Transport of heavily boron-doped synthetic semiconductor diamond in the hopping regime

Toshimaro Sato and Kazutoshi Ohashi
Faculty of Engineering, Tamagawa University, Tamagawagakuen 6-1-1, Machida, Tokyo 194-8610, Japan

Hiroyuki Sugai
Department of Materials Science and Engineering, Japan Atomic Energy Research Institute (JAERI), Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan

Takashi Sumi and Katsuji Haruna
Faculty of Engineering, Tamagawa University, Tamagawagakuen 6-1-1, Machida, Tokyo 194-8610, Japan

Hiroshi Maeta
Hiroshima-Denki Institute of Technology, Nakano Aki-ku 6-20-1, Hiroshima 739-0321, Japan

Norimasa Matsumoto and Hideo Otsuka
Department of Materials Science and Engineering, Japan Atomic Energy Research Institute (JAERI), Tokai-mura, Naka-gun, Ibaraki 319-1106, Japan
(Received 5 April 1999)

We report electrical transport measurements of synthetic diamonds doped with boron about 100 ppm. The resistivity has been measured in the temperature range 20–300 K by the van der Pauw method. We have also investigated infrared absorption coefficient at room temperature. Furthermore, we have studied the effect of P^{+9} ion irradiations with 150 MeV which introduce donor defects and also the influence of the annealing after the irradiation. The key features of the present measurement are as follows: (i) The observed temperature dependence of resistivity shows characteristic features of the variable-range-hopping (VRH). A crossover from $T^{-1/4}$ behavior of Mott VRH to the $T^{-1/2}$ form of Efros VRH is found to occur at 100 K. (ii) Below 50 K we have observed the hard gap T^{-1} form. The width of the hard gap is about 10 meV. (iii) The experimental results are quantitatively explained by the theory of VRH. (iv) The observed width of the optical hard gap is equal to that of the hard gap obtained from resistivity. (v) The annealing effects appear only in the hard gap region and do not appear in the variable-range-hopping region. This result leads to the speculation that the hard gap is weakened by the lattice defects.

I. INTRODUCTION

In 1952 Custers[1] discovered that the natural diamonds show significant electrical conductivity at room temperature and transmit ultraviolet light (type II). He called these very rare p type semiconducting diamonds type IIb diamonds in which borons were major impurities with concentrations less than 1 ppm. Today, the development of high-pressure synthesis technique allows to grow large single diamond crystals and the chemical vapor deposition (CVD) makes it possible to produce diamond films. Semiconducting diamond is potentially one of the best materials for high-quality electronic devices. Despite the remarkable progress, the growing and doping technology of diamonds has not yet been established to the control process well enough it is for Si and other semiconductors of commercial use. This fact prohibits a wide application of semiconducting diamonds to electronic devices. Further, diamonds exist only as p type semiconductor with the only acceptor being boron.

In 1962 Wilson[2] has measured the electrical conductivity in the temperature range 88 to 293 K on boron-doped natural and synthetic diamonds and obtained nearly 30 discrete activation energies ranging between 0.0029 and 0.087 eV. These data are interpreted as evidence for impurity conduction or hopping transport, which is commonly observed in heavily doped and highly compensated semiconductors at low temperatures.[3] The impurity conduction mechanism has been investigated by Mott.[4] He has pointed out that in compensated semiconductor, impurity conduction is possible by direct transfer of carrier from an occupied site to an empty site of major impurity. In 1970 Williams, Lightowlers and Collins[5] made dc electrical conductivity measurement in the temperature range from 80 to 450 K on boron-doped synthetic semiconducting diamonds. Their results confirm that the acceptor is responsible for the semiconducting properties of synthetic semiconducting diamonds, and yield activation energies of the order of 0.35 eV. Furthermore, they show that, for heavily doped synthetic diamonds, impurity conduction is the dominant conduction process at low temperatures.

There are several hopping mechanisms depending on the temperature range, the magnitude of the overlap of the wave functions and the impurity bandwidth. The temperature dependence of the hopping resistivity ρ is given by the hopping formula:

$$\rho(T)=\rho_0 \exp\left(\frac{T_m}{T}\right)^m, \tag{1-1}$$

 ©2000 The American Physical Society

where T is the temperature and T_m is a constant. In the case of nearest-neighbor hopping model (NNH),[6] where tunneling occurs to the nearest accessible sites, m is unity corresponding to simple activated behavior. At low temperatures, it is energetically favorable to hop over larger distances than nearest neighbor (variable-range hopping, VRH). In the case of VRH predicted by Mott[7] the exponent is $m = 1/4$. Mott has predicted VRH of this form on the assumption that the density of states (DOS) near the Fermi energy is constant (or a slowly varying function of energy). The Coulomb interaction in this disordered system with strongly localized electronic states plays an important role. The long-range unscreened Coulomb repulsion between the electrons in localized states reduces the single-particle DOS near the Fermi energy. At zero temperature it is expected that the DOS is zero at the Fermi energy but it is finite at energies different from the Fermi energy. This soft gap is called as Coulomb gap.[8,9] The depletion of single-particle excitations near the Fermi energy certainly influences the transport properties of the system under considerations. This hopping mechanism is called as Efros-Shklovskii VRH (Efros VRH). The Coulomb gap yields VRH with an exponent $m = \frac{1}{2}$ instead of $\frac{1}{4}$. But an assumption of a parabolic single-particle DOS to calculate the transport behavior has been questioned by a number of authors. Particularly, Pollak[10] criticizes that Efros VRH is derived from a one-particle DOS, which cannot be used to evaluate transport properties of interacting particles. Moreover, Efros VRH is concerned primarily with non-interacting hopping excitations of single particles. Pollak has argued that the low-energy excitations of the system cannot be described by non-interacting one-electron hopping and that the inclusion of many-electron effects generally leads to further reduction of the DOS near the Fermi energy where there are effectively no states within a narrow range of energy.[11,12] This gap is called as hard gap. One possible manifestation of a hard gap is that upon lowering temperature, the resistivity shows a crossover from the form given by VRH to an activated form $m = 1$ associated with transitions across the hard gap. There is recent experimental evidence that a crossover occurs in some materials at very low temperatures to this new regime where the resistivity depends more strongly on the temperature with an exponent m larger than $m = \frac{1}{2}$. A crossover with decreasing temperature to simply activated conduction ($m = 1$) has been found in an $Cd_{0.91}Mn_{0.09}Te$:In,[13] ion-implanted Si:P, B,[14] ion-implanted Si:As[15] and insulating Si:B (Ref. 16) samples. In these insulating Si:B samples the activation energy is about 0.03 meV, so that it is possible to observe the resistivity of activated form for temperatures below about 1 K.

Experimentally, there still remains the controversies concerning Coulomb gap. Namely, there are two classes of crossovers from Mott $T^{-1/4}$ VRH to $T^{-\gamma}$ VRH with the exponent γ considerably greater than $\frac{1}{2}$. In the first case, the exponent γ firmly tends to 1. In the second case of crossovers, the exponent of the resistivity smoothly increases from the Mott value of $\frac{1}{4}$ to values, which, although greater than $\frac{1}{2}$, are still small than 1. If we can present such experimental data in the liquid nitrogen temperature region that the resistivity follows the Mott $T^{-1/4}$ VRH law at first and then the Efros $T^{-1/2}$ law, before changing to the activated T^{-1} behavior at lower temperatures, these experimental results should yield more information to settle the controversies. As Massarani, Bourgoin, and Chrenko[17] has pointed out, a semiconducting diamond represents in principle an ideal system for studying hopping conduction in crystalline material. Due to the high energy level of the boron acceptor level E_A (0.35 eV above the valence band), the conduction in the valence band becomes negligible at relatively high temperature (20-300 K). Hence, the hopping conduction can be studied in a very large temperature range up to 200 K. Furthermore, boron concentrations as high as 100 ppm induce a large hard gap width to be about 10 meV so that the crossover from VRH to the simply activated conduction with decreasing temperature should be observed around 50 K. In this paper, we report our measurement results, which demonstrate that low-temperature resistivity below 50 K of boron-doped diamonds exhibits simply activated behavior. We have also performed 150 MeV P^{+9} irradiations, which introduce donor defects (i.e., new compensating centers), in order to study the variations of conductivity with changes in donor concentration.

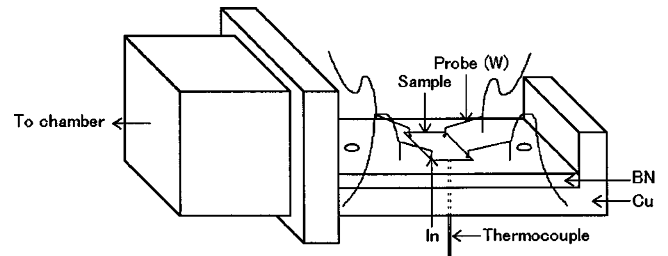

FIG. 1. The schematic diagram of the holder.

II. EXPERIMENTAL METHOD

The samples examined are boron-doped systhetic diamonds grown by Sumitomo Denko Co. Ltd. The crystal size is $3.0 \times 3.0 \times 0.3\ \mathrm{mm}^3$, with the plane surface of (100) crystallographic planes. These diamonds contain boron, whose concentration is about 100 ppm. Details on the determination of boron concentration by means of x-ray diffraction method can be found elsewhere.[18] The samples are placed in a liquid-herium cryostat equipped with a temperature stabilizer in the temperature range 20–300 K. The specimens are fixed by the use of the holder described in Fig. 1. The resistivity is measured by using the van der Pauw method. The sample holder has been designed in order to allow both good thermal contact with helium exchange tube of the cryostat and good electrical insulation, so that each diamond is mounted on a BN plate. The BN plate is chemical stable at low temperatures and a good electrical insulator and also a good thermal conductor. Throughout the experiments, the temperature of the diamonds is measured by using AuFe-Chromel thermocouple. Four electrical pressure contacts, consisting of 0.1-mm diameter tungsten wires etched to a fine point, are arranged on the surface of the diamond. Furthermore, to improve good electrical contact between tungsten wire and the specimen the In sheet is inserted to achieve an ohmic contact.

In order to know the compensation effect, we have performed 150 MeV P^{+9} irradiation, which introduce donor defects (i.e., new compensating centers), in order to study the

variations of conductivity in the hopping range with changes in donor concentration and to verify that these variations can be accounted for the hopping mechanism. Specimens have been irradiated with 150 MeV P^{+9} ions up to the influence of about 10^{14} ions/cm^2 using the Tandem accelerator at JAERI. The temperature of the specimen during ion irradiation is kept at 20 K. The electrical conductivity before and after the irradiation has been measured.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The probability that a carrier hops from an occupied site to an unoccupied site, separated by a distance R, depends on the overlap of the wave function of the two sites and on the dispersion ε in energy of the associated localized states. This probability is given by

$$P=\nu_{\mathrm{ph}}\exp\left(-2\alpha R-\frac{\varepsilon}{k_BT}\right), \tag{3.1}$$

where ν_{ph} is a factor depending on the phonon frequency, α^{-1} is the localization length characterizing the extension in space of the wave functions, and ε is the energy difference between the two localized states.

In the case where $\varepsilon/k_BT\ll 2\alpha R$, P is maximum for R minimum: the carriers hop from one site to the nearest-neighboring site [nearest-neighbor hopping regime (NNH)].[6] Then the conductivity, occurring through thermally activated hops, is characterized by a constant activation energy ε:

$$\sigma=\sigma_0\exp\left(-\frac{\varepsilon}{k_BT}\right). \tag{3.2}$$

The activation energy ε is interpreted as being the energy necessary for the carrier to surmount the Coulomb potential which exists between the occupied and the unoccupied sites. The Bohr radius of the ground state of the doping impurity is small when a hydrogen model for the hole-bound of the boron impurity is assumed, that is $a_B=3.00$ Å. In this expression we use the relative dielectric constant κ of diamond to be 5.66.[19] In the previous paper we have determined the boron concentration contained in our specimen to be about 100 ppm by means of the x-diffraction method.[18] We can estimate the doped boron concentration per unit volume. The mass density of diamond is $\rho_D=3.514$ g/cm^3 (Ref. 20) and the volume per unit mol is $V_{\mathrm{mol}}=3.415$ cm^3. Noticing the number of atoms per unit mol is equal to Avogadro number ($N_A=6.0225\times10^{23}$/mol), the boron concentration per unit volume of the specimen containing 100 ppm boron is equal to $n_B=1.76\times10^{19}$/cm^3. As the boron concentration increases, the wave functions of adjacent impurity centers overlap to yield a metallic conduction. The impurity concentration n_c at which the finite overlap of the wave functions of adjacent centers occurs is given by

$$n_c=\frac{3}{4\pi}a_B^{-3}=8.85\times10^{21}\ \mathrm{cm}^{-3}. \tag{3.3}$$

By comparing n_B with n_c the impurity concentrations as high as 100 ppm do not result in a metallic conduction. Such high concentration induces a large impurity bandwidth, corresponding to a large spread in the energy of the localized states of the impurity centers, which makes it possible to observe the transition between the two hopping regimes at a relatively high temperature: hopping through nearest-neighbor centers (NNH) and hopping through moderate distant impurity centers (VRH). The distance between the boron impurity is given by

$$r_{B-B}=\left(\frac{3}{4\pi n_B}\right)^{1/3}=23.8\ \text{Å}, \tag{3.4}$$

so that the magnitude of Coulomb interaction between the defects is as follows

$$w=\frac{e^2}{\kappa r_{B-B}}=107\ \mathrm{meV}. \tag{3.5}$$

Following to Massarani[17] we assume that the impurity bandwidth is caused by the Coulomb interaction between the nearest-neighbor boron impurities. Hence, for the boron concentration of 1.76×10^{19} cm^{-3} the impurity bandwidth becomes $w=107$ meV. The energy difference between the two localized states ε, which corresponds to the interaction energy of electron with the hole left behind, is equal to $w=107$ meV, so that w/k_BT at $T=300$ K is given by

$$\frac{w}{k_BT}=4.13. \tag{3.6}$$

On the other hand, by assuming the localization length α^{-1} to be equal to the Bohr radius we have the following result as

$$2\alpha R=\frac{2r_{B-B}}{a_B}=15.9. \tag{3.7}$$

Hence, ε/k_BT is not negligible compared to $2\alpha R$ even at $T=300$ K. When ε/k_BT is not negligible compared to $2\alpha R$, that occurs at low temperature or for large hopping energy, the hopping probability is maximum when $2\alpha R+\varepsilon/k_BT$ is minimum. The hopping distance R and the hopping energy ε are related to each other by the three-dimensional (3D) normalization equation of the one particle DOS $g(\varepsilon)$ expression

$$\frac{4\pi}{3}R^3\int_0^{\epsilon}g(\varepsilon)d\varepsilon=1, \tag{3.8}$$

where ε is the one-particle energy measured from the Fermi energy E_F. This is called variable-range hopping (VRH). On the assumption that the DOS $g(E)$ near the Fermi energy is constant g_F, Mott[7] has predicted VRH form for the resistivity of 3D systems;

$$\rho=\rho_0\exp\left[\left(\frac{T_{1/4}}{T}\right)^{1/4}\right]. \tag{3.9}$$

In this case $T_{1/4}=\beta\alpha^3/k_Bg_F$ where $\beta=5.7$. The Mott law, Eq. (3.9), has been more rigorously confirmed by Ambegaokar, Halperin, and Langer[21] by use of a percolation method and dimensionless constant β to be approximately 16 is estimated. But there exists a considerable discrepancy as regards the values of the coefficient β; 1.5 given by Mott,[22] $24/\pi=7.6$ given by Mott[23] and 22.8 given by Skal and Shklovskii.[24]

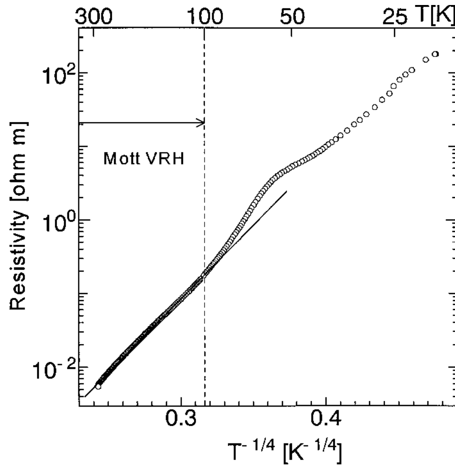

FIG. 2. Resistivity ρ versus $T^{-1/4}$. The solid line shows the fit to the $T^{-1/4}$ law.

The theory of VRH has been developed assuming a constant DOS in a region extending to several k_BT around the Fermi level. This is justified when the temperature range in which the VRH mechanism is operative is small, or when the states are uniformly distributed. The DOS at the Fermi level g_F is then estimated as being the ratio

$$g_F = \frac{n_B}{w} = 1.64\times 10^{20}\,\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}. \tag{3.10}$$

A semilogarithmic plot versus $T^{-1/4}$ is shown in Fig. 2, which suggests that the VRH mechanism may be valid in this system above 100 K. Equation (3.9) is fitted in Fig. 2 to the experimental data using $T_{1/4}$ as a variable parameter. The value of $T_{1/4}$ obtained by the fitting is

$$(T_{1/4})^{1/4} = 46\,\mathrm{K}^{1/4}. \tag{3.11}$$

The theoretical value of $T_{1/4}$ is given as

$$(T_{1/4})^{1/4} = \left(\frac{5.7\alpha^3}{k_B g_F}\right)^{1/4} = 62.2\,\mathrm{K}^{1/4}. \tag{3.12}$$

For the Mott theory to be valid, the electron must ''hop'' a mean distance $\bar{R}_{\mathrm{hop,Mott}}$ that is greater than the nearest-neighbor impurity separation and considerably greater than the localization length α^{-1}. The mean hopping distance $\bar{R}_{\mathrm{hop,Mott}}$ can be derived directly from Mott's arguments and will play important roles shortly in determining criteria. At 100 K the hopping distance has been estimated to be

$$\bar{R}_{\mathrm{hop,Mott}} = \left(\frac{1}{\alpha}\right)\left(\frac{9}{8\pi\beta}\right)^{1/4}\left(\frac{T_{1/4}}{T}\right)^{1/4} = 29.6\ \text{Å} \tag{3.13}$$

This mean hopping distance is nearly equal to the average distance between the boron impurity $r_{B\text{-}B} = 23.8$ Å. Schirmacher[25] has suggested that the most common hops occur either directly between the initial and final sites or indirectly via a third additional site.

Subsequent work has demonstrated that long-range Coulomb interactions cause a depletion of single-particle states near the Fermi energy. By considering one-electron transitions, Eflos[9] found a parabolic ''Coulomb gap'' of the parabolic form $\varepsilon^2 = |E - E_F|^2$. The following parabolic form of the DOS in the immediate vicinity of E_F is given;

$$g(\varepsilon) = g_0 \varepsilon^2 \tag{3.14}$$

with

$$g_0 = \left(\frac{3}{\pi}\right)\left(\frac{\kappa^3}{e^6}\right), \tag{3.15}$$

where κ is the dielectric constant and e is the elementary charge. Efros[9] calculated the constant by a mean-field method. The Coulomb gap is called a ''soft gap'' because the density of states goes smoothly to zero with a parabolic dependence. The width of the gap Δ is given by the following equation as

$$\Delta = \left(\frac{g_F}{g_0}\right)^{1/2}. \tag{3.16}$$

Since long-range dissociation of electrons from holes costs energy in the presence of a gap, it is natural to expect that the gap will impede dc conductivity. Assuming that the conductivity is determined by the single-particle DOS, Efros has shown that a parabolic gap yields VRH with an exponent $\frac{1}{2}$ instead of $\frac{1}{4}$, that is

$$\rho = \rho_0 \exp\left[\left(\frac{T_{1/2}}{T}\right)^{1/2}\right] \tag{3.17}$$

with

$$T_{1/2} = \frac{e^2\beta\alpha}{k_B\kappa}, \tag{3.18}$$

where the coefficient β is equal to 2.8 according to Shklovskii[26] or $\beta = 0.57$ according to Adkins.[27] Thus, there exists a discrepancy as regards the value of β. On deriving Eq. (3.17) it is assumed that there are primarily non-interacting hopping excitations of single particles. A one-particle DOS and its use to calculate the transport behavior has been questioned by a number of authors as pointed out in the Introduction. A parabolic gap in DOS at the Fermi level is undoubtedly recognized in many computer simulation.[28–31] The Efros law is certainly observed in various materials. Massey and Lee also reported a direct observation of the parabolic gap in boron-doped silicon by tunneling spectroscopy.[32,33] However, Efros $T^{-1/2}$ are still under discussions. But in this paper we obey Efros VRH model. In Fig. 3 we show a semilogarithmic plot of the resistivity versus as $T^{-1/2}$, which suggest that Efros VRH mechanism may be valid in this system between 50 and 100 K. The dc electrical resistivites ln ρ fall on straight lines over a considerable range of temperature, showing the $m = \frac{1}{2}$ behavior expected from the Coulomb gap model. Equation (3.17) is fitted in Fig. 3 to the experimental data. The value of $(T_{1/2})^{1/2}$ obtained by the fitting is as follows

$$(T_{1/2})^{1/2} = 92.9\,\mathrm{K}^{1/2}. \tag{3.19}$$

On the other hand, the theoretical value is given as follows

$$(T_{1/2})^{1/2} = 166\,\mathrm{K}^{1/2}. \tag{3.20}$$

The theoretical value is about two times larger than the experimental value. We must notice that the above consider-

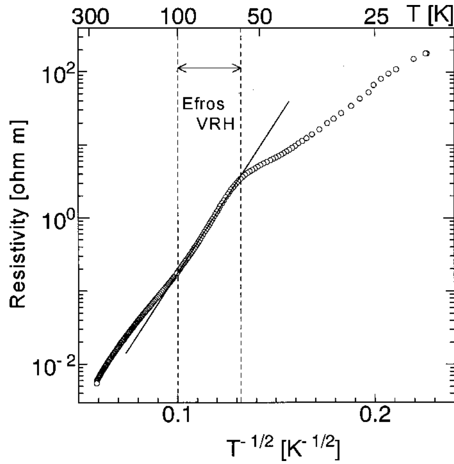

FIG. 3. Resistivity ρ versus $T^{-1/2}$. The solid line shows the fit to the $T^{-1/2}$ law.

ation does not take into account the ''weakening'' or ''smearing'' of the gap due to finite-temperature effects. If the temperature is raised above zero, ''thermal smearing'' of the Fermi surface will increase the DOS in the gap from zero at E_F to a finite value, which is stated by Mott and Kaveh[34] to be of the order of $k_BT/w^2r_{B-B}^3$, where w is the band width and r_{B-B} is the distance between neighboring impurity sites. Shlimak *et al.*[35] refer to this effect as the ''temperature-induced smearing of the Coulomb gap.'' His measurements of the VRH conductivity on samples of ion-implanted Si:As show that the integrated DOS in the optimal band in the vicinity of the Fermi level increases with increasing temperature. Sartestani, Schreicher, and Vojta[30] have investigated the Coulomb gap at finite temperature by means of a Monte Carlo method and found that the Coulomb gap is filled with increasing temperature. If the DOS in the vicinity of the Fermi level increases with increasing temperature, the apparent half-width of the Coulomb gap Δ decreases with increasing temperature so that apparent $(T_{1/2})^{1/2}\approx\Delta^{1/3}$ also decreases with increasing temperature. On the other hand, Perez-Carrido *et al.*[36] studied by computer simulation the effects of Coulomb interactions on the conductivity by considering the many-electron configurations of the system and obtained the characteristic temperature $T_{1/2}$, which is a factor of 10 smaller than Efros prediction. In our experiment $T_{1/2}(\text{experiment})/T_{1/2}(\text{Efros})=0.31$.

Davies[11] and Chicon *et al.*[12] studied the consequences of stabilizing the ground state against certain many-electron transitions, obtaining hard gaps (i.e., gaps stronger than parabolic) in the DOS. The hard gaps are produced by the existence of a relatively large density of compact low-energy one-electron excitations. Such compact electron-hole pairs requires only a small energy to move the electron from one site to the other. The separated electron-hole pairs generate electric dipole moments. This polarization releases a relaxation energy which lowers the total energy of the excitation. This effect makes DOS a stronger function of energy E near E_F, that is many-electron transitions in stabilization of the ground state result in stronger (exponential) functional dependence of DOS on E (so called as hard gap). The stronger dependence is confined to a rather narrow regime around E_F. In the hard gap there are effectively no states within a narrow but finite range of energy, E_H, with $E_H\approx\Delta/5$ where Δ is the Coulomb gap. One possible manifestation of a hard gap is, upon lowering temperature, the appearance of a crossover from a resistivity given by VRH to an activated form associated with transitions across the hard gap,

$$\rho=\rho_0\exp\left(\frac{E_H}{T}\right). \tag{3.21}$$

Such a crossover is opposite to the most common crossover from nearest-neighbor hopping to VRH with decreasing temperature. There is recent experimental evidence that a crossover occurs in some materials at very low temperature to a new regime where the resistivity depends on the temperature with an exponent equal to 1.

We may estimate the Coulomb gap as follows

$$\Delta=\left(\frac{g_F}{g_0}\right)^{1/2}=\left[\frac{\pi}{3}\frac{g_Fe^6}{\kappa^3}\right]^{1/2}=616k_B=0.053\,\text{eV}. \tag{3.22}$$

Hence, as a result of assuming the parabolic Coulomb gap the width of the Coulomb gap is nearly equal to 53 meV and this value is equal to half of the impurity bandwidth. The energy width of hard gap is determined from

$$E_H=\frac{\Delta}{5}=10.6\,\text{meV}. \tag{3.23}$$

A semilogarithmic plot versus T^{-1} is shown in Fig. 4. As shown in the figure the present work demonstrates the crossover from an $\exp(T_{1/2}/T)^{1/2}$ to an $\exp(E_H/T)$ in the boron-doped diamond, as the temperature is reduced below 50 K. Equation (3.21) is fitted in Fig. 4 to the experimental data. The value of $E_H=11$ meV is obtained. The resistivity of our samples is consistent with simply activated conduction. We note that nearest-neighbor hopping, which has a similar temperature dependence, generally entails large energy, compared with 11 meV found for the sample. Moreover, Mott VRH and Efros VRH is observed at higher temperatures, ruling out the possibility that the activated conduction found at lower temperature is due to nearest-neighbor hopping.

We attribute the simply activated conduction in boron-doped diamond below 50 K to the presence of a gap in the DOS near the Fermi energy. In order to obtain more definite information about the hard gap, we investigates room-temperature infrared absorption coefficient of the boron-doped diamond. The optical absorption is measured in the range 20 meV-1 eV. By assuming the allowed direct transition the optical gap E_H is obtained by extrapolating a plot of the square of the absorption intensity A^2 against $h\nu$ and using the relation: $A^2\approx(h\nu-E_H)$. This relation is shown Fig. 5. In this figure the straight line represents the case of the optical hard gap to be about 11 meV. At room temperature the Coulomb gap does not completely disappeared due to the smearing.

Furthermore, we have performed phosphorus (P) ion irradiation on synthetic boron-doped diamonds and studied the effects of P ion radiation on electrical conductivity. Figure 6 shows the behavior of the resistivity as a function of P dose at 20 K. Below $F_{\min}=0.625\times10^{14}$ ions/cm^2 the resistivity decreases from 167 Ωm value down to 100 Ωm for $F_{\min}$ dose. This peculiar non-monotonic behavior has been found

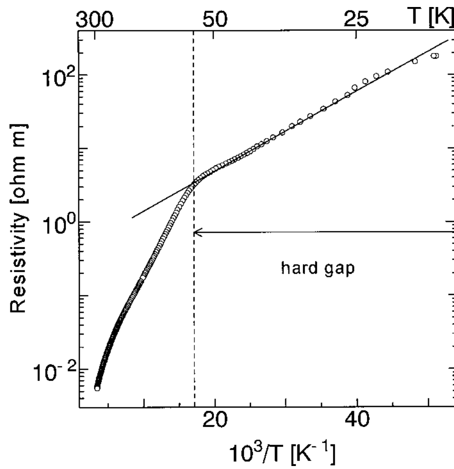

FIG. 4. Resistivity ρ versus T^{-1}. The data has been fit with simple activation conduction.

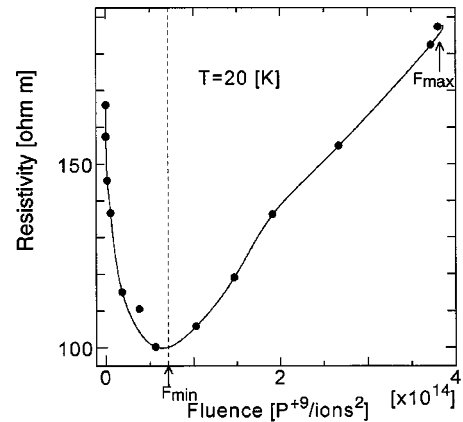

FIG. 6. Resistivity of boron-doped diamond irradiated with 150 MeV P^{+9} ion.

by other groups.[37,38] They reported that there appeared three distinct regions: for low implantation dose, the resistivity falls to a shallow minimum as shown by $F_{\rm min}$ in Fig. 6, it then increases to a maximum to which the $F_{\rm max}$ in Fig. 6 nearly corresponds, and the resistivity falls sharply from the maximum. In the low-dose regime, isolated point defects are responsible for the drop of the resistivity. With increased implantation dose, which covers the region where the resistivity rises, partial ion-induced graphitization takes place. For dose around the resistivity maximum intense graphitization sets in.

The temperature dependence of electrical conductivity for B-doped diamond of 3.80×10^{14} ions/cm^2 implantation dose has been measured in the range 20–300 K. The resistivity of the specimen after the irradiation of 3.80×10^{14} ions/cm^2 is nearly equal to that of the specimen before the irradiation at 20 K. The results are shown in Fig. 7. Under this implantation the graphitization is estimated to begin. The influence of the annealing appears only in the lowest temperature region and does not appear in the variable range hopping regions. This result leads to the following speculation that the hard gap itself may be disturbed by the annealing and its width reduces to 9.9 meV after 4 months. In the hard gap nearby electrons capable of low-energy excitation become important. The low-energy excitations are transitions to nearby vacant sites. Such compact electron-hole pairs are likely to be influenced by the surrounding state, so that the resistivity in hard gap region may be affected by the annealing. On the other hand, in Mott VRH and Efros VRH the hopping range is comparatively large so that the influence of the surrounding state appears only weakly. Therefore, the annealing effect does not appear in VRH ranges. According to this speculation defects seem to act to weaken the hard gap. As pointed out in the Introduction, experimental studies show that two classes of crossovers from Mott $T^{-1/4}$ VRH to the $T^{-\nu}$ VRH with the exponent ν considerably greater than $\frac{1}{2}$. In the first case, the exponent ν firmly tends to 1 in the lowest temperature such as the present results of the semiconducting diamond. In the second class of crossovers, there is no clear picture of the three VRH regimes. This case may be considered as a result of the weakening of the hard gap due to crystal imperfections, so that there appear soft gaps harder than Coulomb gap at Fermi energy in this case.

In summary, this paper described transport properties of the boron-doped diamond as a function of temperatures. There is strong evidence to suggest that electrical transport occurs by variable-range-hopping. Above 100 K the Mott VRH is observed. Upon decreasing temperature a transition from Mott VRH to Efros VRH is observed in this system

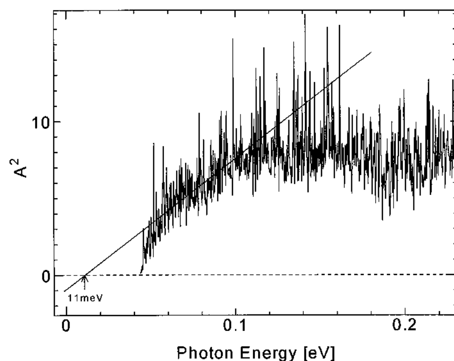

FIG. 5. Absorption spectrum of boron-doped diamond. A^2 versus $h\nu$. The data has been fit with $A^2=(h\gamma-E_H)$ where optical gap $E_H=11$ meV.

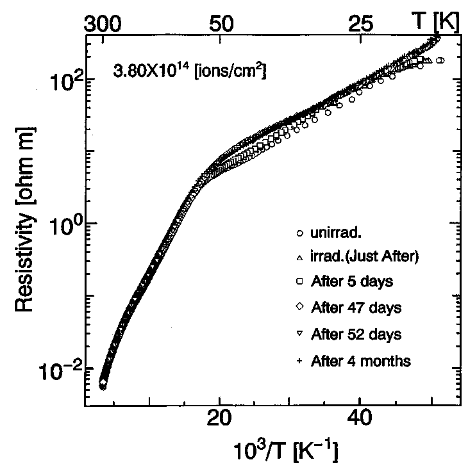

FIG. 7. Resistivity ρ versus T^{-1} after the irradiation of 3.80×10^{14} ions/cm^2.

between 50 and 100 K. Furthermore, below 50 K the simple activated conduction due to the hard gap is observed. The width of the hard gap is 10 meV in diamonds containing 100 ppm borons. More definite information about the hard gap has been obtained by measuring absorption coefficient of the boron doped diamond at room temperature. The observed optical hard gap width is equal to that of the electrical transport result. Finally, we have performed phosphorous ion irradiation and investigated the influence of the annealing. The annealing effect appears only in the hard gap region. This result leads to the speculation that the hard gap itself is influenced by the lattice defects.

ACKNOWLEDGMENT

We are grateful to Professor M. Inoue for many helpful discussions on the subject of this paper. We also thank the technical staff of the Accelerator Division at JAERI for their great help.

[1] J. F. H. Custers, Physica (Amsterdam) **18**, 489 (1952); Nature (London) **176**, 173 (1955).
[2] W. B. Wilson, Phys. Rev. **127**, 1549 (1962).
[3] N. F. Mott and W. D. Twose, Adv. Phys. **10**, 107 (1961).
[4] N. F. Mott, Can. J. Phys. **34**, 1356 (1956).
[5] A. W. S. Williams, E. C. Lightowlers, and A. T. Collins, J. Phys. C **3**, 1727 (1970).
[6] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[7] N. F. Mott, J. Non-Cryst. Solids **1**, 1 (1968).
[8] M. Pollak, Discuss. Faraday Soc. **50**, 13 (1970); Philos. Mag. **23**, 519 (1971).
[9] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975); J. Phys. Solid State Phys. **9**, 2021 (1976).
[10] M. Pollak, Philos. Mag. B **65**, 657 (1992).
[11] J. H. Davies, Philos. Mag. B **52**, 511 (1985).
[12] R. Chicon, M. Ortuno, B. Hadley, and M. Pollak, Philos. Mag. B **58**, 69 (1988); Phys. Rev. B **37**, 10 520 (1988).
[13] I. Terry, T. Penney, and S. von Molnar, Phys. Rev. Lett. **12**, 1800 (1992).
[14] J. Zhang, W. Cui, M. Juda, D. McCammon, R. L. Kelley, S. H. Moseley, C. K. Stahle, and A. E. Szymkowiak, Phys. Rev. B **48**, 2312 (1993).
[15] R. W. van der Heijden, G. Chen, A. T. A. M. de Waele, H. M. Gijsman, and F. R. B. Tielen, Solid State Commun. **78**, 5 (1991).
[16] P. Dai, Y. Zhang, and M. P. Sarachik, Phys. Rev. Lett. **69**, 1804 (1992).
[17] B. Massarani, J. C. Bourgoin, and R. M. Chrenko, Phys. Rev. B **17**, 1758 (1978).
[18] T. Saotome, K. Ohashi, T. Sato, H. Maeta, K. Haruna, and F. Ono, J. Phys.: Condens. Matter **10**, 1267 (1998).
[19] M. I. Eremets, Semicond. Sci. Technol. **6**, 439 (1991).
[20] R. Berman, *The Properties and Growth of Diamond*, edited by G. Davies (Institute of Electrical Engineers, London, 1994), p. 13.
[21] V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).
[22] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990), p. 50.
[23] N. F. Mott, *Conduction in Non-Crystalline Materials* (Clarendon, Oxford, 1993), p. 32.
[24] A. S. Skal and B. I. Shklovsii, Fiz. Tverd. Tela (Leningrad) **16**, 1820 (1974) [Sov. Phys. Solid State **16**, 1190 (1974)].
[25] W. Schirmacher, Phys. Rev. B **41**, 2461 (1990).
[26] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1994), p. 240.
[27] C. J. Adkin, J. Phys.: Condens. Matter **1**, 1253 (1989).
[28] J. H. Davies, P. A. Lee, and T. M. Rice, Phys. Rev. B **29**, 4260 (1984).
[29] A. Mobius, M. Richter, and B. Drittler, Phys. Rev. B **45**, 11 568 (1992).
[30] M. Sarvestani, M. Schreicher, and T. Vojta, Phys. Rev. B **52**, R3820 (1995).
[31] F. Epperlein, M. Schreiber, and T. Vojta, Phys. Rev. B **56**, 5890 (1997).
[32] J. B. Massey and M. Lee, Phys. Rev. Lett. **75**, 4266 (1995).
[33] M. Lee and J. B. Massey, Phys. Status Solidi **205**, 25 (1998).
[34] N. F. Mott and M. Kaveh, Adv. Phys. **34**, 329 (1985); **34**, 367 (1985).
[35] I. Shlimak, M. Kaveh, R. Ussyshbin, V. Ginodman, S. D. Baranovskii, P. Thomas, H. Vaupel, and R. W. van der Heijden, Phys. Rev. Lett. **75**, 4764 (1995).
[36] A. Perez-Garrido, M. Ortuno, E. Cuevas, J. Ruiz, and M. Pollak, Phys. Rev. B **55**, R8630 (1997).
[37] S. Prawer, F. Ninio, and I. Blanchonette, J. Appl. Phys. **68**, 2361 (1990).
[38] M. S. Dresselhaus and R. Kalish, *Ion Implantation in Diamond, Graphite and Related Materials* (Springer-Verlag, Berlin, 1992), p. 130.