# MODEL OF THERMAL CONDUCTIVITY OF ANISOTROPIC NANODIAMOND

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Dependence of thermal conductivity of nanocrystalline diamond on grain size and shape is theoretically investigated. Nanodiamond is considered as two-phase material composed of diamond grains characterizing by three main dimensions and segregated by thin graphite layers with electron, phonon or hybrid thermal conductivity. Influence of type of thermal conductance and thickness of boundary layer on thermal conductivity of nanodiamond is analyzed. Derived dependences of thermal conductivity on grain dimensions are compared with experimental data.

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## INTRODUCTION

As it is known, monocrystalline diamond has the highest thermal conductivity within solid materials, fivefold exceeding that of copper. On the contrary, low thermal conductivity of ultrananocrystalline diamond (UNCD) materials which is in several hundred times less than that of diamond requires special accounting at calculation of thermal conditions in processes where they are used [1, 2]. At present methods of growth of UNCD coatings with required grain size are developed [3], so understanding of these properties and possibility to control them are very important for practical use of UNCD materials. In view of small sizes of grains they boundary layers significantly determine thermal properties of UNCD. Dependence of thermal conductivity of isotropic UNCD on effective size of grain was theoretically investigated in ref. [4]. In proposed model describing structure of nanodiamond by only two parameters, the effective grain size *D* and the effective thickness *d* of boundary graphite layer with electron conductivity, the analytical expression for thermal conductivity was obtained. This expression describes reasonably the UNCD thermal conductivity in a wide range of parameters *D* and *d*. However, derived formula is inapplicable for calculation of thermal conductivity of anisotropic diamond coatings with phonon or hybrid thermal conductivity of boundary layers.

The goal of the paper is the theoretical investigation of dependence of thermal conductivity of anisotropic UNCD on characteristic dimensions of crystal grain and on thickness and physical properties of boundary layer.

## THEORETICAL INVESTIGATION

Let nanodiamond is a composite consisting of diamond grains ($sp^3$-bond carbon) separated by thin graphite layers ($sp^2$-bond carbon). It can be supposed that graphite is amorphized because of heightened imperfection of boundary layer. According to this conception one should determine thermal conductivity of nanodiamond as the corresponding value of a two-component composite material. To solve this problem we have to know some characteristics of each component and take into consideration how change these characteristics for nanometer-sized objects.

In the course of analysis we replace the real UNCD structure with the model one which includes all basic elements of heat transfer in two-component material.

Fig. 1 shows scheme of UNCD crystalline and equivalent modeling structure to be used for calculation of effective thermal conductivity of UNCD. Also, Fig. 1 shows the model of the elementary cell consisting of diamond gain surrounded with graphite shell which is marked by grey color. The shell thickness does not exceed 1 nm. We shall characterize the elementary cell by dimensions X, Y, Z of the diamond grain along three orthogonally related directions ($x, y, z$ axes) and by boundary shell thickness *d*. We suppose that nanodiamond is an orthotropic material. It corresponds to properties of deposited UNCD coatings possessing different grain dimensions in the plane of the coating and in perpendicular direction. In the general case, dimensions X, Y, Z are different.

The effective thermal conductivity $\lambda^{ef}$ of orthotropic material is a second-rank tensor associating gradient of temperature T with heat flow density $\vec{q}$: $q_i = -\lambda_{ik}^{ef}(\partial T/\partial x_k)$. In Cartesian coordinate system $x, y, z$ which is associated with X, Y, Z dimensions tensor $\lambda^{ef}$ has only diagonal elements and the basic Fourier conduction law transforms to more simple form $q_x = -\lambda_x^{ef}(\partial T/\partial x)$; $q_y = -\lambda_y^{ef}(\partial T/\partial y)$; and $q_z = -\lambda_z^{ef}(\partial T/\partial z)$, where $\lambda_x^{ef}$, $\lambda_y^{ef}$ and $\lambda_z^{ef}$ are the tensor eigenvalues which are equal to thermal-conductivity coefficient in direction of axes x, y, z, correspondingly. Determination of $\lambda_x^{ef}$, $\lambda_y^{ef}$ and $\lambda_z^{ef}$ permits to determine temperature field in UNCD material.

Diamond heat conduction has purely phonon nature and may be interpreted as diffusion of thermal phonons. The thermal conductivity of single crystal diamond connected with middle phonon path l by relation $\lambda = \rho C s l/3$, where $r, C, s$ are the mass density, the specific heat capacity, and the longitudinal sound velocity in single crystal diamond, correspondingly. Taking $\lambda \approx 2000$ W/(m·K) we get the next assessment for the mean phonon path: $l = 220$ nm. Obtained value

may considerably exceed characteristic dimension of nanodiamond grain. Supposing that phonons are reflected on crystalline interface we conclude that characteristic dimension of nanodiamond grain is parameter determining the effective phonon path in nanodiamond.

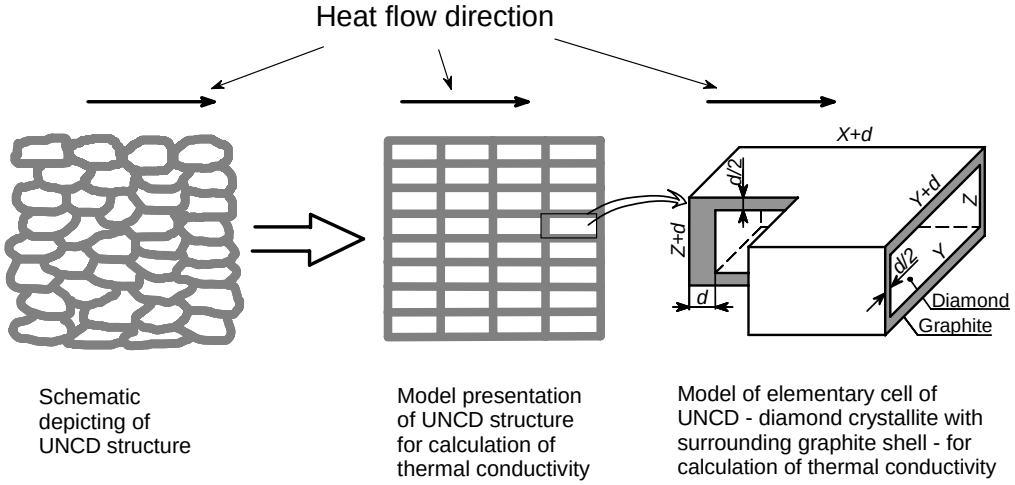


*Fig. 1. Scheme of UNCD crystalline and equivalent model structure to be used for effective thermal conductivity calculation. Isometric display of model grain is shown on the right*

In case of orthotropic crystalline diamond the effective phonon path depends on direction. Particularly, one can use the following approximation to determine the effective phonon path $l_x$ in direction of *x*-axis: $l_x^{-1} = l^{-1} + (2/X)$. Using this equation we can write expression for thermal conductivity of diamond phase along *x*-axis in form:

$$\lambda_x(X) = \frac{1}{3}\rho C s \cdot \frac{lX}{2l + X}. \qquad (1)$$

We can easily write similar expressions for thermal conductivity of diamond phase along *y*-axis and *z*-axis.

Equation (1) does not take into account dependence of thermal conductivity of crystalline diamond on thermal resistance of amorphized graphite layer between grains. At present this boundary resistance is unknown. As graphite is semimetal its thermal conductivity can be mainly conditioned by electron transport. In this case one can estimate value of thermal conductivity of boundary layer using formula $\kappa_b = l_e v_F/3$, where $l_e$ is the free path length of conduction electron with the Fermi energy $\varepsilon_F$. For graphite we can accept $\varepsilon_F = 0{,}026$ eV. Using formula $v_F = \sqrt{2\varepsilon_F/m_e}$, where $m_e$ is electron mass we obtain $v_F \approx 10^5$ m/s. The free length of conduction electron at room temperature exceeds considerably the interatomic distance *a*: $l_e$ = (200...250)·*a*. Taking into account that thickness of boundary layer *d* is approximately equal to 2*a* we can put for the effective path of electron $l_e = d/2$. In this case thermal conductivity of boundary layer material is equal to:

$$\lambda_b(d) \approx \rho_G C_G \frac{dv_F}{6}, \quad (d \text{ і } 2a), \qquad (2)$$

where $\rho_G$ and $C_G$ are the mass density and the specific heat capacity of graphite, correspondingly.

Thus we see that thermal conductivity of boundary layer is directly proportional to layer thickness *d* if the heat transfer is conditioned by electron transport.

If thermal conductivity of boundary layer depends on phonon transport then one should make double replacement in equation (2): $d \to 2a$; $v_F \to s$. Here $s \approx 1{,}47\cdot 10^3$ m/s is the longitudinal sound velocity in graphite. It is easy to see, that the phonon thermal conductivity $\lambda_b(d) = \rho_G C_G a s/3$ is considerably less (in ~ 70 times) than the electronic one and does not depend on thickness of boundary layer. In the general case, both mechanisms can contribute to heat conductance of boundary layer depending on a coating growth process, doping, etc. Hence, thermal conductivity of boundary layer can possess any value from interval determined by both above mechanisms.

Let's determine effective thermal conductivity of UNCD taking into consideration the effect of boundary layer. Apply the basic Fourier conduction law to heat transport through the elementary cell (see Fig. 1). Let temperature of left and right boundaries of the cell are $T_1$ and $T_2$, correspondingly where $T_1 > T_2$. Then the heat flow $Q_x$ from left to right is equal to

$$Q_x = -\lambda_x^{ef} S \frac{\partial T}{\partial x} = \lambda_x^{ef} (Y + d)(Z + d)\frac{T_1 - T_2}{X + d}. \qquad (3)$$

On the other hand, we can represent the heat flow *Q* as a sum $Q_x = Q_{1x} + Q_{2x}$. Here $Q_{1x}$ is the heat flow passing through graphite layer having cross section square $S_1 = (Y + d)(Z + d) - YZ$ and thickness $X + d$. $Q_{2x}$ is the heat flow passing through bilayer with cross section square of $S_2 = YZ$, thickness of graphite layer $d$ and thickness of diamond layer *X*. The heat flow $Q_{1x}$ is equal to

$$Q_{1x} = -S_1 \lambda_b \vec{\nabla} T = \left[(Y + d)(Z + d) - YZ\right]\lambda_b \frac{T_1 - T_2}{X + d}. \qquad (4)$$

To find $Q_{2x}$ we use continuity of the heat flow on the boundary between layers. It permits determining temperature $T^*$ on the boundary:

$$T^* = \frac{T_1 \lambda_b X + T_2 \lambda_x d}{\lambda_b X + \lambda_x d}. \qquad (5)$$

Using (5) we can write expression for $Q_{2x}$:

$$Q_{2x} = YZ\lambda_b \frac{T_1 - T^*}{d} = \lambda_b \lambda_x YZ \frac{T_1 - T_2}{\lambda_b X + \lambda_x d}. \qquad (6)$$

Using (3), (4), (6) we obtain equation for determining $\lambda_x^{ef}$. Finally, we have the following expression for the effective $\lambda_x^{ef}(X,Y,Z,d)$ in direction of x-axis:

$$\lambda_x^{ef} = \lambda_b(d)\left[1 + \frac{XYZ\left[\lambda_x(X) - \lambda_b(d)\right]}{\left(\lambda_b(d)X + \lambda_x(X)d\right)(Y+d)(Z+d)}\right]. \qquad (7)$$

Analogous expressions for thermal conductivities $\lambda_y^{ef}$ and $\lambda_z^{ef}$ along *y*- and *z*-axes directions one can get by circular permutations $X \to Y \to Z \to X$:

$$\lambda_x^{ef} = \lambda_b(d)\left[1 + \frac{XYZ\left[\lambda_y(Y) - \lambda_b(d)\right]}{\left(\lambda_b(d)Y + \lambda_y(Y)d\right)(Z+d)(X+d)}\right],$$

$$\lambda_z^{ef} = \lambda_b(d)\left[1 + \frac{XYZ\left[\lambda_z(Z) - \lambda_b(d)\right]}{\left(\lambda_b(d)Z + \lambda z(Z)d\right)(X+d)(Y+d)}\right].$$

## CALCULATION RESULTS AND DISCUSSION

Assuming $X = Y = Z$ in (7) we get expression for thermal conductivity of isotropic bicomponent material:

$$\lambda^{ef}(X,d) = \lambda_b(d)\left[1 + \frac{X^3\left(\lambda_x(X) - \lambda_b(d)\right)}{\left(\lambda_b(d)X + \lambda_x(X)d\right)(X+d)^2}\right].$$

Obtained expression represents physically reasonably dependence of thermal conductivity of composite material on component parameters. Particularly, the effective thermal conductivity tents to zero (to infinity) at $\lambda_b \to 0$ $(\lambda_b \to \infty)$. It takes place because the boundary layer plays role of binding agent or matrix into which embed diamond grains which are thermally isolated one from another. That is why the effective thermal conductivity does not tent to zero (to infinity) at $\lambda_x \to 0$ $(\lambda_x \to \infty)$. Thus, influence of components in considered case is nonequivalent. That is why the expression is asymmetric relatively double replacement $\lambda_b \to \lambda_x$ and $X \leftarrow d$. Also, we have $\lambda_x^{ef} = \lambda_x$ at $\lambda_b = \lambda_x$ and $\lambda_x^{ef} \to \lambda_b$ at $X \to 0$ that corresponds to transfer to homogeneous material. Fig. 2 illustrates dependence of effective thermal conductivity $\lambda_{ef}$ of isotropic UNCD on grain dimension $X$ at different thicknesses $d$ of boundary layer. Calculation was performed for two kinds of thermal conductivity of boundary layer, namely, electron (upper group of curves) and phonon (lower group of curves) thermal conductivity. The mean phonon path $l$ is equal to 220 nm.

In case of electronic nature of thermal conductivity the boundary layer thickness influences on UNCD thermal conductivity $\lambda_{ef}$ only at ultimately small grain sizes $X < 10$ nm, and $\lambda_{ef}$ increases with $d$.

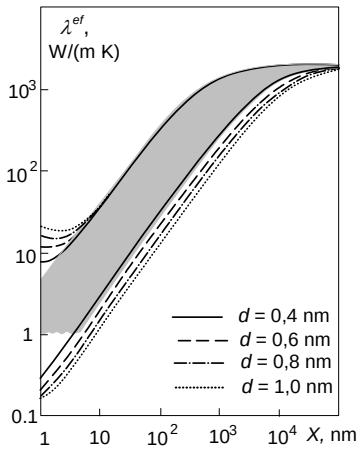


*Fig. 2. Dependence of thermal conductivity $\lambda_{ef}$ of isotropic UNCD on grain size X at different thicknesses of boundary layer d. Upper (lower) group of curves corresponds to electron (phonon) thermal conductivity of boundary layer. Area of experimentally determined thermal conductivity [5] is signed by grey color*

In case of phonon mechanism domination $\lambda^{ef}$ decreases with $d$ in all range of grain sizes $X$. The phonon path $l$ in the grain material practically does not influences on $\lambda^{ef}$ at $X \le l$. Calculation shows (see Fig. 2) that UNCD thermal conductivity at grain sizes 2…10 nm can be less than 10 W/(m·K) in accordance with experimental data [2] whereas thermal conductivity of polycrystalline coating is equal to 1800…2200 W/(m·K).

Also, Fig. 2 displays the range where experimentally determined values of thermal conductivity lie (area bounded by dashed curves and marked by grey color) [5]. As it can see from figure the analytical results do not contradict to experimental observations. If thermal conductivity of boundary layer includes contributions of both electron and phonon transport then curve $l^{ef}(X)$ will lie between upper and lower curves in marked range.

At present time experimental data on thermal conductivity of UNCD in the range of ultimately small grain sizes $X \sim 1$ nm where influence of boundary layer is appreciable are very poor. So, derived model could clarify nature of thermal conductivity of boundary layer.

Fig. 3 illustrates influence of thermal conductivity of isotropic nanodiamond on the phonon path length $l$ in monocrystalline diamond. Solid (dashed) curves correspond to case $l$ = 220 nm ($l$ = 110 nm). Curves 1 (curves 2) were calculated in supposition of electron (phonon) nature of thermal conductivity of boundary layer. Thickness of boundary layer $d$ was equal to 0.4 nm.

As one can see from Fig. 3, thermal conductivity $l^{ef}$ of nanocrystalline diamond with grain size $X < 100$ nm does not depend practically on thermal conductivity of corresponding monocrystalline diamond, which is directly proportional to the phonon path $l$. Thereagainst, $l^{ef}$ strongly depends on thermal conductivity of boundary layer.

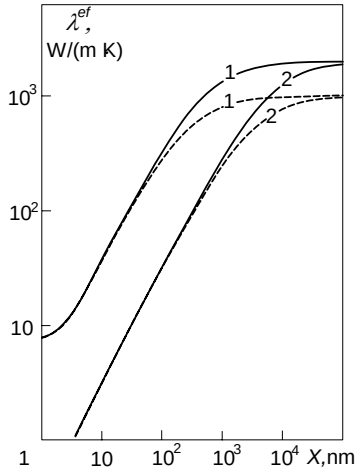


*Fig. 3. Thermal conductivity of isotropic UNCD for two different phonon paths l in monocrystalline diamond: l = 220 nm (the solid curves), l = 110 nm (the dashed ones). Curves 1(curves 2) correspond to electron (phonon) thermal conductivity of boundary layer*

Let nanodiamond grain is characterized by different dimensions $X,Y,Z$. In this case all tensor eigenvalues are different. Fig. 4 shows functions $\lambda_x^{ef}(X)$, $\lambda_y^{ef}(X)$, $\lambda_z^{ef}(X)$ in case when the following proportion between grain dimensions takes place $X:Y:Z = 4:2:1$ (dashed curves 1, 2, 3, respectively). Solid curve corresponds to the effective thermal conductivity of isotropic UNCD. Thermal conductivity of boundary layer was calculated by equation (3) i. e., has electron nature.

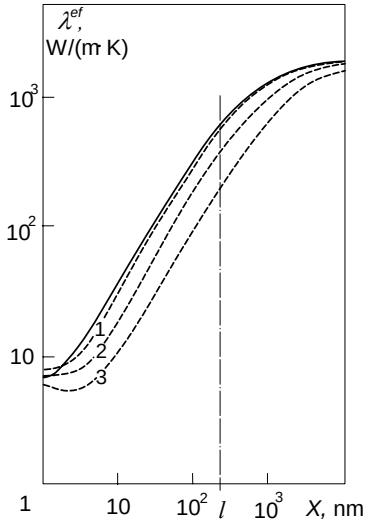


*Fig. 4. Thermal conductivities $l_x^{ef}, l_y^{ef}, l_z^{ef}$ of orthotropic UNCD with the following proportion of grain dimensions $X:Y:Z = 4:2:1$ (dashed curves 1, 2, 3, respectively). Solid curve is dependence $l^{ef}(X)$ for isotropic nanodiamond ($X = Y = Z$)*

As a rule, UNCD films growing by plasma-ion deposition have isotropic structure in the plane of substrate (*yz*-plane), at that crystalline grains can be elongated in direction of growth (*x*-axis). For this case we have to accept Y = Z. Fig. 5 illustrates this case in supposition $X:Y:Z = 10:1:1$. Calculation are performed at $d = 0.4$ nm in supposition of electron nature of heat transport through boundary layer.

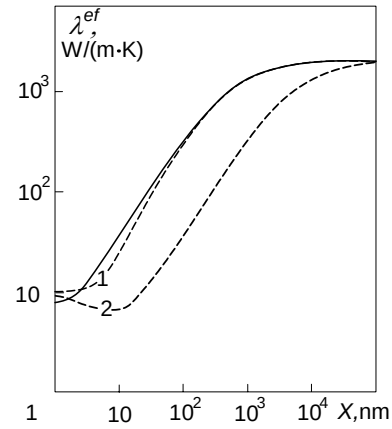


*Fig. 5. Thermal conductivities $l_x^{ef}, l_y^{ef}$, of orthotropic UNCD with the following proportion of grain dimensions $X:Y:Z = 10:1:1$ (dashed curves 1, 2, respectively). Solid curve is dependence $l^{ef}(X)$ for isotropic nanodiamond*

As it can see from Figs. 4, 5, structural anisotropy considerably influences on value of thermal conductivity in different directions. One need to take into account this effect at calculation of thermal conditions of devices based on nanocrystalline coatings.

## CONCLUSIONS

In the model describing structure of orthotropic crystalline diamond by four parameters – effective dimensions *X, Y, Z* of the diamond grain and thickness of boundary layer *d* – expressions for eigenvalues of thermal conductivity tensor were derived. Obtained expressions provide physically grounded characterization of UNCD thermal conductivity in the vast range of grain dimensions from 1 nm and more.

Calculation shows that anisotropy considerably influences on value of thermal conductivity in different directions.

According to derived model thermal conductivity of isotropic UNCD increases with grain size from 5 to 2200 W/(m·K). The last corresponds to thermal conductivity of polycrystalline diamond at $X > 10^3$ nm.

Influence of boundary layer on UNCD thermal conductivity $l^{ef}$ depends considerably on nature of its thermal conductivity. In case of domination of electron thermal conductivity the boundary layer thickness *d* affect $l^{ef}$ only at grain sizes $X < 10$ nm, and $l^{ef}$ increases with *d*. In case of phonon thermal conductivity domination UNCD thermal conductivity $l^{ef}$ decreases with *d* in all range of grain sizes *X*.

Obtained in the model values of thermal conductivity as well as their behavior depending on grain size in case of isotropic UNCD are in accordance with known experimental data. For thorough testing proposed model one should carry out thermal conductivity measurements in range of grain sizes from

1 nm to 100 nm at reliable controlling thickness of boundary layer.

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## REFERENCES

1. D.M. Gruen // *Annu. Rev. Mater. Sci.* 1999, v. 29**,** p. 211.

2. V. Ralchenko, S. Pimenov, V. Konov, et al. // *Diamond and Related Materials.* 2007, v. 16**,** p. 2067.

3. I.I. Vyrovets, V.I. Gritsyna, S.F. Dudnik, O.A. Opalev, E.N. Reshetniak, V.E. Strel'nitskij // *Physical Surface Engineering***.** 2010, v. 8**,** p**.** 4 (in Russian).

4. S.F. Dudnik, A.I. Kalinichenko, V.E. Strel'nitskij. // *The Journal of Kharkov National University N 916, Physical series "Nuclei, Particles, Fields".* 2010, N 3/47/, p. 94 (in Russian).

5. M.A. Angadi, T. Watanabe, A. Bodapati, X. Xiao, O. Auciello, J.A. Carlisle, J.A. Eastman, P. Keblinski, P.K. Schelling, and S.R. Phillpot // *J. Appl. Phys*. 2006, v. 99, p. 114301.

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## МОДЕЛЬ ТЕПЛОПРОВОДНОСТИ АНИЗОТРОПНОГО АЛМАЗА

***С.Ф. Дудник, А.И. Калиниченко, В.Е. Стрельницкий***

Теоретически исследуется зависимость теплопроводности нанокристаллического алмаза от величины и формы кристаллита. Наноалмаз рассматривается как двухфазный материал, состоящий из алмазных зерен, характеризующихся тремя главными размерами и разделенных тонкими графитовыми слоями с электронной, фононной или смешанной теплопроводностью. Анализируется влияние типа теплопроводности пограничного слоя и его толщины на теплопроводность наноалмаза. Полученные зависимости теплопроводности наноалмаза от размеров зерна сравниваются с имеющимися экспериментальными данными.

## МОДЕЛЬ ТЕПЛОПРОВІДНОСТІ АНІЗОТРОПНОГО АЛМАЗУ

***С.Ф. Дуднік, О.І. Калініченко, В.Є. Стрельницький***

Теоретично досліджується залежність теплопровідності нанокристалічного алмазу від величини й форми кристаліту. Наноалмаз розглядається як двофазний матеріал, що складається з алмазних зерен, що характеризуються трьома головними розмірами, та розділених тонкими графітовими прошарками з електронною, фононною або змішаною теплопровідністю. Аналізується вплив типу теплопровідності прикордонного шару і його товщини на теплопровідність наноалмазу. Отримані залежності теплопровідності наноалмазу від розмірів зерна порівнюються з наявними експериментальними даними.