Relative importance of grain boundaries and size effects in thermal conductivity of nanocrystalline materials

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A theoretical model for describing effective thermal conductivity (ETC) of nanocrystalline materials has been proposed, so that the ETC can be easily obtained from its grain size, single crystal thermal conductivity, single crystal phonon mean free path (PMFP), and the Kaptiza thermal resistance. In addition, the relative importance between grain boundaries (GBs) and size effects on the ETC of nanocrystalline diamond at 300 K has been studied. It has been demonstrated that with increasing grain size, both GBs and size effects become weaker, while size effects become stronger on thermal conductivity than GBs effects.

As a critically important physical property, thermal conductivity of nanocrystalline materials is of quite general interest due to its significant technological importance in many practical applications of such materials, including bioMEMs¹, thermal barrier coatings² and micro-/nanoelectomechanical devices¹, to name just a few. It is well known that nanocrystalline materials are structurally characterized by a large volume fraction of grain boundaries (GBs)⁴. Generally, GBs can be considered as an obstacle for heat transmission. Therefore, thermal conductivity of nanocrystalline materials is lower than that of the corresponding single crystal materials, and it decreases with decreasing grain sizes⁵.

Many efforts have been devoted to the research on nanocrystalline materials thermal conductivity²,⁵–⁷, and some equations to model effective thermal conductivity (ETC) have been developed. In 1998, a Kapitza resistance-EMA (effective medium approaches) model to describe the ETC for common polycrystals with isotropic, equisized spherical crystallites has been proposed by Nan and Birringer⁵, where the ETC can be described as

\[ K \approx K_0 \frac{1}{1 + 2R_K K_0/d} \] (1)

In (1), \( K_0 \) is single crystal thermal conductivity (W/m·K), \( R_K \) is Kapitza thermal resistance from GBs (m²·KW⁻¹), and \( d \) is grain size (nm).

By considering that each grain boundary region is shared by two grains, Eq. (1) has been revised by Yang et al. in 2002², which led to the following expression:

\[ K = \frac{K_0}{1 + R_K K_0/d} \] (2)

It is different from Eq. (1) only by the absence of a coefficient factor 2 for \( R_K \).

Although Eq. (2) has been widely used to study the ETC for many nanocrystalline materials²,⁵–⁷, in fact, its value calculated by Eq. (2) is usually larger than almost all of the experimental or simulated values²,⁵,⁷. A persuasive explanation for this inconformity is that an intragranular thermal transmission property may change with grain size⁸. It is collectively known as size effects of thermal properties. The reason for these effects is that the phonon mean free path (PMFP) is reduced due to increased phonon scattering in the intragranular with decreasing grain size. By considering size effects of thermal properties¹⁴–¹⁷, a new type ETC formula¹⁵,¹⁶ for nanocrystalline materials has been suggested as

\[ K = \frac{K_{\text{intra}}}{1 + R_K K_{\text{intra}}/d} \] (3)

where \( K_{\text{intra}} \) is the intragranular thermal conductivity (W/m·K), and \( R_K \) is the Kapitza thermal resistance (intergranular thermal resistance). In this theoretical model, the ETC for nanocrystalline materials is not only
affected by the Kapitza thermal resistance, but also by size effects. As a result, an agreement between calculated and experimental results has been reached.

Although Eq. (3) has been proved to be reasonable for calculating the ETC of nanocrystalline materials, it is not a convenient model for applications, especially in the process of computing intragranular thermal conductivity. To make Eq. (3) better amenable to practical application, a simple theoretical ECT model for nanocrystalline materials has been proposed in this work by considering both single crystal thermal properties and the Kapitza thermal resistance. By comparing our theoretical predictions with simulated results for the ECT of nanocrystalline diamond at 300 K as well as experimental ETC of nanocrystalline silicon at 300 K, a good agreement between them has been obtained, which proves the rationality behind our ECT formula. Although the effect of both GBs and size effects can be expressed by using the grain size in this ECT formula, the mechanisms of action in these two factors on ETC are totally different, and further the contribution of these two factors on ETC may be different for different materials and grain sizes. Therefore, it is necessary to study the effect of each factor on ETC separately. In this work, the relative importance of these two factors on ETC are totally different, and further the contribution of these two factors on ETC may be different for different materials and grain sizes.

For Eq. (3), the greatest challenge in quantitatively predicting the ETC for nanocrystalline materials is to calculate intragranular thermal conductivity $K_{\text{intra}}$. To calculate the intragranular thermal conductivity, kinetic theory has been used, leading to the following expression:

$$K_{\text{intra}} = \frac{1}{3} CV\Lambda_{\text{intra}}.$$  \(4\)

$\Lambda_{\text{intra}}$ is the intragranular PMFP due to size effect of thermal properties, and the value of $\Lambda_{\text{intra}}$ is correlated with single crystal PMFP $\Lambda_0$, as well as with an additional PMFP $\Lambda_{\text{add}}$ due to decreased grain sizes.

By using Matthiessen’s rule, their relationship can be written as

$$\Lambda_{\text{intra}}^{-1} = \Lambda_0^{-1} + \Lambda_{\text{add}}^{-1}.$$  \(5\)

As a result, intragranular PMFP $\Lambda_{\text{intra}}$ can be expressed as

$$\Lambda_{\text{intra}} = \frac{\Lambda_0\Lambda_{\text{add}}}{\Lambda_0 + \Lambda_{\text{add}}}.$$  \(6\)

Assuming that the acoustic velocity and heat capacity are not affected by grain size, when Eq. (6) is inserted into Eq. (4), the intragranular thermal conductivity can be described as

$$K_{\text{intra}} = \frac{1}{3} CV\Lambda_0 \frac{\Lambda_{\text{add}}}{\Lambda_0 + \Lambda_{\text{add}}} = \frac{K_0}{1 + \Lambda_0/\Lambda_{\text{add}}},$$  \(7\)

where $K_0$ is the corresponding single crystal thermal conductivity ($WmK$).

Hence, the intragranular thermal conductivity $K_{\text{intra}}$ can be considered as a function of the corresponding single crystal thermal conductivity $K_0$ and PMFP $\Lambda_0$, as well as grain size induced PMFP $\Lambda_{\text{add}}$. It is well known that $\Lambda_{\text{add}}$ is related to grain size $d$. For a definitive material under a given temperature, single crystal thermal conductivity $K_0$ and PMFP $\Lambda_0$ can be regarded as constants. Therefore, the intragranular grain thermal conductivity can be described as a function of grain size $d$. According to Ref. 21, the thermal conductivity of nanocrystalline materials can be modeled by an exponential function of defect concentration. In this work, we assume that the grain boundary is a type of defect, and that the intragranular grain thermal conductivity can be expressed as an exponential function of grain size $d$. Therefore, we have

$$K_{\text{intra}} = \frac{K_0}{1 + \Lambda_0/d^z},$$  \(8\)

where $z$ is the exponent ranging from 1/2 to 3/4 according to phenomenological theory.

Now, by combining the equations (3) and (8), the ETC of nanocrystalline materials can be written as

$$K_{\text{nearest}} = \frac{K_0/(1 + \Lambda_0/d^2)}{1 + R_K[K_0/(1 + \Lambda_0/d^2)]/d}.$$  \(9\)

To determine an affirmative value of $z$, a simulated ETC of nanocrystalline silicon at 500 K is used to fit Eq. (9) by using the least square method. At the same time, in this calculation we use the single crystal silicon thermal conductivity $K_0$ at 500 K from experimental data ($77W/mK$)\(^4\), $R_K$ value ($1.06 \times 10^{-9} m^3K^{-1}$) and $\Lambda_0$ (17.6 $nm$) from simulation\(^2\). As a result, the determined value of $z$ is 0.75 with a correlation coefficient about 0.93, which shows that the value of $z$ agrees with the phenomenological theory.

Finally, the ETC of nanocrystalline materials can be described as

$$K_{\text{nearest}} = \frac{K_0/(1 + \Lambda_0/d^{0.75})}{1 + R_K[K_0/(1 + \Lambda_0/d^{0.75})]/d}.$$  \(10\)

By using this equation, the ETC of nanocrystalline materials can be easily obtained based only on its grain size $d$, single crystal thermal conductivity $K_0$, single crystal PMFP $\Lambda_0$, and the Kapitza thermal resistance $R_K$.

To further validate this equation, our present theoretically predicted ETC of nanocrystalline diamond has been compared with molecular dynamic (MD) simulated results. The MD calculated ETC of nanocrystalline diamond at room temperature is shown in Fig. 1 with a grain size range from 2 to 13.3 $nm$. By comparing our simulated results with previously reported ETC values for nanocrystalline diamond\(^5\), we confirm that a good agreement has been obtained. This has also confirmed that the MD simulation parameters used in this work are reliable.

In order to get theoretical values of ETC for nanocrystalline diamond from Eq. (10), the single crystal diamond thermal conductivity and the Kapitza resistance of crystalline diamond grain boundary have also been calculated by using MD simulation, and details for these calculations can be found in supplementary document (Supplementary discussions 2 and 3). The calculated values of $K_0$ and $R_K$ are 1265 $Wm^{-1}K^{-1}$ and 0.143 $\times 10^{-9} m^3K^{-1}$, respectively. Both calculated values of $K_0$ and $R_K$ are consistent with the previously reported results\(^9,20,25,26\), confirming that our computational method is reliable. The value of single crystal PMFP $\Lambda_0$ used in the calculation has been chosen as 180 $nm$, which is in the range of previously reported values (150 $nm$\(^2\) and 400 $nm^2$). By comparing ETCs of nanocrystalline diamond obtained from MD simulations with theoretical analysis based on our model (as plotted in Fig. 1), a good agreement between them has been observed, demonstrating that
our newly developed model for ETC is effective for nanocrystalline materials. In addition, a good agreement between our model and experimental ETC\textsuperscript{4,7,17} for nanocrystalline silicon at 300 K (refer to Supplementary discussion 4 and Fig. S7) has also been observed, which further confirmed that our model is valid.

Since both, the effect of GBs and size effects of thermal properties, are considered in our calculations, the ETC of nanocrystalline diamond is much smaller than the single crystal diamond thermal conductivity, and it decreases with the reduced grain sizes. The reduction of thermal conductivity in nanocrystalline diamond compared with single crystal is caused by two factors: GBs and size effects of thermal properties. The relative importance of these two groups of effects on the reduced thermal conductivity of nanocrystalline materials is a very important issue for the study of nanocrystalline materials thermal conductivity. In this work, the relative importance of these two effects on the reduced thermal conductivity of nanocrystalline materials has been studied by using nanocrystalline diamond as a prototype. Note that the thermal resistance of nanocrystalline diamond $R_{\text{pol}}$ can be divided into two parts, one is the intragranular thermal resistance ($R_{\text{intr}}$) caused by size effects, and the other one is the intergranular thermal resistance ($R_{\text{int}}$) caused by GBs. The plots of intragranular thermal resistance ($R_{\text{intr}}$), intergranular thermal resistance ($R_{\text{int}}$), and total thermal resistance ($R_{\text{pol}}$) of nanocrystalline diamond have been obtained as functions of grain size, based on Eq. (10). They can be seen in Fig. 2 (a). Note that theoretical results from our theoretical model agree well with the results obtained by MD simulations. With the increasing grain size, the intragranular thermal resistance $R_{\text{intr}}$ and intergranular thermal resistance $R_{\text{int}}$ both decrease. When the grain size is large enough (or $1/d$ tends to 0), the intragranular thermal resistance approaches to the single crystal thermal resistance, while the intergranular thermal resistance tends to zero. These results demonstrate that with increasing grain size, both the effect of GBs and the size effects become weaker.

To better understand the relative importance of GBs and size effects of thermal properties on the reduced thermal conductivity of nanocrystalline diamond, the ratio of intragranular thermal resistance, as well as the intergranular thermal resistance, to the total nanocrystalline diamond thermal resistance ($R_{\text{intr}}/R_{\text{pol}}$ and $R_{\text{int}}/R_{\text{pol}}$) have been calculated. These characteristics have been plotted in Fig. 2 (b). As can be seen from Fig. 2 (b), $R_{\text{intr}}/R_{\text{pol}}$ is larger than $R_{\text{int}}/R_{\text{pol}}$ throughout, and with increasing grain size, the value of $R_{\text{intr}}/R_{\text{pol}}$ is increasing, while the value of $R_{\text{int}}/R_{\text{pol}}$ is decreasing. It indicates that with increasing grain size, size effects of thermal properties become stronger than the GBs effect on nanocrystalline diamond thermal conductivity at 300 K. When the grain size is less than 10 nm, $R_{\text{intr}}/R_{\text{pol}}$ is less than 0.65, and $R_{\text{int}}/R_{\text{pol}}$ is larger than 0.35, the effect of GBs and size effects of thermal properties both play a very important role for ETC. When the grain size is 100 nm, $R_{\text{intr}}/R_{\text{pol}}$ is 0.79, and $R_{\text{int}}/R_{\text{pol}}$ is 0.21, size effects of thermal properties become much stronger than the effect of GBs on ETC, and both effects are still very important. When grain size is 1000 nm, $R_{\text{intr}}/R_{\text{pol}}$ is 0.92, and $R_{\text{int}}/R_{\text{pol}}$ is 0.08, size effects of thermal properties are still relatively stronger than the effect of GBs on ETC. When the grain size is 10000 nm, $R_{\text{intr}}/R_{\text{pol}}$ is 0.99, and $R_{\text{int}}/R_{\text{pol}}$ is only 0.01, at that time, both effects have almost no influence on ETC, and the nanocrystalline diamond thermal conductivity becomes very close to the corresponding single crystal thermal conductivity. Analysis of relative importance of size effects and GBs on ETC shows that besides GBs, size effects also play a very important role in the reduced ETC, which is a good reason for the inconformity between previous theoretical results and simulated or experimental ones\textsuperscript{4,7,17}, and that can be explained by decreasing intragranular PMFP and increasing GB number due to decreasing grain size.

In addition, the thermal transmission of nanocrystalline silicon at 500 K\textsuperscript{17} have also been studied on the basis of Eq. (10). As shown in Fig. 1 and Fig. 2 (a), the simulated values of thermal conductivity and thermal resistance of nanocrystalline silicon\textsuperscript{17} at 500 K conform well with our theoretical model. With increasing grain size, both the effect of GBs and size effects of thermal properties on ETC both become weaker. However, the relative importance of GBs and size effects of thermal properties on ETC for nanocrystalline silicon at 500 K is different from that of nanocrystalline diamond at 300 K. For nanocrystalline silicon at 500 K, the effect of GBs is stronger than size effects on ETC when $d < 40$ nm, whereas a crossover is observed at $d = 40$ nm, while for $d > 40$ nm, the size effects of thermal properties are stronger. This difference indicates that besides grain size, perhaps material kind and temperature are also important factors that affect the relative importance of GBs and size effects of thermal properties on ETC. Moreover, the relative importance of GBs and size effects for nanocrystalline silicon at 300 K has also been analyzed by applying our theoretical model. Although the trend is the same as that of nanocrystalline silicon at 500 K and nanocrystalline diamond at 300 K, the critical grain size is different for different materials and temperature (Detail in Supplementary discussion 5).
In summary, a theoretical model for describing the ETC has been proposed in this work. By using this theoretical model, the ETC for nanocrystalline materials can be easily obtained by using only its grain size, single crystal thermal conductivity, single crystal PMFP, and the Kaptiza thermal resistance. The effectiveness of this model has been verified by comparing simulated value of ETC for nanocrystalline diamond at 300 K as well as experimental ETC for nanocrystalline silicon at 300 K with theoretical results based on this model. The relative importance of GBs and size effects of thermal properties on ETC of nanocrystalline diamond at 300 K has been studied by using this equation. With increasing grain size, both the effect of GBs and size effects of thermal properties become weaker, and the size effects become stronger than the GBs effect on thermal conductivity. This novel theoretical model provides a convenient path to the calculation of nanocrystalline materials thermal conductivity. It is expected that it will greatly contribute to in-depth understanding of the thermal properties of nanocrystalline materials.

**Methods**

In this work, the nanocrystalline diamond ETC are calculated by using the non-equilibrium molecular dynamics (NEMD) simulations\(^2\). This methodology uses an idea of imposing heat flux through the structure under study and determining a temperature gradient that develops as a consequence of the imposed flux\(^1\). The heat flux is introduced by continuously transferring energy from 'cold' regions, located at the ends of the simulation cell, to 'hot' regions, located at the middle of simulation model, as shown in Fig. 3 (a). Then, the ETC can be calculated from the heat flux and temperature gradient shown in Fig. 3 (b) by using the Fourier's law\(^2\) (refer to supplementary discussion 1 about the detail of the computational method used here). In order to carry out the simulation by using NEMD, the atomic models of nanocrystalline diamond are generated using the three-dimensional Voronoi tessellation method\(^3\), which has been widely used in creating random grain structures for nanocrystalline materials simulation\(^4-7\). Fig. 4 shows a typical nanocrystalline diamond structure with periodic boundary conditions in all three-directions. In these simulations, C-C bonding interactions have been described by Tersoff potential and an NPT ensemble has been used. We use the atmospheric pressure and temperature 300 K.

The atomic coordinates and the overall periodic dimensions of the simulation cell were first optimized using the gradient-based minimization method implemented to minimize the stress. NEMD simulations have then been carried out on the relaxed structure to make the system equilibrated at room temperature with a time step of 0.1 fs for \(2 \times 10^5\) steps. Then, by imposing a heat flux, the canonical ensemble has been performed consecutively for \(10^6\) steps to allow the systems reaching the steady-state regime. Finally, the temperature profiles have been obtained by averaging every \(10^5\) MD steps. In our simulations, the effects of domain size on ETC have been considered\(^1\). Four models with different domain sizes and the same grain size (2.43 nm) are listed in Fig. 5, as well as the separate ETCs calculated. It can be seen that the variation between the results obtained with these models is very small, although the simulation domain sizes are quite different.

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