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The Electrical and Optical Properties of Thin Film Diamond

Alan T. Collins

Wheatstone Physics Laboratory, King's College London, Strand, London, WC2R 2LS, UK

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Abstract: The electrical properties of thin film diamond grown by chemical vapour deposition (CVD) follow the behaviour expected from the analyses of electrical transport measurements in natural and high-pressure synthetic diamond. In addition, scattering at grain boundaries in boron-doped polycrystalline material leads to very low carrier mobilities; surface states at the grain boundaries can also compensate an appreciable fraction of boron acceptors in lightly doped films. Very heavily doped films exhibit a metallic conductivity which decreases with increasing temperature. Improvements in manufacturing techniques over the last five years have enabled free-standing plates of CVD diamond to be produced which are virtually transparent in the visible spectral region. Hydrogen and silicon are known to produce absorption bands; the latter is incorporated in the bulk of the diamond, but the hydrogen-related bands are believed to result from H–C complexes associated with non-diamond carbon at the grain boundaries. There are a large number of cathodoluminescence systems unique to CVD diamond; these are produced by recombination at as-yet unidentified defect centres, probably present in a relatively low concentration.

1 ELECTRICAL PROPERTIES

With certain exceptions, the electronic properties of CVD diamond can be understood using data established for bulk diamond. The major differences occur with polycrystalline CVD diamond in which scattering at the grain boundaries drastically reduces the carrier mobilities and, at low doping levels, electronic surface states at the grain boundaries act as donors which compensate p-type acceptors. We will begin by reviewing work carried out on bulk diamond to see how this relates to CVD diamond.

1.1 Acceptors and donors in diamond

Nitrogen and boron are the only elements that significantly affect the bulk electrical conductivity of diamond; in addition, a hydrogen-terminated surface also gives rise to p-type conduction.[1,2]

Nitrogen is the dominant impurity in the majority of diamonds. Most diamonds produced commercially by high-pressure synthesis (referred to hereafter as "synthetic diamond") and a small fraction (about 0.1%) of natural diamonds are type Ib, meaning that the nitrogen is present in isolated substitutional form; typical concentrations are 40 ppm for natural type Ib diamonds and a few hundred ppm for standard synthetic diamonds. Almost all natural diamonds are predominantly type IaA, meaning that the nitrogen is present as nearest-neighbour pairs; here the nitrogen concentration can be as high as 3000 ppm. For the rare type IIa natural diamonds the nitrogen concentration is less than about 10 ppm. Isolated substitutional nitrogen is generally present as a trace impurity in CVD diamond, although in the highest quality undoped material the concentration may be no more than 0.01 ppm.

The isolated nitrogen and the A form of nitrogen both behave as donors; however, the ionisation energies are high — around 1.7 eV and 4.0 eV, respectively. Nitrogen-containing diamonds are therefore good electrical insulators at room temperature. At higher temperatures (>200°C), conductivity associated with the 1.7 eV donor leads to a deterioration of the insulating properties of diamond compared, for example, with sapphire.[3]

Amongst natural diamonds significant electrical conductivity at room temperature occurs only for the very rare type IIb diamonds, in which boron is the major impurity. These diamonds are p-type semiconductors with typical boron concentrations rather less than 1 ppm and an acceptor ionisation energy of 0.37 eV. Synthetic diamond containing up to 1000 ppm of uncompensated boron can be produced by removing nitrogen from the growth capsule and adding boron. Boron-doped CVD diamond, again with boron concentrations much higher than those found in natural type IIb diamonds, is readily grown by adding a gaseous compound of boron to the plasma.

1.2 p-type conductivity

For a partially compensated p-type semiconductor, with an acceptor concentration sufficiently small that there is no degeneracy, the hole concentration at temperature T may be written as:[4]

$$p(p+N_D)/(N_A-N_D-p) = (2/g_a)(2\pi m^* kT/h^2)^{3/2}\exp(-E_A/kT) \qquad (1)$$

where N_A and N_D are the acceptor and donor concentrations, g_a is the ground state degeneracy factor for the acceptor, m^* is the density of states effective mass for the holes and E_A is the acceptor ionisation energy.

At high temperatures p approaches the saturation value $N_A - N_D$; at low temperatures $p \ll N_A$ or N_D and, provided the acceptor concentration is sufficiently low to avoid impurity band conduction, eqn (1) approximates to:

$$p \propto (N_A/N_D - 1)T^{3/2}\exp(-E_A/kT) \qquad (2)$$

The concentration of free holes can be determined from the Hall coefficient, R, using:

$$p = r/Re \qquad (3)$$

where r is the ratio of the Hall mobility μ_H to the conductivity mobility μ_c and e is the electronic charge. The value of r depends on the scattering processes; in the case of a non-degenerate semiconductor a number of simplifying assumptions lead to $r = 3\pi/8$ for acoustic phonon scattering and $r = 315\pi/512$ for ionised impurity scattering.[5] Phonon scattering is the dominant mechanism at high temperatures, and standard analysis[5] suggests the mobility will vary as $T^{-3/2}$. In practise, the high temperature mobility $\mu(T)$ of natural type IIb diamond varies approximately as:[6]

$$\mu(T) = \mu(290) \times (T/290)^{-S} \qquad (4)$$

with S around 2.8.

Most workers have analysed their Hall effect data using eqn (1) with $g_a = 2$ and eqn (3) with $r = 3\pi/8$. Elsewhere,[7] I have argued that $g_a = 4$ may be more appropriate, and perhaps even $g_a = 6$ at high temperatures. This makes relatively little difference to the analysis, since effectively $(m^*)^{3/2}/g_a$ in eqn (1) is an adjustable parameter used to obtain the best fit to the experimental data.

Figure 1 shows a plot of hole concentration versus reciprocal temperature obtained by Williams[8] for a natural type IIb diamond. We note that this approaches saturation at high temperatures, as expected from eqn (1) and varies almost linearly at lower temperatures as expected from eqn (2). Williams found that when the values for N_A, N_D and E_A that gave the best fits were substituted into eqn (1), m^* was approximately constant at around 0.75 m_e below room temperature, and decreased in a non-monotonic way at higher temperatures (m_e is the rest mass of the electron).

From measurements on 5 diamonds Collins and Williams[9] quote an average value of $E_A = 368.5 \pm 1.5$ meV, determined using eqn (2) in the

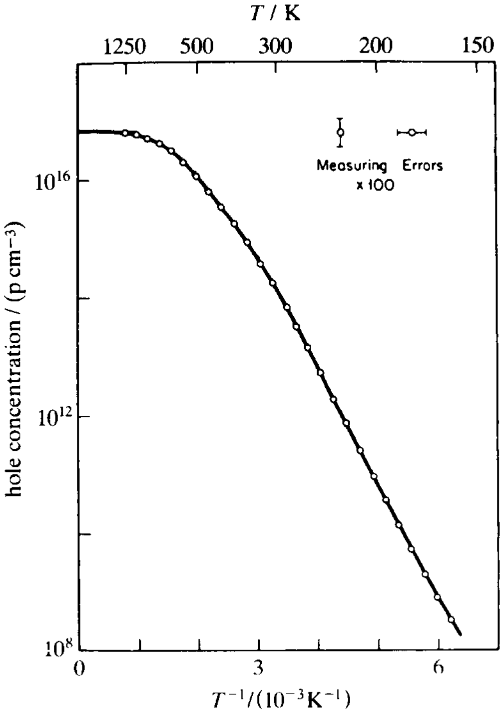

Fig. 1. Hole concentration in a natural semiconducting diamond as a function of reciprocal temperature, derived from the Hall coefficient (eqn (1)) with $r = 3\pi/8$.

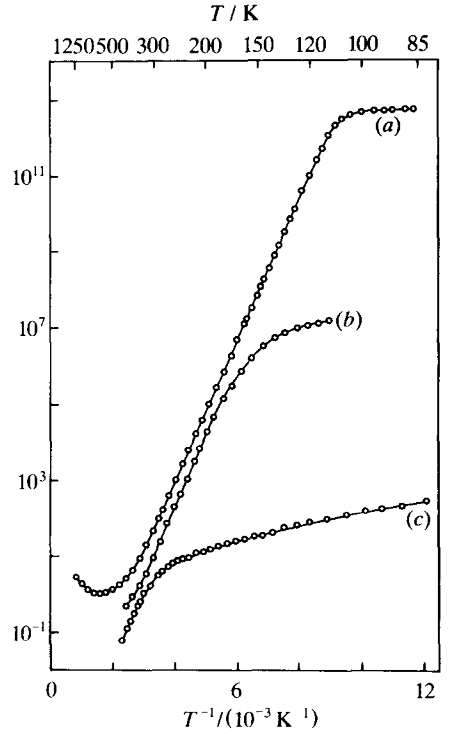

Fig. 2. Resistivity as a function of reciprocal temperature for (a) a natural type IIb diamond, and for synthetic type IIb diamonds with (b) $(N_A - N_D) = 3 \times 10^{17}$ cm^{-3} and (c) $(N_A - N_D) = 10^{18}$ cm^{-3}.

temperature interval 160–330 K. Impurity concentrations for these diamonds were determined[10] as N_A between 48 and 83 × 10^{15} cm^{-3} and N_D between 0.9 and 15 × 10^{15} cm^{-3}. The highest value of N_A/N_D was 56. Substitution of these data in eqn (2) shows that this approximation becomes inaccurate at temperatures above 330 K. At and below this temperature the approximation also requires $N_D \gg 4 \times 10^{13}$ cm^{-3}, and this condition is well-satisfied.

The hole mobilities at 290 K for the diamonds used by Collins and Williams[9] lay in the range 700–2010 cm^{2}V^{-1}s^{-1}, and similar data had been obtained by many previous workers. More recently measurements on natural type IIb diamonds have yielded[11,12] rather lower values between 130 and 518 cm^{2}V^{-1}s^{-1}. At temperatures above room temperature the mobilities of all specimens decrease rapidly, in accordance with eqn (4).

1.3 Impurity conduction and hopping conduction

Figure 2 shows the resistivity as a function of reciprocal temperature for a natural semiconducting diamond and two boron-doped synthetic diamonds. For the natural diamond we see that there is a shallow minimum in the resistivity curve; this is because the carrier concentration has almost reached saturation (eqn (1)) but the mobility is still decreasing at higher temperature (eqn (4)). Between about 400 and 120 K the log(resistivity) increases linearly with an activation energy of 0.37 eV, and at 120 K there is a sharp knee beyond which the resistivity increases very gradually at lower temperature. Curve (b) for the first synthetic diamond has a substantial linear section with a change of slope to a lower value at about 160 K, and curve (c) for the second synthetic diamond has a short section, parallel to that for the other two diamonds, and a change of slope to a lower value at about 280 K. The neutral acceptor concentrations for (b) and (c) were estimated optically to be 3 × 10^{17} cm^{-3} and 1 × 10^{18} cm^{-3}, respectively.[13]

The behaviour shown in Fig. 2 can be understood if the conductivity s is expressed as a sum of three terms:[14]

$$\sigma = \sigma_1 \exp(-E_1/kT) + \sigma_2 \exp(-E_2/kT) + \sigma_3 \exp(-E_3/kT) \tag{5}$$

The activation energy E_1 is the normal acceptor ionisation energy, associated with transitions from the acceptor ground state to the valence band, and is observed in all samples provided the acceptor concentration is not too high. The activation energy E_2 can only be observed in the intermediate concentration range and is associated with conduction in an impurity band. When the acceptor concentration is small E_2 is close to E_1, but when the acceptor concentration is increased, so that there is an appreciable overlap between the wavefunctions of neighbouring centres, E_2 is reduced. Finally, at the acceptor concentration for which the metal–insulator transition occurs, $E_2 \rightarrow 0$. For boron in diamond this transition occurs[13] at a concentration around 2 × 10^{20} cm^{-3}. The activation energy E_3 is most prominent for specimens with a relatively low impurity concentration, and is interpreted in terms of the energy associated with the tunnelling transition ("hopping") of a hole from an unoccupied to an occupied acceptor site.

In Fig. 2(a) the change of slope in the resistivity curve for the natural diamond is interpreted[9] as hopping conductivity associated with activation energy E_3, whereas all three conductivity mechanisms are believed[13] to be operative for the synthetic diamonds in Fig. 2(b) and (c). For the diamond used to obtain Fig. 2(c) the data may also be fitted, in the temperature range 80–250 K, to Mott's formula[15] for variable-range hopping. In this case:

$$\log\sigma = A - BT^{-1/4} \tag{6}$$

where A and B are constants. In this process carriers prefer to hop to a distant site which has a similar energy, rather than to nearest neighbours which have significantly different energy. Massarani *et al.* have also extensively investigated conductivity mechanisms in boron-doped synthetic diamond, and find that for heavily doped samples the behaviour at low temperatures is dominated by variable-range hopping.[16] They confirmed that the activation energy exhibited a $T^{3/4}$ dependence, as expected for variable-range hopping.

1.4 Polycrystalline CVD films

Diamond films grown on non-diamond substrates are invariably polycrystalline, and doping with boron produces semiconducting material. Von Windheim *et al.*[12] report that the carrier concentration shows a very sharp drop with decreasing dopant density. They note that similar data are observed in B-doped polycrystalline silicon, and attributed this to surface states at grain boundaries acting as trapping centres. The grain boundaries also cause severe scattering of the carriers, so that mobilities are typically[17] in the range 1–30 $cm^2V^{-1}s^{-1}$.

At high doping levels impurity conduction is observed, as in synthetic type IIb specimens, and for doping levels around 10^{21} cm^{-3} metallic conduction is obtained. In that case the conductivity of the material *decreases* as the temperature is increased.[18]

When a lightly boron-doped layer is grown on top of an oriented textured film with {100} faces, mobility values up to 165 $cm^2V^{-1}s^{-1}$ may be obtained[17] and the acceptor ionisation energies for such films are around 0.35 eV, close to the value for natural type IIb diamond.

1.5 Homoepitaxial CVD diamond layers

In this section we will consider two representative studies — that by Fujimori *et al.*[19] using a microwave plasma with doping by B_2H_6, and that by Visser *et al.*[20] using the hot-filament technique and boron-doping by out-diffusion of the BN substrate holder. Both groups find that growth on to a {100} oriented diamond substrate produces a higher quality layer than on a {110} oriented substrate, that boron incorporation is lower in the {100} layer and that the hole mobility is very much lower in the {110} layers. The quality of homoepitaxial layers on {111} substrates is also poor. It is found that {110} and {111} layers contain a high density of stacking faults, where the tetrahedral diamond packing sequence is disrupted by the hexagonal (Lonsdalite) sequence.[21]

Figure 3 shows the mobilities of the CVD layers grown by Fujimori *et al.* plotted as a function of the carrier concentration measured at room temperature.

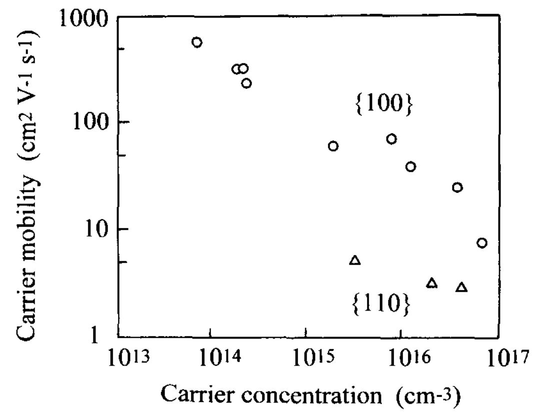

Fig. 3. Relationship between carrier mobility and carrier concentration of boron-doped epitaxial films deposited on {100} and {110} substrates.

We see that as the carrier concentration increases from 7 × 10^{13} to 7 × 10^{16} cm^{-3} the mobility of the {100} layers falls from 600 to less than 8 $cm^2V^{-1}s^{-1}$. The mobilities of all the {110} layers are less than 6 $cm^2V^{-1}s^{-1}$. Gildenblat *et al.*[21] have gathered together the {100} data in Fig. 3 with data inferred from measurements on natural and synthetic type IIb diamonds and shown there is a general decreasing downward trend in mobility values with increasing carrier concentration. Fujimori *et al.* have also shown that the temperature dependence of the mobility for boron-doped CVD diamond is similar to that observed for natural type IIb diamond (eqn (4)) with S around 3.0 for the lightly doped material, decreasing to 2.2 for more heavily doped layers.

Visser *et al.*[20] show conductivity data from 110 to 500 K for four pairs of diamonds with different impurity concentrations. Each pair had a {100} and a {110} layer produced in the same growth run. The conductivity curves are very similar to those obtained on boron-doped synthetic diamonds (Section 1.3), showing a change in activation energy at 225 K for the lowest doping and around 310 K for the highest doping. They show that their data can be fitted using just two activation energies — E_1 and E_3 of eqn (5). Their low-temperature data also fitted the Mott $T^{-1/4}$ law (eqn (6)) very closely, and they conclude that the dominant process at low temperatures may be variable-range hopping.

Visser *et al.*[20] also carried out Hall effect measurements as a function of temperature. They find that they cannot fit the data using eqn (1) with the effective mass value $m^* = 0.75\ m_e$ used for natural type IIb diamond (Section 1.2). For their most lightly doped {100} sample they find $m^* = 0.35\ m_e$

and $N_D/N_A = 0.008$. The room-temperature carrier concentration and Hall mobility for this specimen were 1.3×10^{14} cm^{-3} and 590 cm^{2}V^{-1}s^{-1}, respectively. These values are similar to the most lightly doped sample studied by Fujimori *et al.*[19]

1.6 Hydrogen in CVD diamond

Virtually all CVD diamond is grown in the presence of large quantities of hydrogen; if the shut-down sequence of the growth system leaves the CVD film exposed to a hydrogen plasma then undoped films have a similar conductivity to that of doped films.[21] Gildenblat *et al.*[21] showed that the conductivity of the undoped films can be removed by chemical cleaning, and is simply due to a surface conducting layer. They showed that such a conducting layer could also be produced on a natural type IIa diamond exposed to the hydrogen plasma. More recently it has been shown that hydrogenation of the surface leads to a p-type conducting layer and that it is possible to fabricate a field effect transistor using this layer.[2]

1.7 n-type conductivity

No technique has been found to produce a useful level of n-type conductivity in either synthetic or CVD diamond. At high temperatures natural type IIa diamond and many samples of CVD diamond exhibit a small amount of n-type conduction with an activation energy of about 1.6–2.0 eV.[3] This is probably associated with the small concentrations of isolated substitutional nitrogen.[22]

2 OPTICAL PROPERTIES

In this section we will review briefly the improvements in the optical quality of CVD diamond that have been achieved over the last five years and discuss those defects unique to CVD diamond that produce absorption and luminescence bands.

2.1 Optical windows

Figure 4 shows the absorption spectra in the visible and ultraviolet spectral regions of a single crystal of CVD diamond, and three diamond films around 10–20 μm thick, produced in the late 1980s.[23] The single crystal, about 50 μm thick, was pale yellow, and the three films, grown using CH_4 concentrations of 0.3, 0.5 and 1.0%, were yellow, pale brown and dark brown, respectively. A number of major manufacturers (Crystallume, De Beers, Norton, Raytheon, etc.) are now producing free-standing plates of CVD diamond up to 1 mm or more in thickness which are virtually transparent in the visible region. Figure 5 shows the absorption spectrum[24] for De Beers Diafilm® and it is clear that the absorption coefficient associated with defects in this material is dramatically lower than for the films illustrated in Fig. 4. Apart from some absorption in the ultraviolet spectral region the CVD window material compares favourably with a natural type IIa diamond. This improvement in quality has come about partly by operating the growth equipment at very high power densities, but the exact details are a closely guarded commercial secret.

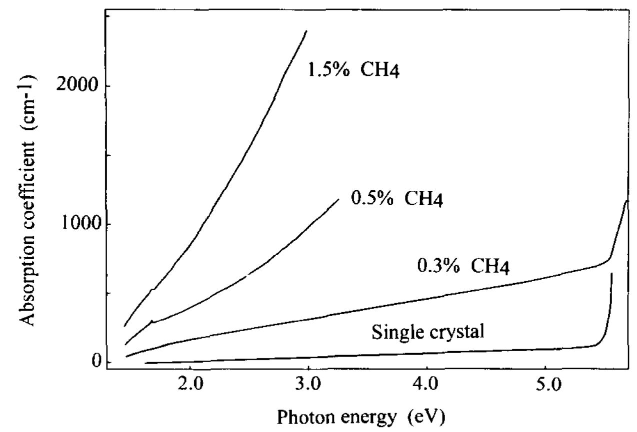

Fig. 4. Absorption spectra of a single crystal diamond and three polycrystalline diamond films, all grown using microwave-assisted CVD.

2.2 Absorption bands associated with hydrogen

Many samples of CVD diamond exhibit the C–H stretch and bend modes in the infrared absorption spectra at around 3000 and 1400 cm^{-1}. Sussmann[24] has shown that these bands are strong in

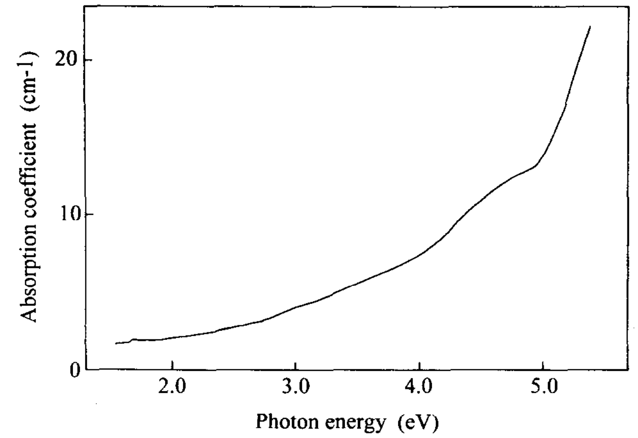

Fig. 5. Absorption spectrum of De Beers Diafilm® (calculated from data in Ref. 24).

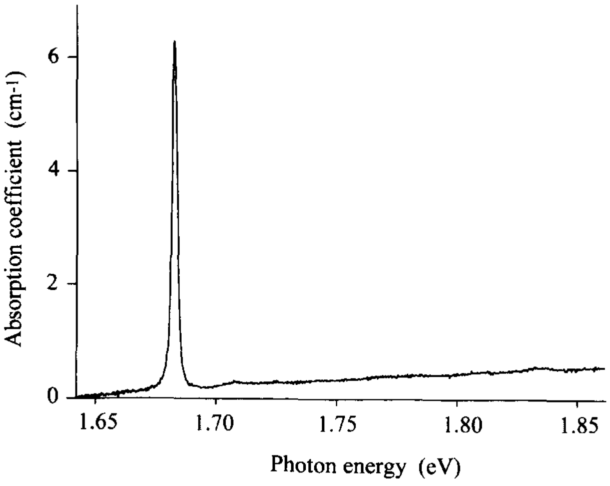

Fig. 6. The 1.681 eV absorption band at 77 K.

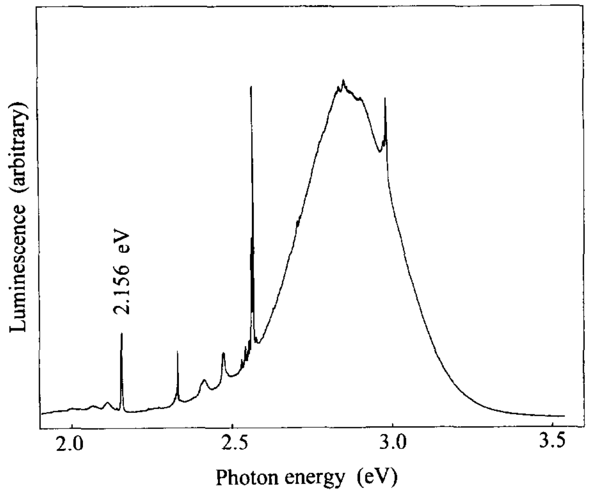

Fig. 7. Cathodoluminescence spectrum from a flame-grown CVD diamond, recorded with the specimen at 77 K.

poor quality CVD diamond ("dark" CVD), but virtually absent in the highest quality transparent material. This strongly suggests that the hydrogen is bonded to the non-diamond carbon at the grain boundaries, and is not incorporated in the bulk of the crystal.

2.3 Absorption associated with silicon

CVD diamond frequently exhibits a luminescence system with a zero-phonon line at 1.681 eV. Vavilov *et al.*[25] were the first to observe this line in CVD diamond, and they showed that it could also be created in natural diamond by implantation of silicon ions. Collins *et al.*[23] observed the 1.681 eV line *in absorption* in some of their specimens (it is just visible in the spectra from the more strongly absorbing films shown in Fig. 4), indicating that the defects responsible must be present in appreciable concentration. Recently it has been demonstrated[26] that the intensity of the absorption band can be substantially increased if the CVD diamond is subjected to radiation damage, followed by annealing at about 800°C. That work suggests that the defect responsible for the 1.681 eV absorption system is a vacancy trapped at a silicon atom. In some cases the 1.681 eV absorption is strong in the as-grown diamond (perhaps because vacancies are introduced during growth) and a typical example is shown in Fig. 6.

2.4 Cathodoluminescence

Figure 7 shows a cathodoluminescence spectrum from a diamond film grown by the combustion flame technique. The sharp line labelled 2.156 eV is also observed in natural and synthetic diamond and is associated with a nitrogen-vacancy complex. The remaining lines shown in Fig. 7 are unique to CVD diamond; they are also observed in material grown by the microwave and hot-filament methods,[27] but are not normally as sharp as observed in Fig. 7. Thin films of diamond grown by the combustion flame technique are extremely fragile; this suggests that the intergranular bonding is weak and this would imply that the random strain in the grains is low. This conjecture is consistent with the emission lines being sharpest in such material.

3 SUMMARY

The electrical properties of thin film diamond are fully consistent with the models used for natural and synthetic diamond when the additional phenomena associated with grain boundaries are taken into consideration. Appreciable quantities of optically active hydrogen and silicon are present in some CVD diamond. The hydrogen is believed to be bonded to non-diamond carbon at the grain boundaries. Small concentrations of presently unidentified defects produce characteristic cathodoluminescence from nominally undoped thin film diamond grown by the microwave, hot-filament or combustion flame techniques.

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