Transport properties of n-type ultrananocrystalline diamond films

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We investigate transport properties of ultrananocrystalline diamond films for a broad range of temperatures. Addition of nitrogen during plasma-assisted growth increases the conductivity of ultrananocrystalline diamond films by several orders of magnitude. We show that films produced at low concentration of nitrogen in the plasma are very resistive and electron transport occurs via a variable range hopping mechanism while in films produced at high nitrogen concentration the electron states become delocalized and the transport properties of ultrananocrystalline diamond films can be described using the Boltzmann formalism. We discuss the critical concentration of carriers at which the metal to insulator transition in ultrananocrystalline diamond films occurs and compare our results with available experimental data.

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I. INTRODUCTION

Ultrananocrystalline diamond (UNCD) films have many potential applications in high-temperature electronics because of the highest n-type conductivity and carrier concentration demonstrated for phase-pure diamond thin films.[1–3] Experimentally, n-type conductivity of UNCD can be tuned within several orders of magnitude by nitrogen addition to the feed gas during plasma-assisted growth. Without the nitrogen addition to the plasma, the resulting films are quite resistive, but addition of more than about 8% of nitrogen leads to a metallic behavior. Interestingly, the grain size increases from 4 to 16 nm, as well as the grain boundary width from about 0.5 to 2.2 nm with N concentration increase from 0% to 20%, but the overall fraction of diamond phase remains consistently very high.[4] At the same time, nitrogen concentration in the films remains nearly the same, suggesting that change in the carrier concentration due to higher number of nitrogen donors cannot be invoked to explain the increase of conductivity. It was shown by careful Hall measurements[5] that the conductivity is n-type, and that carrier concentrations in the films increase much more than carrier mobilities with increase in feed gas nitrogen concentration. Therefore, these studies suggested that there is a metal-insulator transition in UNCD upon nitrogen addition, and that this transition is triggered by changes in UNCD grain and grain boundary sizes.

Theoretical tight-binding studies[6] of UNCD without nitrogen suggested a hopping transport mechanism, where the donor sites are located in the grain boundaries and the bulk of the grains is electrically inactive. Here high-angle high-energy grain boundaries were considered to be a model of general grain boundaries of UNCD. The donor states were calculated to be carbon π states and dangling bond states in the grain boundaries. The hopping conductivity of UNCD was estimated to be $10^{-6}(\Omega\,\mathrm{cm})^{-1}$, 3 to 7 orders of magnitude higher than in chemical vapor deposition (CVD) diamond.

Self-consistent charge density functional based tight-binding studies[7] of nitrogen sites in the bulk and in the grain boundaries found energies, geometries and electronic structure of nitrogen in UNCD at low and high nitrogen concentrations. First, it was found that nitrogen is energetically preferred in the grain boundary relative to the bulk diamond sites in the grains. Second, nitrogen was found not to be a shallow donor, being preferentially in nondoping configurations. Third, electrons from high-lying donor states formed upon nitrogen addition transfer down in energy to the Fermi level, located in the π-state region. This causes an upward shift of the Fermi level with increase in nitrogen concentration. Calculated density of states (DOS) for diamond grain boundaries with and without nitrogen are shown in Fig. 1 along with a scheme of electron levels in the latter case.

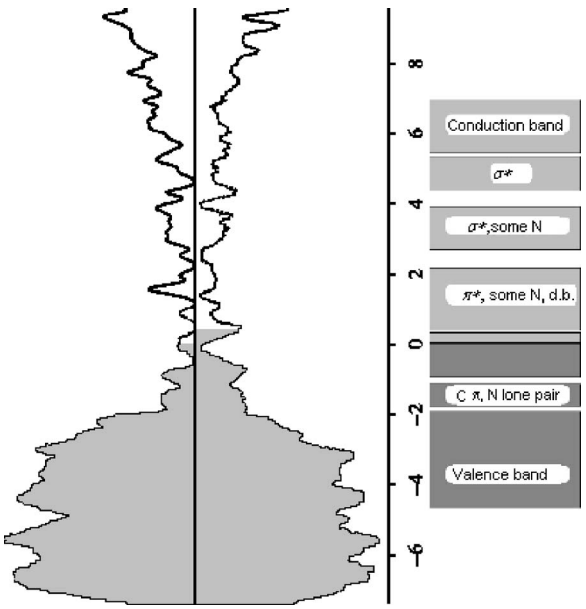

FIG. 1. Calculated DOS for diamond with Σ13 grain boundary and without (left) or with (right) nitrogen (relative to the Fermi level of undoped system). Occupied states are shaded. Sketch of electron levels in the presence of nitrogen is shown on the right. The data are taken from Ref. 7.

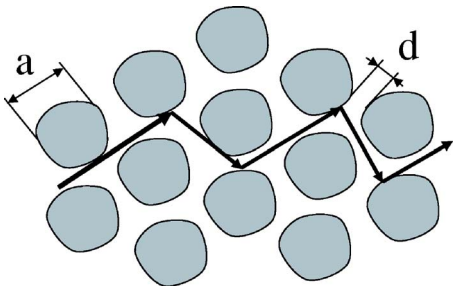

FIG. 2. (Color online) Sketch of ultrananocrystalline diamond film with a schematic electron path. The grey regions are insulating grains with a and d being the characteristic grain size and distance between the grains respectively.

In addition, the connectivity of the π bonds in the grain boundaries improves upon nitrogen addition. This Fermi level shift and improved connectivity were proposed to be responsible for the increase in hopping conductivity.

However, there is still no satisfactory mesoscopic description of UNCD transport properties. No explanation was provided previously for the transition from hopping to semimetallic regime with increase in N concentration. In this paper we consider theoretically transport properties of UNCD films in the temperature range

$$10\ \mathrm{K} < T < 700\ \mathrm{K}, \tag{1}$$

and investigate UNCD conductivity within approximations developed for an array of metallic and semiconducting grains[8,9] in both Ohmic and non-Ohmic regimes.

II. INSULATING REGIME

For low concentrations of nitrogen ($<1\%$ in the feed gas), the resistance of UNCD films per square is $R \sim 10-100\ \mathrm{M}\Omega \gg R_c$, where $R_c = 6.25\ \mathrm{k}\Omega$ is the quantum resistance. In this case, UNCD films are insulators.

The characteristic grain sizes, see Fig. 2, of UNCD films are in the range

$$4\ \mathrm{nm} < a < 16\ \mathrm{nm} \tag{2}$$

and characteristic width of the grain boundaries is

$$0.5\ \mathrm{nm} < d < 2.2\ \mathrm{nm}. \tag{3}$$

The charging energies $E_c = e^2/\kappa d$, with κ being the dielectric constant, corresponding to these grain boundary widths are

$$\frac{1}{\kappa} 10^3\ \mathrm{K} < E_c < \frac{1}{\kappa} 4 \times 10^4\ \mathrm{K}. \tag{4}$$

Assuming that the dielectric constant for UNCD films is $\kappa \sim 3-6$ from Eq. (4), it follows that the temperature T satisfies the inequality

$$T < E_c. \tag{5}$$

In this temperature range the activation conductivity,

$$\sigma \sim \exp(-E_c/T) \tag{6}$$

(tunneling between the nearest neighbors), is suppressed and electron transport occurs through tunneling via several grains.

Below we assume that the concentration of donors in the grain boundaries n_d satisfies the condition

$$n_d \xi^3 \ll 1, \tag{7}$$

where ξ is the localization length. Using the fact that

$$\xi \sim d \sim 1\ \mathrm{nm}, \tag{8}$$

we obtain the following condition for concentration of donors:

$$n_d \ll 10^{21}\ \mathrm{cm}^{-3}. \tag{9}$$

We first consider phonon-assisted (Ohmic) transport in UNCD films and later discuss the non-Ohmic regime.

A. Ohmic transport

Following the Mott-Efros-Shklovskii theory[10,11] we write the hopping conductivity in the following form:

$$\sigma \sim \exp\left(-\frac{r}{\xi} - \frac{e^2}{\kappa r T}\right), \tag{10}$$

where ξ is the localization length (ξ is of the order of a boundary width d). Equation (10) is valid for three-dimensional (3D) samples and thick films with the sample thickness L larger than the optimal hopping length r_{opt} defined below. This is a typical case for UNCD films, which are grown to thicknesses of μm.[2] Minimizing Eq. (10) with respect to the hopping distance r, we obtain the optimal hopping length

$$r_{\mathrm{opt}}(T) = \xi \sqrt{\frac{e^2}{\kappa \xi T}} = \xi \sqrt{\frac{T_0}{T}}, \tag{11}$$

where $T_0 = e^2/\kappa\xi$ is the characteristic energy scale. From Eq. (11) follows that the hopping length $r_{\mathrm{opt}}(T)$ increases with decreasing temperature. Using the fact that the hopping length

$$r_{\mathrm{opt}}(T) = N(T) a, \tag{12}$$

where $N(T)$ is the number of grains in one hop, we obtain

$$N(T) = \frac{\xi}{a} \sqrt{\frac{T_0}{T}}. \tag{13}$$

For temperatures $T \leqslant 300$ K and $T_0 \sim 40\,000$ K one obtains

$$N \sim 2. \tag{14}$$

With increase in temperature the number of grains N in one hop will decrease, leading to the hopping distance $r_{\mathrm{opt}}(T)$ of the order of the grain size. Also, increase in nitrogen concentration is shown to lead to increase in the grain size. With increase in the grain size a (and proportional increase in the grain boundary width d) N will decrease as $\sqrt{a}$. Substituting Eq. (11) into Eq. (10) we finally obtain

Efros-Shklovskii-type[12] of conductivity behavior

$$\sigma \sim \exp(-\sqrt{T_0/T}). \tag{15}$$

Equation (15) is valid for temperatures $T<T_0$. At temperatures $T\sim T_0$ the hopping distance $r_{\mathrm{opt}}(T)$ becomes of the order of a grain size and Eq. (10) does not work anymore. In this temperature range the conductivity obeys the Arrhenius law (6).

We would like to discuss the possibility of the observation of the Mott law in UNCD films. In semiconductors, the Efros-Shklovskii law may turn to the Mott behavior with the increase of temperature. This happens when the typical electron energy ε involved in a hopping process becomes larger than the width of the Coulomb gap Δ_c, i.e., when it falls into the flat region of the density of states where Mott behavior is expected. To estimate the width of the Coulomb gap Δ_c, one compares the ES expression for the density of states

$$\nu(\Delta_c) \sim (\kappa/e^2)^D |\Delta_c|^{D-1}, \tag{16}$$

where D is the dimensionality of a sample, with the bare density of states ν_0, i.e., the DOS in the absences of the long-range part of the Coulomb interactions. Using the condition $\nu(\Delta_c)\sim\nu_0$ we obtain

$$\Delta_c = \left(\frac{\nu_0 e^{2D}}{\kappa^D}\right)^{1/(D-1)}. \tag{17}$$

Inserting the value for the bare DOS, $\nu_0=1/E_c\xi^D$, into Eq. (17) we finally obtain

$$\Delta_c \sim E_c. \tag{18}$$

Equation (18) means that there is no flat region in the density of ground states and, thus, the Mott regime is difficult to observe in UNCD films. At first glance, this conclusion contradicts numerically obtained results using tight-binding methods[6,7] since nonzero densities of states at the Fermi level was obtained as a result of these calculations. However, there are relatively few states in the numerical studies because of the number of atom limitations on the size of the unit cells, which leads to uncertainties in the peak positions larger than typical values of Coulomb gap of several 10 K. In addition, Coulomb gap existence is based on excitonic effects, which are not explicitly taken into account in the tight-binding simulations. In other words, tight-binding simulations are not designed to accurately reproduce the functional form of DOS in the immediate vicinity (within several tens of Kelvins) of the Fermi level.

B. Non-Ohmic transport

Here we consider non-Ohmic conductivity in the temperature range in which the Ohmic conductivity is given by Eq. (15). In the presence of electric field E, the hopping conductivity is given by the following expression:

$$\sigma \sim \exp\left[-\frac{r}{\xi} - \frac{e^2}{\kappa r T} + \frac{eEr}{T}\right]. \tag{19}$$

1. Weak electric field

In a weak electric field, $eE\xi<T$, the last term in the right-hand side (rhs) of Eq. (19) is not important and the optimal hopping length is given by Eq. (11). Using Eqs. (19) and (11) one obtains for the hopping conductivity in a weak electric field the following expression:

$$\sigma \sim \exp(-\sqrt{T_0/T})\exp[(eE\xi/T)\sqrt{T_0/T}]. \tag{20}$$

From Eq. (20) follows that the Coulomb term becomes of the order of the electric field term at fields

$$E^* \sim T/e\xi. \tag{21}$$

2. Strong electric field

For electric fields $E>E^*$, where the field E^* is defined by Eq. (21), the first term in the rhs of Eq. (19) is not important. The optimal hopping length in this regime is temperature independent and is given by the following expression:

$$r_{\mathrm{opt}}(E) = \xi\sqrt{E_0/E}, \tag{22}$$

where $E_0=e/\kappa\xi^2=T_0/e\xi$ (we note that $E_0\gg E^*$). Using Eq. (22) one obtains for the hopping conductivity in a strong electric field[13]

$$\sigma \sim \exp(-\sqrt{E_0/E}). \tag{23}$$

We note that (i) for very strong electric fields, $E\sim E_0$, where the field E_0 is defined below Eq. (22), the hopping picture does not work anymore since the hopping length becomes of the order of the localization length, $r_{\mathrm{opt}}(E_0)\sim\xi$ and (ii) The current density j can be expressed in terms of conductivity as follows: $j=\sigma E$, where the conductivity σ is given by Eqs. (20) and (23) depending on the strength of the electric field E.

III. METALLIC REGIME

The transition from the hopping regime to degenerate semiconductor regime in UNCD is associated with a strong increase in the number of carriers, whereas the mobility of carriers is not strongly affected. This was demonstrated in Hall measurements.[5] Also, higher nitrogen concentration is related to increase in grain size and grain boundary width. For relatively large concentrations of nitrogen in the plasma ($\gg 5\%$), the UNCD film resistance becomes less than the quantum resistance, $R\sim 100\ \Omega \ll R_c$. As a result, the electron states become delocalized and the transport properties of UNCD films can be described using the Boltzmann equation.

There are several scattering mechanisms which contribute to the resistance R of a sample:[14] (1) scattering of electrons on static impurities R_{ei}, (2) electron-phonon scattering R_{e-ph}, and (3) electron-electron scattering R_{e-e}. At high temperatures the interference between different mechanisms can be neglected and the total resistance consists of a sum of resistances

$$R = R_{ei} + R_{e-ph} + R_{e-e}, \tag{24}$$

where $R_{ei}=\alpha\tau_{ei}^{-1}$, $R_{e-ph}=\alpha\tau_{e-ph}^{-1}$, $R_{e-e}=\alpha\tau_{e-e}^{-1}$. Here $\alpha=m^*/(e^2n_e)$ with m^* being the effective mass of an electron

and τ_{ei}, τ_{e-ph}, and τ_{e-e} are the characteristic scattering times due to scattering of electrons on static impurities, phonons, and electrons, respectively. We would like to comment on the validity of Eq. (24). Writing Eq. (24) we assume that different scattering mechanisms are independent. This is indeed the case at not very low temperatures when the scattering lengths $L_{e-ph}=u/T$, with u being the phonon speed and $L_{e-e}=v_F/T$ are smaller than the elastic mean free path, $l=v_F\tau_{ei}$. Using the condition $\max(L_{e-ph},L_{e-e})\simeq l$ one can find the characteristic temperature $T^*=\tau_{ei}^{-1}$. For temperatures $T>T^*$ the interference among different mechanisms is not important and Eq. (24) is valid. Below we discuss different contributions to the resistance of UNCD films.

Assuming that the mean free path of an electron is of the order of the grain boundary width d for elastic scattering time one obtains $\tau_{ei}^{-1}\sim v_F/d$, where v_F is the Fermi velocity. The electron-phonon scattering time τ_{e-ph} is given by the following expression:[14]

$$\tau_{e-ph}^{-1}=\begin{cases} T & T>\omega_D, \\ T\left(\dfrac{T}{\omega_D}\right)^4 & T<\omega_D, \end{cases} \tag{25}$$

where ω_D is the Debye temperature (for UNCD films $\omega_D\sim 1000$ K). For the temperature range considered here, only the $T<\omega_D$ regime is relevant. For electron-electron scattering time τ_{e-e} one finds $\tau_{e-e}^{-1}=T^2/\mu$, where μ is the chemical potential. Using Eqs. (24) and (25) for temperatures $T<\omega_D$ we obtain the following expression for the total resistance R of a sample:

$$R=(m^*/e^2n_e)(v_F/d+T^5/\omega_D^4+T^2/\mu). \tag{26}$$

For temperatures $T<\omega_D$ the last two terms in the rhs of Eq. (26) are small therefore the resistance R is almost temperature independent.

IV. CROSSOVER FROM INSULATING TO METALLIC REGIME

In this section we discuss crossover from insulating (hopping) to semimetallic regime in UNCD films. To find a critical concentration of carriers n_c at which the crossover from insulating to semimetallic regime occurs following the Mott's approach,[10] we compare two characteristic lengths: the screening length $r_e\approx\frac{1}{2}\frac{\xi}{(\xi^3n)^{1/6}}$ and the localization length ξ. In the metallic regime the screening length r_e is small and the localization length ξ is large while in the insulating regime the situation is the opposite. The crossover region between the two regimes can be defined as $r_e\sim\xi$. Using the above condition we obtain the following expression for the critical concentration of carriers:

$$n_c\sim\frac{1}{(4\xi)^3}. \tag{27}$$

Since the localization length ξ is of the order of the distance between the grains, $\xi\sim d$, see Eq. (8), from Eq. (27) follows that the larger the distance between the grains the smaller the critical concentration n_c is needed to achieve the metal to insulator crossover. For a realistic $d\sim 1$ nm we obtain the following estimate for the critical concentration $n_c\sim(10^{19}-10^{20})$ cm^{-3}, which appears to be plausible.[2]

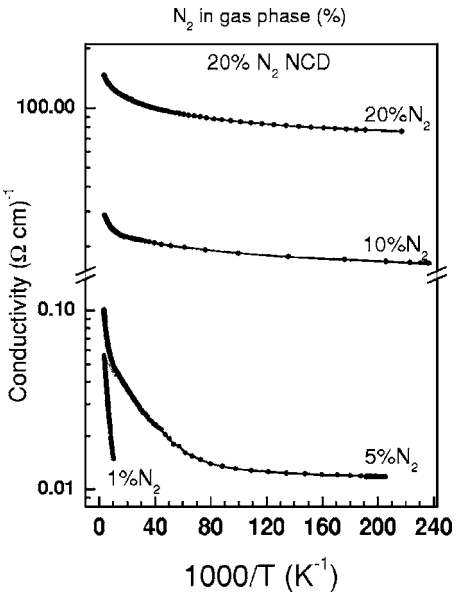

FIG. 3. Dependence of the conductivity of UNCD films on temperature. Different curves correspond to different nitrogen concentrations in the feed gas during film growth. Reproduced from Ref. 2.

V. COMPARISON WITH EXPERIMENT

In this section we compare our results for resistivity of UNCD films with available experimental data from Refs. 2 and 3. These data are shown in Fig. 3. One can distinguish two qualitatively different regimes for conductivity behavior: (i) metallic, $\sigma>1\ \Omega^{-1}$ cm^{-1} and (ii) semiconducting, $\sigma\leqslant 1\ \Omega^{-1}$ cm^{-1}.

To compare our results for resistivity R in the metallic regime, Eq. (26), with experimental values we have taken reasonable estimates for the critical carrier concentration of $n_e\sim n_c\sim 10^{20}$ cm^{-3} and v_F of 10^8 cm/s. From Eq. (26), we obtain the specific resistivity of UNCD to be $R\sim 0.1\ \Omega$ cm. We note that Eq. (26) was estimated to be valid above temperatures $T^*=10-50$ K.

In the semiconducting regime the conductivity behavior of UNCD films is described by Eq. (15). Since the energy scale T_0 in Eq. (15) is inversely proportional to the localization length ξ one can see that at fixed temperature T the conductivity σ is very sensitive to the value of localization length. This fact is in perfect agreement with experimental data in Fig. 3.

The transport properties of UNCD films have been discussed in several publications.[3,15,16] Our treatment does not contradict the proposed DOS behavior.[3] In fact, electron densities in this work are consistent with our treatment. The main difference between previous considerations and our work is based on our description of experimental data using two regimes: (i) extended electronic states, Sec. III and (ii) localized electronic states, Sec. II. All previous interpreta-

tions of experimental data were based on electron hopping theory only.

VI. CONCLUSIONS

We studied transport properties of UNCD films as a function of temperature and concentration of nitrogen during plasma-assisted growth. We show that for UNCD grown in low concentration of nitrogen ($<1\%$ in the feed gas) the electron transport occurs via a variable range hopping mechanism while for films grown at high nitrogen concentration the electron states become delocalized and the transport properties of ultrananocrystalline diamond films can be described using the Boltzmann equation. Our results are in agreement with available experimental data.

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