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Defects at low temperature in electron-irradiated diamond

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Man-made boron-doped diamonds have been irradiated with energetic electrons. The effect of the dose, for irradiations performed around 15°K, and the effect of the temperature (in the range 15–250°K) upon the conductivity measured at 12°K have been studied. Isochronal annealing, performed in the temperature range 15–350°K, has shown the presence of several stages associated with the thermal release of carriers from traps and of a recovery stage around 260°K. The activation energy for the recovery of the defect has been measured (1.3 eV) and the recovery kinetics determined. A level situated at about 20 meV below the conduction band has been associated with the defect. It is proposed that this recovery stage (around 260°K) is due to the recombination of vacancy-interstitial pairs through the mobility of the interstitial.

I. INTRODUCTION

Microscopic techniques [e.g., electron paramagnetic resonance (EPR), optical absorption and luminescence, sometimes complemented by uniaxial or hydrostatic stress] have been used in the study of defects in diamond. Very few impurities or defects have been identified: substitutional nitrogen (using EPR), substitutional boron (using activation analysis and conductivity) and a triangular arrangement of nitrogen atoms (the N_3 system, seen in absorption and emission). Electron irradiation has been used extensively in attempts to identify the defects present before irradiation or produced by irradiation.[1] It has been observed that, while some of the defects produced were intrinsic, others were associated with impurities. But no defect identification has been made; at most it is reasonable to ascribe an absorption at 1.673 eV (labeled GR1), which anneals around 800 °C, to the vacancy.[2,3] Neither the interstitial nor the vacancy-interstitial pair have been detected; the two annealing stages which occur below 800 °C (around 300 and 500 °C) with the same activation energy of 1.3 eV are believed to be associated with the interstitial.[4]

It has been impossible up to now to obtain a perspective upon the defect production and recovery processes in irradiated diamond. One of the reasons for this is that the measurements performed are all microscopic measurements (when, for instance, the disappearance of an optical band is observed there is no assurance that the resultant defects will give rise to other optical bands). The study of macroscopic properties, i.e., of electrical properties (which count all the defects present on which free carriers have been trapped), are needed. Only very few electrical measurements have been made in irradiated semiconducting diamonds[5-8]; Clark *et al.*[5] showed that the introduction of defects results in the production of donor levels and, from the variation of the defect creation rate with the energy of irradiation, they obtained a value of 80 eV for the threshold energy for displacement. Unfortunately these electrical measurements were performed at room temperature; they therefore imply that no defect recovery takes place below this temperature. In light of the observations made in silicon and germanium (for instance a mobility of the interstitial and of the vacancy at very low temperatures) this assumption has few chances to be verified. Actually, Horzowski and Lourens[7] noted that the dependence of the resistivity upon the dose of irradiation is consistent with a recovery occurring during the course of the irradiation (at room temperature).

Macroscopic measurements after irradiation at very low (liquid helium) temperature of the defect creation rate and annealing studies from this temperature are therefore of a fundamental interest. They will permit the determination of the stability and mobility of the primary defects (interstitials, vacancy-interstitial pairs) below room temperature. The importance of the behavior of these defects upon the formation of the more complex defects present at room temperature has been demonstrated in the case of silicon.

The aim of this paper is to study the creation of defects by electron irradiation around helium temperature and their recovery in the temperature range ~4–350 °K using electrical measurements. We perform conductivity measurements in synthetic boron-doped diamonds; the conductivity in these diamonds occurs through thermally activated holes in the valence band between 1000 and 200 °K and through an hopping mechanism below 100–150 °K. The description of the samples and of the experimental setup used in these experiments can be found elsewhere[9] and will not be repeated here. Only in the second section we shall describe brief-

ly how the experimental results are analyzed in order to get the defect concentration introduced by irradiation and what are the precautions which have to be taken in the course of the measurements. The paper will be divided in two parts: creation of defects (Sec. III), and recovery of defects (Sec. IV), each part containing a description of the experimental results and a discussion. The determination of the threshold energy for atomic displacement, deduced from the study of the defect creation rate vs the energy of irradiation, will be the subject of another paper.[10] There will be a final section in which conclusions upon the nature of the defects observed will be drawn from the results obtained.

II. TECHNIQUE OF ANALYSIS

We have shown[9] that, in boron-doped diamonds sufficiently doped such as the one we used in this study, the conductivity σ occurs through a variable range hopping mechanism below about 150 °K; then the conductivity, which obeys the Mott's law, is very sensitive to a variation ΔN_D in the concentration N_D of the centers which compensate the boron impurities, thus allowing the conduction (through hops of holes from occupied to unoccupied boron sites) to take place. If σ_i is the initial conductivity, corresponding to a concentration N_D of the compensating centers, it can be demonstrated[11] that the conductivity σ corresponding to $N_D + \Delta N_D$ is given by

$$\ln\sigma = \ln\sigma_i - \beta\Delta N_D , \tag{1}$$

when ΔN_D is small compared to $N_A - N_D$ (N_A is the boron concentration). β is given by

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

when $1 - K \ll 1$ (K is the compensation: $K = N_D/N_A$), e is the electronic charge, χ the dielectric constant and T the temperature. α^{-1} is a length characterizing the extension in space of the wave function of a hole on boron. We have shown[9] that the variation of σ with temperature and with the density of state at the Fermi level in various samples follows the Mott's theory when α^{-1} is on the order of 2×10^7 cm; this is the value which we shall consider.

Electron irradiation produces two effects. First it introduces defects which, because they are donor centers,[5] introduce a variation ΔN_D of the compensating center; this quantity ΔN_D will be obtained from the conductivity using formulas 1 and 2 after formula 1 has been verified. The (initial) values of the concentrations N_A and N_D in the samples used in this study are given in Table I. As discussed in Ref. 9 the values of N_A and N_D we determined in sample GE5A are such that they correspond to a very small value of the density of states at the Fermi level and we concluded that the hopping conduction does not occur in the boron impurity band but on other centers. Consequently the results obtained with this sample cannot be analyzed quantitatively in the hopping regime and the sample has been used mostly for measurements in the regime in which the conduction takes place in the valence band.

In case of measurement above approximately 150 °K, temperatures at which the electrical conduction takes place in the valence band, the concentration of the defects introduced is equal to the variation of the free hole concentration p. This hole concentration is given by

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

where m^* is the effective hole mass and E_A the energy level of boron in the forbidden gap. A change ΔN_D in the concentration of the compensating centers results in a change in the hole concentration, from p_i to p, such that

$$\frac{p_i}{p} = \frac{N_A - N_D}{N_D} \frac{N_D + \Delta N_D}{N_A - N_D - \Delta N_D} = 1 + \frac{\Delta N_D/N_A}{K[1 - K - (\Delta N_D/N_A)]} .$$

ΔN_D is then calculated from

$$\Delta N_D = \frac{N_A K(1-K)}{1 - K + K(p_i/p)} \left(\frac{p_i}{p} - 1\right) \tag{3}$$

after p has been deduced from σ. To be able to make this deduction we have considered the mobility measured in similar samples by Dean *et al.*[12] The variation of this mobility because of the irradiation is neglected. Indeed Clark *et al.*[5] have shown that the mobility changes are on the order of 30% for 5×10^{16} electrons cm^{-2} at 1.5 MeV; the doses we used being on the order 10^{16} cm^{-2} at 0.5–0.7 MeV (energies for which the cross section for displacement is 0.3–0.5 times the cross section for displacement at 1.5 MeV[10]) the variations of mobility we expect are on the order of few per cent (assuming a linear variation of the mobility with the dose, which is verified for other semiconductors). The effective mass m^* is taken equal to the free electron mass, value close to the value found by Dean *et al.*[12] in the samples the mobility of which we used.

Second, electron irradiation, through ionization, changes the distribution of the population of the carriers trapped on the deep levels associated with the compensating centers and on the boron level (situated at $E_A = 0.37$ eV above the valence band). At low temperature, because thermal excitation of carriers from the deep levels cannot

TABLE I. Concentrations (cm^{-3}) of boron impurities (N_A) and of compensating centers (N_D) in the samples used in this study. The way these concentrations are obtained is exposed in detail in Ref. 9.

Sample	$N_A - N_D$	N_A	N_D	$K = N_A/N_D$
GE 48	6.5×10^{16} (optical measurements)	1.69×10^{18}	1.62×10^{18}	96%
GE 5A	9×10^{16} (electrical measurements)	9×10^{16}	2×10^{14}	0.2%

take place, the ionization results in a metastable state in which the concentration of the compensating center (N'_D) is different from the concentration at equilibrium (N_D). Because $N_D - N'_D$ happens to be small compared to $N_A - N_D$, N'_D can also be calculated, using formulas 1 and 2, from the value σ_0 of the conductivity in this metastable state. This is this value N'_D which has to be considered next, for the evaluation of the concentration of the defects introduced by irradiation. Actually when an ionization, such as by uv illumination, x-ray irradiation or low-energy-electron irradiation, is used the conductivity increases until it reaches a saturation value σ'_0. When the ionization is stopped, the conductivity decreases rapidly, then slowly; after several minutes (5 min) the changes in conductivity are such that they are negligible during the time to make one measurement (several minutes); a value σ_0 of the conductivity is then measured (Fig. 1). The way the changes of conductivity $\Delta\sigma$ due to defect introduction are obtained is then the following: the high-energy-electron irradiation performed is always such

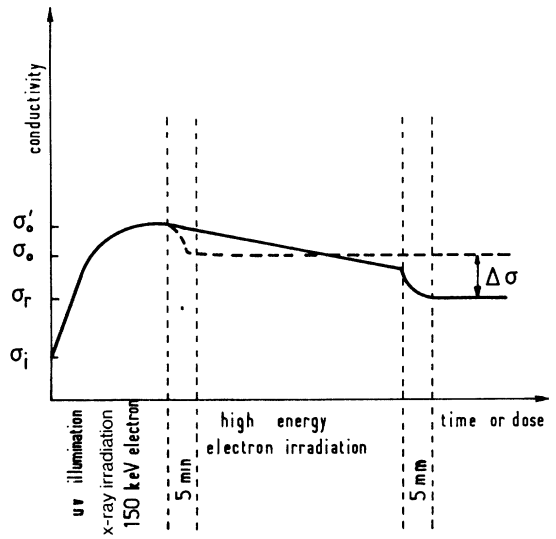

FIG. 1. Schematic diagram illustrating the way measurements of changes in conductivity due to defect introduction are obtained.

that the saturation value σ'_0 is reached even for the lowest doses used. After the desired dose has been obtained, the irradiation is stopped and the measurements are taken 5 min later. The change of conductivity observed, from σ_0 to σ_r (Fig. 1), is due only to the defects created by the irradiation provided that the distribution of the carrier population among the different compensating centers is the same (i.e., that the metastable state reached after high-energy irradiation is the same that after ionization). This is a correct approximation since the concentration of the defects introduced never exceeded 5×10^{15} cm^{-3} while N_A and $N_A - N_D$ are on the order of 10^{18} cm^{-3} and 10^{17} cm^{-3}, respectively. (This necessitates the calculation of the new value $N'_D - \Delta N_D$ of the concentration of the compensating centers after each irradiation.) When the temperature is raised some of the excited centers can release thermally the trapped carriers and come back to their equilibrium charge state[13] (thermal release of carriers is observed around 160, 230, and 300 °K). The ionization, which decreases the compensation, induces an increase of conductivity while the introduction of defects, which increases the compensation, induces a decrease of conductivity because the compensation is larger than 0.5 (in sample GE48).

III. CREATION OF DEFECTS

A. Experimental results

Irradiations with successive doses ϕ of 0.5-MeV electrons have been performed around 15 °K in sample GE48 and the conductivity σ measured at 12 °K. The results are given in Fig. 2. A series of irradiations at 0.5 and 0.7 MeV have also been performed at 80 °K in sample GE5A; each irradiation was followed by heating up to 200 °K for 10 min[14] and σ was then measured in the temperature range 120–200 °K; the results are given in Fig. 3. Another series of irradiations at different temperatures, ranging from 20 to 200 °K, has also been performed with approximately the same doses of 0.7-MeV electrons in sample GE48; the varia-

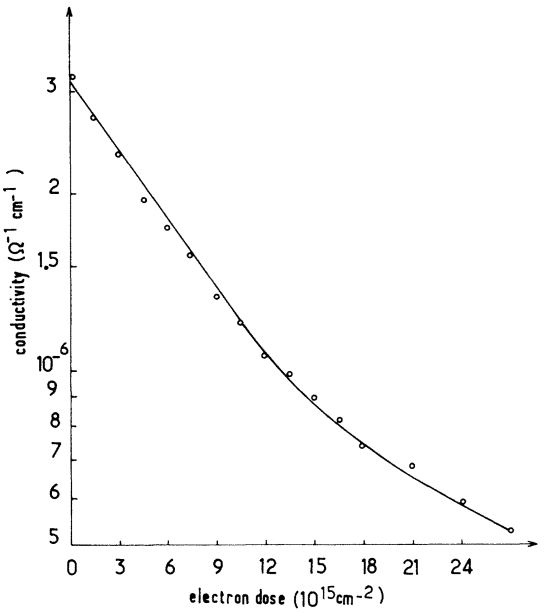

FIG. 2. Variation of the conductivity at 12 °K vs electron dose for irradiation at 0.5 MeV in sample GE 48.

tions of σ measured at 12 °K vs dose are given in Fig. 4.

B. Discussion

At low temperature where the defects created are not mobile and for low doses of irradiation, there is no interaction between the defects themselves or between defects and impurities; under these circumstances the concentration of defects ΔN_D introduced is proportional to the dose of irradiation ϕ. Figure 2, which shows that for doses lower than 10^{16} cm^{-2} σ varies exponentially with ϕ, gives therefore a verification of the validity of formula 1; results of Fig. 4 show that this variation of σ vs ϕ is also verified in different conditions. For doses larger than 10^{16} cm^{-2} a slight deviation in the linearity of $\ln\sigma(\phi)$ is observed. This is a consequence of the fact that the distribution in depth of the defects introduced is not uniform; as a result, in the more damaged part of the sample, the concentration of defects is such that the approximation $\Delta N_D \ll N_A - N_D$ (used to deduce formula 1) is no longer valid. Moreover, if ΔN_D is not negligible in front of N_D, the large defect concentration

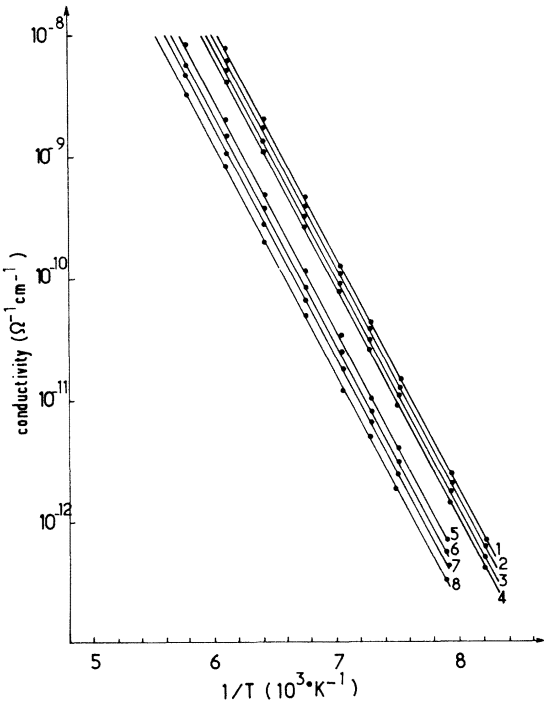

FIG. 3. Variation of the conductivity vs temperature after successive doses at 0.5 and 0.7 MeV in sample GE 5A irradiated at 80 °K.

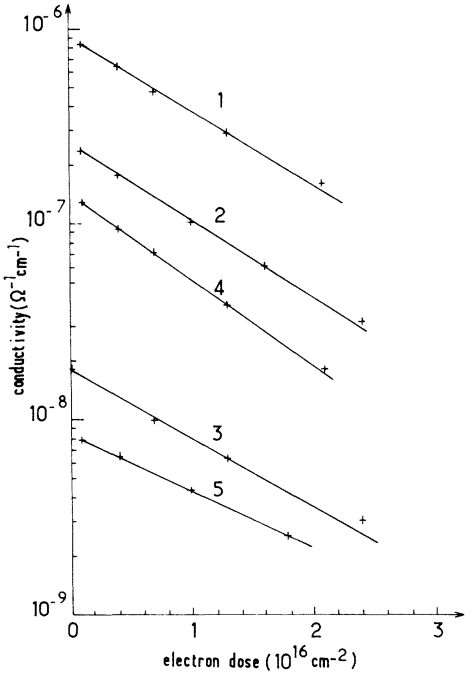

FIG. 4. Variation of conductivity at 12 °K vs dose of 0.7 MeV electrons in sample GE 48. The irradiations are performed at temperatures: 1-20 °K; 2-40 °K; 3-80 °K; 4-100 °K; 5-200 °K in the following order: 1, 2, 4, 3, 5.

can introduce a non-negligible change in the metastable equilibrium of the carrier population among the compensating centers and our method for the evaluation of $\Delta\sigma$ does not apply anymore. The defect creation rate, defined as $\tau = \Delta N_D/\phi$, can be calculated from formula 1:

$$\tau = \ln(\sigma/\sigma_i)/\beta\phi \,. \tag{4}$$

For sample GE48 (in which $\beta = 1.25 \times 10^{-16}$ cm^3) irradiated at 0.5 MeV (Fig. 3), one gets $\nu = 0.6$ cm^{-1}.

Figure 5 gives the variation of ΔN_D, calculated using formula 3, with the dose of irradiation at 0.5 and 0.7 MeV. The defect creation rates that we deduce in the linear range (i.e., for doses larger than 2 to 3×10^{16} cm^{-2}) of $\Delta N_D(\phi)$ are 3×10^{-2} cm^{-1} at 0.5 MeV and 1.2×10^{-1} cm^{-1} at 0.7 MeV. This defect creation rate at 0.5 MeV, obtained with the results corresponding to a regime of conduction in the valence band, is ten times smaller than the defect creation rate obtained, in the other sample, from results in the hopping regime; this is not surprising in view of the facts that the concentrations N_A and N_D are not determined with a good accuracy and that approximations have been made for some of the parameters used (m^*, μ, α). The absolute value of the defect creation rate can only be known within a factor of 10; consequently it is necessary, in order to study the variation of the defect creation rate with various parameters (such as temperature and energy of irradiation), to use the same sample.

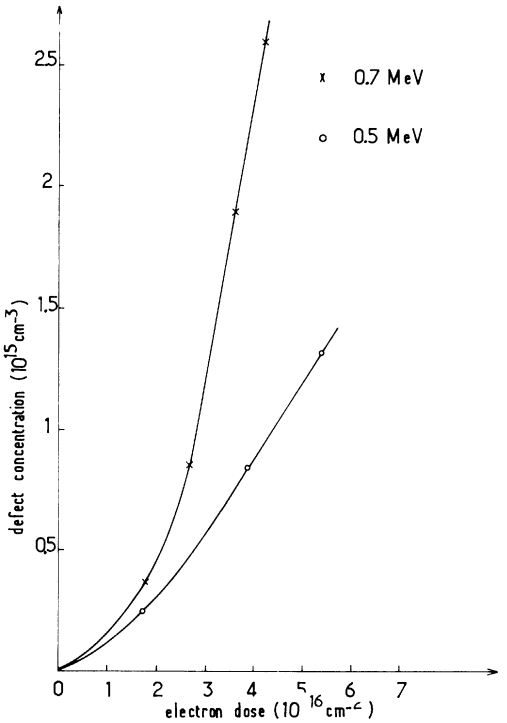

FIG. 5. Variation of the defect concentration introduced at 0.5 and 0.7 MeV with the dose of irradiation.

The variation of the defect creation rate with the temperature is obtained from the results given in Fig. 4 using formula 1 (since the measurements are performed at 12 °K). In the calculation the variation of N_D after each irradiation is taken into account. As shown in Table II this defect creation rate is nearly constant up to 100 °K; it decreases of about 25% at 200 °K. Such a decrease could be due to the fact that some of the defects anneal during the irradiation since the first recovery stage begins at 240 °K, as we shall see in Sec. IV.

The study of the variation of the defect creation rate with the energy of irradiation is the subject of another paper.[10]

IV. ANNEALING OF DEFECTS

A. Experimental results

In order to study the possible recovery stages of the defects created at 15 °K, we performed first isochronal annealing of the conductivity (measured at 12 °K) between 20 and 350 °K. As we discussed briefly in Sec. II the existence of traps, excited at low temperature by the irradiation, can also give rise to stages when they thermally release carriers; but they can be distinguished from the defect annealing stages because: (i) they are also produced by x-ray irradiation, low-energy-electron irradiation or uv illumination; (ii) they can be found again when the sample is reexcited at low temperature; (iii) they correspond to decreases of conductivity while the annealing of defects corresponds to increases of conductivity (in the particular sample used whose compensation is larger than 0.5). Figure 6 shows that after 0.7 MeV electron irradiation (curve 2) two stages, at 50 and 260 °K, appear in addition to the stages at 160, 230, and 300 °K (curve 1) due to the thermal release of carriers. A detailed study[13] of these stages allowed us to attribute the 260 °K stage to a defect annealing stage and the 50 °K stage to the thermal release of carriers from this defect. Indeed: (i) the 260 °K stage cannot be found again after a warming up to 300 °K followed by a new excitation at low temperature (and a subsequent iso-

TABLE II. Defect creation rate at 0.7 MeV.

Irradiation temperature (°K)	20	40	80	100	200
Creation rate (cm^{-1}) (± 0.05)	0.40	0.45	0.45	0.50	0.30

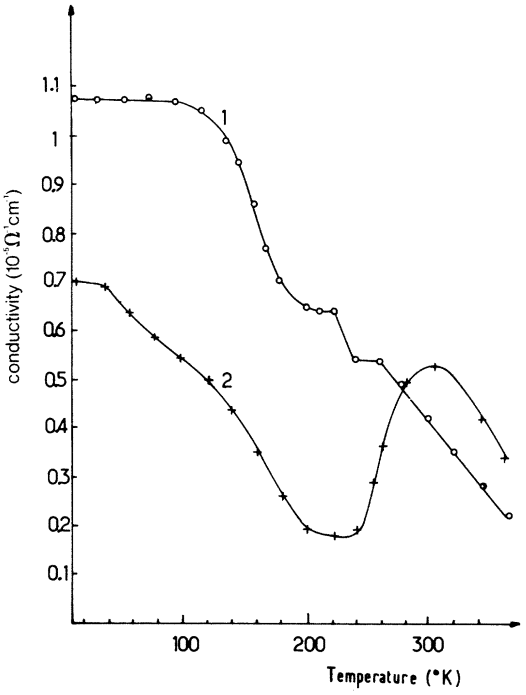

FIG. 6. Isochronal annealing (20 °K/10 min) of the conductivity measured at 12 °K of sample GE 48 after 0.7 MeV irradiation (curve 2) and uv illumination or x-ray irradiation (curve 1).

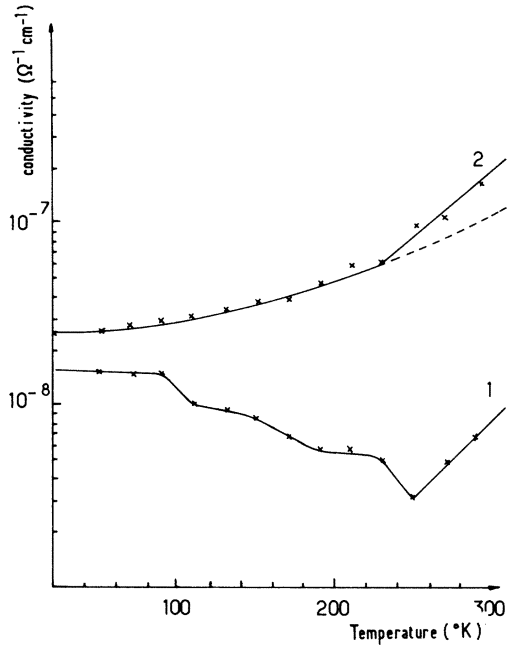

FIG. 7. Isochronal annealing (20 °K-10 min) of the conductivity measured at 12 °K before (curve 1) and after (curve 2) excitation by 150 keV electron irradiation.

chronal annealing); (ii) it corresponds to an increase of resistivity; (iii) the 50 °K stage corresponds to a decrease of conductivity and can be observed after warming up at 200 °K followed by a new excitation at low temperature; (iv) the 50 °K stage cannot be observed after warming up around 300 °K followed by a new excitation at low temperature; it is therefore connected to electrically active defects which recover between 200 and 300 °K, i.e., to the defects found at 260 °K.

In an attempt to eliminate the variation of conductivity due to the thermal release of carriers we made the measurements with the traps always in the same metastable state. For this we operated in the following way: after annealing at a given temperature the sample is cooled to 12 °K and measurements are taken (curve 1 of Fig. 7); then the traps are put back in the metastable state they had just after irradiation by a small irradiation of low-energy (150 keV) electrons (1 min of irradiation with a flux of 0.1 μA cm^{-2}) and the measurement is taken again (curve 2 of Fig. 7). The change of conductivity of the sample, once excited, should reflect, in principle, only the annealing of the defects. This is indeed observed: curve 2 (Fig. 7) exhibits only one stage, starting at 240 °K; the slight continuous increase of conductivity of this curve can be attributed to a cumulative effect of the excitation on the deep traps which are not de-excited at the annealing temperatures.

We have then studied the annealing kinetics of the 260 °K stage using isothermal annealings at different temperatures. Because changes of conductivity are not detectable around 260 °K the measurements have been done at 12 °K. Figure 8 shows the variation of the recovered fraction

$$a = (\ln\sigma - \ln\sigma_0)/(\ln\sigma_\infty - \ln\sigma_0) \quad (5)$$

(where σ_∞ is the conductivity once the annealing has been completed) at 255 °K. Figure 9 gives the variation of the annealed fraction at two temperatures $T_1 = 255$ °K and $T_2 = 270$ °K.

B. Discussion

If we assume that the annealing obeys a law

$$dN/dt = -KN^n \quad (6)$$

with $K = K_0 e^{-E/kT}$ (N defect concentration, n order of reaction, E activation energy for the annealing, K_0 jump frequency), then the order of reaction can be deduced experimentally from an isothermal curve by using the logarithmic form of Eq. (6):

$$\ln(da/dt) = n \ln(1 - a) + \text{const}.$$

$1-a$ has been plotted vs $\ln(da/dt)$ in Fig. 8. It appears that the slope of $\ln(da/dt)(1-a)$ is not constant, indicating that the recovery occurs through a diffusion process. At most it can be said that, for an unannealed fraction between 0.6 and 0.8, n is on the order of 3, which could be interpreted as a manifestation of the recovery of correlated pairs.[15]

The activation energy E for the recovery can be obtained from the results of Fig. 9 considering the reaction for the recovery under the form

$$dN/dt = -K_0 e^{-E/kT} f(N)$$

(since no order of reaction can be defined). The slopes R_1 and R_2 at two different temperatures T_1 and T_2, measured for the same value N_0 of N give E through:

$$E = k(T_1 T_2/T_2 - T_2)\ln(R_2/R_1). \quad (7)$$

The application of formula 7 in case of Fig. 9 gives $E = 1.3 \pm 0.2$ eV.

V. CONCLUSION

The defects introduced at 15 °K by electron irradiation in diamond have a threshold energy for displacement (35 eV) close to the theoretical value of the threshold energy for the creation of vacancy-interstitial pairs[10]; the total number of the defects created is in good agreement with the calculated number of vacancy-interstitial pairs.[10] Here we have found that these defects recover around 260 °K with an activation energy of 1.3 eV. The fact that this stage is the first recovery stage (assuming no stages in the temperature range 0–20 °K) corroborates the conclusion that this stage has to be attributed to the recombination of vacancy-interstitial pairs. The absence of a dependence of the defect creation rate upon the temperature below 150–200 °K suggests that, if there are close pairs, the barrier for the recombination of the interstitial in the vacancy is large compared to $kT \simeq 13$–17 meV. Some of these pairs could be correlated since the order of reaction seems to be equal to 3 during part of the recombination process.

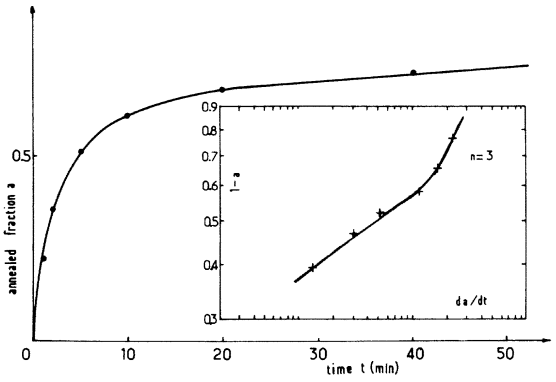

FIG. 8. Isothermal annealing of the logarithm of the conductivity at 260 °K.

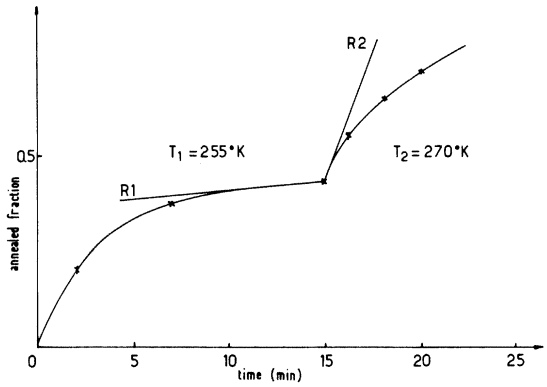

FIG. 9. Isothermal annealing of the logarithm of the conductivity at 255 and 270 °K.

The recombination occurs through the diffusion of one of the elements of the pairs. The element which becomes mobile is most probably the interstitial since the identification of the vacancy in the GR1 center which recovers around 800 °C is very reasonable. Another argument suggests that the defect which disappears in the 260 °K stage is indeed the interstitial: the interstitial is expected to be a donor and the study of the 50 °K stage (correlated with the disappearing defects) has shown that it is due to the thermal release of carriers from a donor level situated at about 20 meV below the conduction band.[13] Then the value of the activation energy for the diffusion of the interstitial is 1.3 eV. This activation energy being the same as in the two stages appearing above room temperature (300 and 500 °C), it is reasonable to conclude that, as suggested by Clark and Palmer,[4] these two stages are also due to the mobility of interstitials which escape trapping from impurities.[16]

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[1]For reviews on radiation damage in diamond see: C. D. Clark and E. W. J. Mitchell, *Radiation Effects in Semiconductors*, edited by J. W. Corbett and G. D. Watkins (Gordon and Breach, N. Y. 1971), p. 257; J. W. Corbett, Solid State Phys. Suppl. 7, edited by F. Seitz and D. Turnbull (Academic Press, N.Y., 1966), p. 144; E. W. J. Mitchell, *Physical Properties of Diamond*, edited by R. Berman (Clarendon, Oxford, 1965), Chap. 15.

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[12]P. J. Dean, E. C. Lightowlers, and D. R. Wright, Phys. Rev. 140, A352 (1965).

[13]The study of these traps through thermoluminescence and thermally excited conductivity will be the subject of another paper.

[14]As we shall see in Sec. IV, the first annealing stage of the defects introduced occurs around 260 °K. The heating is done in order to prevent the measurements to be perturbed by the thermal excitation of carriers (see Sec. II) without inducing defect annealing.

[15]A reaction having an order of 3 is equivalent to a $t^{-1/2}$ (t : time) dependence of the annealed fraction. As shown by Zizine [J. Zizine, *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum, New York, 1968), p. 186.], such a reaction is, for long enough times, characteristic of the recombination of correlated pairs through diffusion.

[16]In such a case the recovery is the sum of two processes: the detrapping of the interstitial from the impurity followed by the diffusion of the interstitial; this last process is the dominant one, therefore the only one observed, since the activation energy observed is the activation energy for the interstitial mobility.