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Model for the defect-related electrical conductivity in ion-damaged diamond

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Ion-damaged diamond, with a point-defect density smaller than a critical density of $10^{22}\,\mathrm{cm}^{-3}$, exhibits defect-related electrical conductivity that follows an Arrhenius pattern. Subsequent to isochronal annealing, the activation energies (ϵ_A) for this conductivity were found to increase from 0.35 to 1.15 eV as the annealing temperature (T_a) increased from 200 °C to 1200 °C. We present a quantitative explanation for this substantial increase that is based on the fact that when a vacancy in diamond is neutral, it has a deep localized state occupied by an electron with higher-lying states, which may trap an additional electron, resulting in higher-lying energy *levels* within the band gap. These states may form an energetically higher-lying *band* (the D^- band) in which electrical conduction may take place. The energy gap between the Fermi level and the mobility edge of the D^- band is related to the observed ϵ_A. Since both the shift of the Fermi level and the width and shape of the D^- band depend on the density of defects, the observed ϵ_A depends on the defect concentration, i.e., the degree of defect annealing. This model can account for the experimentally observed variation of ϵ_A with T_a. It can also explain some of the measured large varieties of activation energies reported for diamond ion-implanted with dopant atoms (which were previously interpreted as representing different energy states of the dopants) as attributed to unannealed residual implantation-related defects. The present model should be generally applicable for the description of electrical conduction in wide band-gap semiconductors with deep defect levels inside the forbidden energy gap.

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I. INTRODUCTION

The doping of diamond remains a complicated and problematic issue in diamond technology. This is mainly due to the high formation energy of most potential dopant impurities, but is also related to native defects that may be electrically active.[1] These issues are of particular relevance for the case of diamond doping by ion implantation, where implantation-related defects are inherently introduced into the lattice. The ion energies commonly used for ion-implantation doping are high enough to displace many carbon atoms from their lattice site, thus creating many vacancies and interstitials. Vacancies in diamond can be considered as amphoteric impurities (of either *p* or *n* type) since their charge state depends on the position of the Fermi level.

In intrinsic type-IIa diamond the vacancies are predominantly in the neutral charge state, giving rise to the so-called GR1 absorption line.[2] In semiconducting *p*-type B-doped diamond (where the Fermi level lies about 0.37 eV above the valence band) vacancies act as deep donors, increasing the compensation ratio. It was recently shown[3] that vacancies effectively compensate the boron acceptors in *p*-type diamond, indicating that they preferentially exist in the positive charge state (V^+). The GR1 absorption due to neutral vacancies in irradiated B-doped diamond has been shown to be very weak as long as there are some boron acceptors uncompensated by vacancies.[4] This supports the assumption that vacancies are the compensating donors in diamond. In nitrogen-containing, type-I diamond, for which the Fermi level lies about 1.7 eV below the conduction band, vacancies exist in both the neutral (V^0) and negative (V^-) charging states. Reversible charge transfer between V^0 and V^- was found to occur upon annealing.[2] The effects of native defects on the optical properties of different types of diamond have been extensively studied, and are reviewed in the literature.[2,4]

Recently, we have reported that native defects introduced into type-IIa diamond by ion-induced damage give rise to thermally activated electrical conduction with a wide range of activation energies that depend on defect concentration.[1] This conductivity is always characterized by extremely low mobilities, hence it cannot be used for most device applications. However, it may be mistaken for real chemical doping, especially during the search for new potential dopants, for which the expected activation energy is unknown.

In the present paper we present a model that describes the nature of the defect-related conductivity in ion-damaged diamond and quantitatively explains the dependence of its activation energy on defect concentration. After a review of the relevant experimental results in the next section, we will give the theoretical background and predictions in Sec. III. In Sec. IV we will apply these ideas and present *ab initio* computations for the energetics involved in the formation of charged vacancies in diamond. As will be summarized in our conclusion the computations support the predictions and experimental results.

II. EXPERIMENT

We have recently investigated[1] thermally driven changes in the activation energy of the electrical conductivity in type-IIa diamond damaged by C-ion implantation to doses below the critical damage level (N_C) of 10^{22} vacancies/cm^3.[5] In particular, we followed the temperature dependence of the electrical resistivity of diamond, damaged to the total con-

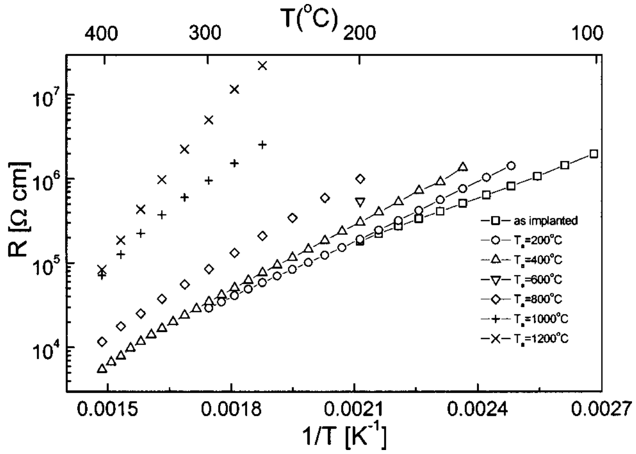

FIG. 1. Temperature dependencies of the logarithm of the resistivity, ρ, of slightly damaged diamond after annealing at T_a as a function of $1/T^{-}$. The linear dependencies demonstrate the activation behavior of the conductivity. The increase in slope of the lines for increasing T_a is indicative of a gradual increase in activation energy upon annealing. (See Ref. 1.)

centration of vacancies of $8\times10^{21}\,\mathrm{cm}^{-3}$ (i.e., below N_C) and subjected to annealing at temperatures (T_a) increasing from room temperature to 1200 °C. The measured temperature dependencies of the electrical resistivity, ρ, determined in the experiment are plotted in Fig. 1. From this figure it can be seen that when the data are plotted as $\log\rho$ vs $1/T$, they follow a linear dependence, indicating a thermally activated behavior of the conductivity. Moreover the activation energy of the conductivity increases with increasing T_a, i.e., with decreasing defect concentration. Activation energies ranging from 0.35 up to 1.15 eV for annealing temperatures 200 °C–1200 °C were deduced, as shown in Fig. 2. We have also found that no Hall effect could be measured, even for the more conductive samples, at any temperature (up to 500 °C), presumably because of the very low carrier mobility.

III. THEORETICAL BACKGROUND AND PREDICTIONS

The above-described experimental results are unusual, insofar as the measured activation energies span an extremely wide range. We now present an explanation for this observation within the theory of impurity band conduction. We start by briefly reviewing those aspects of this theory that are relevant to the present model. For simplicity, we will consider electron conduction, however, the same picture should also be applicable for the case of hole conduction, as will be discussed below.

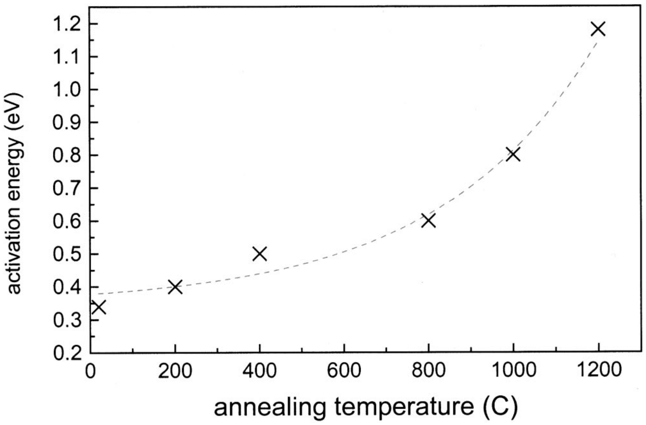

FIG. 2. Activation energy of the conductivity as extracted from the slopes of lines in Fig. 1, plotted as a function of annealing temperature. The dotted line is drawn to guide the eye.

The temperature dependencies of the conductivity in semiconductors are given quite generally by the following expression:[6]

$$\sigma(T)=\sigma_1\exp\left(-\frac{\epsilon_1}{kT}\right)+\sigma_2\exp\left(-\frac{\epsilon_2}{kT}\right)+\sigma_3\exp\left(-\frac{\epsilon_3}{kT}\right), \tag{3.1}$$

where $\sigma_1,\sigma_2,\sigma_3$ are nearly independent of T and $\epsilon_1,\epsilon_2,\epsilon_3$ are activation energies associated with three different conduction mechanisms. The first term represents band conduction, with ϵ_1 being of the order of the donor ionization energy, E_D. The second term, which is connected with conductivity in a defect-related band, will be the subject of extensive discussion below. The third term represents hopping conduction (denoted by HC) between nearest-neighbor donors, which dominates at low temperature and is due to phonon-assisted electron or hole hops from occupied to unoccupied sites within the band gap. This can only occur if some neighboring vacant sites, such as those resulting from compensation, are available. This conduction has a characteristic activation energy ϵ_3, which is small compared to ϵ_1. The electron mobility characteristic for this conduction mechanism is very low due to the localization of the electrons and their motion by tunneling between sites.

Neither band conduction nor HC appear to be suitable for describing the experimentally observed conductivity for the following reasons:

1. Hopping conductivity is unlikely in the case of damaged diamond because the rather high activation energies found here cannot be accounted for theoretically. According to Ref. 6, the maximum activation energies for hopping conductivity for low compensated semiconductors (when the compensation ratio $K=N_A/N_D\ll1$) are given by $0.99e^2N_D^{1/3}/\chi$ where N_A is the concentration of acceptors, N_D that of donors, and χ is the dielectric constant of the material. This yields a maximal activation energy of about 0.5 eV, even for the highest defect concentration N_D of $8\times10^{21}\,\mathrm{cm}^{-3}$. This value is much lower than most of the activation energies experimentally found in damaged diamond.

2. According to the theory of hopping conductivity the activation energy has to *decrease* with decreasing defect concentration, in contrast to the experimentally observed increase.

3. It is implausible to explain the observed dependence of the activation energies on annealing temperature (i.e., on residual defect concentration) in terms of free-carrier conductivity in the conduction band due to the extremely low carrier mobilities found experimentally.

Thus an alternative explanation for the experimentally observed electrical properties of ion-damaged diamond has to be found. We now present one in terms of conduction in the D^- band,[6,7] presumably due to negatively charged donors, which leads to the second term in the expression for $\sigma(T)$ given above.

The D^--band conductivity is attributed to the motion of electrons over singly occupied neutral donors D^0. If the donor level is deep enough, such a defect can trap an additional (extra) electron, forming the D^- center. Electron transport under certain conditions (very low compensation) may occur due to electron activation from an occupied donor to a nearest-neighboring occupied donor and movement in the D^- band. It should be noted that the model described here is also valid for the case of hole conduction due to hole activation from a neutral acceptor A^0 (i.e., occupied with a hole) to a nearby occupied acceptor, forming an A^+ center. We assume the conduction to be by electrons on donor states, however, as will be discussed below, the experimental results on the conductivity in damaged diamond alone cannot discriminate between hole or electron conduction, and the proposed model applies to both.

The model of D^- centers, for shallow hydrogenlike defects, has been successfully applied to explain the results of some experiments related to impurity conduction, luminescence spectra, photoconduction, etc.[7] It has also been applied more recently to explain experimental results on hopping magnetoresistance.[8] Nishimura[9] discussed the conduction in antimony-doped Ge with small compensation in terms of the D^--band conduction in which the activation energy is given by the energy gap between the Fermi level and the bottom of the D^- band.

In Secs. III A and III B below we describe, in general terms, the essentials of the model, while in Sec. IV we consider the suitability of this conduction mechanism to quantitatively describe the experimentally observed conductivity for the case of lightly damaged diamond.

A. Activation energy for D^--band conduction

We use below well-measured quantities such as the ionization energies E^- and E^0 of negative and neutral charged defects rather than quantum-mechanical energies of various many-electron states. The formulas of the statistics of multivalent centers[10] may be written as

$$N^- = \frac{g^-}{g^0} N^0 \exp\left(\frac{E^- - E_F}{kT}\right). \tag{3.2}$$

Here N^- and N^0 are the densities of the negatively charged and neutral defects, respectively, and g^- and g^0 are degeneracy factors of these charge states. The Fermi energy E_F is measured with respect to the bottom of the conduction band E_C so that $E_F > 0$ for E_F located below E_C. Note that the above expression does not depend on the possibility of describing the energetic structure of any defect in a one-electron way, nevertheless, the above expression is similar to that which describes the occupation number of one-electron states with energy E^- and with density of states N (given by $N = g^-/g^0 N^0$). This is the reason why we are using the one-particle description for the states under consideration. The energy E^- differs from E^0 due to the Coulomb repulsion between the two electrons, the exchange interaction of the two electrons, and the lattice distortion caused by the additional electron. Usually[6–8] the difference between E^0 and E^- is called the correlation energy $U = E^0 - E^-$ (see Fig. 3 for a schematic representation of these quantities).

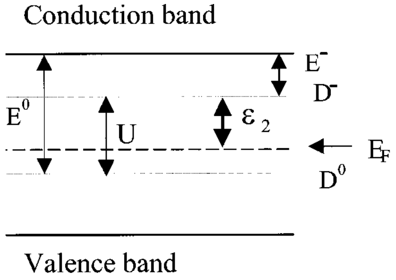

FIG. 3. Schematic drawing of the energy states for a neutral donor (D^0) and a negatively charged donor (D^-). The ionization energies E^0 and E^- of D^0 and D^- states, respectively, and the correlation energy U are indicated with arrows. The energy of activation of the D^- state, ϵ_2, is also shown.

We will now discuss in detail the case $U > 0$ that corresponds to the electronic states of a vacancy in diamond. Note that the expression for N^- reflects the specifics of these states, namely, that states with binding energy E^- do not initially exist in the band, but appear only on those donors that were previously in the neutral state. The activation energy of the E^- state is $\epsilon_2 = E_F - E^-$, and therefore ϵ_2 depends on donor concentration just as do E^- and/or E_F. We now consider these dependencies in detail. First, the binding energy E^- depends on impurity concentration through the quantum-mechanical broadening, caused by the overlap of the wave function of E^- states at neighboring donors, thereby leading to the formation of a D^- band of *delocalized* states. This broadening has been accurately calculated[6] for the case in which the defects are regularly ordered (i.e., on a diamondlike sublattice), yielding a shift of the bottom of the band from the position of the E^- level of an isolated defect by $4Y$, where Y is the overlap integral and the factor 4 is due to the number of nearest neighbors in the diamond lattice. Since the one-electron state with energy E^- is a localized state created by a neutral impurity center D^0, the overlap integral is given by

$$Y = E^- a N^{1/3} \exp\left(-\frac{1}{aN^{1/3}}\right), \tag{3.3}$$

where a is the localization radius of the state with binding energy E^-. For the physically realistic case in which the defects are randomly arranged in the lattice, the above holds for high concentrations when $Na^3 > 0.02$. It is obvious that for low concentrations[6] (where $aN^{1/3} < 1$), the decrease in ϵ_2 is very small due to the exponential dependence of Y on N, and thus has to be taken into account only for the highest donor concentrations.

Second, the position of the Fermi level is determined by the neutrality condition. If the compensation, K, is so small that

$$K \ll \exp\left(-\frac{|E^{0,-} - E_F|}{kT} \right), \tag{3.4}$$

the presence of ionized defects due to compensation can be neglected. In this case the neutrality condition is $N^- = N^+$, and N^+ is, according to Ref. 10,

$$N^+ = \frac{g^+}{g^0} N^0 \exp\left(\frac{E_F - E^0}{kT} \right). \tag{3.5}$$

Here g^+ is the degeneracy factor of positively charged donor states. The position of the Fermi level does not depend on defect concentration and is given by

$$E_F = \frac{1}{2} \left[E^0 + E^- - kT \ln\left(\frac{g^+}{g^-} \right) \right], \tag{3.6}$$

or [neglecting the term $kT\ln(g^+/g^-)$]

$$E_F = E^0 - \frac{U}{2}. \tag{3.7}$$

This ideal case of zero compensation and the D^- band of delocalized states was investigated by Nishimura.[9] In this case the activation energy is expressed by

$$\epsilon_2 = \frac{U}{2} - 4Y. \tag{3.8}$$

It should be noted that while the dependence of ϵ_2 on donor concentration is well described by the above expression, the absolute values of the activation energies calculated according to this formula are more than twice as large as the measured value.[9] For the more realistic case, in which $K \neq 0$, the position of the Fermi level will depend on defect concentration, hence, a correction to this expression should be introduced.

When $K \gg \exp(-|E^{0,-} - E_F|/kT)$ the number of defects ionized by compensation $(2KN_D)$ is higher than the number of thermally ionized ones. Hence, the Fermi level will be located near the donor level. The position of E_F depends on the concentration of major impurities (defects) according to

$$-E_F + E^0 = 0.99 \frac{e^2 N_D^{1/3}}{\chi}. \tag{3.9}$$

This holds for temperatures and compensation that match the requirement

$$1 \gg K > \exp\left(-0.99 \frac{e^2 N_D^{1/3}}{\chi kT} \right), \tag{3.10}$$

which are compatible with the conditions of the present experiment.

Summarizing the above leads to the final equation for the activation energy ϵ_2 and its dependence on donor concentration, N_D,

$$\epsilon_2 = \left(E^0 - 0.99 \frac{e^2 N_D^{1/3}}{\chi} \right) - E^- - 4E^-(Na^3)^{1/3} \exp[-(Na^3)^{-1/3}]. \tag{3.11}$$

[Note that this expression is approximated by Eq. (3.8) above in the ideal case as studied in Ref. 9.] Here and below, $N = N_D(1-K)$ within an accuracy of g^-/g^0. The expression [Eq. (3.11)] can be rewritten as

$$\epsilon_2 = U - 4E^-(Na^3)^{1/3} \exp[-(Na^3)^{1/3}] - 0.99 \frac{e^2 N_D^{1/3}}{\chi} \tag{3.12}$$

using the concept of correlation energy.

It is obvious that the activation energy ϵ_2 depends on donor concentration and *increases* as N_D *decreases*. Indeed, as N_D decreases, the Fermi level moves toward the level E^0, the D^- band shrinks, and ϵ_2 *increases*. The various energies involved in the above discussion are schematically illustrated on the left side of Fig. 4.

In order to be able to evaluate the values of ϵ_2 for a wide range of defect concentrations, as encountered in the present experiment, we have to bridge between the two extreme cases, which can be calculated explicitly, namely, the case of reasonably high concentrations, which we have described above and that of low concentrations. The second case of low defect concentrations can be dealt with in classical terms since classical long-range potential fluctuations dominate. These fluctuations will destroy the delocalization. In this limit ϵ_2 is related to defect concentration by

$$\epsilon_2 = U - \epsilon_p(N_D, K) - 0.99 \frac{e^2 N_D^{1/3}}{\chi}. \tag{3.13}$$

This expression differs from the expression for ϵ_2 given in Eq. (3.12) in that the band of extended states (with a width of $8Y$) does not exist. Instead of the $4Y$, a percolation threshold, ϵ_p, in the classical potential determines the minimum activation energy required to give rise to the hopping conduction.[11] As the potential has a typical energetic scale of $e^2 N_D^{1/3}/\chi$ the most general expression for ϵ_p is given by

$$\epsilon_p = f(K) \frac{e^2 N_D^{1/3}}{\chi}. \tag{3.14}$$

The explicit form of $f(K)$ is known for the case of very low compensation $(K < 10^{-4})$ and is given by[6,11] $f(K) = 0.3K^{1/4}$. In this case the corrections to E_F due to the long-range fluctuations are negligible as they are of the order of $e^2 N_D^{1/3} K^{1/2}/\chi$ and, hence, much less than ϵ_p for $K \ll 1$.

Since the overlap integral Y decreases exponentially as N_D decreases and ϵ_p only decreases as some power of N_D, the following interpolation formula can be written:

$$\epsilon_2 = U - 4E^-(Na^3)^{1/3} \exp[-(Na^3)^{1/3}] - \frac{e^2 N_D^{1/3}}{\chi}(0.99 + 0.3K^{1/4}). \tag{3.15}$$

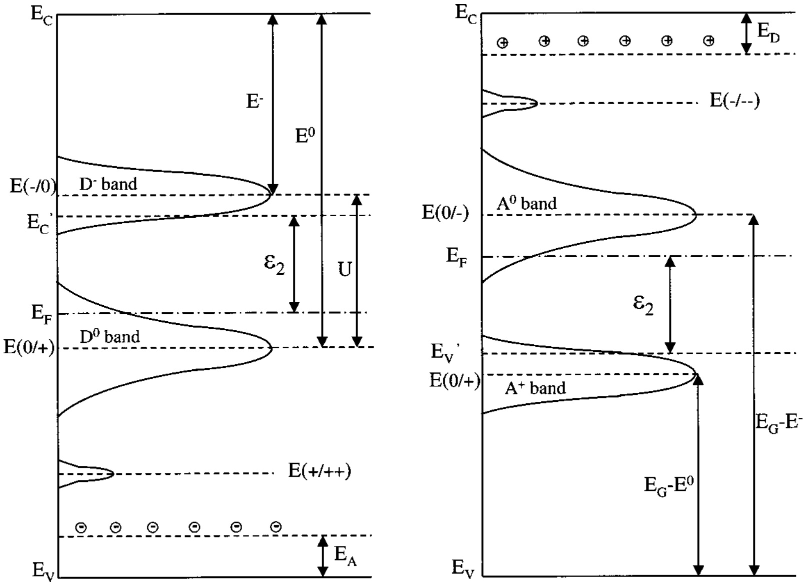

FIG. 4. Bands of localized states induced by neutral vacancies. On the left the major impurity is an acceptor, E_A is the acceptor's hole binding energy, and all acceptors are ionized since $N_A \ll N_V$. E_C' is the mobility edge (percolation threshold) in the D^- band. Electrons occupy all states below E_F. On the right the major impurity is a donor, E_D is the donor's electron binding energy, and all donors are ionized since $N_D \ll N_V$. E_V' is the percolation threshold in the A^+ band. Holes occupy all states above E_F.

Although one could expect that this expression only holds for very small values of K, comparison with the results of the numerical computations of the dependencies $\epsilon_p(K)$ and $E_F(K)$ on K for any compensation K (Ref. 6) shows that the above approximate expression yields rather accurate results (deviating by no more than 10%) even for K values as large as 0.5. (The numerical computations[6] were performed for $0<K<1$ in connection with modeling of the impurity band and with investigation of concentration dependence of activation energy for ϵ_1 conductivity.)

B. Transport in the *D* band

It is clear from the above that the number of electrons in the D^- band is small at reasonable temperatures compared to the number of empty places in the D^0 band since $\epsilon_2 > \epsilon_3$ [$\epsilon_3 = e^2 N_D^{1/3}(0.99-0.3K^{1/4})/\chi$ (Ref. 6)]. Nevertheless, the conduction throughout the D^- band can be favored over hopping between empty states in the D^0 band if the states in the D^- band are delocalized.[7] This holds for[6] $\epsilon_p < Y$, $Na^3 > 0.02$, and $Na_0^3 < 0.02$ (a_0 is the localization radius of the E^0 state). These limitations are rather strict and are satisfied only in a limited range of defect concentrations, N_M, near the Mott transition point $N_M a_0^3 = 0.02$.[7] However it can be shown[12] that carriers in the D^- band have substantially higher mobility than when hopping over empty states in the D^0 band, even when localized. The reason for this effect is a lattice distortion in the vicinity of a defect.[13] If D_i^- and D_j^- are two distinct states in the D^- band, then the transition rates within the D^- band (i.e., $D_i^- + D_j^0 \geqslant D_i^0 + D_j^-$) can exceed those that govern the conduction in the D^0 band (i.e., $D_i^+ + D_j^0 \geqslant D_i^0 + D_j^+$) because of differences in the local distortion (lattice relaxation) around differently charged defects.[12] This effect was not taken into account in previous studies of the ϵ_2 conductivity[7–9] where only shallow levels were considered. It is thus conceivable that despite the smaller number of electrons in the D^- band than in the D^0 band, at a given temperature (decreasing exponentially as T decreases), electron hopping in the D^- band can exceed the D^0-hopping conductivity. Furthermore, at a given temperature, conduction with the D^- band can win the competition with conduction in the conduction band, which has a larger mobility but a substantially lower electron concentration, since $\epsilon_1 > \epsilon_2$.

IV. APPLICABILITY OF THE D^--CONDUCTION MECHANISM TO DAMAGED DIAMOND

We now proceed to demonstrate that the concepts presented above can account for the observed electrical conductivity in ion-damaged diamond and its peculiar dependence on defect concentration (annealing). In particular, we have to show that the dominant defect can bind an extra electron (or hole) and that the creation of a D^- (or an A^+) center is plausible in damaged diamond. We also have to show that all states under consideration lie within the forbidden gap, and hence the conduction mechanism described above is applicable. Our model is based on the following assumptions and theoretical arguments:

1. We assume that C-ion implantation to doses below the critical dose creates defects similar to those due to electron and proton irradiation, i.e., mainly single vacancies will be preferentially formed. This assumption is based on our previous study[3] showing that the effect of proton irradiation on the electrical properties of semiconducting diamond is quite similar to that caused by electron irradiation, despite the fact that protons are 2000 times heavier than electrons. Heavier-ion bombardment (like bombardment with C ions, which is 12 times heavier than with protons) will, most probably, lead to the appearance of the same type of point defects, although the creation of other complex defects is also possible. A similar conclusion was also reached by Prins[14] for the case of oxygen-implanted diamond.

2. We show, theoretically, that vacancies, which can, in principle, exist in diamond in several charge states, are pre-

dominantly present in undamaged type-IIa diamond in the neutral state.

3. We show that the neutral vacancy (V^0) in diamond can bind an additional electron or hole (depending on the position of the Fermi level), thus forming a negatively or positively charged vacancy (V^- or V^+) with binding energies lying within the forbidden gap.

A. The charge states of vacancies in damaged type-IIa diamond

As presented above, the proposed conduction mechanism in ion-damaged diamond is that of electron (hole) motion in the D^- (A^+) band. In order to be able to apply this model to explain the experimental conductivity data for damaged diamond, it is imperative to estimate the probabilities of obtaining the required vacancy states and to evaluate the energetics involved in their formation. To this end, we have performed first-principles *ab initio* computations based on density-functional theory[15] as described below.

Nonlocal norm-conserving pseudopotentials were constructed using the Troullier-Martins[16] procedure, and were implemented in the fully separable form of Kleinman and Bylander.[17] With this choice of pseudopotentials, a kinetic-energy cutoff of up to 50 Ry leads to excellent convergence with respect to the plane-wave basis.

Supercells of 128 atoms in a diamond structure were used, and the special k point proposed by Makov, Shah, and Payne[18] has been employed. No symmetry was assumed for the atomic relaxation. Both local-density approximation[19] and generalized-gradient approximation[20] were used for the exchange-correlation functionals. Similar results were obtained with these two approximations, using the same functional for the pseudopotential generation and the plane-wave calculations. The code used is FHI98MD (Ref. 21) from the Fritz Haber Institute. The formation energy, E^f, of a vacancy in charge state q can be calculated from

$$E^f(q,E_F)=E^{\mathrm{tot}}_{N-1}(q)-\frac{N-1}{N}E^{\mathrm{tot}}_{\mathrm{bulk}}+qE_F, \tag{4.1}$$

where $E^{\mathrm{tot}}_{N-1}(q)$ and $E^{\mathrm{tot}}_{\mathrm{bulk}}$ are the total energy of the sample with $N-1$ atoms ($N=128$) and a vacancy in charge state q and the total energy of the bulk supercell containing N atoms of carbon, respectively. E_F is the Fermi level, measured with respect to the valence-band maximum. The correction to the top of the valence band was introduced for each charge state,[22,23] and was found to be very small compared to the formation energies calculated here. In Fig. 5 we show the formation energies of a vacancy in diamond in its various charged states (V^{++}, V^+, V^0, V^-, and V^{--}) as a function of the Fermi level, calculated from Eq. (4.1).

As can be seen from Fig. 5, for intrinsic diamond (with the Fermi level in midgap) the most abundant charge state is the V^0 state. For slightly n-type diamond, as is expected to be the case for all natural diamonds (even well-selected type-IIa) due to the unavoidable nitrogen contamination (with a deep donor level at 1.7 eV below the conduction-band edge), the Fermi level will lie above the midgap. In this case, V^0 and V^- are expected to be the most abundant charge states of the vacancy.

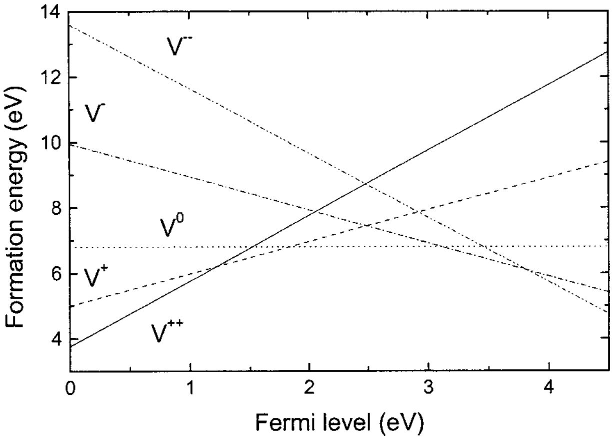

FIG. 5. Formation energies for a vacancy in slightly damaged diamond at different charge states as a function of the Fermi level E_F, measured with respect to the top of the valence band E_V.

The energy required to change the charge on a vacancy from q_1 to q_2 [$E(q_1/q_2)$] is the value of the Fermi energy where the formation energies of the two charge states, q_1 and q_2, become equal. From the crossing points of the appropriate lines in Fig. 5 we find that $E(+/0)=1.9$ and $E(0/-)=3.05\,\mathrm{eV}+E_V$, where E_V is the top of the valence band. The correlation energy (U) associated with the appearance of a negatively charged vacancy V^- is given by the difference between the corresponding ionization energies, i.e., $U=1.15\,\mathrm{eV}$. Justification for this statement is given in the Appendix.

From Fig. 5 one can conclude that the ground states at different charge states are located within the gap of diamond, as required by our theoretical model (see above). Moreover, it was proven in Ref. 24, by a configuration interaction including a model with many-body effects, that the excited states of a vacancy in diamond are also located within the band gap.

It has to be mentioned that calculations similar to ours have been carried out by Bernholc *et al.*[25] with far smaller samples of only 16 and 32 atoms. The formation energy of the neutral vacancy in diamond was found in Ref. 25 to be 7.2 eV, in good agreement with the 6.9 eV found in the present work. A value of $U=0.6\,\mathrm{eV}$ was found by these authors,[25] which is rather small compared to the value of U (1.15 eV) found here. To investigate the reason for this large discrepancy and to see if it has to do with the substantially smaller sample used in Ref. 25, we have recalculated U with a supercell of 64 atoms, and a $2\times2\times2$ Monkhorst-Pack k point.[26] These calculations yielded a value of $U=0.85\,\mathrm{eV}$ showing that U converges to higher values when larger samples are used in the computations. Further proof for this is found in a recent paper[27] in which the convergence of first-principles supercell calculations as a function of the size sample has been demonstrated, for the case of a vacancy in Si. According to Ref. 27 the calculated values for the correlation energies in Si coincide with the experimentally measured values. This is in spite of the fact that the absolute positions of the ionization levels do not coincide with experimental ones even for the largest supercell used in these calculations. Hence, this supports the value of $U=1.15\,\mathrm{eV}$ found here, for the case of the vacancy in diamond.

B. Hole and electron conduction analogy

As shown in the Appendix a vacancy in diamond is an amphoteric defect. Whether it will act as a donor or an acceptor depends on the presence and type of compensating impurities. If the major *impurities* are *acceptors* (for example, due to accidental boron), the Fermi level will be located in the upper half of the V^0 band and neutral vacancies will act as neutral donors, while when negatively charged they will act as D^- centers, as described above in Sec. III.

The complementary picture in which the *compensating impurities* are *donors* (e.g., nitrogen) can be described in a similar way. Now the Fermi level is located in the lower part of the V^- band with most of the band empty of electrons, i.e., filled with holes. These holes have binding energy $E_G - E^-$ (see the Appendix). In this case a neutral vacancy V^0 is analogous to a neutral acceptor A^0 for which the nonbonding hole is attracted to the nuclear charge. A positively charged vacancy V^+ is analogous to an A^+ center and has an additional hole. This hole is localized by the potential of a neutral defect A^0 with binding energy $E_G - E^0$ and $E_G - E^0 < E_G - E^-$, since $E^0 - E^- \equiv U > 0$. The ϵ_2 conduction is associated with the motion of holes over the E^0 states. These holes are activated from empty E^- states to the mobility edge in the A^+ band. The situation is described in Fig. 4. On the left side, the case when the compensating impurity is an acceptor is shown and on the right side, the case of compensation due to donors is demonstrated.

C. Comparison with experiment

The present data, which are sensitive only to the energetics related to transitions between different charge states of the vacancies, cannot distinguish between the above two pictures. Both, however, yield an activation energy for electrical conductivity in damaged diamond that *increases* as the number of defects *decreases*.

Figure 6 shows the dependence of ϵ_2 on vacancy concentration (N_V) as calculated according to Eq. (3.15). (We have used the relations and values $N_D \equiv N_V$, $N = N_V(1-K)$, and $E^- = 1.9\,\mathrm{eV}$, and the number of compensating impurities is $N_K = 10^{16}\,\mathrm{cm}^3$. The results are almost independent of the exact value of E^- since variations in E^- are compensated by small variations of a.) Two parameters that enter into the numerical calculations, namely, the initial number of vacancies (N_{init}) prior to annealing and the localization radius a are not known accurately. It is reasonable to assume a value of N_{init} that is close to that predicted by the transport of ions in matter (TRIM) (Ref. 28) for the damaging implantation. Figure 6 shows the results of calculations using Eq. (3.15) with $N_V = 8 \times 10^{21}$ vacancies/cm^3 for several possible values of a. It is obvious from the figures that the activation energy starts at a very high value and decreases monotonically with increasing defect concentration covering a wide range of energies ranging from about 1.15 eV for low vacancy concentrations to about 0.3 eV (depending on the values used in the calculations) for high concentration of defects. Thus the experimentally observed trend is very well reproduced by the proposed model.

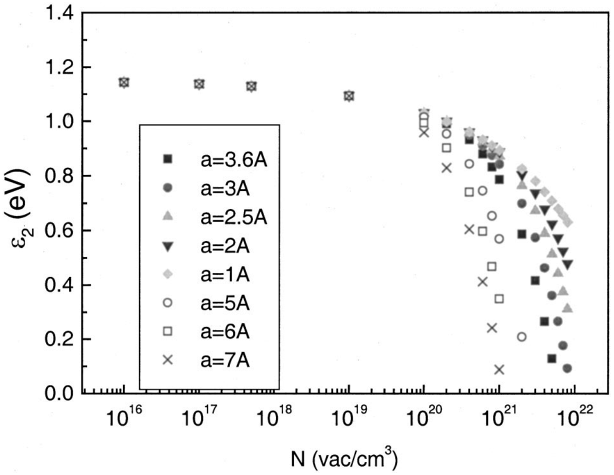

FIG. 6. The dependence of activation energy ϵ_2 on vacancy concentration N_V calculated as functions of N_{init} for several values of a. See the text following Eq. (3.15) for more details.

V. CONCLUSIONS

By invoking conduction in an energy band formed by negatively charged vacancies (the D^- band), we have explained the very large variation in activation energies, measured for diamond damaged by carbon-ion implantation following annealing at different temperatures (ranging from 0.35 eV for as-implanted to 1.15 eV for diamond annealed at 1200 °C). The energies required for exciting electrons into this band depend on its position and width relative to the Fermi level, which, in turn, was shown to depend on the density of defects, i.e., the degree of annealing of the diamond.

Good agreement with the experimental results was obtained. Transport experiments such as those described here are independent of the exact location of the levels involved within the gap. Only *differences* in energies can be observed, but the conductivity type (whether due to hopping of holes or electrons) cannot be determined experimentally.

It is important to note that there is nothing specific in the present model that makes it applicable only to the case of damaged diamond, i.e., the peculiarity of diamond, with its metastable sp^3 bonding with respect to the stable sp^2 bonding and their extremely different electronic properties, is not involved in the present model. Hence, this model should also apply to conduction in other damaged wide band-gap semiconductors if they have defects (vacancies) in different charge states located within the gap among which electron or hole hopping can take place. The conduction in other damaged wide band-gap materials, such as GaN, AlN, SiC, SiO$_2$, or even ternary wide band-gap semiconductors, may thus also be described by the present model.

The case of binary wide band-gap semiconductors may, however, be more complicated than the present case of a monoelemental wide band-gap semiconductor (diamond) due to the larger variety of possible point defects (related to anions and cat-ions). Nevertheless, the general principle invoked here, namely, that of hopping of carriers between differently charged native defects, could also hold for these materials. The existence of defect-related electrical conductivity and the dependence of its activation energies on defect concentration in materials other then diamond has not yet been observed, to the best of our knowledge, hence it awaits verification by future experiments.

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APPENDIX

Here we show that vacancies in diamond can have a charge, q, that is of either positive or negative type. This Appendix uses notation developed in Sec. IV A above. By definition,[10,13] the (hole/electron) ionization energy $E(q/q\pm1)$ of a defect is equal to the difference of total energies of the system in the final state of charge $q\pm1$ and the initial state of charge q. If the electron-ionization energy $E(q/q+1)$ and the hole ionization energy $E(q/q-1)$ are less than the forbidden gap, E_G, the defect in the $q-$ charge state is an amphoteric one.

It follows from Eq. (4.1) that the ionized energy $E(q/q\pm1)$ for a system of $N-1$ atoms and one defect is given by the expression $E(q/q\pm1)=E^{\mathrm{tot}}_{N-1}(q\pm1)-E^{\mathrm{tot}}_{N-1}(q)$. It is connected to $E^f(q,E_f)$ (the formation energy of defects in different charge states) at a given value of the chemical potential, E_F, by the expression

$$E(q/q\pm1)=E^f(q\pm1,E_F)-E^f(q,E_F)-(\pm E_F). \quad \text{(A1)}$$

Since E_F is measured with respect to the top of the valence band, this expression gives the value of the hole ionization energy $E(q/q-1)$. The electron-ionization energy is equal to $E_G+E(q/q+1)$.

Let us now consider several cases in more detail. It is more convenient to use values of the Fermi energy where the formation energies of the two charge states q and $q+1$ (or $q-1$) become equal. Here, $E(q/q-1)=E_F$ and $E(q/q+1)=-E_F$. These values are determined by the crossing points of appropriate lines in the plot of formation energy as a function of Fermi energy (see Fig. 5). Specifically, the electron-ionization energy, $E^0=E_G+E(0/+)$, since E^0 is defined by the transition of an electron from a neutral vacancy to the conduction band: $V^0\rightarrow V^+ + e$. Thus, the neutral vacancy V^0 is a simple donor D^0 with an electron binding energy of $E^0=3.6\,\mathrm{eV}$. The hole ionization energy $E(0/-)$ is defined by the transition $V^0\rightarrow V^- + h$. Thus the neutral vacancy V^0 is a simple acceptor A^0 with hole binding energy $E(0/-)=3.05\,\mathrm{eV}$. Since according to our calculations E^0 and $E(0/-)$ are less than E_G, *a neutral vacancy in diamond is an amphoteric defect*.

Furthermore, the electron-ionization energy of a negatively charged vacancy is defined by the transition $V^-\rightarrow V^0 + e$ and $E^-=E_G+E(-/0)$. In other words, a negatively charged vacancy V^- is an analog of a D^- center with the electron binding energy $E^-=2.45\,\mathrm{eV}$, with respect to such a transition. The transition $V^+\rightarrow V^0+h$ is suitable for ionization of the hole held by an empty state E^0, i.e., a positively charged vacancy V^+: $E(+/0)=E_G-E^0$. From this point of view a positively charged vacancy V^+ is an acceptorlike center A^+ and $E_G-E^0=1.9\,\mathrm{eV}$ is the binding energy of a hole.

To check the accuracy of these estimates it is possible to calculate $E(q/q\pm1)$ for some other suitable values of the Fermi energy. For example, if the position of E_F coincides with E_V,

$$E(q/q\pm1)=E^f(q\pm1,0)-E^f(q,0). \quad \text{(A2)}$$

We can obtain the values of $E^f(+,0)$, $E^f(0,0)$, and $E^f(-,0)$ with the help of Fig. 5: $E^f(+,0)=5$, $E^f(0,0)=6.9$, and $E^f(-,0)=9.9\,\mathrm{eV}$. The resulting ionized energies are given by the following expressions: $E_G-E^-=E^f(-,0)-E^f(0,0)=3.0\,\mathrm{eV}$ and $E_G-E^0=E^f(0,0)-E^f(+,0)=1.9\,\mathrm{eV}$. These values coincide with the values calculated previously to within an accuracy of 0.1 eV.

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