Threshold energy for atomic displacement in diamond

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Man-made boron-doped diamonds have been irradiated with energetic electrons. The effect of the energy of the irradiations, performed around 15°K, upon the conductivity measured at 12°K has been studied. The comparison between the variations, with the energy of irradiation, of the defect introduction rate (deduced from conductivity measurements) and of the cross section for atomic displacement provides a threshold energy of 35 ± 5 eV in good agreement with the theoretical estimates.

I. INTRODUCTION

The threshold energy for displacement T_d is a phenomenological parameter used to describe the probability that a given recoil energy, transmitted to an atom of a solid by energetic particles, produces a displacement: any recoil, smaller than T_d, is ineffective in displacing the atom while any energy greater than T_d has a unity probability of displacing the atom.

In semiconductors there are only two theoretical estimates of this threshold energy, due to Kohn[1] and Baüerlein.[2-4] According to these authors, T_d includes the energy to break four bonds, plus the work required for the displaced atom to pass through the saddle point and go to an interstitial position, plus the energy associated with the lattice distortion around the interstitial. The strain energy term and the potential energy term are assumed to be small in front of the bond-breaking energy; the single-bond energy, taken as one half of the total bond energy per atom, is related to the heat of sublimation corrected for the $s^2p^2 \rightarrow sp^3$ promotion. As discussed by Mitchell[5] and more recently by Corbett *et al.*,[6,7] too much reliance should not be placed on such estimates although they provide values which are in reasonable agreement with the values determined experimentally for germanium and silicon.[8]

But for diamond these theoretical estimates provide values for T_d (24–30 eV) which are quite low as compared to the experimental value (80 eV) found by Clark *et al.*[9] This implies that either the estimation is incorrect or the threshold energy experimentally determined does not correspond to the direct creation of vacancy interstitial pairs. The existence of a threshold energy associated with the creation of a more complex defect is plausible since (i) its determination has been done using irradiations at room temperature, temperature larger than the temperatures at which the first annealing stage (260 °K), due to the recovery of the primary defects,[10] occurs; (ii) the threshold energy (80 eV) determined by Clark *et al.*[9] being nearly two times larger than the theoretical estimate could be attributed to divacancy formation[5]; indeed—as demonstrated in the case of silicon[11]—the threshold energy for divacancy formation is twice the threshold energy for vacancy formation.

The aim of this paper is to describe a measure of the threshold energy for irradiations performed near helium temperature, in such a way that the threshold energy can unquestionably be attributed to the formation of vacancy-interstitial pairs. This threshold energy is obtained from the comparison between the variations, with the incident energy of the electrons used to transmit an energy to the atoms, of the concentration of the defects introduced and of the cross section for atomic displacement. The defect concentration is obtained from conductivity measurements. The samples studied[12] are diamonds doped with a concentration of boron on the order of 10^{17}–10^{18} cm^{-3}, in which the conductivity occurs through a variable range hopping mechanism[13] below 100–150 °K; in such a regime the variation of conductivity due to the introduction of extra compensating centers, such as by irradiation, has been worked out.[14] Because the way the measurements are taken and the experimental setup can be found elsewhere,[12,14] we shall describe in this paper only the experimental results obtained (Sec. II) and the calculation of the cross section for atomic displacement (Sec. III). The comparison between the experimental results and the calculation, from which T_d is deduced, will be made in Sec. IV.

II. EXPERIMENTAL RESULTS

The irradiations are performed around 15 °K and the measurements are taken as 12 °K, temperatures below which no defect recovery occurs.[12] The effect of the energy of irradiation upon the defect creation rate is investigated in the following ways. First we proceeded by successive irradiations with low doses (on the order of 10^{15} cm^{-2}) of various energies ranging from 0.25 to 0.5 MeV; the variations of conductivity σ due to these successive irradiations are shown on Fig. 1. Then we used larger doses (on the order of 10^{16} cm^{-2}) at each different energy; with such doses the variations of conductivity σ are very large and consequently the samples are warmed-up at 350 °K (temperature at which most of the defects created are annealed[12]) between two irradiations at different energies; the results obtained in this way are given on Fig. 2, for energies ranging from 0.3 to 1 MeV.

Figures 1 and 2 show that $\ln\sigma$ varies linearly with the dose ϕ of irradiation, indicating that the formula[12,14] which relates the variation of σ (of initial value σ_i) to the concentration of the compensating centers ΔN_D introduced by irradiation

$$\ln\sigma = \ln\sigma_i - \beta\Delta N_D ,$$

with

$$\beta = 0.66(\alpha^3 e^2/2\chi kT)^{1/4} N_A^{1/6}(N_A - N_D)^{-4/3}$$

verified. In this formula N_A is the acceptor (boron) concentration, χ the dielectric constant, e the electronic charge, and α^{-1} a length which characterized the extension in space of the wave function associated with a hole on a boron site[13] ($\alpha^{-1} \simeq 2\times 10^{-7}$ cm).

The defect creation rate, defined as $\tau = \Delta N_D/\phi$, is related to the slope of $\ln\sigma$ vs ϕ since

$$\tau = \ln(\sigma_i/\sigma)/\beta\phi .$$

The slope of $\ln\sigma(\phi)$ is therefore a measure of τ. Actually the slopes of $\ln\sigma(\phi)$ at identical energies (0.3 and 0.5 MeV; see Fig. 1) are slightly different. This difference can be qualitatively understood by taking into account the concentration of defects accumulated after each irradiation; but this variation of τ between successive irradiations cannot be exactly calculated because the distribution of the defects created is inhomogeneous and varies with the energy of irradiation. The calculated values of ΔN_D for the irradiations described in Fig. 1 are given, together with the corresponding values of τ, in Table I. (For the sample studied $N_A = 1.69\times 10^{18}$ cm^{-3}, $N_D = 1.62 \times 10^{18}$ cm^{-3}, and $\beta = 1.25\times 10^{-16}$ cm^{-3}.) The accuracy upon the absolute values of ΔN_D and τ is poor because: (i) they depend upon the initial values of the concentrations N_A(1.69×10^{18} cm^{-3}) and N_D(1.62×10^{18} cm^{-3}) which are not known with a good accuracy[13]; (ii) the distribution of the de-

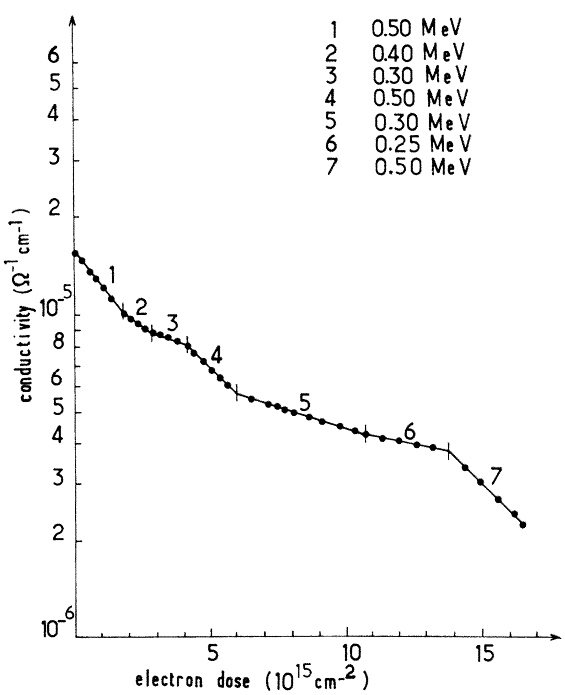

FIG. 1. Variation of conductivity versus dose of electrons of various energies.

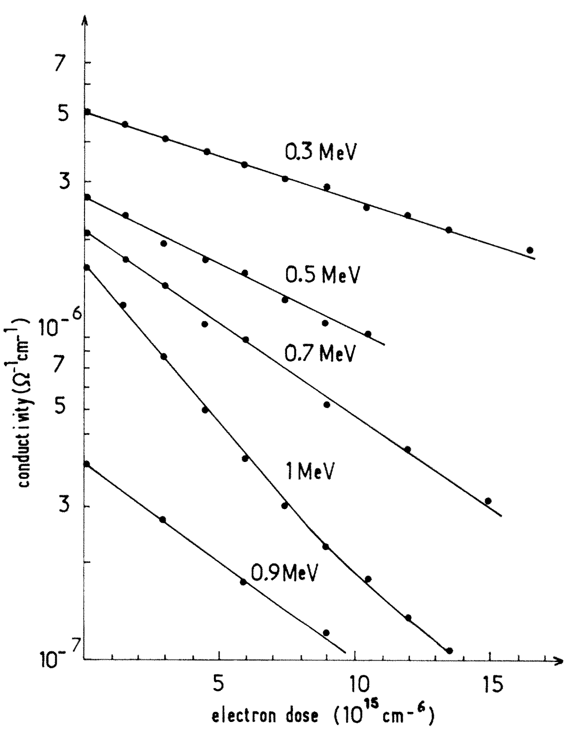

FIG. 2. Variation of conductivity versus electron dose at: 1–0.3 MeV; 2–0.5 MeV; 3–0.7 MeV; 4–0.9 MeV; 5–1 MeV. The irradiations have been performed in the order 1, 2, 3, 5, 4.

TABLE I. Calculated concentrations of the defects introduced (ΔN_D) and of the creation rates (τ), versus the energy E of irradiation (irradiations described in Fig. 1).

Fig. 1	E (MeV)	ϕ (10^{15} cm^{-2})	$\ln(\sigma_i/\sigma_r)$	ΔN_D (10^{15} cm^{-3})	τ (cm^{-1})
1	0.50	1.8	0.39	2.74	1.52
2	0.40	0.9	0.11	0.77	0.86
3	0.30	1.5	0.11	0.76	0.51
4	0.50	1.8	0.36	2.21	1.23
5	0.30	4.8	0.28	1.92	0.40
6	0.25	3.0	0.13	0.90	0.30
7	0.50	2.7	0.52	3.24	1.20

fects being inhomogeneous the values of ΔN_D determined are values averaged over the sample thickness. This is not important in view of the fact that only relative values of τ are needed for the determination of T_d. Relative values of τ, i.e., the slopes of $\ln\sigma(\phi)$, for the irradiations described in Fig. 2, are given in Table II.

III. CALCULATION OF THE CROSS SECTION FOR ATOMIC DISPLACEMENT

The differential cross section ds for the transmission of an energy between T and $T+dT$ by an electron of energy E is given by the Rutherford formula corrected to account for the fact that the electrons are relativistic. This differential cross section, derived by Mott,[15,16] being the sum of two conditionally convergent infinite series, is difficult to calculate and we used the approximation of McKinley-Feshbach[17] valid for carbon.[18] From ds, the total cross section is given by

$$S(E)=\int_{T_d}^{T} g(T)(ds/dT)\,dT\,,$$

where T_m and T_d are respectively the maximum transmitted energy and the minimum energy necessary to displace an atom (threshold energy for displacement). We consider for $g(T)$, the number of displacements due to a primary knock-on of energy T, the Kinchin and Pease model[19]

$$g(T)=0 \quad \text{for } T<T_d,$$

$$g(T)=1 \quad \text{for } T_d<T<2T_d\,,$$

$$g(T)=T/2T_d \text{ for } T>2T_d\,.$$

TABLE II. Slopes of $\ln\sigma(\phi)$, in relative units, versus the energy E of irradiation (irradiations described in Fig. 2).

E (MeV)	0.3	0.5	0.7	0.9	1
$\Delta(\ln\sigma)/\Delta\phi$	4.6	8.8	12.3	13	21

The results of the calculation, performed for various values of T_d, are given on Fig. 3.

Actually the samples used being not infinitely thin, it is necessary to take into account in the calculation the energy losses (due to collisions with the electrons of the solid) with the penetration depth of the electrons. This is done using the electron energy-loss rate $-dE/dR$ deduced from empirical formulas[20]

$$dE/dR=E/R(1.265-0.191\log_{10}E)^{-1} \quad \text{for } E<2.5$$

and

$$dE/dR=0.00189 \quad \text{for } E>2.5$$

(E is the electron energy in MeV and R the range in mg cm^{-2}). The calculation of the cross section S for displacement versus the depth of penetration x we performed is described elsewhere.[21] Examples of the results of the calculation for various

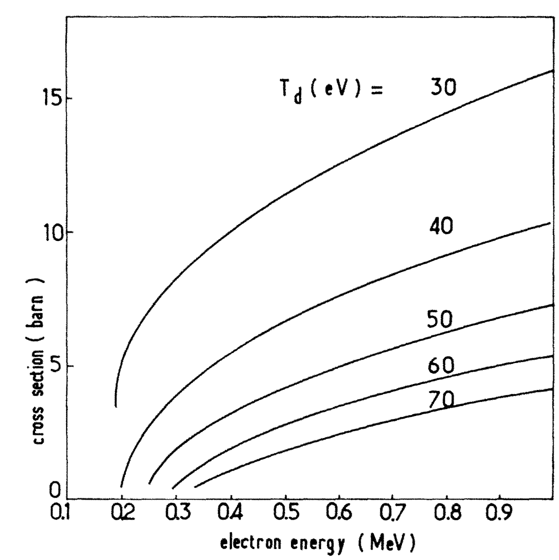

FIG. 3. Cross section for atomic displacement versus incident electron energy for various values of threshold energy T_d.

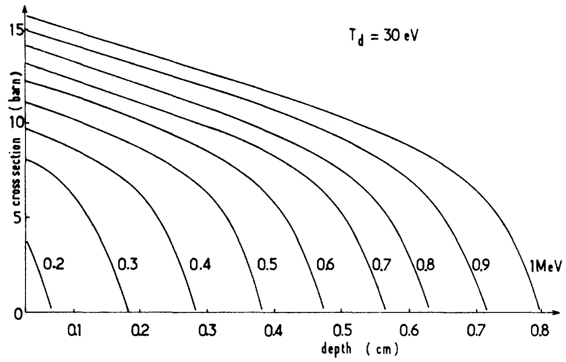

FIG. 4. Cross section for displacement versus the penetration depth of electrons having various incident energies, calculated for a threshold energy of 30 eV.

energies of irradiation and various threshold energies are given in Figs. 4 and 5.

The total number of displacements is given by the integral $\Gamma = N\int_0^d S\,dx$, where d is the sample thickness ($d = 2.5$ mm) and N the number of carbon atoms per unit volume.

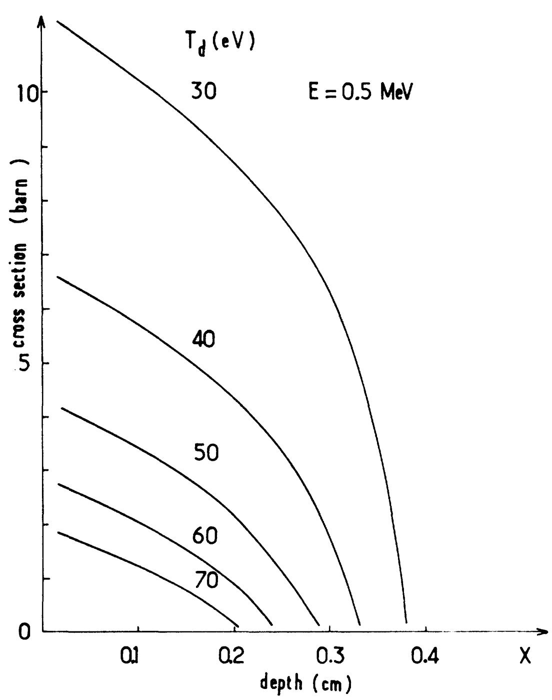

FIG. 5. Cross section for displacement versus the penetration depths of 0.5 MeV electrons calculated for various values of the threshold energy T_d.

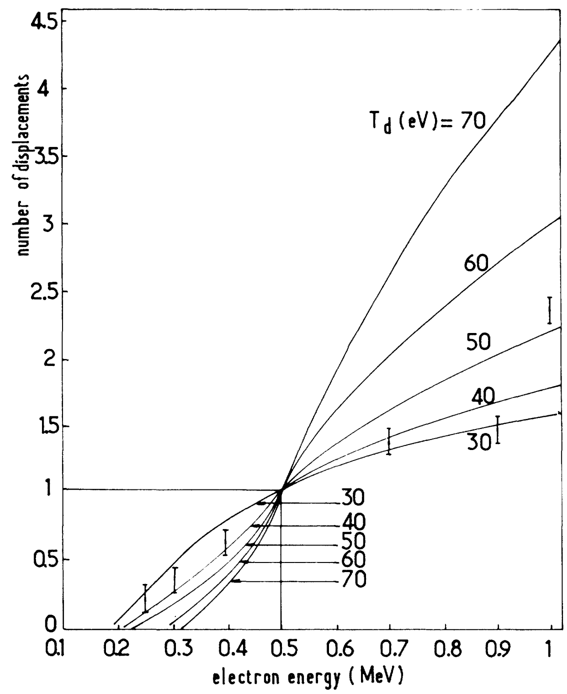

FIG. 6. Total number of displacements versus electron energy calculated for various values of the threshold energy (normalized at 0.5 MeV). Bars correspond to the experimental results.

IV. DISCUSSION

In order to compare the experimental variation of the defect creation rate with the theoretical one, we normalize (at 0.5 MeV) the experimental values of τ or of $\Delta(\ln\sigma)/\Delta\phi$ and the curves giving Γ for various values of T_d. We notice that all the experimental data fall between the theoretical curves corresponding to threshold energies of 30 and 40 eV (Fig. 6) except for the data at 1 MeV. We can therefore conclude that the threshold energy for displacement has a value of 35 ± 5 eV.

Such a value for the threshold energy is in reasonable agreement with the estimates of Kohn and Baüerlein. It is practically half the value determined by Clark *et al.*[9] indicating that, probably, these authors measured the threshold energy for divacancy production; it is possible that they did not observe the threshold at 35 eV because most of the defects that are created at low temperature have disappeared at the temperature at which they performed their irradiations.

These measurements provide therefore a strong evidence that the defects created by low-temperature irradiation, which have been observed[10] to recover around 260 °K, are vacancy interstitial pairs. As seen on Table III, the total number of

TABLE III. Comparison between the total number of displacements Γ calculated for $T_d = 35$ eV and the total number of defects determined experimentally.

Fig. 1	E (MeV)	τd experimental	Γ calculated
1	0.50	0.38	0.35
2	0.40	0.22	0.23
3	0.30	0.13	0.10
4	0.50	0.31	0.35
5	0.30	0.10	0.10
6	0.25	0.08	0.07
7	0.50	0.30	0.35

displacements calculated for $T_d = 35$ eV is in agreement with the evaluation of the total number of defects (τd) made using conductivity measurements.

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