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LETTER TO THE EDITOR

Thermal and optical measurements on vacancies in type IIa diamond

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Abstract. Type IIa diamonds were irradiated below 250 K with electrons of 1·50, 0·60 or 0·35 MeV. The radiation-induced thermal resistivity is shown to correlate with the concentration of neutral vacancies as determined by the strength of the GR 1 optical absorption band. The production of vacancies was found to saturate at high doses and to be as large as previously observed after irradiation at about 500 K.

This Letter reports several extensions of previous work by Burgemeister and Ammerlaan (1980) on radiation damage in diamond. In the earlier work the damage was produced by electrons of 1·50, 0·90 or 0·60 MeV, observed as a reduction of the thermal conductivity between 320 and 450 K, and analysed in terms of a thermal resistivity depending on the vacancy concentration. It was assumed that the displaced carbon atoms have a negligible effect on the high-temperature thermal conductivity. In the present work, this assumption has been verified by correlating the thermal resistivity with the GR 1 optical absorption (Clark *et al* 1956), which is most probably produced by vacancies (Walker 1979, Clark *et al* 1979). It was also assumed previously that recombination of displaced atoms and vacancies was negligible during irradiation. However, since the vacancy concentrations were high (of the order of 0·01 %) the production of damage is beginning to saturate, as we show here by means of a simple model.

In the present work the diamonds were irradiated at temperatures below 250 K for comparison with the 500 K irradiation used earlier (Burgemeister and Ammerlaan 1980). Massarani and Bourgoin (1976) and Collins (1977) have shown that the rate of damage production is larger for irradiations carried out at 100 K than at higher temperatures, even when the specimens are stored at room temperature before measurement (Collins 1977). We show here that there is no detectable difference in damage rates for 250 K and 500 K irradiations.

Type IIa diamonds (which contain only low levels of impurities, see e.g. Sellschop 1979) were selected for this work since the analysis of radiation damage in this type of diamond is more straightforward than for type I diamonds (which contain of the order of 0·1 at.% nitrogen: see Field 1979 for earlier references). For the latter type, Davies (1972) inferred that vacancies may be trapped on nitrogen atoms, and Burgemeister and Ammerlaan (1980) found a thermal resistivity caused by damage combined with nitrogen.

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Rectangular bars of type IIa diamond were prepared with thicknesses much smaller than the ranges of the electrons of the irradiating beams. Two faces of each bar were metal-coated to obtain good thermal contact upon clamping it between copper blocks cooled with liquid nitrogen. Bars were irradiated in this configuration with electrons of 1·50, 0·60 or 0·35 MeV from a Van de Graaff accelerator. Although up to about 10 W was supplied to the specimens by the electron beam, their temperature remained below 250 K as estimated from temperature measurements at various places in the copper blocks.

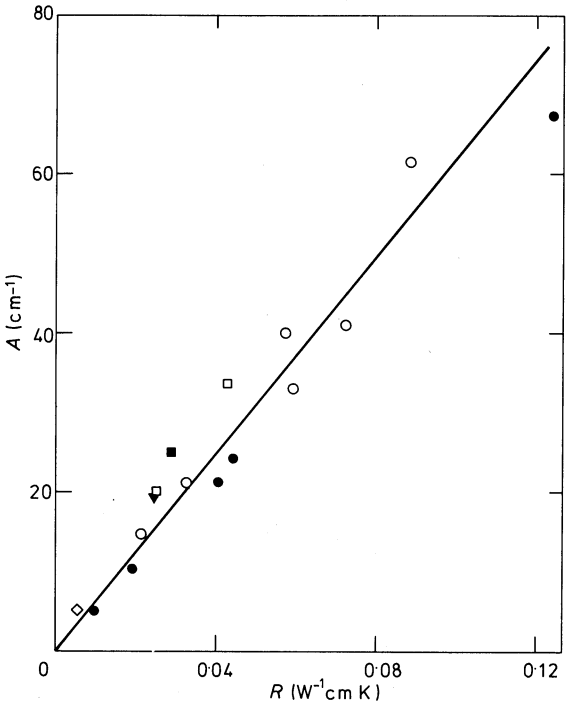

Figure 1. Measured strengths of the GR 1 absorption against measured thermal resistivities of electron-irradiated type IIa diamonds. Vacancies were produced by irradiating the diamonds below 250 K (open symbols) or at about 500 K (full symbols) with electrons of energy E_e to doses between $3{\cdot}1 \times 10^{18}$ and $1{\cdot}19 \times 10^{20}$ cm^{-2}. Symbols correspond to values of E_e as follows: circles, 1·50 MeV; triangles, 0·90 MeV; squares, 0·60 MeV; diamonds, 0·35 MeV.

Before and after each irradiation, the thermal conductivity of the bar was measured at several temperatures between 320 and 450 K. It was found that the thermal conductivity depended on the temperature in the same way as previously found (Burgemeister and Ammerlaan 1980). For each bar, radiation-induced thermal resistivities were derived at 320 and 450 K, and the mean value R is used below. Absorption spectra were measured between 750 and 400 nm at liquid nitrogen temperature. A measure for the strength of the GR 1 absorption is denoted by A and defined as the difference in absorption coefficient between the peak of the sharp 40 meV phonon sideband and the minimum at 716 nm on the short-wavelength side of the band (e.g. Davies and Foy 1980). This definition avoids the uncertainties in defining a baseline under the GR 1 band. The value of A was

found to be the same when the specimens were stored at room temperature or heated for about 1 h at 450 K during measurement of the thermal conductivity.

Figure 1 shows the results for the diamond bars irradiated at temperatures below 250 K (open symbols) compared to those for bars previously irradiated at about 500 K (full symbols). The high correlation (correlation coefficient = 0·97) supports the assumption that vacancies, which produce GR 1 absorption, are the cause of the thermal resistance. The experiment can thus be described by

$$\alpha A = \beta R = n_V \tag{1}$$

where α and β are constants and n_V denotes the number of vacancies per cm^3.

Some systematic scatter as a function of electron energy E_e is observable in figure 1. This is possibly a result of the formation of divacancies at $E_e = 1{\cdot}50$ MeV, since the effect of divacancies on the thermal conductivity is of the same order as that of vacancies,

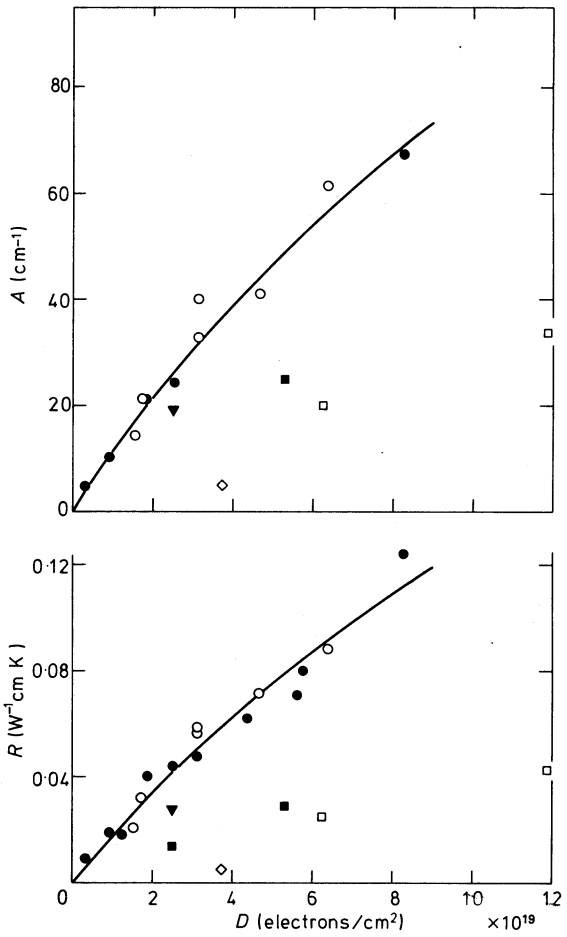

Figure 2. Measured strengths of the GR 1 absorption and measured thermal resistivities against irradiation dose. The curves were fitted to the results of irradiations below 250 K (open symbols) and at about 500 K (full symbols), both with $E_e = 1{\cdot}50$ MeV. Symbols correspond to values of E_e as follows: circles, 1·50 MeV; triangles, 0·90 MeV; squares, 0·60 MeV; diamonds, 0·35 MeV.

whereas divacancies do not give GR 1 absorption. However, this scatter is ignored in the further analysis since the divacancy/vacancy ratio is estimated to be only about 0·03.

Figure 2 shows plots of the measured quantities against the irradiation dose D. The results for specimens irradiated below 250 K were plotted together with those from the earlier specimens irradiated at about 500 K (although A values were not measured for all the previously irradiated specimens).

Figures 1 and 2 both show that the temperature of the specimens during irradiation (250 K or 500 K) did not affect the total amount of damage observed. This implies that by 250 K there is enough thermal energy present to allow recombination of any metastable close vacancy–interstitial pairs (Collins 1977). (The annealing stage at $\sim$260 K reported by Massarani and Bourgoin 1976 and Lomer and Marriott 1979 will, of course, occur in any case during room-temperature storage).

The displacement cross section σ_d is a function of E_e and of the displacement energy of carbon atoms in diamond E_d. The ratio of vacancy production for two E_e values depends on E_d via a difference in σ_d. Graphs of this ratio against E_d were made on the basis of Mitchell's calculations (1965). From the comparison of the experimental results with these graphs, the effective E_d value is found to be 80 ± 20 eV. This effective value might depend to some extent on E_e; it agrees with the results of earlier irradiations above room temperature (Clark *et al* 1961) but is much larger than $E_d = 35$ eV calculated by Bourgoin and Massarani (1976) from low-temperature irradiation (see also Clark and Mitchell 1977).

A displaced carbon atom travels a distance p before encountering a trapping site such as a dislocation or other defect. It might also recombine with a vacancy giving saturation of damage production; the cross section for recombination is given by s. For a small extra dose δD, the vacancy concentration increases approximately as

$$\delta n_V + psn_V\delta n_V = n_C\sigma_d\delta D \tag{2}$$

where n_C is the number of carbon atoms per cm^3. The solution of equation (2) is

$$n_V = [-1 + (1 + 2psn_C\sigma_d D)^{1/2}]/ps. \tag{3}$$

Values of α and β in equation (1) were derived from figure 2 for $E_e = 1{\cdot}50$ MeV in the limit of low dose ($n_V = n_C\sigma_d D$). They are 6×10^{17} cm^{-2} and $3{\cdot}7 \times 10^{20}$ W cm^{-4} K^{-1} respectively, using $n_C = 1{\cdot}77 \times 10^{23}$ cm^{-3} and $\sigma_d = 4{\cdot}03 \times 10^{-24}$ cm^2 (the last value was calculated by Mitchell 1965). The curves in figure 2 were fitted to the results for $E_e = 1{\cdot}50$ MeV, using $ps = 2 \times 10^{-20}$ cm^3 in equation (3) to determine the deviation from linearity in the radiation-induced effects.

Since the GR 1 absorption is attributed to the neutral vacancy (Walker 1979), Coulomb interaction may not be involved in recombination. Then, we expect s to be of the order of the cross section of a typical {110} channel through the lattice, $s \sim 10^{-15}$ cm^2, giving $p \sim 2 \times 10^{-5}$ cm. Displaced carbon atoms will be trapped with a high capture probability by dislocations due to the presence of strain fields around dislocation lines. We note that the value of p is of the order of the typical spacing between dislocations in type IIa diamond (Lang 1979).

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