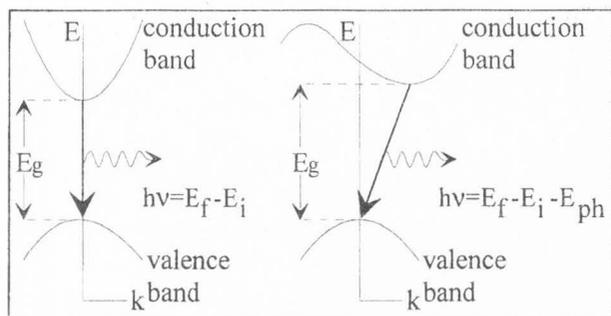
Figure 3. The energy transitions in direct- and indirect-gap semiconductor between initial states E_i and final states E_f. For indirect transitions, the participation of a phonon (E_{ph}) is required.
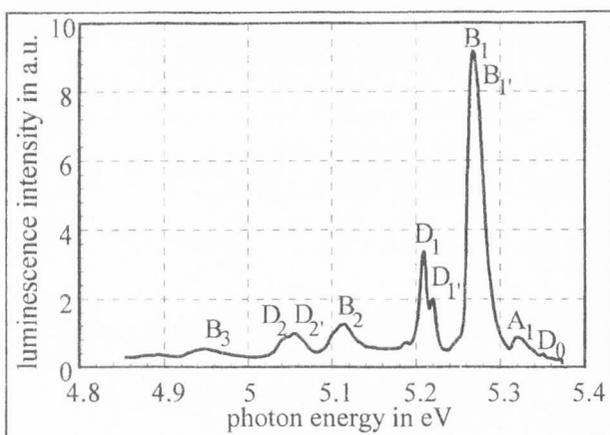

Figure 4. Cathodoluminescence spectrum of the edge recombination from natural p-type diamond at 100K (Dean, 1965).

Edge emission

Diamond is an indirect semiconductor with an energy gap E_g of 5.49 eV valence band maximum at wavevector $k_V = O$, and conduction band minimum at $k_C = 0.79$ along the <100> type axes (Dean, 1965; Kawarada *et al.*, 1990). The energy transitions in a direct and indirect gap semiconductors between initial state E_i and final state E_f are illustrated in Figure 3.

For indirect transitions, a phonon must be created, with its energy $\hbar\omega$ being taken from the energy stored in the exciton. The energy emitted in the photon is given by $\hbar\nu = E_g - E_x - \hbar\omega$, where E_x is the exciton binding energy. Figure 4 shows the edge recombination radiation spectra from natural p-type semiconducting diamond. Free excitons with the emission of phonons of wavevector $\pm k_C$ having values of 87 ± 2 meV (transverse acoustic), 141 ± 1 meV (transverse optic), and 163 ± 1 meV (longitudinal optic) labelled A, B, and C have been found. D_1 and $D_{1'}$ are associated with the
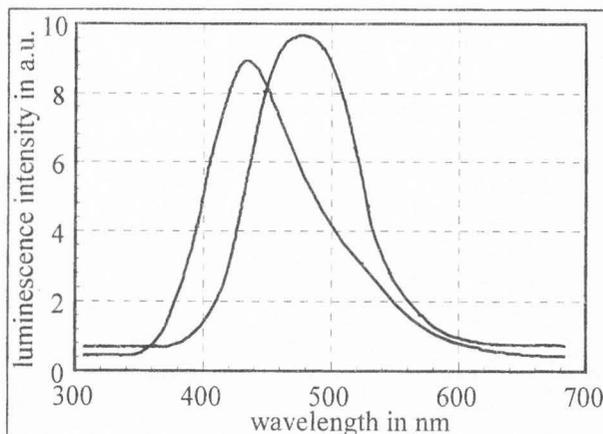

Figure 5. Blue and green luminescence from diamond films (Kawarada *et al.*, 1988).

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recombination of excitons bound to the boron acceptor. In contrast to free exciton case, luminescence from a bound exciton can proceed without creating phonons. Qualitatively, this reflects the localization of the hole on an acceptor centre. The components D_0 and $D_{0'}$ (D_0 not illustrated in Fig. 4) are zero phonons and are quite narrow. They are displaced below the exciton energy gaps E_{gx} and $E_{gx'}$, associated with upper and lower valence band by E_{4x} and $E_{4x'}$, which represent the binding energies of the upper- and lower-valence-band indirect exciton to the neutral acceptor. The peak emission intensity ratio of the bound-exciton relative to that of the free-exciton gives an indication of the uncompensated boron concentration.

Edge emission may only be observed from diamonds that are relatively free from defects. Kaward *et al.* (1990) found that the luminescence is produced only in the <100> growth sectors of CVD particles, due to a lower defect concentration. The ratio between the free-exciton recombination radiation and the band A emission is more than 20 times higher than values of natural diamond ever reported (Kawarada *et al.*, 1994).

Band A

A discussion of CL is incomplete without mentioning of donor-acceptor pair spectra. The "band A" luminescence is commonly observed by CL in all types (Ia, Ib, IIa, and IIb) of natural, synthetic, and CVD diamond. The emission band is broad, and commences from about 2 eV and extends up to 3.5 eV. The mechanism of band A is explained by donor-acceptor (D-A) pair recombination (Dean, 1965). It has been argued that in natural diamond, closely separated D-A pairs predominate resulting blue emission (see eq. 1), while in synthetic diamond, the separation of D-A pairs is larger and green emission occurs (see Fig. 5).
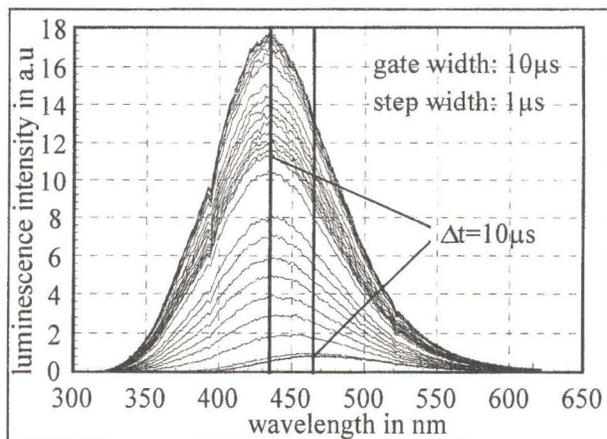
Figure 6. Time resolved cathodoluminescence of natural diamond (gate width = 10 μs step width = 1 μs (Heiderhoff et al., 1994).

Figure 7. Optical absorption of diamond containing nitrogen in the B form (Clark et al., 1992).

When electron-hole pairs are generated by the electron beam, the donor captures an electron and the acceptor captures a hole, releasing an energy given by:

$$E(r) = \{E_g - E_A - E_D + (e^2/4\pi\varepsilon r) - (ea^5/4\pi\varepsilon r^6)\}$$

Here, E_g is the energy gap, E_A and E_D are the acceptor and donor binding energies, ε is the static dielectric constant, "a" is an adjustable parameter in the polarization term and, r is the distance between the donor and acceptor. E will be shared between the photon and the phonons emitted.

Dean proposed that there is only one donor with a binding energy of 3.9 eV. Today, however, we believe that the donor ionization energy in synthetic diamond is about 1.7 eV, which should result in a luminescence band in the ultraviolet region (Collins, 1992).

Kawarada et al. (1988) examined the band A luminescence from undoped and boron doped CVD diamond. In the undoped film, they found that the blue luminescence characteristics such as peak position, half width of the spectra, and the temperature dependence of the intensities are equal to natural diamond IIa, where the luminescence regions are located at dislocations. In both undoped and boron doped diamond films, generally <100> sectors are much more band A luminescent than <111> sectors. In the boron doped CVD diamond, another addition peak appears at 2.3-2.4 eV. It is assumed that the peak relates to the doping boron due to the same dependence in natural type IIb semiconducting diamond.

Time resolved spectra show the presence of at least three bands upon excitation of diamond films. For natural diamond in the Cl spectra, a continuous shift of the band A with time to the green region has been observed
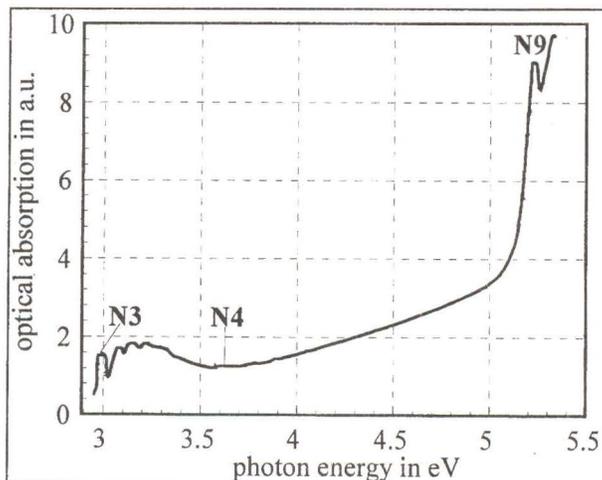
(see Fig. 6; Heiderhoff et al., 1994). For different time delays and windows, different PL spectra are also obtained from CVD diamond films (Pereira et al., 1992). The different spectra showed a dependence on decay and temperature behaviour of the intensities.

Finally, we note that it is better to use the description "band Al" than "donor-acceptor pair recombination," because at present there is no theory which describes all these phenomena.

N-lines

We noted that nitrogen is by far the most common impurity with many forms. The sharp lines at 2.985 eV (415.2 nm), 3.61 eV (344 nm), and 5.26 eV (236 nm) known as N3, N4, and N9 are correlated with different nitrogen impurities.

The N9 line is associated by Davies and Summergill (1973) with B-nitrogen and there is a correlation of the intensities with the concentrations of nitrogen in the B form. Figure 7 shows the optical absorption of diamond containing nitrogen in the B form. The low energy tail tends to be obscured by the N3 and N4 systems.

The N3 system (Clark et al., 1956a) with a zero-phonon line at 2.985 eV is the best known of the naturally occurring vibronic bands. van Wyk (1982) believed it to be three substitutional nitrogen atoms on a <111> plane "bonded" to a common carbon atom or a vacancy. The N3 luminescence band is superimposed on the band A in CL from type IIa diamonds and type IaB diamonds. High concentrations of nitrogen in the A form quench the luminescence, so that many diamonds having a N3 system may still exhibit no luminescence.

A bright yellow linearly polarised CL is observed from the 2.526 eV (490.7 nm) centre in type IaB diamond. This luminescence is associated with a defect
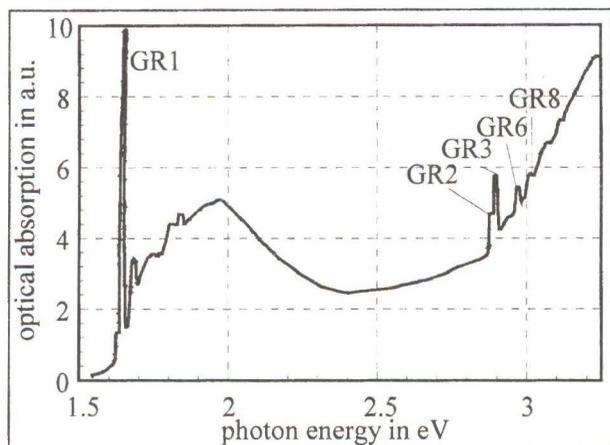
Figure 8. Absorption spectrum of the GR defect (Clark *et al.*, 1992).

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which decorates slip traces and is much stronger at 77K than at room temperature (Collins and Woods, 1982, 1987). The E vector lies in the direction of the slip line.

The bright yellow luminescence is naturally occurring, but can also be generated by plastic deformation. The effects on the zero-phonon line of uniaxial stresses are reported and analysed by Nazare *et al.* (1992), showing that the 2.526 eV transition occurs at a monoclinic I centre between two A' states.

Radiation damage

Radiation damages of all types produce the General Radiation (GR) defect in all diamond types, with the GR1 zero-phonon line at 1.673 eV (740.9 nm) and a series of absorption lines, GR2 to GR8, between 2.88 eV and 3.01 eV (430 nm to 412 nm) due to transitions to higher excited states (Fig. 8). The GR defect has been identified as the neutral vacancy (Clark and Walker, 1972), while the negative vacancy gives rise to the ND1 absorption line at 3.150 eV (393.5 nm; Davies, 1977). In natural type IIb diamonds, the GR1 zero-phonon line is very sharp in PL, but in CL, an additional structure is present, the origin of which is not understood (Collins, 1992).

The neutral and the negative vacancies become mobile for annealing temperatures above 830K, and the bands disappeared after annealing two hours at 1125K. If the sample temperature is kept below 250K during the irradiation, an additional vibronic band with a zero-phonon line at 2.367 eV (523.7 nm) occurs. This peak is unstable to thermal annealing. However, after annealing at 475K for two hours, the system becomes destroyed, and another zero-phonon line at 2.535 eV (489.0) starts growing in intensity. The 2.367 eV system is also bleached by intense light at temperatures < 200K, while at 1.979 eV (626.3 nm) a peak increases.
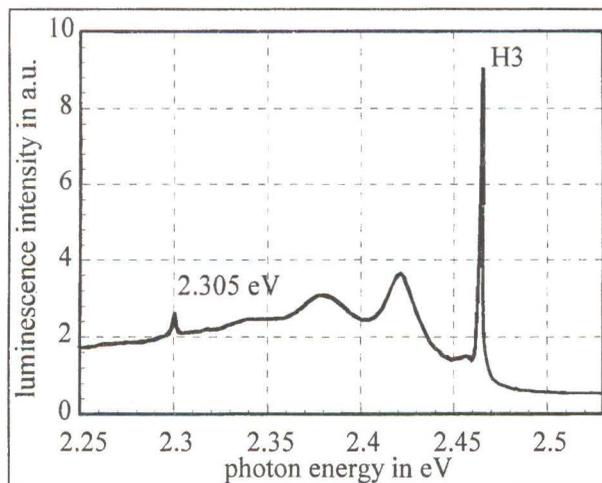

Figure 9. The H3 system observed in cathodoluminescence (Collins, 1992).

Mita *et al.* (1990) have also observed photochromic effects in the H2 systems with a zero-phonon line at 1.257 eV (989.1 nm). The vibronic band is produced in synthetic type Ib diamond by intense radiation damage followed by annealing at about 1775K, with a bleaching of H2 by light with energies higher than 2 eV (600 nm). Diamonds treated in this way contain aggregated nitrogen (ionization energy around 1.7 eV), producing some A nitrogen (ionization energy around 4.0 eV) which have donor-like properties. The Fermi level is therefore closer to the conducting band than in type IaA diamonds. It is proposed that the H2 centre is a negative charge state of the H3 centre and the photochromic effects due to photoionization.

Davies and Summergill (1973) showed that the H3, H4 systems are due to a vacancy trapped at the A form and the B form of nitrogen. The H3 and H4 systems {zero-phonon lines at 2.463 ev (503.2 nm) and 2.499 eV (496.0 nm)} are produced in type Ia diamond by radiation damage and annealing at temperatures above 825K (Clark *et al.*, 1956b). Both centres exhibit strong CL which can be brighter than band A, while no H2 CL can be produced (the reasons are still not understood). However, also an additional peak at 2.305 eV (537.8 nm) on the H3 band occurs, which is absent in the PL spectra (see Fig. 9).

The 575 nm (2.156 eV) system is most intense in CL spectra in nitrogen-doped thermal-CVD diamonds. The emission is strongest in type Ib diamonds which generate an intense pink or orange luminescence following radiation damage and annealing. Collins and Lawson (1989) concluded that the 575 nm system is due to a single nitrogen atom and a vacancy. Collins and Robertson (1985) showed that the zero-phonon line responds relatively rapidly to random stress S and
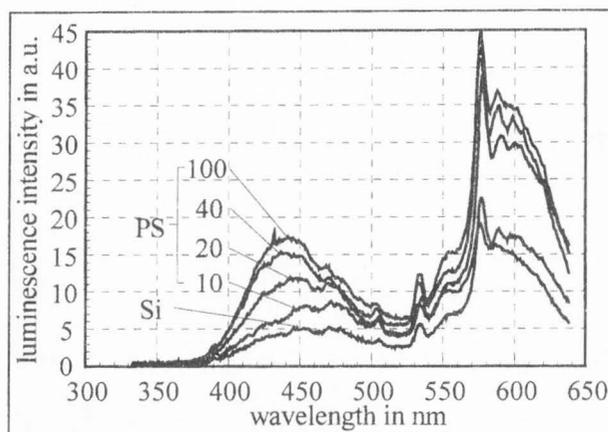
Figure 10. Cathodoluminescence spectra of diamond films grown on Si and PS with anodization current densities of 10, 20, 40, and 100 mA/cm^2 (Heiderhoff *et al.*, 1994).
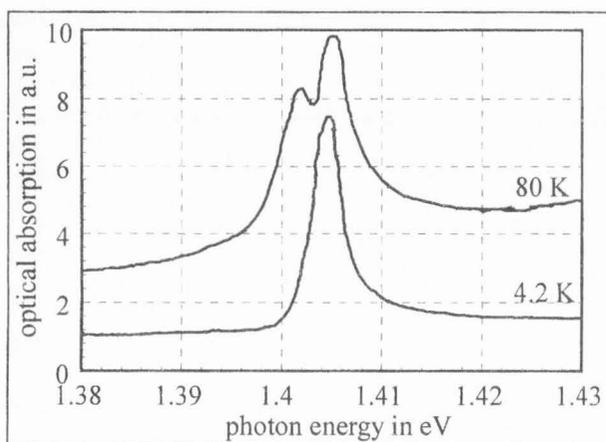

Figure 12. Absorption spectra of the 1.4 eV system (Collins and Spear, 1983).

Figure 11. Cathodoluminescence spectrum of the 5RL system (Collins, 1992).

Figure 13. Cathodoluminescence spectra of the 2.56 eV system (Collins and Spear, 1983).

proposed that S can be estimated from the line width $\Delta\lambda$ using the expression: $\Delta\lambda = S\cdot10$ meV/GPa. Heiderhoff *et al.* (1994) examined microwave plasma-assisted CVD-diamond films grown on porous silicon (PS) to demonstrate the influence of crystal structure and stress. The CL measurements showed that a stress relaxed diamond film can be grown by the use of appropriate PS thicknesses. Additionally, a shift of the band A to the blue region has been observed with increasing porosity, while a shift to the red has been observed with increasing thicknesses (see Fig. 10).

Finally in this section, we note the 5RL system with a zero-phonon line at 4.582 eV (270.5 nm) which is observed in absorption and CL in relatively pure diamonds following primary radiation damage (Collins and Spear,
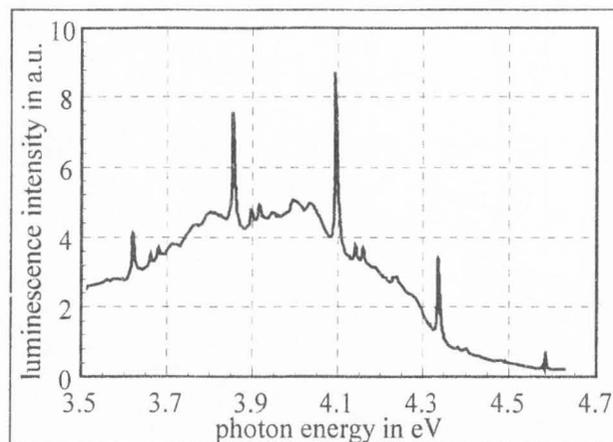
1986). The CL spectrum (Fig. 11) is interesting because it is dominated by a series of peaks spaced at about 0.237 eV. Collins *et al.* (1988) proposed that the centre is caused by the carbon interstitial, because for synthetic diamonds grown from ^{13}C, the spacing of the peaks is reduced, showing that a carbon-carbon vibration is involved.

Ni-lines

The 1.40 eV (885 nm) CL band is observed in all type Ib synthetic diamonds and is particularly intense in specimens using a nickel-based solvent-catalyst (Katsumata, 1992). Cathodoluminescence in the 2.56 eV (484 nm) system tends to be strong when the 1.4 eV luminescence is strong. Typical spectra are shown in Figures 12 and 13.
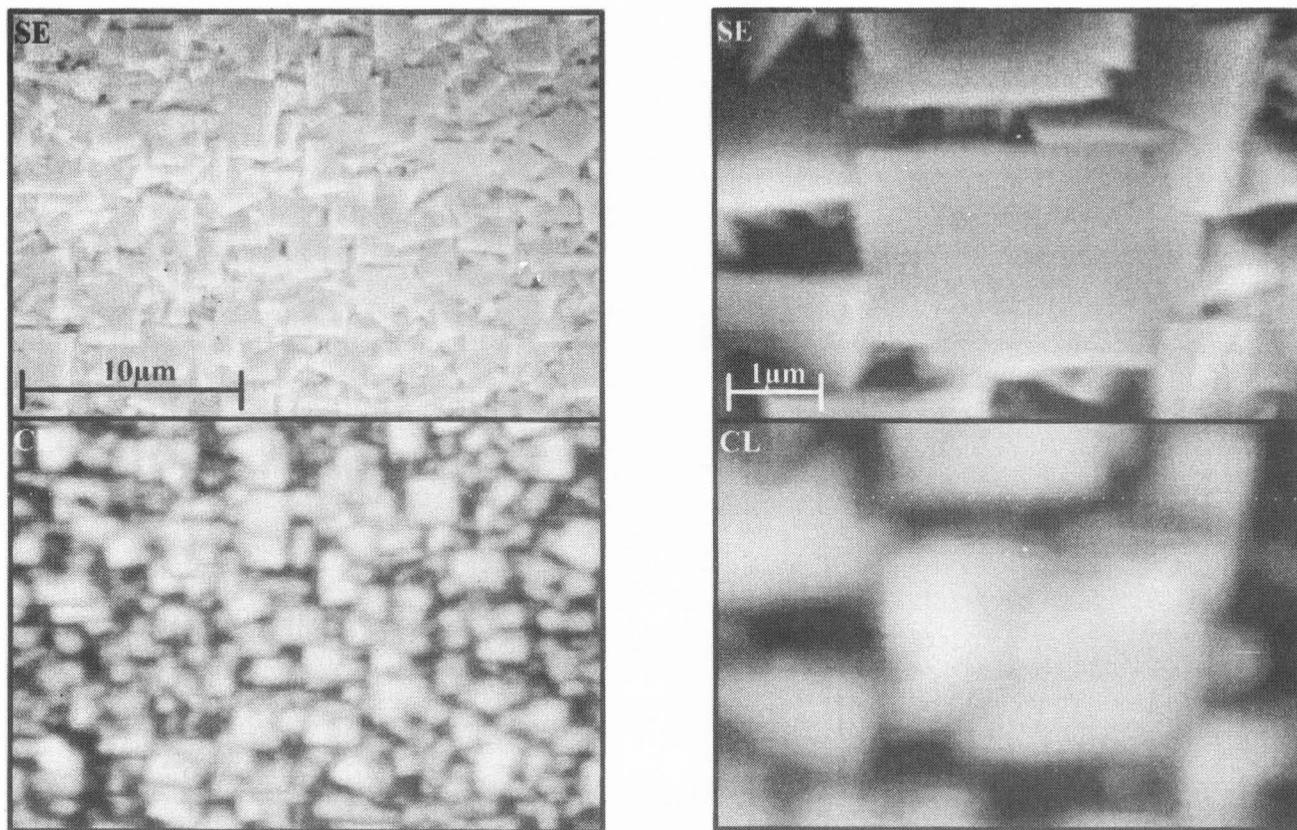
Figure 14. Scanning electron micrographs and CL images of a CVD-diamond film (Heiderhoff *et al.*, 1994).

These lines can also be detected from natural diamonds which have been implanted with Ni$^+$ ions (Gippius *et al.*, 1983). Temperature-dependence measurements showed that the 1.4 eV zero phonon doublet arises from a split ground state and that the 2.56 eV centre appears to make four thermalizing components.

Luminescence Micrographs

Cathodoluminescence is a powerful technique for characterizing diamond films. It allows a high resolution visualization, i.e., of grain boundaries, dislocations, and impurities by spatially luminescence. Figure 14 shows scanning electron microscope (SEM) images and Cl images of a CVD diamond film grown on PS with different magnifications, the second row showing twins and dislocations. Bright regions in monochromatic images are correlated with different facets dependence of the defects (discussed in the previous section) that are presented (i.e., Katsumata 1992; Robins *et al.*, 1992).

Finally, we note that this paper is naturally limited to a selection of optical centres and optical characterisation methods. Significant luminescence bands, defects, and the problems with the models used to interpret the systems were discussed.

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