Bohdan ANDRIYEVSKY

Faculty of Electronics and Computer Sciences, Koszalin University of Technology

Comparative molecular dynamics studies of Si, GaN and SiC thermal conductivity

Abstract. Thermal conductivity of Si, SiC and GaN crystals have been calculated by the reversed non-equilibrium molecular dynamics method using the Forcite program with the Universal force field potentials of the Materials Studio 7.0 package. The dependencies of thermal conductivity on the length of crystal's supercell and density have been obtained and analyzed. Correlation of the degree of hybridization of vibrations of Si and C in SiC and Ga and N in GaN, from the one side, and coefficient of thermal conductivity, from the other one, has been revealed.

*Streszczenie. Obliczono przewodność cieplną kryształów Si, SiC i GaN metodą odwrotnej nierównoważnej dynamiki molekularnej za pomocą programu Forcite przy potencjałach pól siłowych typu Universal z pakietu Materials Studio 7.0. Otrzymano i przeanalizowano zależności przewodności cieplnej kryształów w funkcji długości odpowiedniej superkomórki oraz gęstości. Ujawniono korelację stopnia hybrydyzacji drgań atomów Si i C w SiC oraz Ga i N w GaN, z jednej strony, a współczynnika przewodności cieplnej, z drugiej. (**Porównawcze badania przewodności cieplnej Si, GaN i SiC metodą dynamiki molekularnej**).*

Keywords: semiconductors, coefficient of thermal conductivity, molecular dynamics.
Słowa kluczowe: półprzewodniki, współczynnik przewodności cieplnej, dynamika molekularna.

Introduction

Silicon (Si), silicon carbide (SiC) and gallium nitride (GaN) are semiconductors widely used in electronics. SiC and GaN are known as excellent wide band gap materials for power electronics [1]. Thermal characteristics of these materials are therefore of great interest. Also, thermal characteristics of interfaces between these materials represents still one of the major concerns. Silicon carbide (SiC) and gallium nitride (GaN) are probably more suitable to the demands of high power electronics than Si [2].

In recent years, significant advancements have been achieved in the improvement of material quality and device technology both for SiC and GaN, and several devices have been created: Schottky diodes, *p-n* junction diodes, metal-oxide-semiconductor field effect transistors (MOSFETs), high electron mobility transistors (HEMTs), hybrid MOS-HEMTs, etc. [3 - 5]. Development of the power GaN-based transistors on the basis of epitaxially grown GaN layers over several substrate types (sapphire, Si or SiC) have made possible its applications in millimeter wave communications [6]. HEMTs based on AlGaN/GaN are promising for high-power, high frequency transistors due to their high electron sheet charge densities and high electrical breakdown fields [7]. However, some scientific and technological open issues related to surfaces and interfaces still limit wide practical applications of these novel devices on the basis of SiC and GaN [8].

In the case of the high electron-mobility transistors (HEMTs) based on AlGaN/GaN, a careful study of the efficient heat removal through the substrate is necessary. Such heat removal can be realized by using of GaN composite substrates including high-thermal-conductivity substrates such as SiC [9]. High-power operation exceeding 40 W/mm has been recently reported for a GaN-on-SiC configuration [10]. But localized device level self-heating limits the peak power density and degrades device reliability [11]. The low thermal conductivity of the GaN buffer layer and the high thermal boundary resistances at interfaces in some composite substrates impede efficient heat dissipation from the heated device region. In view of these problems, the theoretical studies of the heat flow characteristics through Si, SiC and GaN semiconductors could be useful.

In the paper, the computational simulations of thermal conductivity of Si, SiC, GaN and SiC-GaN slabs are presented, which have been obtained by using the Non-Equilibrium Molecular Dynamics (NEMD) method with the forcefield interatomic potentials.

Computational method

In this work, the thermal conductivity was computed using the Reversed Non-Equilibrium Molecular Dynamics (RNEMD) computational simulations [12]. In the method, a heat flux through the structure under study is applied and the temperature gradient that develops as a consequence of the imposed flux is determined. The heat flux is introduced by continuously transferring energy from a "cold" slab, located at the middle of the simulation cell, to the "hot" slabs, located at the ends of simulation cell. This is accomplished by exchanging the velocities of the hottest atom in the cold slab with the coldest atom in the hot slab. Calculations were performed using the Thermal Conductivity script (version 2.2) written by Reinier Akkermans for the Forcite application within the Materials Studio 7.0 package of the Biovia company.

The Universal Force Fields (UFFs) were used for all calculations because only these Force Fields (FFs) are accessible in the Materials Studio 7.0 package for the pairs of atoms under study. The parameters of UFFs are generated from a set of rules based on element, hybridization and connectivity. The UFFs were parameterized for the full periodic table and has been carefully validated for the main-group compounds, organic molecules and metal complexes [13]. The Materials Studio package contains a full implementation of the UFFs, including bond order assignment. Parameter generation is based on physically realistic rules. Bond stretching is described by a harmonic term, angle bending by a three-term Fourier cosine expansion, and torsions and inversions by cosine-Fourier expansion terms. The van der Waals interactions are described by the Lennard-Jones potential. Electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) Coulombic term. UFFs have full coverage of the periodic table. UFFs are moderately accurate for predicting geometries and conformational energy differences of organic molecules, main-group inorganics, and metal complexes.

Results and discussion

For the steady state regime of molecular dynamics, the thermal conductivity κ of a material can be obtained from

the below Fourier's heat conduction equation using the averaging over the heat flux $\langle\Phi\rangle$ and temperature gradient $\langle dT/dz\rangle$,

(1) $$\langle\Phi\rangle = \kappa\langle dT/dz\rangle .$$

The brackets, $\langle\rangle$, indicate the average of the quantities over time as well as over the particles in the simulation cell. The atomic coordinates and the overall periodic dimensions of the simulation cell are first optimized until the forces on atoms are less than $4\cdot10^{-5}$ eV/Å. The RNEMD simulations were then carried out on the relaxed structure at the temperature 300 K with a time step of 2.0 fs. The overall simulation time used was near $100 - 300$ ps. The temperature profiles are determined by dividing the structure into slabs that are approximately 10 Å wide.

We have found that the conductivity κ of materials studied are increasing with the unit supercell dimension L_c along z-axis. This increase is caused by the scattering of the low energy phonons at the heat baths (or boundaries) of the system. The mean free path of such phonons could be of the order of hundreds nanometers. Here, one should mention that in the wide band gap and non doped semiconductors and isolators, thermal conductivity is determined mainly by phonons. In the narrow band gap semiconductors and/or wide band gap doped materials, the thermal conductivity of a material is formed also by the weakly bonded electrons. According to the kinetic theory of phonon transport [14], the thermal conductivity is proportional to the mean free path Λ for phonon scattering,

(2) $$\kappa = \rho C_V v \Lambda/3 ,$$

where ρ is density of a material, C_V is the specific heat at constant volume, v is a representative carrier velocity and Λ the carrier mean free path (the average distance traveled between collisions). In the case of phonons scattering at the heat reservoir (crystal supercell), two sources of scattering should be taken into account, phonon-phonon scattering and scattering on the boundaries in a simulation crystal supercell. These both types of phonon scattering decrease the effective thermal conductivity coefficient κ_{eff} and increase the corresponding thermal resistivity κ_{eff}^{-1}, similarly like in the case of serial connection of two electrical resistances, $\kappa_{eff}^{-1} = \kappa_{ph-ph}^{-1} + \kappa_c^{-1}$. With taking into account the proportionality $\kappa \sim \Lambda$ (2), the corresponding effective mean free path L_{eff} may be presented as the following,

(3) $$L_{eff}^{-1} = L_{ph-ph}^{-1} + L_c^{-1} ,$$

where L_{ph-ph} denotes phonon-phonon scattering length and L_c is a scattering length due to the boundaries in a crystal supercell and can be approximated to be the length of the simulation box along the heat flux in RNEMD method. On the basis of this relation, the thermal conductivity κ satisfies the relation

(4) $$\kappa_{eff}^{-1} \sim L_{eff}^{-1} = L_{ph-ph}^{-1} + L_c^{-1} ,$$

which means that a plot of the value κ_{eff}^{-1}, as function of the inverse of the system size L_c^{-1}, should be a linear dependency. In this case, the intercept of the dependency $\kappa_{eff}^{-1}(L_c^{-1})$ is the inverse thermal conductivity $\kappa_{eff}^{-1} = \kappa_1^{-1}$ of the infinitely large supercell box.

The dependency $\kappa_{eff}^{-1}(L_c^{-1})$ obtained in our study for silicon (Fig. 1) is found to be not perfectly linear, however the intercept $\kappa_{eff}^{-1}(L_c^{-1} = 0) = 0.0047$ corresponds to the thermal conductivity $\kappa_{eff}(L_c^{-1} = 0) = 213$ $Wm^{-1}K^{-1}$, which is close to the room temperature reference value of silicon $\kappa = 156$ $Wm^{-1}K^{-1}$ [15] within the uncertainty of 20%.
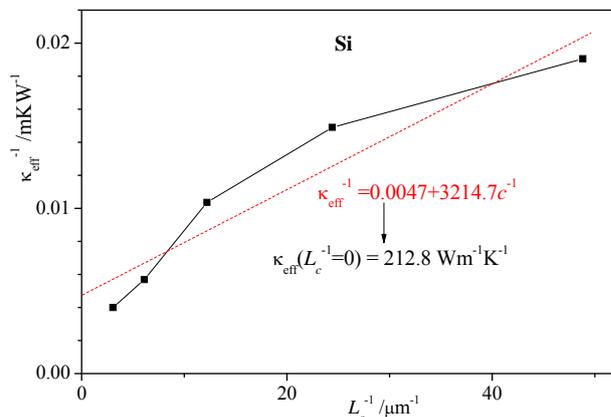
Fig. 1. Inverse of thermal conductivity κ_{eff}^{-1} for silicon as a function of inverse supercell dimension L_c^{-1} along z-axis

Thermal conductivity of SiC and GaN crystals was studied as well in similar way (Fig. 2). The corresponding intercepts $\kappa_{eff}^{-1}(L_c^{-1} = 0)$ and thermal conductivities $\kappa_{eff}(L_c^{-1} = 0)$ have been obtained to be the following. For SiC: $\kappa_{eff}^{-1}(L_c^{-1} = 0) = 0.0132$, $\kappa_{eff}(L_c^{-1} = 0) = 75.7$ $Wm^{-1}K^{-1}$. For GaN: $\kappa_{eff}^{-1}(L_c^{-1} = 0) = 0.0616$, $\kappa_{eff}(L_c^{-1} = 0) = 16.2$ $Wm^{-1}K^{-1}$. The value κ_{eff} for SiC is obtained much larger than that for GaN, what reflects the corresponding reference relation, $\kappa_{SiC} > \kappa_{GaN}$, correctly. However, absolute value of the reference thermal conductivity of SiC is much larger, $\kappa_{SiC} > 360$ $Wm^{-1}K^{-1}$, also, the reference thermal conductivity of GaN is near $\kappa_{GaN} = 130$ $Wm^{-1}K^{-1}$ [16], that is larger than the corresponding calculated value. One of the probable reasons of disagreement the calculated thermal conductivity κ_{eff} ($L_c^{-1} = 0$) and corresponding reference data is a choice of the region at L_c^{-1} axis for performing the linear fitting of the dependencies $\kappa_{eff}^{-1}(L_c^{-1})$, which are nonlinear in fact (Figs. 1, 2). Another reason of this disagreement can be some inaccuracies of the force fields used for the study of SiC and GaN.

The problem of size effect at calculations of the thermal conductivity of semiconductors using the molecular dynamics calculations is known [17]. Depending on the phonon effective mean free path of a material, the molecular dynamics results for the value of thermal conductivity are different [17]. However the molecular dynamics method may be useful when the comparative studies of different materials or one material at different conditions are of interest. In the case of present study, the relation of calculated thermal conductivities $\kappa_{eff(SiC)}/\kappa_{eff(GaN)} = 75.7/16.2 = 4.67$ reflects satisfactorily the relation of reference values of these materials.
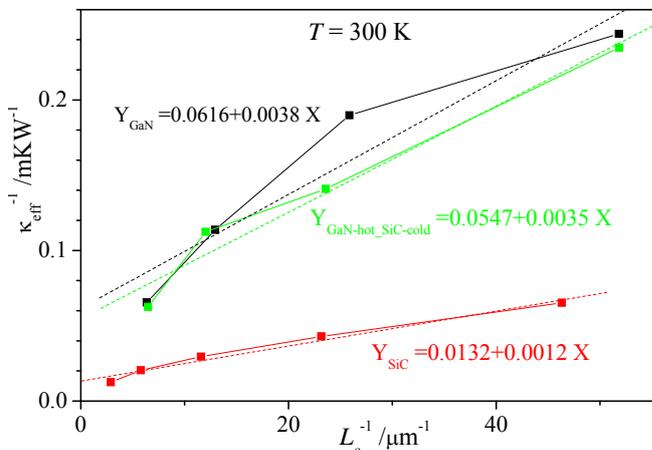
Fig. 2. Inverse of thermal conductivity κ_{eff}^{-1} for SiC, GaN and GaN-SiC as a function of inverse supercell dimension L_c^{-1} along z-axis

Because of the phonon origin of thermal conductivity of SiC and GaN, it is reasonable to study the corresponding phonon spectra and try to find out some features in these spectra, which could be in correlation with the values of thermal conductivities of these materials. Study of the time dependency of the atomic positions during the molecular dynamics run gives possibility to calculate the corresponding time-dependent velocity autocorrelation function (VACF) and its power spectrum (Fourier transformation of VACF), which in fact permit to obtain the frequencies of harmonic movements (vibrations, rotations) of atoms in the material.

The calculated intensities of Fourier transformation of VACF as functions of frequency ν for SiC and GaN crystals are presented in figures 3, 4. The corresponding molecular dynamics runs have been performed for the cubic supercell $3 \times 3 \times 3$ of SiC-β (space group no. 216, $a = b = c = 13.5$ Å, $\alpha = \beta = \gamma = 90°$), and for the wurtzite (hexagonal) supercell $4 \times 4 \times 3$ of GaN (space group no. 186, $a = b = 17.4$ Å, $c = 16.2$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$). In the case of SiC and GaN, the lower and higher frequency ranges may be selected (Figs. 3, 4). In the lower frequency range of SiC spectrum, the intensities of VACF power spectrum are larger for silicon units than for carbon ones. The opposite relation is observed for the higher frequency range of SiC, where the intensities of VACF power spectrum are larger for carbon ions than for silicon ones. Also, in this material, the relatively high hybridization (mixing) of the ionic vibrations of silicon and carbon ions takes place (Fig. 3). Opposite situation is observed for GaN, where such hybridization of the ionic vibrations of gallium and nitrogen ions is very small. Besides, the effective (intensity weighted) frequency ν_{eff} for GaN (1561 cm^{-1}) is larger than for SiC (1044 cm^{-1}). These relative characteristics correlates with the relative magnitudes of thermal conductivity of SiC and GaN. Larger hybridization of the ionic vibrations of Si and C in SiC, in comparison to the smaller hybridization of vibrations of Ga and N in GaN, promotes for the larger magnitude of thermal conductivity of SiC than in GaN. Also, smaller effective frequency ν_{eff} for SiC (1044 cm^{-1}) than for GaN (1561 cm^{-1}) promotes for the larger thermal conductivity of SiC than for GaN at the temperatures not very far from the room one, $T = 293$ K. This conclusion originates from the fact that the temperature $T = 293$ K corresponds to the frequency $\nu = 203.6$ cm^{-1}. Thus, the closer the effective frequency of a material ν_{eff} to the value $\nu = 203.6$ cm^{-1} ($T = 293$ K), the larger the thermal conductivity of a material at this temperature.
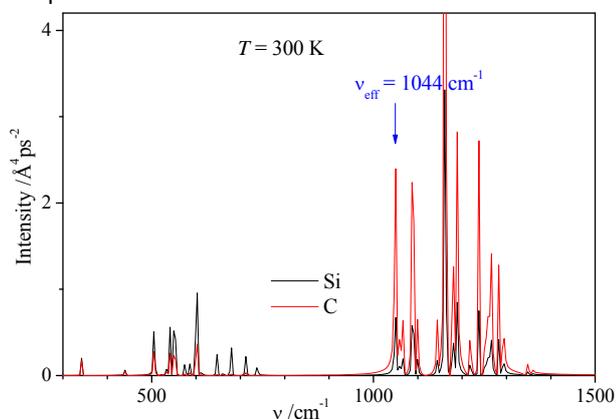
Fig. 3. Intensity of Fourier transformation of VACF as function of frequency ν (power spectrum) for Si and C in SiC at temperature 300 K. The effective (intensity weighted) frequency is equal to $\nu_{eff} = 1044$ cm^{-1}

We have calculated also the influence of hydrostatic pressure on the thermal conductivity of GaN, Si and SiC. This direction of studies is reasonable in view of the known relation (2) for the phonon originated thermal conductivity derived from the kinetic theory [14]. The product $(1/3)v\Lambda$ can be regarded as a diffusion coefficient for phonons, $D_{ph} = (1/3)v\Lambda$ (such form of relation is valid also for the coefficient of atoms diffusion). The relative change $\Delta\kappa/\kappa$ caused by the change of external pressure and therefore of density ρ can be derived from the relation (2) and presented in the form,

$$(5) \qquad \Delta\kappa/\kappa = \Delta\rho/\rho + \Delta C_V/C_V + \Delta D_{ph}/D_{ph} \ .$$

The equation (5) permits in principle to estimate the relative income to the induced change $\Delta\kappa/\kappa$ from the change of density $\Delta\rho/\rho$ and from the rest its parts, $\Delta C_V/C_V$ and $\Delta D_{ph}/D_{ph}$.

Our calculations have revealed that at the external pressure $P = 300$ GPa, the relative changes of density were found to be the following: $\Delta\rho/\rho_{GaN} = 0.0125$, $\Delta\rho/\rho_{SiC-\beta} = 0.052$, $\Delta\rho/\rho_{Si} = 1.11$. Small relative changes of density $\Delta\rho/\rho$ for GaN and SiC-β obtained do not permit to claim of the certain dependencies $\kappa_{eff}(\rho)$. For silicon, the dependency $\rho(P)$ obtained is close to the reference one. The linear fitting of the dependency $\Delta\kappa_{eff}/\kappa_{eff}$ as function of $\Delta\rho/\rho$ has revealed that the applied external pressure of 300 GPa induces the relative changes of density $\Delta\rho/\rho = 1.0$, thermal conductivity $\Delta\kappa_{eff}/\kappa_{eff} = 1.71$ and summary change of the specific heat capacity C_V and phonon diffusion coefficient D_{ph}, $\Delta C_V/C_V + \Delta D_{ph}/D_{ph} = 0.71$.

Conclusions
The phonon parts of coefficients of thermal conductivity of Si, SiC and GaN single crystals have been calculated using the Forcite program and Universal force field potentials in the framework of the Materials Studio 7.0 package. The reversed non-equilibrium molecular dynamics method has been used. The coefficients of thermal conductivity have been calculated for the crystal supercell dimensions $1 \times 1 \times N$, where $N = 40, 80, 160, 320$. The data obtained were fitted by the linear dependency between the inverse thermal conductivity κ_{eff}^{-1} and inverse long supercell length L_c^{-1}. The expected proportionality between these values have been found for Si, SiC and GaN, however clear non-linearity of the dependencies $\kappa_{eff}^{-1}(L_c^{-1})$ have been revealed for three materials studied.

Much higher hybridization (mixing) of the ionic vibrations of silicon and carbon ions have been found in SiC in comparison to the much lower hybridization of vibrations of gallium and nitrogen ions in GaN. This relation promotes for the larger magnitude of thermal conductivity of SiC than GaN.

For GaN and SiC, very small external pressure induced increases of density $\Delta\rho/\rho$ have been found for the value of pressure 300 GPa: near 1% for GaN and near 5% for SiC. For such small changes of density, no clear changes of thermal conductivity have been found. These unexpected results imply for some inaccuracies of the universal force fields used for the pairs Ga - N and Si - C.

REFERENCES

[1] Millan J., IET Circuits, *Devices & System* 1 (2007) 372-379
[2] Ren F., Zolper J.C. (Eds.), Wide Band Gap Electronic Devices, *World Scientific*, Singapore, 2003
[3] Park Y.S., in: Willardson R.K., E.R. Weber (Eds.), SiC Materials and Devices, *Semiconductors and Semimetal*, vol. 52, Academic Press, San Diego CA, 1998
[4] Chen W., Wong K.-Y., Chen K.J., *IEEE Electr. Device L.* 30 (2009) 430
[5] Kikkawa T., *Jpn. J. Appl. Phys.* 44 (2005) 4896
[6] Yanagihara M., Uemoto Y., Ueda T., Tanaka T., Ueda D., *Phys. Stat. Sol.* (a) 206 (2009) 1221
[7] Mishra U.K., Parikh P., Wu Y.F., *Proc. IEEE Micr. Elect.* 90 (2002) 1022-1031
[8] Roccaforte F., Frazzetto A., Grecoa G., Giannazzo F., Fiorenza P., Lo Nigro R., Saggio M., Leszczyński M., Pristawko P., Raineri V., *Appl. Surf. Sci.* 258 (2012) 8324
[9] Cho J., Li Z., Bozorg-Grayeli E., Kodama T., Francis D., Altman D., Ejeckam F., Faili F., Asheghi M., Goodson K.E., *13th IEEE Intersociety Conference on Date of Conference*: May 30 2012-June 1 2012, 435-439
[10] Wu Y.F., Moore M., Saxler A., Wisleder T., Parikh P., *Proc. IEEE DRC Conf. Dig.* (2006) 151
[11] Meneghesso G., Verzellesi G., Danesin F., Rampazzo F., Zanon F., Tazzoli A., Meneghini M., Zanoni E., *IEEE Trans. Device Mater. Rel.* 8 (2008) 332
[12] MullerPlathe F.J., *Chem. Phys.* 106 (1997) 6082
[13] Rappe A.K., Casewit C.J., Colwell K.S., Goddard III W.A., Skiff W.M., *J. Am. Chem. Soc.* 114 (1992) 10024
[14] Ziman J.M., Electrons and Phonons. Oxford University Press, Oxford, 2001
[15] Claudio T., Stein N., Stroppa D.G., Klobes B., Koza M.M., Kudejova P., Petermann N., Wiggers H., Schierning G., Hermann R.P., *Phys. Chem. Chem. Phys.* 16 (2014) 25701
[16] Shibata H., Waseda Y., Ohta H., Kiyomi K., Shimoyama K., Fujito K., Nagaoka H., Kagamitani Y., Simura R., Fukuda T., *Mater. Trans.* 48 (2007) 2782
[17] Sellan D.P., Landry E.S., Turney J.E., McGaughey A.J.H., Amon C.H., *Phys. Rev. B* 81 (2010), 214305

Author: prof. dr hab. Bohdan Andriyevsky, Koszalin University of Technology, Faculty of Electronics and Computer Sciences, Śniadeckich str. 2, 75-453 Koszalin, E-mail: bohdan.andriyevskyy@tu.koszalin.pl.