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Conductivity in boron-doped diamond

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The appearance of additional states of an impurity under high doping levels is discussed. On the basis of a Fermi level calculation, a model for the conductivity of heavily boron-doped diamond is proposed. This model allows one to reproduce the temperature dependence of the conductivity and of the Hall coefficient for different impurity concentrations. The temperature dependence of the conductivity was found to be connected with the coexistence of valence-band and hopping conductivities in a wide temperature range. The hopping conductivity takes place over the additional states of the boron impurity.

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In the early period of semiconductor studies three activation energies ϵ_1, ϵ_2, and ϵ_3 were extracted from resistivity measurements versus temperature for heavily doped semiconductors.[1–4] The theory of this phenomenon was provided by Miller and Abraham.[5] Then Mott formulated the conception of variable-range hopping conductivity.[6] For *n*-type materials ϵ_1 is the activation energy from donor levels to the conductivity band and ϵ_3 is the activation energy for hopping conductivity. It is said that ϵ_2 is the activation energy to the upper Hubbard band or the energy from the D^- state to the mobility edge,[3,4,7] but the origin of ϵ_2 remains unclear.[4] To clarify the peculiarities of the transition from band to hopping conductivity, we introduce an idea connected with the appearance of different states of the main impurity as the doping level increases. Two impurity atoms situated close to each other should be in a state with energy different from the energy of the impurity in its usual position.[8] These states are ground states and in this sense differ from D^- states. As an example, we describe the change in the temperature behavior of conductivity in diamond.

Boron-doped diamond is a very interesting material for the investigation of impurity conductivity.[9–14] This is due to a wide temperature region of hopping conductivity and to an unusual behavior of the Hall coefficient. The recently developed homoepitaxial crystal growth chemical vapor deposition (CVD) technique provides high-quality diamond samples. In a recent paper,[15] an attempt was made to describe the conductivity of diamond by considering both the valence-band and hopping conductivities. However, it still remained unclear if an actual change in the activation energy takes place or if this is only an apparent effect. An unusually high value for the hopping conductivity was obtained as well. That paper does not clarify what physical processes occurring at doping lead to the dramatic change in the conductivity. In the present paper we attempt to establish these reasons and to find theoretically the dependence of the activation energy on temperature at different concentrations of impurity and levels of compensation. Thus in this work we try to establish what the real driving force is for this behavior of conductivity.

Diamond contains both acceptor and donor impurities and in our case the acceptors are boron atoms and the donors are nitrogen atoms with the concentration of acceptors much higher than that of donors. Thus donors act as compensators, and we have a case of weak compensation. It is known that substitutional boron in diamond forms an acceptor ground level with energy $u_1 = 0.37$ eV above the valence band.[9–11] However, and that is the main idea of this paper, it is to be supposed that under high concentrations of impurities the probability of boron atoms occupying nonordinary (additional) positions greatly increases i.e., their nearest environment will consist not only of carbon atoms.[8] These complexes are B-B, B-C-B, B-C-C-B, B-N-B, B-N-C-B, and so on.[8] This type of nontrivial state will form shallow accepter levels[8] with energy u_2 lower than the energy u_1. What fraction of the boron atoms will occupy these states depends on both statistical laws and conditions of sample growth. One may assume that the number of the additional boron states, N_2, depends on the total boron concentration N_{B} according to the following statistical law: $N_2 = N_{\mathrm{B}}^2 V_0$ ($V_0 \simeq 5$ nm^3 is the volume of the interaction area). For example, when $N_{\mathrm{B}} = 10^{19}$ cm^{-3} we have $N_2 = 5 \times 10^{17}$ cm^{-3}.

The additional states of boron are composed of levels that occupy a span of 0.07 eV above the valence band.[14] We will assume that all these states have the energy $u_2 = 0.06$ eV above the valence band. This is correlated with the results of conductivity measurements of stratified mesa structures.[16] Note that this value is close to the first excited state energy that is observed in optical measurements.[9] But it should be stressed that in the general case the energy u_2 does not necessarily coincide with the value of the first excited state energy. As all samples studied in this work were prepared following one and the same CVD technology, one may suppose that the degree of compensation $K = N_D / N_{\mathrm{B}}$ is the same for all samples and small. Thus, when the boron concentration increases, the concentration of levels with energies u_1 and u_2 will also increase. As the concentration of donors N_D increase more slowly than the concentration N_2, for sufficiently high boron concentration $N_{\mathrm{B}} > N_{cr}$, we will get $N_2 > N_D$ (we use $N_{cr} = 2 \times 10^{18}$ cm^{-3} and $K \simeq 0.01$ in our calculations). In this case donors compensate only the states with energy u_2, because $u_2 < u_1$, and thus the behavior of the conductivity changes dramatically. Therefore at high boron concentrations we have a completely different behavior

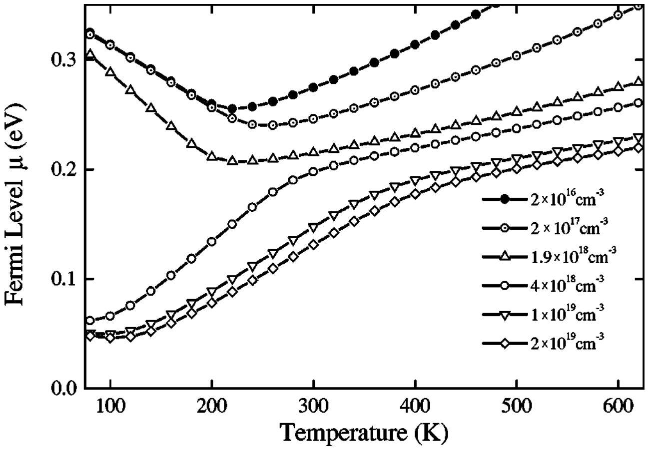

FIG. 1. Temperature dependence of the Fermi level μ for different concentrations of boron according to Eq. (3).

of conductivity and other quantities related to electron properties. It is well known that the Fermi energy depends strongly on temperature for the weak compensation case.

It is useful to remember[3] that, if the Fermi energy E_f has a linear temperature dependence like $E_f - E_v \simeq a + bT$, then by measurement of the thermoactivated behavior of the conductivity, $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ (k is the Boltzmann constant) we can determine an activation energy E_a equal to the constant a, and the constant b leads to renormalization of the preexponential factor $\sigma_0[\sigma_0' = \sigma_0 \exp(-b/k)]$. The preexponential factor σ_0' decreases for positive b or increases for negative b. As we can see below, it is necessary to take this into account in discussing experimental data.

The following program is realized: the temperature dependence of the Fermi level as a function of impurity concentration is calculated (see Fig. 1); on the basis of this calculation the hole concentrations in the valence band and impurity levels are determined; and then the temperature dependences of the conductivity and of the Hall coefficient are described for different impurity concentrations. In so doing we base our calculations on experimental results for the conductivity and Hall measurements (see Fig. 2 and Fig. 3). Details of the sample preparation and experimental procedure have been reported previously.[13] From Figs. 2–3 we note that conductivity properties change dramatically in the transition to heavily doped samples. Moreover, the temperature dependence of the Hall coefficient has a minimum, opposite to what we see in other materials[2,3] in the same measurements. The description of these peculiarities will give insight into the problem of hopping conductivity. To describe this behavior we start with the Fermi level determination.

Thus the starting point in our consideration is the supposition that there are two types of acceptor level with energies u_1 and u_2, above the top of the valence band, and with concentrations N_1 and N_2, respectively ($N_1 + N_2 = N_B$). All energy intervals are measured from the top of the valence band. Therefore we determine the Fermi level μ as the Fermi energy counted from the top of the valence band ($\mu = E_f - E_v$). The energy distribution of holes is given by Fermi-Dirac statistics. In the case of weak compensation the number of free states on the acceptor levels is limited and, therefore, the Fermi level μ depends strongly on temperature and should be calculated from the condition that the total number of holes N is conserved: $N = p_v(T) + p_1(T) + p_2(T)$, where $p_v(T), p_1(T)$, and $p_2(T)$ are the hole concentrations at the valence band and at the levels u_1 and u_2, respectively ($N = N_1 + N_2 - N_D$). It is equivalent to the electrical neutrality condition. Thus we obtain the following equation for the Fermi level:

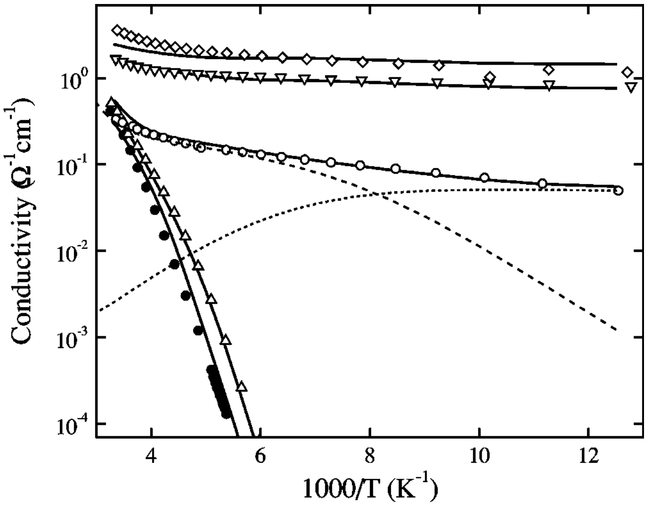

FIG. 2. Experimental (symbols) and theoretical (lines) temperature dependences of conductivity σ for different concentrations of boron in the stream BH_2/CH_4 (see Ref. 13): ◇, 5000 ppm (2×10^{19} cm^{-3}); ▽, 2500 ppm (1×10^{19} cm^{-3}); ○, 1000 ppm (4×10^{18} cm^{-3}); △, 5 00 ppm (1.9×10^{18} cm^{-3}); ●, 5 ppm (2×10^{16} cm^{-3}). Boron concentrations used in the theoretical calculations are given in parentheses. Dashed line is the valence-band conductivity σ_v and dotted line is the hopping conductivity σ_h, for $N_B = 4 \times 10^{18}$ cm^{-3}.

$$N = \int_{-\Delta_v}^{0} f(\mu,\varepsilon) n_v(\varepsilon) d\varepsilon + \sum_{i=1}^{2} \int_{u_i}^{\tilde{u}_i} f(\mu,\varepsilon) n_i(\varepsilon) d\varepsilon, \quad (1)$$

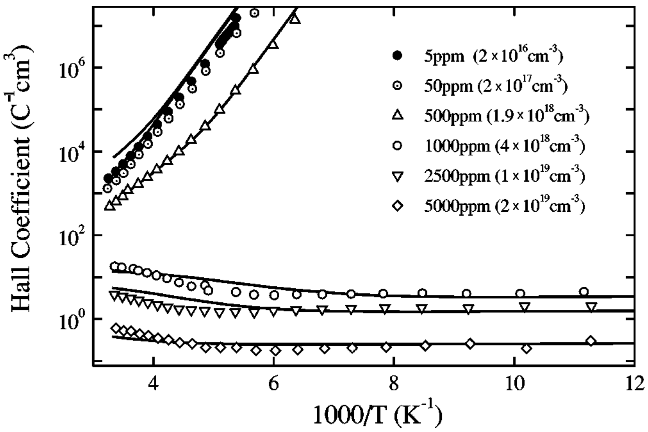

FIG. 3. Experimental (symbols) and theoretical (lines) temperature dependences of the Hall coefficient R_H for different concentrations of boron in the stream BH_2/CH_4 (see Ref. 13). Boron concentrations used in the theoretical calculations are given in parentheses.

where $N=N_1+N_2-N_D$, $f(\mu,\varepsilon)=\{1+g^{-1}\exp[(\mu-\varepsilon)/kT]\}^{-1}$ is the Fermi-Dirac distribution for holes, g is the degeneracy of the levels ($g=1$ for the valence band and $g=2$ for the acceptor levels), ε is the energy of holes, which is measured from the top of the valence band, Δ_v, n_v are the width of the valence band and the effective density of states at the valence band, $n_i(\varepsilon)$ is the effective density of states of the level with energy $u_i, \tilde{u}_i$ is the energy of the top of this level, and Δ_i is the width of this level ($\Delta_i=\tilde{u}_i-u_i$). We shall assume that the diamond samples are nondegenerate semiconductors; then $\exp(-\mu/kT)\ll 1$. We also assume that the width of each of the levels is much smaller than the value of $u_2(\Delta_1,\Delta_2\ll u2)$. For the density of states at the valence band we have $n_v(\varepsilon)=(2\pi)^{-1}(2m_p/\hbar)^{3/2}\varepsilon^{1/2}$ for the parabolic band case, where m_p is the hole effective mass. As a result, Eq. (1) is easily rewritten in the form

$$N=N_v\exp\left(-\frac{\mu}{kT}\right)+\sum_{i=1}^{2}\frac{N_i}{1+g^{-1}\exp[(\mu-u_i)/kT]}. \quad (2)$$

Here, N_v is the effective density of states at the valence-band edge, $N_v\equiv N_v(T)=2(m_pkT/2\pi\hbar^2)^{3/2}$. For the valence-band hole concentration $p_v(T)$, we have $p_v(T)=N_v(T)\exp[-\mu(T)/kT]$.

Now we can obtain the value of the Fermi level from Eq. (2) numerically. However, taking into account that in the temperature interval studied ($T<1500$ K) the energy u_1 is always much larger than kT, Eq. (2) can be reduced to a quadratic one with respect to a variable $A(\mu)=\exp(-\mu/kT)$. Then we obtain the following expression for the Fermi level $[\mu\equiv\mu(T)]$:

$$\mu(T)=u_1-kT\ln(B+\sqrt{B^2+C}), \quad (3)$$

$$B=\frac{N+(N-N_1)\exp[(u_1-u_2)/kT]-N2-p_{2v}(T)}{2[N_1+N_2+p_{2v}(T)-N]},$$

$$C=\frac{N\exp[(u_1-u_2)/kT]}{N_1+N_2+p_{2v}(T)-N},$$

where $p_{2v}(T)=N_v(T)\exp(-u_2/kT)$. Numerical calculations show that the value obtained from Eq. (3) is in good agreement with the exact value for the Fermi level obtained from the solution of Eq. (2). The temperature dependence of the Fermi level is shown in Fig. 1. For temperature $T<300$ K we get for $N>N_1$

$$\mu(T)\simeq u_2+kT\ln\left(\frac{N_1+N_2+p_{2v}(T)-N}{N-N_1}\right), \quad (4)$$

and for $N<N_1$

$$\mu(T)\simeq u_1-kT\ln\left(\frac{N_1}{N_1-N}\right). \quad (5)$$

Thus $\mu(T)=u_1-\alpha_1kT$ for $N<N_1$ and $T<300$ K and we will observe the activation energy $E_a=u_1$. For high concentrations of impurity, $N>N_1$, we have from Eq. (4) $\mu(T)\simeq u_2-\alpha_2kT$ for $T<100$ K, and, for the temperature range $100<T<300$ K, $\mu(T)\sim kT\ln[N_v/(N-N_1)]$. This means that the activation energy is equal to zero and the density of valence-band holes is equal to $N-N_1$. Thus this temperature region corresponds to a regime of saturation of the impurity state with energy u_2. For high temperatures ($T>350$ K) and for any concentration of impurities we have $\mu(T)\approx(u_1-u_2)/2+kT\ln(N_v/N)/2$. This temperature interval was not investigated in this work, but we can find this behavior in the experiments of Ref. 14.

The total conductivity consists of the valence-band conductivity and the hopping conductivity: $\sigma=\sigma_v+\sigma_h$. The valence-band conductivity is calculated with the formula $\sigma_v(T)=e\mu_vp_v(T)\equiv e\mu_vN_v(T)\exp[-\mu(T)/kT]$, where μ_v is the valence-band hole mobility and e is the charge of an electron. We have taken into account that the temperature dependence of the hole mobility μ_v is connected with the mobility from ionized impurities μ_i and with the mobility from phonons $\mu_{ph}:\mu_v=(\mu_i^{-1}+\mu_{ph}^{-1})^{-1}$. As the impurity density increases the mobility connected with ionized impurities μ_i provides the main contribution to the mobility μ_v, and the mobility changes according to the law $\mu_v\simeq(AN_2T^{-3/2}+BT^{3/2})^{-1}$, where we take $A=5\times10^{-16}$ V s K$^{3/2}$ cm and $B=4\times10^{-8}$ V s K$^{-3/2}$ cm^{-2}. The expression for the hopping conductivity is $\sigma_h=\sigma_0\exp[-(T_0/T)^{1/4}]$, where $\sigma_0=e\mu_hp_2(T)$ and μ_h is the hopping mobility ($\mu_h=20$ cm^2 V^{-1} s^{-1}). On the basis of the results for high boron concentrations, when the hopping mechanism of conductivity is obviously dominating, let us assume that $T_0=\beta/N_2(\beta=10^{19}$ K cm$^{-3})$. Then we get the temperature dependence of conductivity $\sigma(T)$ that is shown in Fig. 2. Thus the temperature dependence of the conductivity is determined by the coexistence of the valence-band and hopping conductivities in a wide temperature range. The hopping conductivity occurs over the additional states of boron and can be assisted by the excited states of boron in the usual position or by D^- states.

To describe the Hall measurement we use the well-known[2] formula for the Hall coefficient $R(T)$:

$$R(T)=\frac{p_v\mu_v\mu_{vH}+p_2\mu_h\mu_{hH}}{e(p_v\mu_v+p_2\mu_h)^2}. \quad (6)$$

Here μ_{vH} and μ_{hH} are the Hall mobilities for each conductivity mechanism, respectively. The temperature dependence of the Hall coefficient is shown in Fig. 3. There we have used an idealized formula for the the relations $\mu_{vH}/\mu_v\sim2$ and $\mu_{hH}/\mu_h\sim0.1$. For better agreement betweeen theory and experiment it is important to know the actual temperature behavior of this relation. The specific feature of the Hall coefficient is connected with the fact that the temperature dependence of mobility μ_v is strong even compared with the temperature dependence of the valence-band hole concentration over the transition region of temperature.

Thus it is shown that the temperature dependence of the conductivity is connected with the coexistence of band and hopping conductivity in a wide temperature range. A scenario of the transition to hopping conductivity for heavily doped diamond is as follows. As the temperature decreases, first the band conductivity with activation energy u_1 is observed, and then a gradual transition to the state where only holes thermoactivated from the level u_2 participate in the valence-band conductivity takes place. At the same time, the hopping conductivity in the levels u_2 increases and at lower temperatures, when thermoactivation from the level u_2 weakens, it becomes dominating. In fact, the change of Fermi level with temperature can be interpreted as the observation of ϵ_2. In the general case the hopping conductivity occurring on the levels u_1 and u_2 depends on what has taken place earlier: the concentration of the additional boron states exceeds that of the donors or the hopping conductivity on levels u_1 becomes high enough to exceed the valence-band conductivity. In the second case, as the doping level increases, a transition from hopping conductivity in the level u_1 to hopping conductivity in the level u_2 should take place.

In any case, a transition to hopping conductivity in the levels u_2 and the corresponding appearance of the effective activation energy ϵ_2 will occur when the donor concentration is sufficiently low, and the situation with N_2 larger than N_D is easily achieved. It is interesting that previously it was also emphasized[1–4] that a low value of the degree of compensation accompanies the observation of the activation energy ϵ_2. In our case ϵ_2 is due to the transition from valence-band conductivity with holes activated from the level u_1 to hopping conductivity in the level u_2 via the temperature change of the activation energy that follows the temperature change of the Fermi level. Thus ϵ_2 is a manifestation of the temperature change of the Fermi energy in a certain temperature range. For very high boron concentrations one should consider a large number of additional states. A great number of states with different energies close together are possible, leading to the smearing of the level u_2. Taking this into account might slightly modify the results but will not change the main conclusions of this work.

The following conclusions can be made. Additional states arise as the doping level increases and at low temperatures conductivity is due to both the thermal activation from shallow levels and the hopping mechanism. As the energy of the levels of the additional states is close to that of the level of an excited boron state in the conventional position, hopping conductivity occurs along the additional boron states assisted by the excited boron states in the conventional position. This leads to high hopping conductivity. At very high doping the conductivity is mainly of hopping character because the number of the additional states greatly increases with doping.

The same mechanism should be taken into account when the problem of impurity conductivity in other materials is discussed.[3,4]

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