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2D-Modeling for the temperature-composition dependent thermal conductivity of Al<sub>m</sub>N<sub>n</sub> compounded semiconductor materials

Yanan Xu1,2, Mukti Rana and Matthew Tanzy
The Division of Physics, Engineering, Mathematics and Computer Science, Delaware State University, 1200 N. DuPont Highway, Dover, DE 19901, United States of America
1 Author to whom any correspondence should be addressed.
2 These authors contributed equally to this work.
E-mail: yxu@desu.edu, mrana@desu.edu and mtanzy@desu.edu

Abstract

The quantitative effect on the thermal conductivity of Aluminum Nitride (AlN) regarding to Al mole fraction and temperature has not been reported computationally. Therefore, the goal of this study is to investigate the impact of Al mole fraction and temperature on the thermal conductivity of Al<sub>m</sub>N<sub>n</sub> numerically based on Boltzmann Transport equation by considering phonon scattering mechanisms. The theoretical thermal conductivity of Al<sub>m</sub>N<sub>n</sub> versus Al mole fraction and temperature is showed in this study. It is found that Point-defect and Umklapp scatterings are dominant scattering mechanisms for the thermal conductivity of Al<sub>m</sub>N<sub>n</sub>. The calculated thermal conductivity of Al<sub>m</sub>N<sub>n</sub> is verified through the comparison of experimental data versus Al mole fraction and temperature.

1. Introduction

Thermoelectrical and pyroelectrical materials are able to convert heat into electricity. But at the same time, they result in high temperature due to Joule heating [1] and [2]. During this process, heat dissipation would diminish the device performance and lifetime. Therefore, the development of thermal-electrical materials is limited because of their relatively low efficiency and high commercial cost.

It is imperative to develop materials with high conductivity to improve efficiencies of thermal-electrical materials. In Aluminum Nitride (AlN) based semiconductor materials, thermoelectric and pyroelectric properties have attracted many researchers’ attention. This is because these properties enable potential applications of composite semiconductor materials for Al<sub>m</sub>N<sub>n</sub> in fields such as optoelectrical devices, precision instruments and medical equipments, etc. Here, m is the Al mole fraction in the composite alloy and m ≥ n. For example, AlN based semiconductor materials play a significant potential applications in opto-electrics operating at deep ultraviolet since these materials’ high thermal conductivity properties [3–6] and [7]. However, so far its knowledge is very limited in the field of the quantitative description of thermal conductivities with respect to Al mole fraction m and temperature T in composite semiconductor of Al<sub>m</sub>N<sub>n</sub>.

In order to have a better understanding of the property for AlN based semiconductor alloy, the thermal conductivity property of Al<sub>m</sub>N<sub>n</sub> about different Al mole fraction m under varied temperature T based on the Boltzmann Transport equation (BTE) is modeled in this work. To simplify the original expression, it first rewrities the composite alloy Al<sub>m</sub>N<sub>n</sub> as a new form of AlN<sub>x</sub>, where x = m/n and 0 < x ≤ 1. After that, the thermal conductivities of AlN<sub>x</sub> is studied by considering phonon scattering processes. The phonon scattering processes are represented by relaxation times which are functions of frequency and temperature. The phonon scattering processes describe phonon properties including normal scattering τ<sub>NN</sub>, Umklapp scattering τ<sub>Um</sub>, Point-defect scattering τ<sub>PD</sub>, Boundary scattering τ<sub>B</sub> and Dislocation scattering τ<sub>Disl</sub>. The BTE is solved by the Relaxation Time Approximation (RTA) method [8, 9] and [10] regarding to the temperature T and ratio of x = m/n, where 0 < x ≤ 1. It is found that Point-defect and Umklapp scattering are dominant scattering mechanisms for the thermal conductivity of AlN<sub>x</sub>. The computed thermal conductivity of AlN<sub>x</sub> in this model is verified through
2. Analytical model for $Al_mN_n$

In this section, we use the virtual phonon model for $Al_mN_n$ to determine its thermal conductivity. Here, $m \geq n$ and $m$ and $n$ are the mole fraction of Aluminum and Nitride in the composite alloy of $Al_mN_n$, respectively. If we assume $m$ is the 'unit', then the amount of mole fraction for Nitride equals to the ratio value $x = \frac{n}{m}$. Under this idea, $Al_mN_n$ could be rewritten as the new form of $AlN_x$, where $0 < x \leq 1$ and the mole fraction 'unit' is 1 in the former expression whereas the mole fraction 'unit' is $m$ in the latter expression. In composite semiconductor materials, most heat is carried by phonon [19] and [20] due to thermal conductivity by phonon is $10^3$ times larger than the electrons, which can be modeled by using the BTE [10, 21, 22] and [23]. The solution of this integral equation is obtained by the use of RTA [8, 9] and [23]. The theoretical model is calculated based on the BTE leading to the lattice thermal conductivity in $AlN_x$ as the following [23] and [24]:

$$\kappa_{\text{conduction}} = \kappa_A + \kappa_B,$$

where

$$\kappa_A = \frac{k_b T^3}{2\hbar^2 \pi^2 V} \int_0^{\Theta/T} \tau_N(z) \frac{2z^4 e^z}{(e^z - 1)^2} dz,$$

$$\kappa_B = \frac{k_b T^3}{\hbar^2 \pi^2 V} I_1,$$

$$I_1 = \int_0^{\Theta/T} \frac{\tau_N(z)}{\tau_C(z) \tau_R(z)} \frac{2z^4 e^z}{(e^z - 1)^2} dz,$$

$$I_2 = \int_0^{\Theta/T} \frac{\tau_N(z)}{\tau_R(z)} \frac{2z^4 e^z}{(e^z - 1)^2} dz,$$

$$\tau_R = \frac{\hbar \omega}{k_b T}.$$

Here, $k_b$ is the Boltzmann constant, $T$ is the temperature, $h$ is the plank constant, $\Theta$ is the Debye temperature, $\omega$ is the phonon frequency, $\tau_N$ is the phonon scattering time due to normal scattering, $\tau_R$ is the combined scattering time due to all resistive processes, and $\tau_C$ is the combined scattering mechanism of normal process $\tau_N$ and resistive process $\tau_R$. The scattering mechanism of $\tau_N$ and $\tau_R$ will be detailed after parameters of virtual atomic mass $M$, virtual atomic radius $\delta$, and average group velocity $V$ are explained.

In this model, we assume atoms are randomly mixed to form composite alloys. These atoms are arranged in an disordered lattice. The idea of the virtual phonon model is to replace the disordered lattice by the ordered virtual relation with atoms from constituent materials. Following this idea, we describe the disordered alloy structure quantitatively by the ordered virtual relation in terms of virtual atomic weight, volume and lattice s.

The virtual atomic mass $M$ of the composite semiconductor material is assumed to be the weighted average mass of different components. For the $AlN_x$ alloy, $M$ is

$$M = (1 - x) \times M_{Al} + x \times M_{AlN},$$

where $0 < x \leq 1$, $M_{Al}$ and $M_{AlN}$ are the virtual mass of Al and AlN components in the composite material. The virtual atomic radius $\delta$, also known as the characteristic length scale of the lattice, is given by the equation [25]:

$$\delta = (1 - x) \times \delta_{Al} + x \times \delta_{AlN},$$

where $\delta_{Al}$ and $\delta_{AlN}$ are the characteristic length of Al and AlN, respectively. $\delta_{Al}$ and $\delta_{AlN}$ are defined by the cubic root of atomic volume in Al and AlN. For AlN$_x$ virtual crystal, one can get its elastic constants $C_{ij}$ from the work [26] of Al and AlN and equation (4). Once virtual elastic parameters $C_{ij}$ are obtained, we get longitudinal sound velocities $V_L$ and transverse sound velocities $V_T$ through paper [19]. The average phonon group velocity $V$ under the assumption of the Debye frequency is the mean cut off frequency of three acoustic branches, i.e., longitudinal $V_L$ and transverse $V_{T1}$ and $V_{T2}$, which is

$$V = \frac{3}{V_L^{-1} + V_{T1}^{-1} + V_{T2}^{-1}}.$$

The normal scattering $\tau_N$ describing the phonon-phonon scattering phenomenon is represented by [27]

$$\tau_N^{-1}(z) = \frac{k_b^2 \gamma_0 V_0}{2 M \hbar^2 V^3} \left( \frac{k_b}{\hbar} \right)^2 z^2 T^5.$$
Here, \( V_0 \) is the volume per atom and \( \gamma \) is the Grüeisen parameter which is defined as the following:

\[
\gamma = -\frac{d \ln \Theta}{d \ln \delta^3}, \tag{7}
\]

where \( \Theta \) is the Debye temperature of the virtual lattice.

The resistive scattering \( \tau_R \) includes Umklapp scattering \( \tau_{Um} \), Boundary scattering \( \tau_B \), Point-defect scattering \( \tau_{pD} \), and Dislocation scattering \( \tau_{Dis} \).

The phonon-phonon scattering factor where momentum is not conserved and is represented as the Umklapp scattering in the following:

\[
\tau_{\text{Um}}^{-1}(z) = \frac{h}{MV_0^2 \Theta} \left( \frac{k_b}{\hbar} \right)^2 \exp \left( -\frac{\Theta}{3T} \right). \tag{8}
\]

Al vacancies in AlN, bonding play a dominant role due to the mass difference between the original Al/AlN atoms and impurity atoms [23, 28, 29] and [30] and the strain induced on lattice from different atoms’ characteristic length [29] and [30]. These vacancies lead to a larger local distortion than the one by substitutional defects, because of bond breaking and atomic scattering rearrangements and this local distortion causes further phonon scattering. This process is described by Point-defect scattering represented as the following:

\[
\tau_{pD}^{-1}(z) = \frac{8\pi^2}{4\pi V^2} \sum \xi \left[ \left( \frac{M_i - M}{M} \right)^2 + \epsilon \left( \frac{\delta_i - \delta}{\delta} \right)^2 \right]. \tag{9}
\]

Here, \( i \) is the type of atoms, \( \xi \) represents the fraction mole of constituent type \( i \), \( M_i \) is the atomic mass of atom type \( i \), and \( \epsilon \) is considered as a phenomenological parameter specific for given materials system [19, 29–31] and [32]. The strain field factor \( \epsilon \) is defined in the form [29] and [30]

\[
\epsilon = \frac{2}{9} \left( 6.4 \times \frac{1 + V}{1 - V} \right)^2, \tag{10}
\]

where \( \epsilon \) is due to the ionic radius mismatch in the host sites.

Boundary scattering [33]:

\[
\tau_B^{-1} = V/d, \tag{11}
\]

where \( V \) is the average phonon group velocity, \( d \) is grain or crystallite size in polycrystalline material [33].

Dislocation scattering is due to the elastic strain field of the dislocation lines and the strain field of the dislocation lines mediated by the higher order terms in the potential energy of real crystals [8]. The Dislocation \( \tau_{pD} \) is a combined mechanisms [27, 32, 34] and [35] of Core dislocation scattering \( \tau_{\text{Core}} \), Edge scattering \( \tau_{\text{Edge}} \), Screw scattering \( \tau_{\text{Screw}} \) and Mixed scattering \( \tau_{\text{Mixed}} \). These mechanisms are described as the following [23, 27] and [32]:

\[
\tau_{\text{Core}}^{-1}(z) = \frac{\eta N_0 k_b T}{h} \frac{V_{\text{eff}}^{4/3}}{V^2} \gamma^2 z, \tag{12a}
\]

\[
\tau_{\text{Edge}}^{-1}(z) = \frac{2^{7/2} k_b T}{\hbar} \frac{\eta N_0 b_s^2}{b_E^2} \gamma^2 z \left( \frac{1}{2} + \frac{1}{24} \left( \frac{1 - 2\nu}{1 - \nu} \right)^2 \left( 1 + \sqrt{2} \left( \frac{V_L}{V_T} \right)^2 \right) \right)^2, \tag{12b}
\]

\[
\tau_{\text{Screw}}^{-1}(z) = \frac{2^{7/2} k_b T}{\hbar} \frac{\eta N_0 b_s^2}{b_E^2} \gamma^2 z, \tag{12c}
\]

\[
\tau_{\text{Mixed}}^{-1}(z) = \frac{2^{7/2} k_b T}{\hbar} \frac{\eta N_0 b_s^2}{b_E^2} \gamma^2 z \left( b_s^2 + b_E^2 \right) \left( \frac{1}{2} + \frac{1}{24} \left( \frac{1 - 2\nu}{1 - \nu} \right)^2 \left( 1 + \sqrt{2} \left( \frac{V_L}{V_T} \right)^2 \right) \right). \tag{12d}
\]

Here, \( N_0 \) is the density of the dislocation lines of all types; \( \eta \) is the weight factor which accounts for the mutual orientation when dislocations perpendicular to the temperature gradient \( \eta = 1 \), otherwise \( \eta = 0.55 \); \( \nu = C_{12}/(C_{11} + C_{12}) \) is the Poisson’s ratio; \( b_s \) is the Burgers vectors’ magnitude for the Screw dislocations; \( b_E \) is the Burgers vectors’ magnitude for the Edge dislocations; \( b_M = b_s + b_E \) is the Burgers vectors’ magnitude for the Mixed dislocations; \( V_L \) is the longitudinal phonon velocity; \( V_T \) is the transverse phonon velocity [27, 32, 34] and [35]. The constants and parameters used in the calculations are showed in table 1.
3. Results

In Figure 1, it shows the example of phonon scattering rates versus mole fraction $x$ for AlN$_x$ around temperature $T = 300$ K. It is found that Point-defect scattering and Umklapp scattering are the two dominant scattering mechanisms across the range of mole fraction.

Figure 2 shows the thermal conductivity of AlN$_x$ as a function of temperature for the Nitrogen concentration of $x = 0.32788, x = 0.49062, x = 0.59265, x = 0.69449, x = 0.79633, x = 0.85743$ and $x = 0.89816$. The calculated thermal conductivity of AlN$_x$ increases as temperature increasing from 0K to around 60 K. When the temperature surpasses around 60 K, its thermal conductivity decreases with the increasing temperature. The simulated thermal conductivity increases as $x$ increases from $x = 0.32788$ to $x = 0.89816$ shown in this graph. The wave shape of the calculated thermal conductivity in Figure 2 is consistent with the Wurzite thermal conductivity [10, 12] and [11].

We have also analyzed the impact of mole fraction $x$ on the thermal conductivity in AlN$_x$. Figure 3 shows the calculated thermal conductivity for AlN$_x$ across the mole fraction range $x$ in (0, 1) around $T = 973.15$ K. Results from Zhang et al [13], Couturier et al [14], Granta et al [15], Chedru et al [16], Mizuuchi et al [17] and Lee et al [18] are included to do the comparison with the theoretical work in this study. The calculated thermal conductivity of AlN$_x$ is somewhat overestimated for $x$ in (.05,.3) [18]. However, the experimental data deviates even after $x = .4$ through work [13–17] and [18].

| Description                  | Parameter | Value/Expression |
|------------------------------|-----------|------------------|
| Molar mass(amu)              | $M_{Al}$  | 26.982           |
|                              | $M_{AlN}$ | 40.99            |
| Density(kg/m$^3$)            | Al       | 2700             |
|                              | AlN      | 3266             |
| Debye temperature(K)         | Al       | 390              |
|                              | AlN      | 1150             |
| Elastic constants(Gpa)       | $c_{11}$ in Al | 106.2         |
|                              | $c_{12}$ in Al | 61.3           |
|                              | $c_{44}$ in Al | 28.5           |
|                              | $c_{11}$ in AlN | 410            |
|                              | $c_{12}$ in AlN | 149            |
|                              | $c_{44}$ in AlN | 125            |
| Poisson’s ratio              | $\nu$    | $C_{12}/(C_{11} + C_{12})$ |
| Dislocations to the temperature gradient | $\eta_{as perpendicular}$ | 1 |
|                              | $\eta_{as orientated randomly}$ | 0.55 |
| Density of the dislocation lines(g/m$^3$) | $N_D$ | 1e+16 |
| Film thickness(m)            | $d$      | 1e-6             |

Figure 1. AlN$_x$ phonon scattering rate versus mole fraction $x$ around temperature $T = 300$ K.
4. Conclusion

Thermal conductivities for Al$_m$N$_n$ are calculated in this work based on varied mole fraction $x = \frac{m}{m+n}$ and temperatures using the Boltzmann Transport equation. The accuracy of the theoretical thermal conductivity is confirmed by comparing with the experimental data. Point-defect and Umklapp scattering are identified as the dominant phonon scattering characteristics across the mole fraction $x$ range and temperature range. Dislocation scattering is similarly found to be the dominant scattering process for the thermal conductivity of Al$_m$N$_n$ alloy under certain conditions. The thermal conductivities from this model show qualitative agreement with the experimental data under certain conditions.

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ORCID iDs

Yanan Xu https://orcid.org/0000-0003-1070-0759
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