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## LETTER TO THE EDITOR

# Intrinsic and extrinsic cathodoluminescence from single-crystal diamonds grown by chemical vapour deposition

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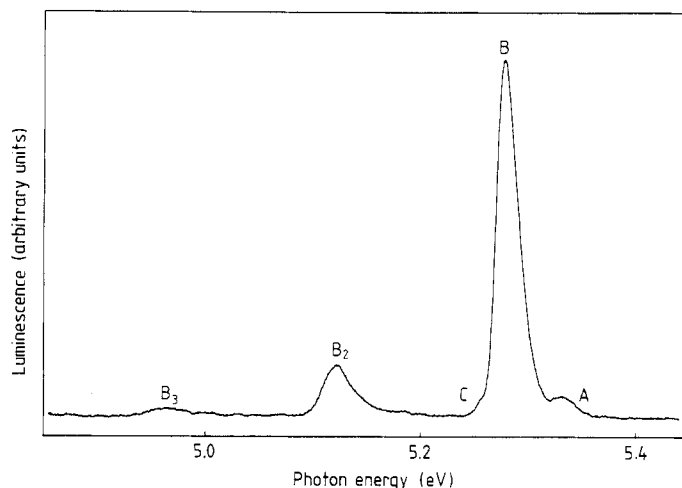
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**Abstract.** We have analysed the cathodoluminescence spectra from single-crystal diamonds grown by the decomposition of a methane–hydrogen mixture in a microwave plasma. Crystals grown using methane concentrations of  $\leq 1\%$  exhibit strong 'edge emission' at around 5.3 eV due to the recombination of free excitons in association with momentum-conserving phonons. When the CH<sub>4</sub> concentration is increased to 2% the edge emission becomes relatively weak, implying a degradation of crystal quality. All the diamonds exhibit bright blue luminescence in the visible spectral region due to donor–acceptor pair recombination. An emission line at 2.985 eV may be the N3 zero-phonon line which is commonly observed in natural diamonds; other emission lines are unique to these diamonds prepared by chemical vapour deposition. The widths of the zero-phonon lines suggest that the material is heavily strained.

In this Letter we present the first spectroscopic analysis of the cathodoluminescence produced in single-crystal diamonds grown by chemical vapour deposition (CVD). In many respects the spectra are characteristic of natural diamonds with very low impurity concentration; some features are, however, unique to CVD diamond.

Following the initial work, which demonstrated that diamond can be nucleated and grown, on non-diamond substrates, from the vapour phase (Spitsyn *et al* 1981, Matsumoto *et al* 1982a, b, Kamo *et al* 1983), a large number of laboratories have begun investigating the growth and characterisation of this material. Most of the work has concentrated on the production of thin polycrystalline films, and reviews of progress in this area are given by De Vries (1987) and Angus and Hayman (1988).

Although diamond films may be deposited on a number of materials (Kamo *et al* 1983), silicon wafers are frequently used in studies of the growth mechanisms. Light abrasion of the polished silicon wafer with diamond paste provides a large number of nucleation sites for diamond growth. Gas mixtures of methane and hydrogen have been investigated most widely, although other hydrocarbons can be used. Typical growth conditions use CH<sub>4</sub> concentrations between 0.5 and 3%, a total pressure about 40 Torr and a substrate temperature about 850 °C. Microwave power is used to maintain a glow discharge in the gas mixture, and the substrate temperature depends on the gas pressure and the microwave power (Kamo *et al* 1983).



**Figure 1.** Edge emission from a CVD single-crystal diamond, grown using 1.0% methane. The crystal temperature was 77 K and the accelerating voltage 45 kV. The labelling of the peaks follows the notation of Dean *et al* (1965).

If the typical growth conditions are maintained for several tens of hours the silicon substrate will be covered in a layer of polycrystalline diamond several tens of  $\mu\text{m}$  thick. However, if the substrate is examined with a scanning electron microscope after, say, 3 h, individually seeded single crystals with dimensions around  $2 \mu\text{m}$  are observed (Kamo *et al* 1983). These microcrystals have well defined habits with  $\{100\}$  and  $\{111\}$  faces appearing predominantly. After a prolonged growing time these microcrystals coalesce, and are overgrown, to produce a polycrystalline film.

In the present investigation we have used the typical growth conditions for microwave CVD summarised above, but with a *highly polished* silicon substrate, and, additionally, a low concentration of admixed water vapour. The nucleation sites on such a substrate are widely spaced, and, by extending the growth time to about 250 h, single crystals about  $100 \mu\text{m}$  across and  $25 \mu\text{m}$  thick have been produced. Although many of the crystals are twinned, a significant number exhibit well defined  $\{100\}$  and  $\{111\}$  facets. Diamonds produced using  $\text{CH}_4$  concentrations of 0.5, 1.0 and 2.0% have been examined.

The cathodoluminescence spectra from these crystals were measured using a custom-built electron gun operating at typically 45 kV and  $10 \mu\text{A}$ , with a spot size about  $300 \mu\text{m}$  in diameter. (Lower voltages could also be used, when required.) Most measurements were made with the diamonds at 77 K, and to achieve this the silicon substrate was clamped to a copper cold finger; thermal contact was ensured by a layer of In–Ga eutectic placed between the silicon and copper. (This alloy is a liquid at temperatures above  $16^\circ\text{C}$ .) Spectra were recorded using a Spex 1500 monochromator fitted with a  $1200 \text{ grooves mm}^{-1}$  grating blazed at 500 nm and an EMI 9789Q photomultiplier. A micro-computer system has been used to replot the spectra on a linear energy scale, but the shapes of the spectra have not been corrected for the wavelength-dependent response of the optical system.

Figure 1 shows the intrinsic edge emission for a diamond grown using 1.0%  $\text{CH}_4$ . The features A, B and C are due (Dean *et al* 1965) to the recombination of a free exciton with momentum-conserving phonons having energies of  $87 \pm 2 \text{ meV}$  (transverse

acoustic),  $141 \pm 1$  meV (transverse optic) and  $163 \pm 1$  meV (longitudinal optic). In many spectra we recorded, the feature C cannot be resolved. The low-energy threshold of each peak occurs at an energy given by

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

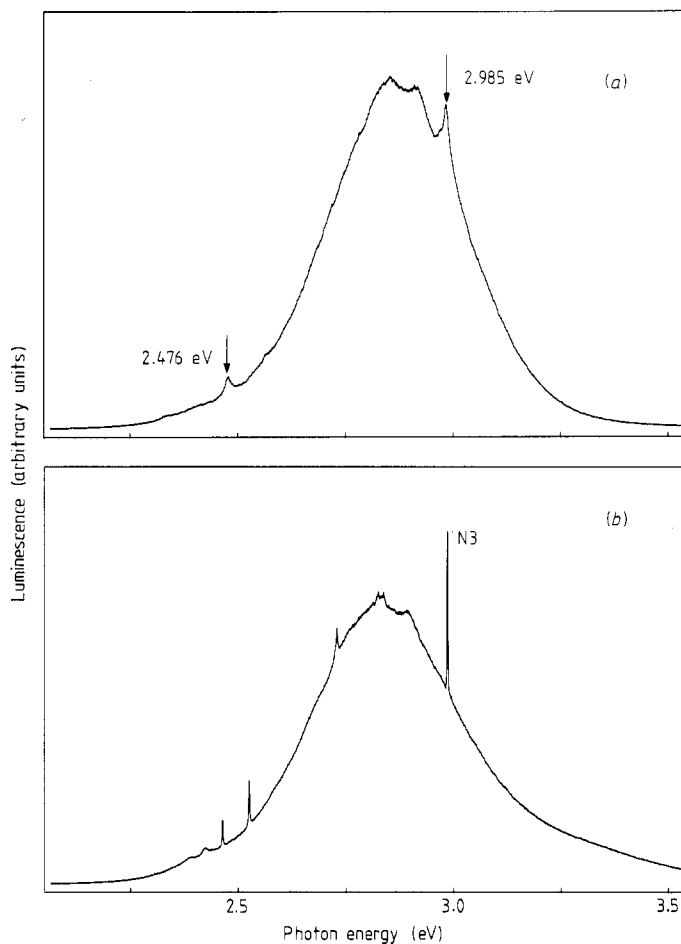
where  $E_g$  is the energy gap (5.49 eV at 77 K),  $E_x$  is the exciton binding energy and  $\hbar\omega$  is the energy of the corresponding phonon. Phonon replicas,  $B_2$  and  $B_3$ , of the major peak are also clearly visible. This intrinsic emission is only observed in diamonds that are relatively free from defects (Dean *et al* 1965). The luminescence shown in figure 1 was considerably stronger than in some relatively pure natural diamonds examined under the same conditions, indicating that this CVD diamond is extremely pure with few structural defects. Luminescence of similar intensity was observed from the diamonds produced using 0.5%  $\text{CH}_4$ , but for the diamonds made using 2% methane the luminescence was very much weaker than that shown in figure 1. The simplest interpretation of these results is that the quality of the diamond deteriorates as the concentration of methane in the gas mixture (and therefore the rate of crystal growth) is increased.

All three batches of CVD diamond exhibited bright blue cathodoluminescence, and in figure 2 we compare the emission from a crystal grown using 1% methane (figure 2(a)) with that for a natural type IIa diamond—i.e. one with very low nitrogen concentration (figure 2(b)). Superficially the two spectra appear very similar; most of the luminescence originates from the broad band (band A) which in natural diamond has been attributed to the recombination of electrons and holes at close-separation donor–acceptor pairs (Dean 1965). Superimposed on the band A in figure 2(b) are four zero-phonon lines, including the N3 line at 2.985 eV. The spectrum for the CVD diamond (figure 2(a)) also has a moderately sharp line at 2.985 eV, but inspection of the apparent phonon replicas at lower energies shows that they do not coincide with those in the N3 vibronic band. The line at 2.985 eV has additional structure on the low-energy side and, if this is associated with an electronic transition, it is possible that its phonon sideband is masking that of the 2.985 eV line. At present we are unable to determine whether the latter line is indeed the N3 zero-phonon line, or whether we have a different optical centre which coincidentally has its zero-phonon line at a nearly identical energy.

We also observe in figure 2(a) an emission line at  $2.476 \pm 0.003$  eV, and, not shown here, diamonds grown from the 0.5%  $\text{CH}_4$  mixture exhibit a sharp emission line at  $3.853 \pm 0.005$  eV. Neither of these lines has been documented for natural diamonds, or diamonds produced by high-pressure synthesis.

Finally, in this initial study of single-crystal CVD diamond, we have noted that the line at 2.985 eV becomes progressively broader as the methane concentration in the plasma is increased; furthermore, in a given diamond, the line is generally narrower if a 15 kV electron beam is used instead of the normal 45 kV. The penetration depths of 15 keV and 45 keV electrons are respectively 2.5  $\mu\text{m}$  and 19  $\mu\text{m}$  (using the relationship given by Davies 1979), and the increase in linewidth as the volume of the crystal sampled is increased implies that the material is very highly strained. This internal strain evidently becomes greater as the rate of crystal growth is increased (by increasing the methane concentration). The presence of strain and structural imperfections unique to vapour-deposited diamonds has also been inferred from earlier Raman scattering measurements (Matsumoto *et al* 1982a).

This investigation shows that cathodoluminescence spectroscopy is a very sensitive technique for the characterisation of CVD single-crystal diamond. For crystals grown using low concentrations of methane (0.5 to 1.0%) the intensity of the intrinsic edge



**Figure 2.** (a) Cathodoluminescence from a CVD single-crystal diamond, grown using 1.0% methane. Accelerating voltage 15 kV. (b) Cathodoluminescence from a type IIa natural diamond, obtained using an accelerating voltage of 45 kV. The N3 zero-phonon line at 2.985 eV is labelled. Both spectra were recorded with the diamonds at 77 K.

emission indicates that the material is remarkably free from impurity or structural defects. In the visible spectral region the band A emission spectrum is very similar to that for natural diamond. This, in itself, is surprising since the model proposed to account for this band assumes the existence of *close-separation* donor-acceptor pairs (Dean 1965). In natural diamonds, it is argued, these form by the diffusion of donors and acceptors, at elevated temperatures, over periods of millions of years. It is not self-evident how such pairs can be produced during the growth of CVD diamond. A similar puzzle would surround the formation mechanism of N3 centres if these are found to be responsible for the emission line at 2.985 eV in the CVD diamond. Our current understanding is that, in natural diamonds, N3 centres (three substitutional nitrogen atoms symmetrically surrounding a vacancy) are formed when A centres (nearest-neighbour substitutional nitrogen pairs) aggregate to form B centres (four nitrogen atoms and a vacancy); again this process requires substantial periods of time at high geological temperatures (Woods 1986).

Clearly there is a great deal to learn about the growth of CVD diamond crystals; in addition the production of single crystals, free from strain and defects, is one of the major technological challenges in this area. Further studies of this material will doubtless also lead to a better understanding, both of natural diamond and diamond produced by high-pressure synthesis.

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