PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Optical and Electronic Properties of Semiconducting Diamond

Alan T. Collins

Phil. Trans. R. Soc. Lond. A 1993 **342**, 233-244
doi: 10.1098/rsta.1993.0017

The optical and electronic properties of semiconducting diamond

By Alan T. Collins
*Wheatstone Physics Laboratory, King's College London, Strand,
London WC2R 2LS, U.K.*

In this paper I review the evidence that shows that the optical and electronic properties of semiconducting diamond can be understood in terms of boron acceptors partially compensated by deep donors. In natural semiconducting diamond, in which the total impurity concentration is less than 1 ppm, there is a lot of fine structure in the acceptor absorption spectrum that is not fully understood, and the electrical conductivity is primarily associated with the thermally activated excitation of holes from the acceptor ground state to the valence band. Some of the problems regarding the analysis of Hall effect data in this material are discussed, including the temperature dependences of the scattering mechanisms, of the contribution from the split-off valence band and of the population of excited states. There are no adequate theoretical descriptions of any of these processes, and this leads to some uncertainties in the values of the parameters derived from the temperature dependence of the Hall coefficient. For boron-doped synthetic diamond, and thin film diamond grown by chemical vapour deposition (CVD), the defect concentrations are generally much higher, and much more inhomogeneous, than in natural semiconducting diamond. This results in a substantial broadening of the acceptor absorption spectrum and the electronic properties are greatly modified by increasing contributions from impurity band conduction as the acceptor concentrations are increased, leading to very low mobility values. For both polycrystalline and single crystal homoepitaxial CVD diamond, measurements of the electrical properties can be completely invalidated by the presence of a surface layer of non-diamond carbon.

1. Introduction

Since the speculation by Davis *et al.* (1988) and others, that thin film semiconducting diamond exhibits considerable potential for opto-electronic devices, there has been renewed intensive activity in the study of the optical and electronic properties of diamond, following almost two decades of relative quiescence. In this review I consider those aspects of the early work that have particular relevance to contemporary studies and briefly examine some of the conclusions of recent investigations.

Natural semiconducting diamond (type IIb diamond) was first reported by Custers (1952). Electrical transport measurements (for a review see Collins & Lightowlers 1979) established that this material is a partially compensated semiconductor, and that the acceptor is boron with an ionization energy of 0.368 eV. That work is discussed further in §3*a*. Nitrogen acts as a deep donor in diamond, and is normally the major impurity in both natural and synthetic diamond; these diamonds are therefore electrical insulators. (I use the word synthetic to mean those

Phil. Trans. R. Soc. Lond. A (1993) **342**, 233–244

Printed in Great Britain

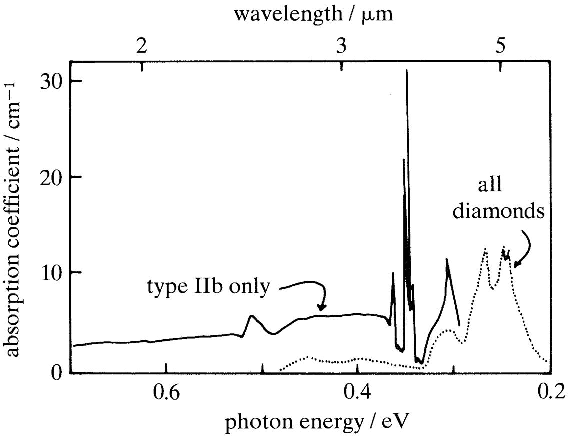

Figure 1. Acceptor absorption in a natural type IIb diamond at 77 K. Redrawn from Smith & Taylor (1962).

diamonds grown by the high temperature, high pressure process.) Huggins & Cannon (1962) first showed that semiconducting type IIb diamond can be grown by excluding nitrogen and incorporating boron during growth. This material had the morphology and dimensions of abrasive grit and presented a considerable challenge in the determination of its optical properties (Collins *et al.* 1965) and electronic properties (Lightowlers & Collins 1966; Williams *et al.* 1970).

2. Optical properties

Luminescence spectra from diamond, including bound exciton recombination and the 'band A' system in natural and synthetic semiconducting diamond, have been reviewed recently by me (Collins 1992). In this section I therefore consider only the optical absorption associated with the boron acceptor.

(*a*) *Natural type IIb diamond*

Transitions from the boron acceptor to the valence band give rise to a series of excited state transitions which start at 0.304 eV and merge with the photoionization continuum at about 0.37 eV. Figure 1 shows this additional absorption produced in a type IIb diamond (Smith & Taylor 1962), superimposed on the two- and three-phonon combination bands which are present in all diamonds. The photoionization continuum extends into the red part of the visible spectrum, and gives type IIb diamonds their characteristic blue colour. Absorption due to the higher-energy excited states is shown in more detail in figure 2. Six of the peaks in this spectrum disappear when the sample is cooled to 4.2 K and Crowther *et al.* (1967) have associated this effect with a 2.1 meV splitting of the acceptor ground state. These latter authors carried out uniaxial stress measurements on the acceptor spectrum, and were able to propose a plausible classification scheme for the peaks at energies below 0.348 eV, but the full complexity of this spectrum is still not understood.

(*b*) *Synthetic type IIb diamond*

Absorption spectra made on synthetic semiconducting diamond by Collins *et al.* (1965) resembled the spectrum shown in figure 1, but even at low neutral acceptor concentrations the peaks were much broader and the fine structure shown in figure

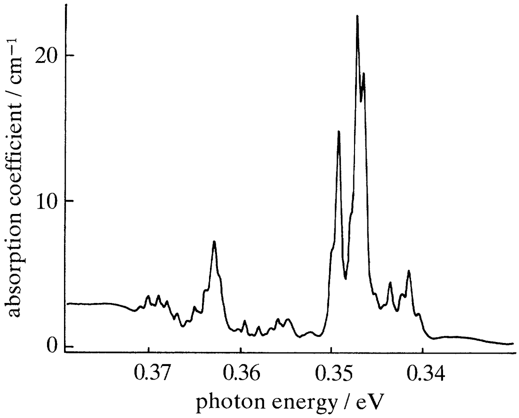

Figure 2. Excited state region of the acceptor spectrum in a natural type II b diamond at 77 K. Redrawn from Lawson (1991).

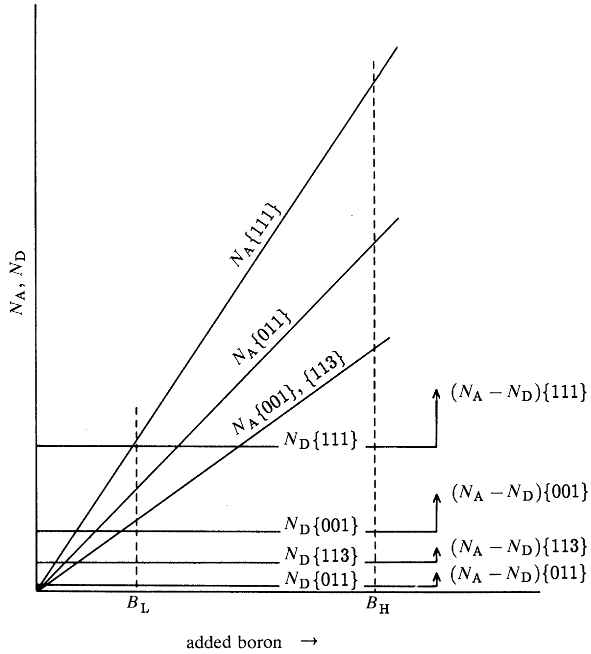

Figure 3. Relation between the nitrogen donor concentration, the boron acceptor concentration and the neutral acceptor concentration in the major growth sectors of synthetic diamond, shown as a function of the added boron concentration. See text for details. Redrawn from Burns *et al.* (1990).

2 could not be detected. As the acceptor concentration increased (assessed semi-quantitatively from the depth of blue coloration association with the photoionization continuum) the peaks became progressively smeared out and merged with the photoionization continuum. Type II b diamonds with much better quality than those used by Collins *et al.* may now be grown by the temperature gradient method (Strong & Chrenko 1971), but in most cases the absorption peaks are still very much broader than those observed in natural type II b diamond; furthermore the broadening of the spectrum is far more severe in some growth sectors than others (Burns *et al.* 1990).

To understand this latter phenomenon we need to consider the way different impurities are incorporated into the different growth sectors of synthetic diamond. This can be summarized on a diagram of the type originally proposed by Kanda *et al.* (1987) and extended by Burns *et al.* (1990), shown in figure 3. This diagram will also have considerable implications for the boron doping of diamond grown by chemical vapour deposition (CVD).

The four horizontal lines on figure 3 indicate the relative concentrations of isolated substitutional nitrogen in the major growth sectors; the {111} sectors contain most nitrogen, and the {011} sectors least. Optical transitions from the nitrogen donor to the conduction band give synthetic diamonds a characteristic yellow colour, and in a polished section of diamond the different nitrogen concentrations in the different growth sectors are evident from the depth of yellow coloration. The gradients of the diagonal lines on figure 3 show the rates at which boron is incorporated into the different growth sectors. A given growth sector becomes semiconducting when the boron concentration exceeds the nitrogen concentration. The horizontal lines are effectively the origins for the *uncompensated* acceptor concentrations ($N_A - N_D$) in the corresponding growth sectors, as indicated on the right of the diagram. We see that the {011} sector is the first to acquire semiconducting properties, and that at relatively low boron concentrations, B_L, ($N_A - N_D$) is highest in this growth sector. Again this effect is visible by eye, because at boron concentrations between 0 and B_L some growth sectors are blue while others are still yellow. At higher boron concentrations, B_H, the neutral acceptor concentration is highest in the {111} sectors.

If there is a significant source of nitrogen in the growth capsule, and a sufficient quantity of boron is added to produce semiconducting diamond, then, although the electrically active boron concentration may be small, the total impurity concentration can be quite large. The relatively high concentration of defects, compared with less than 1 ppm in natural type IIb diamond (see §3*a*) almost certainly accounts for the much greater linewidths observed in the acceptor absorption spectrum (Rooney 1992). This effect is expected to be most pronounced in the {111} growth sectors (see figure 3), as observed experimentally (Burns *et al.* 1990; Rooney 1992). If the nitrogen in the growth capsule is very efficiently 'gettered', by adding materials such as Ti and Zr, the resulting crystals are sometimes semiconducting by virtue of the 'accidental' boron present; in one such crystal grown from ^{13}C, examined by Lawson (1991), the linewidths in the acceptor spectrum were very much sharper than those in the specimens examined by Burns *et al.* (1990), and it was possible to determine the isotope shifts of the major features in the spectrum.

(*c*) *Semiconducting* CVD *diamond*

For CVD diamond grown in a low pressure plasma the nitrogen content is normally very low, but can, nevertheless, be detected using luminescence spectroscopy (Collins 1992). Semiconducting CVD diamond may readily be produced by doping with boron in one of the ways discussed later in §3*d*. The experience with synthetic diamond described in §2*b* suggests that the boron distribution in polycrystalline CVD diamond (which certainly contains both {111} and {001} growth sectors) will be inhomogeneous, and that the rate of incorporation of boron in homoepitaxial material will be greatly influenced by the orientation of the substrate. We shall see below that this is indeed the case.

3. Electrical transport measurements

Most of our information about the electronic properties of semiconducting diamond has come from Hall effect and conductivity studies (for reviews see Kemmey & Wedepohl 1965; Collins & Lightowlers 1979). Here I re-iterate and extend some of this earlier work.

(*a*) *Hall effect measurements*

Hall effect measurements on natural semiconducting diamond have generally been made with the sample geometry in its traditional form of two contacts on opposite faces of a rectangular block. After a correction has been made for the finite length to width ratio of the specimen (Isenberg *et al.* 1948) the concentration p of free holes may be determined from the Hall coefficient R using

$$p = r/Re, \tag{1}$$

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; for a non-degenerate semiconductor a number of simplifying assumptions lead to $r = \frac{3}{8}\pi = 1.18$ for acoustic phonon scattering and $\frac{315}{512}\pi = 1.93$ for ionized impurity scattering (Sze 1981). Phonon scattering is the dominant mechanism at high temperatures and analysis suggests the mobility will vary as $T^{-\frac{3}{2}}$, compared with $T^{\frac{3}{2}}$ for ionized impurity scattering (Sze 1981). In practice the high-temperature mobility of Si, Ge and diamond varies as T^{-S} with S around 2.6 for Si and 2.8 for diamond. This brief summary indicates one (of many) problems in fitting Hall effect data to theoretical formulae. The parameter r is almost certainly temperature dependent, and there is no obvious way to calculate the actual value. Generally r is set to 1 or $\frac{3}{8}\pi$ in the analysis of the data, and variations between the calculated and experimental data may be attributed at least in part to the temperature dependence of r.

For a partially compensated p-type semiconductor, with an acceptor concentration sufficiently small that there is no degeneracy, the hole concentration p at temperature T may be written as (Blakemore 1962)

$$\frac{p(p+N_D)}{(N_A-N_D-p)} = \left(\frac{2}{g_a}\right)\left(\frac{2\pi m^* kT}{h^2}\right)^{\frac{3}{2}} \exp\left(-E_A/kT\right), \tag{2}$$

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 ionization energy.

Mitchell (1963) proposed that g_a should be set to 2; however, setting $g_a = 2$ implies that there is a single, spherically symmetrical valence band with a scalar effective mass m^*. For acceptors in silicon and germanium, Sze (1981) states that g_a should be 4 because the valence band is doubly degenerate at $k = 0$. In diamond the situation is more complicated; Rauch (1962) has shown from cyclotron resonance studies that two bands are degenerate at $k = 0$ with masses $0.70 \pm 0.01\ m_e$ and about $2.1\ m_e$, with a third band split off by 6 ± 1 meV with a mass of $1.06\ m_e$, where m_e is the mass of a free electron. Thus, in equation (2) we should certainly set $g_a = 4$, and at high temperatures $g_a = 6$ may be more appropriate. Assuming a simple Boltzmann distribution, the contribution from the split-off band will vary from 60 to 95% in the temperature range 150–1250 K covered in figure 4.

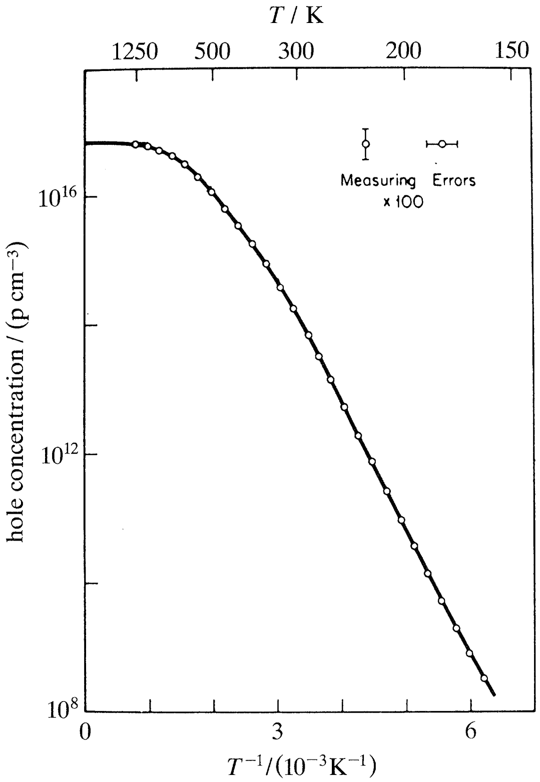

Figure 4. Hole concentration in a natural semiconducting diamond as a function of reciprocal temperature, derived from the Hall coefficient (equation (1)) with $r = \frac{3}{8}\pi$. Redrawn from Collins & Lightowlers (1979).

Note from equation (2) that when $T \rightarrow \infty$, p tends to $N_A - N_D$. In practice, for the typical acceptor and donor concentrations of 5×10^{16} and 5×10^{15} cm^{-3} encountered in natural diamond, p is within 2 or 3% of saturation at $T = 1250$ K. This temperature represents a realistic upper limit for Hall effect measurements on diamond, and for the more heavily doped synthetic and CVD specimens it becomes progressively more difficult to approach the saturated carrier concentration as the acceptor concentration is increased.

At low temperatures $p \ll N_A$ or N_D, and, provided the acceptor concentration is sufficiently low to avoid impurity band conduction (discussed later), equation (2) approximates to

$$p \propto T^{\frac{3}{2}} \exp(-E_A/kT). \qquad (3)$$

From measurements on 5 diamonds Collins & Williams (1971) quote an average value of $E_A = 368.5 \pm 1.5$ meV, determined using (3) in the temperature interval 160–330 K.

At intermediate temperatures there is a further complication that may make it difficult to fit the data using (2). An acceptor impurity is neutral whether it has a hole bound in the ground state at energy E_A above the valence band, or in an excited state rather closer to the valence band. This situation is discussed by Blakemore (1962). In diamond, because there is a superficial similarity of the energies of the excited states with those calculated by the Bohr model, it may be necessary to take the

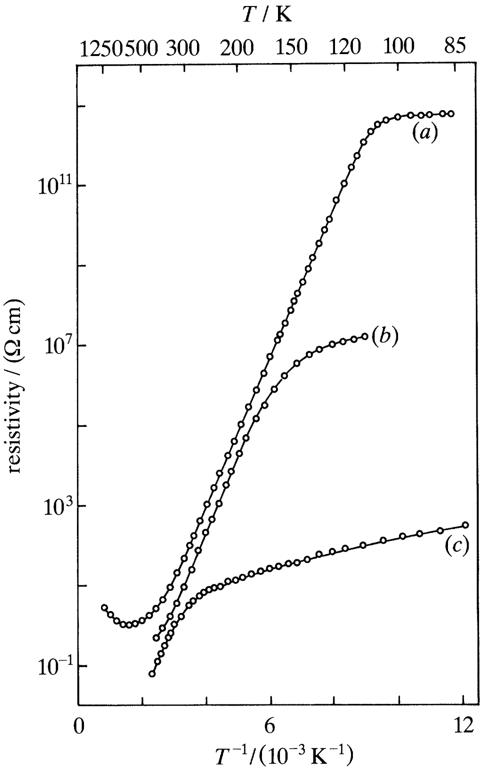

Figure 5. Resistivity as a function of reciprocal temperature for (*a*) a natural type IIb diamond, (*b*) a synthetic type IIb diamond with $(N_A - N_D) = 3 \times 10^{17}\ \mathrm{cm}^{-3}$ and (*c*) as *b* with $(N_A - N_D) = 10^{18}\ \mathrm{cm}^{-3}$. Redrawn from Collins & Lightowlers (1979).

population of these states into account when analysing the temperature dependence of the carrier concentration.

Following Mitchell (1963), Collins & Williams (1971) disregarded all the complexities described above and based their analyses on (2) with $g_a = 2$. They found that when the values for N_A, N_D and E_A that gave the best fits were substituted into (2), and m^* calculated from the experimental data over the range of temperatures used, this effective mass appeared to be constant at around $0.75\,m_e$ below room temperature, but decreased appreciably at higher temperatures in a non-monotonic fashion. In the light of the above discussion we recognize that m^* has simply been used as an adjustable parameter, and that much of the apparent variation with temperature is due to the temperature variation of r, to the temperature dependence of the contribution from the split-off band, to the neglect of the contribution from excited states and to a probable small variation of E_A with temperature.

(*b*) *Resistivity measurements*

In figure 5 the resistivity is shown as a function of reciprocal temperature for a natural diamond and two synthetic diamonds. Dealing first with the natural diamond (*a*) we see that at around 650 K there is a shallow minimum in the resistivity curve; this is because the carrier concentration has almost reached saturation (figure 4) but the mobility is still decreasing at higher temperatures. Between about 400 K 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 temperatures. 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 $3 \times 10^{17}\ \mathrm{cm^{-3}}$ and $1 \times 10^{18}\ \mathrm{cm^{-3}}$ respectively (Williams *et al.* 1970). These latter authors based their analysis of these data on the model discussed earlier by Davis & Compton (1965). The conductivity may be expressed as a sum of three terms

$$\sigma = \sigma_1 \exp(-E_1/kT) + \sigma_2 \exp(-E_2/kT) + \sigma_3 \exp(-E_3/kT). \tag{4}$$

The activation energy E_1 is the normal acceptor ionization 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 acceptor centres E_2 is reduced. Finally, at the acceptor concentration for which the metal–insulator transition occurs, $E_2 \rightarrow 0$. 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 of a hole from an unoccupied to an occupied acceptor site.

In figure 5*a* the change of slope in the resistivity curve for the natural diamond is interpreted as tunnelling conductivity with activation energy E_3 (Collins & Williams 1971), whereas all three conductivity mechanisms are believed to be operative for the synthetic diamonds in figure 5*b*, *c* (Williams *et al.* 1970). The latter authors were also able to demonstrate that the Hall coefficient for their synthetic diamonds went through a maximum at the onset of impurity band conduction, as expected theoretically (Davis & Compton 1965).

Although the work of Williams *et al.* appears plausible it is now recognized that the distribution of acceptor and donor impurities in synthetic diamond is very dependent on the growth sector (§2*b*), and it would be dangerous to try to extract too much information from these early measurements.

(*c*) *Differential capacitance measurements*

If the capacitance C of a Schottky barrier diode is measured as a function of the reverse voltage V for a p-type semiconductor, the uncompensated acceptor concentration is given by

$$N_A - N_D = 2[A^2 \epsilon e\, \mathrm{d}(1/C^2)/\mathrm{d}V]^{-1}, \tag{5}$$

where A is the area of the diode, ϵ is the permittivity and e the electronic charge. This method has been used to measure the acceptor concentrations in both synthetic (Glover 1973) and natural (Lightowlers & Collins 1976) semiconducting diamond. It is also an ideal method to study thin films of CVD diamond, since the depletion layer thickness in a reverse-biased diode is less than 1 μm for acceptor concentrations around $5 \times 10^{16}\ \mathrm{cm^{-3}}$. In the natural diamonds examined by Lightowlers & Collins the ratios N_D/N_A determined from Hall effect measurements lay in the range 3 to 50.

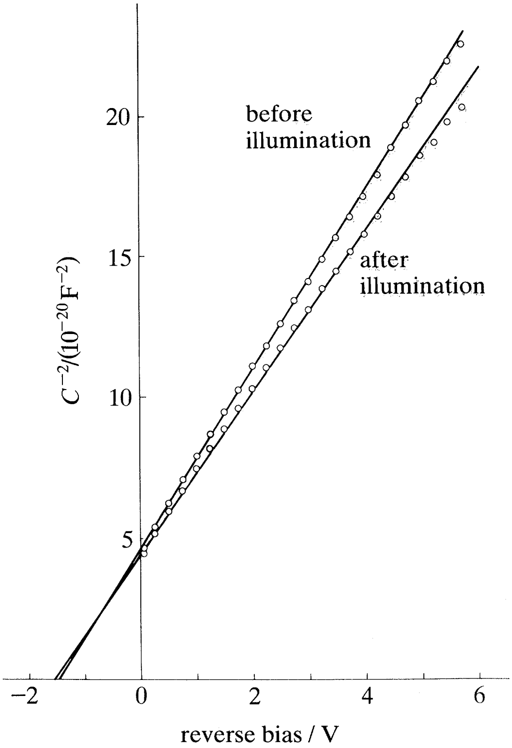

Figure 6. $1/C^2$ against V plots for a 0.5 mm diameter gold Schottky barrier diode on a natural semiconducting diamond before and after illumination which neutralizes the compensated donors. The lines are least squares fits to the experimental points. From Lightowlers & Collins (1976).

These authors showed that by illuminating a reverse biased Schottky diode with visible light the compensated donors could be neutralized. Hence a plot of $1/C^2$ against V before and after illumination yields both $(N_A - N_D)$ and N_A respectively. Typical plots are shown in figure 6, and the ratio of N_D/N_A is comparable with that determined from the temperature dependence of the Hall effect. Lightowlers & Collins showed that the boron concentrations measured by a nuclear technique, in the same area as that probed by the Schottky diode, exhibited a good correlation with N_A in the five diamonds studied earlier by Collins & Williams (1971). The values of N_A were, however, almost a factor of 2 lower than those determined from the Hall effect measurements. This discrepancy may be associated with the oversimplified theoretical treatment of the Hall data, discussed earlier. However, to yield saturation values of the hole concentration almost a factor of 2 lower than those shown in figure 4 apparently requires reducing the high-temperature value of r in (1) to 0.6. This is outside the range calculated from standard scattering theories, but it must be remembered that these theories also fail to predict the correct value of S in the T^{-S} temperature dependence of the mobility.

(*d*) CVD *diamond*

Semiconducting CVD diamond may be made very easily by incorporating boron during growth. Many research groups have produced polycrystalline material, usually on silicon substrates, that have enabled crude rectifiers to be constructed (see, for example, Landstrass *et al.* 1991). However, the electrical transport properties of these films are difficult to interpret because of the scattering of carriers at grain boundaries, and because the non-diamond carbon frequently present at the grain boundaries may be electrically conducting (Shiomi *et al.* 1990; Muto *et al.* 1991). We will restrict our attention, therefore, to thin films of boron doped diamond grown epitaxially on a diamond substrate.

In many cases the techniques used for doping are rudimentary; for example, Gildenblat *et al.* (1990) either place boron powder on the substrate holder, or periodically insert a boron rod into the microwave plasma. Janssen *et al.* (1992) produced semiconducting diamond inadvertently as the plasma in their hot filament reactor slowly decomposed the hexagonal BN substrate holder. On the other hand Shiomi *et al.* (1991) have adjusted the B concentration in their samples in a more rigorous manner by adding controlled amounts of B_2H_6 to the gas stream.

In view of the experience with high-pressure synthetic diamond (§2*b*) it is not surprising that the growth rate of epitaxial CVD diamond, and the degree of boron incorporation, depend on the orientation of the substrate (Janssen *et al.* 1992). Cathodoluminescence measurements show that the boron doped films are frequently inhomogeneous (Janssen *et al.*); furthermore the photoluminescence band in the Raman spectrum of a boron doped layer grown by Grot *et al.* (1991) shows clear evidence that this material contains optical centres involving nitrogen and vacancies (Collins 1992). Thus, although it is possible to grow boron doped single crystal diamond by the CVD process, the quality of the films is not comparable with that of the carefully selected natural type IIb diamonds studied by Collins & Williams (1971) and Lightowlers & Collins (1976).

Gildenblat *et al.* (1990) made the important observation that when their homoepitaxial diamond layers were removed from the microwave reactor there was little difference between the sheet resistance of undoped and boron doped samples. However, after chemical cleaning in an oxidizing solution the sheet resistivity of the undoped layers was greater than 10^8 kΩ per square, while that of the boron doped layers remained low at 60 kΩ per square or less. Gildenblat *et al.* attributed this behaviour to the presence of a surface conducting layer. If, after chemical cleaning, the high resistivity undoped layers were re-introduced to the hydrogen plasma in the microwave reactor their resistivity again dropped to a low value. This reduction in resistivity was also observed when an insulating natural type IIa diamond was exposed to the hydrogen plasma. Albin & Watkins (1990) have proposed that the increased conductivity on hydrogenation is due to the diffusion of hydrogen into the diamond and the passivation of deep traps. The simpler explanation of a surface conducting layer that can be removed by chemical cleaning (Gildenblat *et al.*) carries more conviction.

Gildenblat *et al.* have used the differential capacitance technique described above to measure acceptor concentrations in their films, and show a $1/C^2$ against V plot which yielded an acceptor concentration of 3.2×10^{17} cm^{-3}. Temperature dependence measurements on the series resistance of another Schottky diode yielded an activation energy of 0.15 eV in the temperature range 26–580 °C. The same research group has used a method of selective deposition to grow a film with the conventional Hall effect geometry (Grot *et al.* 1991). Here the temperature dependence of resistivity yielded an activation energy of 0.31 eV, and room-temperature Hall effect data indicated a hole concentration of 10^{14} cm^{-3} and a Hall mobility of 290 cm^2 V^{-1} s^{-1}. This compares with values of 1200 to 2000 cm^2 V^{-1} s^{-1} obtained on high-quality natural type IIb diamond (Collins & Lightowlers 1979).

Other groups (for example Geis 1990; Shiomi *et al.* 1991) have also made electrical transport measurements on boron doped homoepitaxial CVD diamond and found acceptor activation energies ranging from 0.002 to 0.39 eV, and mobilities which are much lower than those obtained with natural type IIb diamond.

Much of the behaviour observed for boron doped CVD diamond is consistent with the analysis of impurity band conduction in synthetic diamond by Williams *et al.* (1970). However, in view of the findings of Gildenblat *et al.* of a conducting surface layer present on as-grown films, the relatively poor quality of many films (as evidenced from photoluminescence and cathodoluminescence measurements (Collins 1992; Janssen *et al.* 1992)) and the known experimental problems with making reliable electrical transport measurements on diamond, much of the information in the literature needs to be approached with a considerable degree of caution.

4. Conclusions

All of the experimental work on natural, synthetic and CVD semiconducting diamond indicates that the optical and electronic properties may be understood in terms of boron acceptors, with an ionization energy of 0.368 eV, partially compensated by a smaller concentration of deep donors. The donors are isolated substitutional nitrogen atoms in synthetic diamond, and assumed to be nitrogen in natural diamond. The total impurity concentration in natural type IIb diamond is less than 1 ppm, and the much higher defect concentrations generally present in doped synthetic and CVD diamond lead to considerable broadening of the acceptor infrared absorption spectrum, to impurity band conduction and relatively low mobility values.

At a more detailed level the fine structure in the acceptor absorption spectrum is not properly understood. Furthermore, Hall effect data can only be analysed approximately because the temperature dependence of the scattering mechanisms, of the contribution from the split-off valence band and of the population of excited states cannot be determined with any certainty.

The distribution of neutral acceptors in synthetic and CVD diamond is extremely inhomogeneous, and it is important that the limitations of the samples, and of the theoretical understanding of the defect centres, are recognized in the ongoing research in this area.

References

Albin, S. & Watkins, L. 1990 In *Diamond, silicon carbide and related wide bandgap semiconductors* (ed. J. T. Glass, R. Messier & N. Fujimori). Materials Research Society Symposium Proceedings, vol. 162, pp. 303–308.

Blakemore, J. S. 1962 *Semiconductor statistics*. Oxford: Pergamon Press.

Burns, R. C., Cvetkovic, V., Dodge, C. N., Evans, D. J. F., Rooney, M-L. T., Spear, P. M. & Welbourn, C. M. 1990 *J. Crystal Growth* **104**, 257–279.

Collins, A. T. 1992 *Diamond Related Mater.* **1**, 457–469.

Collins, A. T., Dean, P. J., Lightowlers, E. C. & Sherman, W. F. 1965 *Phys. Rev.* A **140**, 1272–1274.

Collins, A. T. & Lightowlers, E. C. 1979 In *The properties of diamond* (ed. J. E. Field), pp. 79–105. London: Academic Press.

Collins, A. T. & Williams, A. W. S. 1971 *J. Phys.* C **4**, 1789–1800.

Crowther, P. A., Dean, P. J. & Sherman, W. F. 1967 *Phys. Rev.* **154**, 772–785.

Custers, J. F. H. 1952 *Physica* **18**, 489–496.

Davis, R. F., Sitar, Z., Williams, B. E., Kong, H. S., Kim, H. J., Palmour, J. W., Edmond, J. A., Ryu, J., Glass, J. T. & Carter, Jr, C. H. 1988 *Mater. Sci. Engng* B **1**, 77–104.

Davis, E. A. & Compton, W. D. 1965 *Phys. Rev.* **140**, A2183–A2194.

Geis, M. W. 1990 In *Diamond, silicon carbide and related wide bandgap semiconductors* (ed. J. T. Glass, R. Messier & N. Fujimori). Materials Research Society Symposium Proceedings, vol. 162, pp. 15–22.

Gildenblat, G. Sh., Grot, S. A., Hatfield, C. W., Wronski, C. R., Badzian, A. R., Badzian, T. & Messier, R. 1990 In *Diamond, silicon carbide and related wide bandgap semiconductors* (ed. J. T. Glass, R. Messier & N. Fujimori) Materials Research Society Symposium Proceedings, vol. 162, pp. 297–302.

Glover, G. H. 1973 *Solid State Electron.* **16**, 973–983.

Grot, S. A., Hatfield, C. W., Gildenblat, G. Sh., Badzian, A. R. & Badzian, T. 1991 In *New diamond science and technology* (ed. R. Messier, J. T. Glass, J. E. Butler & R. Roy), pp. 949–955. Pittsburgh: Materials Research Society.

Huggins, C. M. & Cannon, P. 1962 *Nature, Lond.* **194**, 829–830.

Isenberg, I., Russel, B. R. & Greene, R. F. 1948 *Rev. Sci. Instrum.* **19**, 685–688.

Janssen, G., van Enckevort, W. J. P., Vollenberg, W. & Giling, L. J. 1992 *Diamond Related Mater.* **1**, 789–800.

Kanda, H., Ohsawa, T. & Fukunaga, O. 1987 In *Abstracts of the Second Meeting of 'Diamond'*, pp. 23–24. Tokyo, Japan. (In Japanese.)

Kemmey, P. J. & Wedepohl, P. T. 1965 In *Physical properties of diamond* (ed. R. Berman), ch. 12. Oxford: Clarendon Press.

Landstrass, M. I., Moyer, D., Yokota, S. & Plano, M. A. 1991 In *New diamond science and technology* (ed. R. Messier, J. T. Glass, J. E. Butler & R. Roy), pp. 969–974. Pittsburgh: Materials Research Society.

Lawson, S. C. 1991 PhD thesis, University of London, U.K.

Lightowlers, E. C. & Collins, A. T. 1966 *Phys. Rev.* **151**, 685–688.

Lightowlers, E. C. & Collins, A. T. 1976 *J. Phys.* D **9**, 951–963.

Mitchell, E. W. J. 1963 In *Proc. First Int. Cong. on Diamonds in Industry* (ed. P. Greene), pp. 241–251. London: Industrial Diamond Information Bureau.

Muto, Y., Sugino, T. & Shirafuji, J. 1991 *Appl. Phys. Lett.* **59**, 843–845.

Rauch, C. J. 1962 In *Proc. Int. Conf. on Physics of Semiconductors* (ed. A. C. Stickland), pp. 276–280. London: The Institute of Physics and the Physical Society.

Rooney, M-L. T. 1992 *J. Crystal Growth* **116**, 15–21.

Shiomi, H., Nishibayashi, Y. & Fujimori, N. 1991 In *New diamond science and technology* (ed. R. Messier, J. T. Glass, J. E. Butler & R. Roy), pp. 975–980. Pittsburgh: Materials Research Society.

Shiomi, H., Tanabe, K., Nishibayashi, Y. & Fujimori, N. 1990 *Jap. J. appl. Phys.* **29**, 34–40.

Smith, S. D. & Taylor, W. 1962 *Proc. phys. Soc.* **79**, 1142–1143.

Strong, H. M. & Chrenko, R. M. 1971 *J. phys. Chem.* **78**, 1835–1843.

Sze, S. M. 1981 *Physics of semiconductor devices*, 2nd edn. New York: Wiley.

Williams, A. W. S., Lightowlers, E. C. & Collins, A. T. 1970 *J. Phys.* C **3**, 1727–1735.