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Crossover between Mott's and Arrhenius' laws in the temperature dependence of resistivity of highly boron-doped delta-layers in artificial diamond

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Experimental temperature dependence of the resistivity of thin (1–3 nm) highly boron-doped (close to the threshold of the phase transition into a state with a metallic-type conductivity) delta-layers in chemically vapor deposited (CVD) diamond in a broad temperature range from ~ 100 to ~ 500 K can be described by Mott's two-dimensional law (hole „hops“ between localized states with a temperature-dependent average „hop“ length) in a low temperature region and Arrhenius' law (hole „hops“ between the nearest localized states) in a high temperature region. The crossover between them takes place at 230–300 K. The potentials of hole localized states are of a long-range, e. g. Coulomb's, type, the static dielectric permittivities of delta-layers are by several times larger than those of undoped CVD diamond.

Keywords: CVD diamond, Arrhenius law, Mott's law, doped δ-layers, „jump“ conductivity, phase transition insulator–metal.

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1. Introduction

Thin (several lattice constants thick) heavily doped layers (so-called δ-layers) in diamond produced by chemical vapor deposition (CVD) [1–8] are considered to be a promising tool for increasing the mobility of charge carriers. High values of the latter are required for various electronic applications, such as fast CVD-diamond-based field-effect transistors [9,10]. The increase in the mobility of charge carriers in such layers compared to the case of homogeneous alloying is due to the quantum effect of their partial penetration from the quantum well formed by their parent ionized impurity atoms in the δ-layer into the undoped diamond surrounding this layer. As a result, their scattering on these atoms decreases, leading to an increase in their mobility. However, no such increase in hole mobility was observed [8,11] in many experiments with boron-doped δ-layers in CVD-diamond. Consequently, further experimental and theoretical investigation of the conductivity of such layers, especially the influence of their thicknesses on it, is necessary.

The purpose of the present paper — is to measure the resistance dependences of several highly boron-doped (with concentration close to the threshold of phase transition to the metallic conduction state) δ-layers in CVD-diamond over a wide temperature range from ~ 100 to ~ 500 K and modelling them using the theories of „jump“ conductivity and percolation. To this end, two approaches to such modelling, applicable in the low and high temperature ranges, are discussed in the next section. In Section 3, the results of these approaches are compared with experimental data, and conclusions are drawn about the intrinsic characteristics of heavily boron-doped δ-layer in CVD diamond from the condition of their best fit. The conclusion summarizes the main results of the paper.

2. Methodology for calculating temperature dependences of resistances of heavily boron-doped delta layers in CVD-diamond

Let a thin heavily boron-doped δ-layer in CVD diamond have a thickness d (the full width of the boron atom concentration distribution over half of its peak value at the center of the layer) of the order of a few nanometers and the peak concentration of boron atoms N_a in it is close to $10^{21}\,\mathrm{cm}^{-3}$, but below the phase transition threshold of the insulator–metal [12] (the actual parameters of δ-layers will be given in the next section). This δ-layer is between thick deliberately undoped layers of CVD diamond.

First, we consider the interval of sufficiently low temperatures (its upper boundary will be determined from the analysis of experimental data, see further), where hole „hops“ occur mainly between localized states with energies close to the chemical potential μ [13]. In this energy area, the density of localized states is small, but despite the low temperatures, about half of them are occupied by holes, and the other half are empty. As a result, there are some holes in these states and they can „jump“ from one state to another without violating the Pauli principle, which provides conductivity.

Let the characteristic scale of the wave functions corresponding to these states be equal to l. In the theory of „jump“ conductivity [13], the average distance between localized states is usually assumed to be greater than $2l$, so that the wave function of a hole occupying some state near another state is proportional to $\exp(-r/l)$, where r — the distance between these two states. Then the probability of transition of a hole from the occupied state i with energy e_i, $e_i < \mu$, and radius vector $\mathbf{r}_i$ to the unoccupied state j with energy e_j, $e_j > \mu$, and radius vector $\mathbf{r}_j$ is proportional to

$$\exp\left(-\frac{2r_{ij}}{l} - \frac{e_j - e_i}{k_\mathrm{B}T}\right),$$

where $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ — the distance between these states, T — the absolute temperature, k_B — the Boltzmann constant [13].

In the theory of „jump“ conductivity [13], it is shown that the sample resistance R is proportional to

$$\exp\left(\frac{2r_{ij}}{l} + \frac{e_j - e_i}{k_\mathrm{B}T}\right), \tag{1}$$

where r_{ij} as well as $e_j - e_i$ correspond to the „optimal jump“, i. e., „jump“ for which the degree of the exponent is minimal. This minimum is found by considering that the length of the „jump“ r_{ij} is related to the energies of the corresponding states e_i and e_j by the formula $r_{ij} \approx N^{-1/2}(e_i, e_j)$, where $N(e_i, e_j)$ — the two-dimensional density of localized states with energies lying in the interval from e_i to e_j [13]. The use of exactly two-dimensional rather than three-dimensional density of states is due to the fact that for „optimal jump“ r_{ij} is greater than or of the order of the thickness of the δ-layer d (see next section).

To find $N(e_i, e_j)$, note that when the entire hole system is in the ground quantum state (i.e., absolute temperature is zero), the localized state i is occupied and the localized state j is not occupied only if the inequality [13] is fulfilled

$$e_j - u(r_{ij}) - e_i > 0. \tag{2}$$

Here, $u(r_{ij})$ — the potential energy of electrostatic interaction of holes in the localized states i and j. The origin of this condition is due to the fact that the energy e_j of the unoccupied localized state j contains a contribution from the electrostatic energy of the hole in the occupied localized state i. Therefore, when a hole „hops“ from a localized state i to a localized state j, its energy changes from e_i to $e_j - u(r_{ij})$. When the whole hole system is in the ground quantum state, this change must be positive, otherwise the localized state j would be occupied in this state, and localized state — non occupied.

To instantiate the shape of $u(r_{ij})$, consider that near the phase transition insulator−metal, the static dielectric constant of the δ-layer ε_d is much larger than the static dielectric constant $\varepsilon \approx 5.7$ of the surrounding intentionally undoped CVD diamond [12]. In this case, the Coulomb interaction energy of holes can be represented by the formula

$$u(r) \approx \frac{e^2}{\varepsilon_\mathrm{eff} r}, \tag{3}$$

where e — elementary charge, ε_eff — effective static permittivity, $\varepsilon < \varepsilon_\mathrm{eff} < \varepsilon_d$. Substituting (3) in (2), we obtain

$$N(e_i, e_j) < \left[\frac{(e_j - e_i)\varepsilon_\mathrm{eff}}{e^2}\right]^2. \tag{4}$$

Since $N(e_i, e_j)$ must be positive, inequality (4) means that there is a so-called Coulomb gap in the density of states [13], i.e. $N(e_i, e_j) \to 0$ at $e_j \to e_i \to \mu$. It is shown in [13] that in this case, $N(e_i, e_j)$ is of order of the right-hand side (4), i.e.

$$N(e_i, e_j) = \left[\frac{(e_j - e_i)\varepsilon_\mathrm{eff}}{\pi e^2}\right]^2. \tag{5}$$

Then, minimizing (1),

$$\frac{2N^{-1/2}(e_i, e_j)}{l} + \frac{e_j - e_i}{k_\mathrm{B}T},$$

with respect to $e_j - e_i$, it is easy to obtain that for „optimal jump“

$$e_j - e_i = \sqrt{\frac{2\sqrt{\pi}e^2 k_\mathrm{B}T}{\varepsilon_\mathrm{eff} l}} \quad \text{and} \quad r_{ij} = \sqrt{\frac{\sqrt{\pi}e^2 l}{2\varepsilon_\mathrm{eff} k_\mathrm{B}T}},$$

i.e., the length of such a jump depends on temperature (specifically, inversely proportional to the square root of temperature, two-dimensional Mott's law [12]). Substituting this into (1), we obtain that

$$R \propto \exp\left[\left(\frac{T_0}{T}\right)^{1/2}\right], \tag{6}$$

where

$$T_0 = \frac{8\sqrt{\pi}e^2}{k_\mathrm{B} l \varepsilon_\mathrm{eff}}. \tag{7}$$

It is known that near the phase transition insulator−metal, the localization length l grows proportionally to $\sqrt{\varepsilon_d} \sim \sqrt{\varepsilon_\mathrm{eff}}$ [12,14]. Therefore, further, we will assume that $l \approx r_\mathrm{B}\sqrt{\varepsilon_\mathrm{eff}/\varepsilon}$, i.e., we will believe that the localized states of holes in the intentionally undoped CVD-diamond are associated with the usual acceptor states near negatively charged boron ions, and the localized states of holes in the heavily doped δ-layer are formed by clusters of such ions with sizes of the order of l. Here, $r_{\mathrm{B}} = \hbar^2\varepsilon/(e^2 m_h) \approx 7.2\,\mathrm{Å}$ — the Bohr radius for localized hole states near negatively charged boron ions in intentionally undoped CVD diamond, $\hbar$ — Planck's constant, $m_h = 0.4m_e$ — the average effective mass of a hole [15], m_e — the mass of a free electron.

Secondly, let us consider the interval of sufficiently high temperatures (its lower boundary approximately coincides with the upper boundary of the interval of sufficiently low temperatures discussed above and, like the latter, will be determined from the analysis of experimental data, see hereafter), when „jumping“ conductivity is mainly due to hole „hopping“ between localized states with energies close to the energy of the isolated acceptor state [13]. In this energy area, the density of states is large, but only an exponentially small fraction of them are occupied by holes (in the case of a compensation factor close to unity) or only an exponentially small fraction of them are not occupied by holes (in the case of a compensation factor close to zero). In both cases, the resistance ofδ-layer is determined by the hole hopping between the nearest localized states and is inversely proportional to this exponentially small fraction [13], that is

$$R \propto \exp\left(\frac{|\mu|}{k_{\mathrm{B}}T}\right), \tag{8}$$

where μ — the chemical potential counting downward from the energy of the isolated acceptor state. In the case of a near unity compensation factor $\mu < 0$, whereas in the case of a small compensation factor $\mu > 0$. Thus, R looks like the Arrhenius formula [13],

$$R \propto \exp\left(\frac{E_a}{k_{\mathrm{B}}T}\right),$$

with temperature-independent activation energy $E_a = |\mu|$. According to [13] for both of these cases,

$$|\mu| \approx \frac{e^2 N_a^{1/3}}{\varepsilon_{\mathrm{eff}}(1-c)^{1/3}}, \tag{9}$$

where c — compensation factor, $c \equiv N_d/N_a$, N_d — donor concentration.

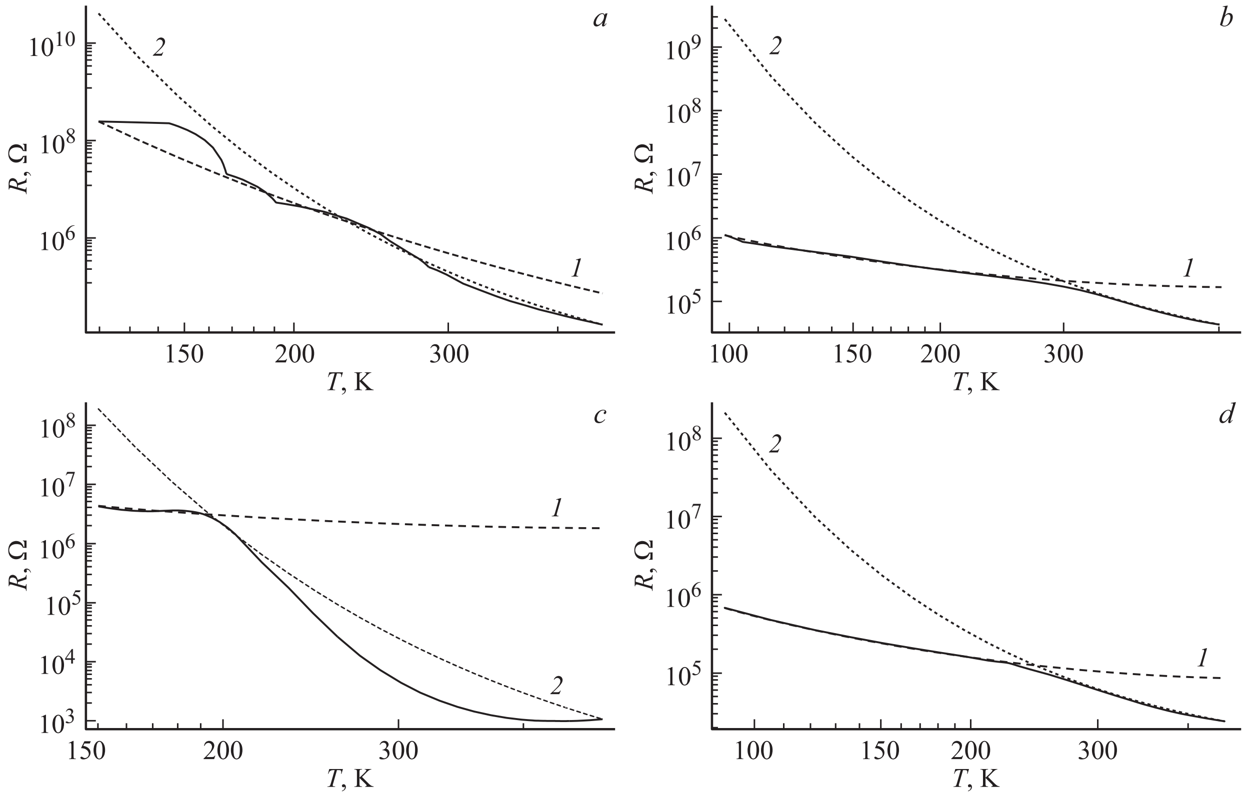
3. Experimental methodology and comparison of experimental and theoretical temperature dependences of resistances of heavily boron-doped delta layers in CVD-diamond

To establish the temperature dependences of the pre-exponential factors in (6) and (8), it is necessary to compare the results of theoretical models with experimental data. The drawing shows the experimental temperature dependences of the resistances R of δ-layers for structures S42, S45, S082, and S085. Measurements were performed both on δ-layers grown directly on the surface of undoped CVD-diamond film (e.g., structure S42, film thickness $3\,\mu$m, ohmic contacts to the δ-layer Ti/Mo/Au) and on layers buried in this film (e.g., structure S45, film thickness 220 nm, depth of δ-layer 20 nm, Ti/Al ohmic contacts to reduce contact resistance were made to an additional strongly boron-doped δ-layer grown on the film surface with parameters similar to those of the buried layer, but etched in the area between the contacts to prevent current flowing through it from contact to contact). Measurements were performed using the Van-der-Pau method. For structures with buried δ-layers, it was verified that the conductivity is indeed determined by these layers (test measurements of resistances were made after etching the structures between contacts to depths greater than the depths of buried δ-layers, and these resistances were found to be 10^4-10^5 times higher than the resistances of the same structures before etching).

The temperature dependences of the resistances of δ-layers in the figure are quite strong, which indicates that their conductivity is not metallic and its conditioned by holes „hops“ between localized states.

Consider the low temperature area (6). According to Miller's–Abrahams theory and percolation theory [13], in a two-dimensional situation (when the resistance δ-layer is of the order of the resistance of a rectangular parallelepiped with height d and width and length, equal to the correlation radius of the critical subnetwork) the temperature dependence of the pre-exponential factor in (6) has the form $T^{3/2}$ if the wave function of the localized hole state declines as $\exp(-r/l)$, or $T^{-1/2}$ if it declines as $r^{-1}\exp(-r/l)$. The first case is characteristic for long-range, e.g. Coulomb, potentials of localized states of holes, whereas the second — for short-range, e.g. shielded, potentials of such states [16]. The calculations show that in the second case, the best agreement with low-temperature experimental data is obtained at relatively small $T_0 \sim 10^3$ K. According (7), such T_0 requires large $\varepsilon_{\mathrm{eff}} \sim 150$. Then, to obtain from (9) $|\mu|$ best fitted to the high-temperature experimental data, it is necessary to take the compensation factor very close to unity, which seems unrealistic. Therefore, it will be assumed hereafter that in the low temperature area, the pre-exponential factor in (6) varies with temperature as $T^{3/2}$. This means that the potentials of localized states of holes are long-range, e.g. Coulomb potentials.

In the high temperature area (8) in the case of long-range potentials, according to Miller's–Abrahams theory and percolation theory [13,14], in the two-dimensional (and three-dimensional) situation, the pre-exponential factor in the temperature dependence of the resistance is directly proportional to the temperature T.



Experimental temperature dependence of the δ-layer resistance R (solid curve) and its low-temperature (10) (dashed curve *1*) and high-temperature (11) (dashed curve *2*) theoretical approximations for the structures S42 (*a*), S45 (*b*), S082 (*c*), and S085 (*d*). Dimensions of all structures (length × width × thickness) 3.5 × 3.5 × 0.5 mm.

Experimentally measured and theoretically calculated parameters of samples

Sample	d, nm	N_a, cm^{-3}	T_{low}, K	$R(T_{\text{low}})$, Ohm	T_{high}, K	$R(T_{\text{high}})$, Ohm	T_0, K	ε_{eff}	l, nm	c
S42	1	$9 \cdot 10^{20}$	119.7	$2.46 \cdot 10^8$	450	$1.66 \cdot 10^4$	$5 \cdot 10^4$	6.27	0.76	0.1
S45	2	$7 \cdot 10^{20}$	98.5	$1.11 \cdot 10^6$	500	$4.29 \cdot 10^4$	$6 \cdot 10^3$	25.8	1.5	0.95
S082	3.3	$2 \cdot 10^{20}$	150	$4.25 \cdot 10^6$	480	$1.07 \cdot 10^3$	$5 \cdot 10^3$	28.3	1.6	0.9983
S085	2.3	$8 \cdot 10^{20}$	91	$6.77 \cdot 10^5$	449.9	$2.41 \cdot 10^4$	$6 \cdot 10^3$	25.8	1.5	0.88

Thus, in the low temperature area, the resistance of δ-layer is approximated by the formula

$$R = R(T_{\text{low}}) \left(\frac{T}{T_{\text{low}}} \right)^{3/2} \exp\left[\left(\frac{T_0}{T} \right)^{1/2} \right] \Big/ \exp\left[\left(\frac{T_0}{T_{\text{low}}} \right)^{1/2} \right], \tag{10}$$

where $R(T_{\text{low}})$ — the resistance of δ-layer at the lower boundary T_{low} of the low-temperature range and T_0 is given by (7). In the high temperature area, it is defined by the expression

$$R = R(T_{\text{high}}) \frac{T}{T_{\text{high}}} \exp\left(\frac{|\mu|}{k_{\text{B}} T} \right) \Big/ \exp\left(\frac{|\mu|}{k_{\text{B}} T_{\text{high}}} \right), \tag{11}$$

where $R(T_{\text{high}})$ — the resistance of δ-layer at the upper boundary T_{high} of the high-temperature range and $|\mu|$ is given by (9).

The table summarizes the experimentally measured parameters d, N_a, $R(T_{\text{low}})$ and $R(T_{\text{high}})$, and the theoretically calculated parameters T_{low}, T_{high}, T_0, ε_{eff}, l and c, providing the best fit of the low (10) and high-temperature (11) theoretical approximations to the experimental data for CVD diamond samples S42, S45, S082, and S085 with δ-layers. These approximations are also shown in the drawing.

The table shows that the parameters of structures S45, S082 and S085 (both experimental and theoretical) are quite close. These structures are characterized by a large compensation degree of the order of 90% and large ε_{eff}, indicating that the heavily boron-doped δ-layers in them are near the insulator–metal phase transition threshold. In contrast, the S42 structure is weakly compensated ($\sim$ 10%), has an ε_{eff} close to the static dielectric constant ε of undoped diamond, indicating that it is quite far from the threshold of this transition. This is probably due to the thinness of the δ-layer in this structure, although the peak concentration of boron atoms in it is even higher than in structures S45, S082 and S085.

The figure shows that the transition from the low (10) to the high-temperature area (11) for structure S42 occurs at $T \sim 230\,\mathrm{K}$, for structure S45 — at $T \sim 300\,\mathrm{K}$, for structure S082 — at $T \sim 200\,\mathrm{K}$, and for structure S085 — at $T \sim 250\,\mathrm{K}$.

Calculations show that the „optimal“ jump length r_{ij} in the low temperature range exceeds $2.5d$ in structure S42 and of the order of d in structures S45, S082, and S085. This justifies the use of the above two-dimensional density of states. Moreover, for all structures, the optimal length of the „jump“ r_{ij} in the low-temperature area is several times larger than the average distance between boron atoms, so that such „jumps“ can indeed occur, which also justifies the theoretical approach used.

4. Conclusion

Thus, it is shown that the experimental temperature dependences of resistances of strongly boron-doped (with peak concentrations of boron atoms close to $10^{21}\,\mathrm{cm}^{-3}$) δ-layers grown in deliberately undoped CVD diamond with thicknesses $\sim 1-3\,\mathrm{nm}$ and non-metallic (i. e. which takes place below the insulator–metal phase transition threshold) type of conductivity in a wide temperature range from ~ 100 to $\sim 500\,\mathrm{K}$ can be explained by „jump“ conductivity of holes that are in localized states in the impurity energy band. For temperatures smaller than 230–300 K (depending on the sample), they are described by the two-dimensional Mott law (which is due to „hops“ of holes between localized states with a temperature-dependent — inversely proportional to the square root of the temperature — average length of the „hops“. For higher temperatures, they are described by the Arrhenius law (which is due to „jumps“ of holes between the nearest localized states). The potentials of localized states are probably long-range, e.g. Coulomb potentials. The static dielectric constants of δ-layers should be several times larger than those of intentionally undoped CVD diamond, due to their proximity to the insulator–metal phase transition threshold.

The obtained results help to better understand the physics of hole „jump“ conduction in heavily boron-doped δ-layers of CVD-diamond just below the threshold of their phase transition to the state with metallic type of conduction. However, further experimental and theoretical studies of this phenomenon are needed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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