SPECTROSCOPIC STUDIES OF SYNTHETIC DIAMONDS GROWN BY THE TEMPERATURE GRADIENT METHOD

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Optical absorption and cathodoluminescence (CL) techniques have been used to study synthetic diamonds produced by the temperature-gradient method. These crystals grow relatively slowly, compared with diamond abrasive grit, and exhibit a high degree of impurity segregation in the different growth sectors. Diamonds studied have been grown using Ni, Fe, Fe–Ni and Co–Fe solvent-catalysts, with and without nitrogen-getters added. Polished slices of diamond have been used to examine the segregation of optical centres in the [100], [111], [110] and [113] growth sectors, and to identify the defects responsible for the polarised green and near-infrared CL. The results also confirm, and extend, earlier work showing that nickel is incorporated in a number of optical centres in synthetic diamond.

1. Introduction

The growth of large, gem-quality synthetic diamond by the temperature-gradient method was pioneered by General Electric3). More recently Sumitomo has developed this process to produce heat sinks and wire-drawing dies on a commercial basis2). De Beers has also been producing large synthetic diamonds on an experimental basis since the 1970s3).

Nitrogen, in single substitutional form, is normally the major impurity in synthetic diamond, unless nitrogen-getters are added to the growth capsule. Absorption associated with this nitrogen, at wavelengths shorter than about 600 nm (energies greater than about 2 eV), gives the crystals a yellow or brown colour. The colour is not uniformly distributed, but is much stronger in the {111} growth sectors and very weak in the {110} and {113} sectors4). In addition the nitrogen produces absorption in the infrared one-phonon region, with a characteristic peak at 1130 cm\(^{-1}\) and a sharp line at 1344 cm\(^{-1}\); the intensities of these absorption features are also proportional to the nitrogen concentration.

The work reported in this paper has led to a better understanding of the segregation of defects, and confirmed earlier speculation about the nature of the optical centres responsible for the polarised CL from the cubic {100} and octahedral {111} growth sectors. The measurements support conclusions, reached from studies of diamond abrasive grit, that a number of absorption and CL systems are associated with the use of Ni (or a Ni alloy) as the solvent-catalyst during diamond growth5).

2. Experimental

The following diamonds have been used in this investigation: De Beers diamonds with standard nitrogen concentrations, grown using Co–Fe or Fe–Ni; De Beers diamonds with low nitrogen concentrations, grown using Fe–Ni with Al–Ti getters, or grown using Co–Fe or Fe with gettering by Al; diamonds grown at the National Institute for Research in Inorganic Materials (NIRIM), Japan, using Ni, either on its own or with different concentrations of Zr as a getter; and diamonds with standard nitrogen concentrations from Sumitomo. Cathodoluminescence and optical absorption spectra in the ultraviolet, visible and near infrared spectral regions, and infrared absorption spectra in the 1500 to 800 cm\(^{-1}\) region, have been measured using standard techniques. Polished slices of diamond have been used to examine the segregation of optical centres in the {100}, {111}, {110} and {113} growth sectors.

3. Results

3.1 Absorption measurements

When diamonds are grown using Co–Fe, the absorption in the visible region is normally only that associated with the nitrogen impurity, and as increasing amounts of nitrogen-getters are added the characteristic yellow colour becomes progressively paler. However, a broad absorption band in the red part of the spectrum is sometimes present in diamonds grown at low temperatures, and this gives such crystals a dark green colour. The absorption, which is the subject of current investigations by the author, is not uniformly distributed but occurs in distinct growth bands.

The situation is quite different when a Ni solvent-catalyst is used. In Fig. 1 we show the absorption spectra for three diamonds grown at NIRIM. Spectrum (a) is for a diamond grown without nitrogen-getters. The nitrogen content is about 450 ppm, and the specimen has a yellow-brown body colour due to the strong absorption in the blue region of the visible spectrum. In addition to the absorption due to nitrogen there is very strong absorption in the optical systems with zero-phonon lines at 1.883 eV and 2.51 eV. Figure 1(b) shows the spectrum for a diamond grown using Ni with 3.4% Zr as getter. This crystal has a bright yellow-green colour, with a nitrogen content around 60 ppm. The 1.883 eV and 2.51 eV systems are still present in considerable strength, but the spectrum is dominated by the broad-band absorption with a maximum near 1.4 eV. It is the tail of this band that is responsible for the green tinge in the colour of the diamond. A small amount of absorption in the 1.40 eV zero-phonon lines can be seen superimposed on the maximum of the band. This spectrum is similar to those for a number of General Electric diamonds investigated previously\(^5\). The broad band is rather stronger, and the 1.40 eV system far more intense, in the spectrum shown in Fig. 2(c). By contrast the 1.883 eV and 2.51 eV zero-phonon lines are much weaker. The diamond used to obtain this spectrum was grown with 5% Zr added to the Ni solvent-catalyst. The broad, structured peak, with a maximum near 1.8 eV, invariably accompanies the 1.40 eV absorption system and, together with the tail of the broad band mentioned above, produces in this diamond substantial absorption at the red end of the visible spectrum. A polished near-central slice of a similar diamond was also examined and it was noticed that the octahedral sectors were green in colour whereas the remaining sectors were virtually colourless; the 1.40 eV absorption was confined to these \{111\} growth sectors. The use of nickel also produces additional absorption in the one-phonon region\(^5\), and this, too, is present only in the \{111\} sectors.

Fig. 1. Absorption spectra of synthetic diamonds grown at NIRIM, recorded with the samples at 77K.
Fig. 2. Absorption spectra of a De Beers pale green diamond, recorded with the crystal at 77K.

All four of the absorption systems shown in Fig. 1 (in addition to that caused by nitrogen alone) have been attributed previously to the use of Ni for the diamond synthesis\(^5\). The results shown here confirm that conclusion, but it is clear that the intensity of each absorption band depends on the chemistry in the growth capsule, and probably also the temperature and pressure used for synthesis. Diamonds produced for commercial applications (by Sumitomo, for example) have medium nitrogen concentrations, and are probably made using a Ni alloy, rather than pure Ni. In many samples it is possible to see a faint trace of the 1.883 eV and 2.51 eV absorption lines that feature so prominently in Fig. 1(a).

In Fig. 2(a) we show the absorption spectrum of a De Beers pale green diamond from the near-infrared region to the absorption edge at 5.5 eV. This crystal was grown using an Fe–Ni solvent-catalyst with Al and Ti getters. From 1.0 to 2.6 eV the spectrum is very similar to that in Fig. 1(c), except that the absorption is about 5 to 10 times weaker. The pale green colour is clearly due to the transmission window produced by the increasing absorption at the red and blue ends of the visible spectrum. From 2.5 to 5.5 eV the spectrum is virtually the same as for a natural type Ib diamond with low nitrogen concentration, except for the absorption lines near 3.1 eV, shown in more detail in Fig. 2(b). The 1.40 eV zero-phonon doublet for the pale green diamond is shown in Fig. 2(c), and it can be seen how very much sharper the components are than in the General Electric abrasive grit studied previously\(^6\). At low temperatures (around 10K) the low energy component of the doublet becomes very weak, as expected from the work of Collins and Spear\(^5\), and the high-energy line becomes extremely sharp, enabling structure due to the 5 stable isotopes of Ni to be resolved\(^6\).

Strong and Cherenko\(^1\) reported that colourless diamonds can be grown using Fe as the solvent-catalyst with Al as the getter. That has been confirmed in the present investigation, and spectroscopic examination shows that the 1.4 eV broad band, and the sharp lines at 1.40 eV, 1.883 eV, 2.51 eV and 3.1 eV are all absent in diamonds grown by this process. The diamonds examined had only a very weak ultraviolet absorption, similar in shape to that in Fig. 2(a) for energies above 2.5 eV (but without the sharp lines at 3.1 eV).

3.2 Cathodoluminescence measurements

In Fig. 3 we show the visible CL from three different external faces of synthetic diamonds, grown using Fe–Ni and containing medium to high nitrogen concentrations, with the specimens cooled to 77K. The emission from \{100\} faces is
The emission from \{111\} faces, with the diamond cooled to 77K, is predominantly due to the 2.56 eV (484 nm) vibronic band (Fig. 3(b)). Temperature-dependence measurements show that the intensity of this bright green luminescence decreases with increasing temperature, and is difficult to detect at temperatures above 200K. This explains why room-temperature CL studies generally show very weak visible emission from \{111\} faces and growth sectors. We have also noted that luminescence in the 1.40 eV vibronic band, not shown in Fig. 3, is produced only in the \{111\} growth regions. Unlike the 2.56 eV system, however, this luminescence is not quenched at room temperature.

One of the notable features of Fig. 3 is the very high degree of impurity segregation in the different growth sectors. The 2.56 eV emission from the \{100\} face is very weak, there is a negligible amount of H3 luminescence detected from the \{111\} face, and both of these systems are virtually absent from the spectrum recorded for the \{110\} face (Fig. 3(c)). Luminescence from the \{110\} and other minor growth sectors therefore appears blue.

At 77K the zero-phonon region of the 2.56 eV system is a complex of 4 lines, three of which are “frozen out” at about 5K\(^5\). Residual structure on this low-temperature line was originally thought, during the course of the present work, to be due to isotope-splitting associated with the 5 stable isotopes of nickel; this conclusion was reached in the light of the work by Nazaré \textit{et al.}, who have observed isotope splitting in the 1.40 eV and 2.51 eV absorption lines\(^6\). To check this proposal the zero-phonon region of the 2.56 eV system has recently been remeasured with the diamond cooled to 4.2K. Figure 4 shows that there is, indeed, a substantial amount of fine structure present, but this structure does not bear the simple relationship to the abundances of the isotopes of nickel which is observed with the 1.40 eV and 2.51 eV systems. Although there is little doubt that nickel is involved in the 2.56 eV centre, the origin of the structure shown in Fig. 4 remains obscure.

3.3 \textit{Polarised cathodoluminescence}

Woods and Lang first observed polarised green emission from the \{100\} growth sectors of synthetic diamond\(^3\). They assumed that this was donor-
acceptor pair recombination. More recently Dodge\textsuperscript{37} has described a process by which H3 centres can be produced during synthesis, and he assumed that the polarised green emission was associated with these H3 centres. That proposal has been checked in the present investigation. Figure 5 shows the H3 CL from a cubic growth sector of a diamond slice polished approximately parallel to a [100] face. (The growth planes studied were therefore nearly perpendicular to the surface.) The polariser was rotated to maximise the intensity of the H3 luminescence, then turned through 90° to record the second spectrum. This result demonstrates conclusively that it is the H3 CL from {100} sectors that is polarised, as surmised by Dodge\textsuperscript{37}, and that the H3 dipole moments lie almost exclusively in the {100} growth planes. The luminescence collected from an external face, however, is unpolarised because of the 4-fold symmetry.

Lang\textsuperscript{8} observed partially polarised near-infrared emission from the {111} growth sectors of a polished slice of synthetic diamond. From the known response of the filter and photographic film used to record the luminescence, Lang concluded that he was detecting CL in the 1.40 eV system. In the present work we have carried out the first spectroscopic examination of CL from the same diamond slice as that used by Lang. Figure 6 confirms that the polarised infrared emission from the {111} sectors is indeed due to the 1.40 eV system. Here, too, because of the 3-fold symmetry, the luminescence from an external face is unpolarised.

![Image](image_url)

**Fig. 6.** Polarised 1.40 eV CL from a {111} sector of a polished slice of synthetic diamond; (a) and (b) are respectively for the polariser set parallel and perpendicular to the growth planes.

### 4. Conclusions

We have shown in this paper that the absorption spectra of diamonds grown by the temperature-gradient method using an Fe–Ni solvent-catalyst without nitrogen-getters generally contain two vibronic systems with zero-phonon lines at 1.883 eV and 2.51 eV that are absent in diamonds grown using Co–Fe. These absorption lines are very much stronger when pure Ni is used as the solvent-catalyst. When nitrogen-getters are added to the pure Ni, a broad absorption band which peaks near 1.4 eV and a vibronic absorption band with a zero-phonon doublet at 1.40 eV (with an accom-
panying structured absorption band at around 1.8 eV) are produced with different relative intensities in different diamonds. These absorption bands result in a green colouration which can be particularly pronounced in diamonds with low nitrogen concentration. Absorption topographs show that the 1.40 eV system occurs only in the {111} growth sectors.

The 1.40 eV system and the broad 1.4 eV band are also observed in diamonds grown using Fe–Ni with nitrogen-getters added, but at a relatively lower intensity than when pure Ni is employed, resulting in a pale green colour. The ultraviolet absorption of these diamonds is very similar to that for a natural type Ib diamond, except for a series of lines around 3.1 eV. The absence of the 3.1 eV system in diamonds grown using Fe–Al indicates that these absorption lines may also be Ni-related.

Cathodoluminescence measurements show that the H3 emission is restricted to the {100} growth sectors (and external faces), and that the H3 luminescence from the {100} sectors of a near-central section of diamond is strongly polarised, with the electric dipole lying in the growth plane. Luminescence from the 1.40 eV and 2.56 eV (484 nm) systems is observed only from the {111} growth sectors (and external faces). The 2.56 eV CL is quenched at temperatures above about 200K and the {111} sectors appear (to the eye) relatively inert at room temperature; infrared luminescence in the 1.40 eV vibronic band is, however, undiminished at this temperature. The 1.40 eV CL from the {111} sectors of a slice of diamond is partially polarised, with the electric dipoles lying preferentially in the growth planes, but the 2.56 eV system shows no such polarisation phenomena. CL in the 2.56 eV and 1.40 eV systems is very much weaker in diamonds grown using Co–Fe than those grown with Fe–Ni.

These findings substantially confirm the conclusions reached from studies of synthetic diamond grits, that absorption in the 1.40 eV, 1.883 eV and 2.51 eV vibronic systems and the 1.4 eV broad band, together with strong CL in the 1.40 eV and 2.56 eV systems, are characteristic of diamonds grown using Ni, or a Ni alloy. The isotope splittings in the 1.40 eV and 2.51 eV zero-phonon lines found recently by Nazaré et al. prove this point beyond question for those two systems.

The polarisation data on the H3 system give strong support to the model proposed by Dodge in which the H3 centres are incorporated during synthesis on the {100} growth planes. In addition, it has been confirmed spectroscopically that the polarised CL from the {111} growth planes is due to the 1.40 eV system, as proposed by Lang. Absorption associated with the 1.40 eV centre is also confined to the {111} sectors and exhibits pronounced polarisation behaviour. Presumably, a mechanism similar to that proposed by Dodge is responsible for the segregation of Ni-related defects into the {111} sectors.

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