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PHONON THERMAL CONDUCTIVITY OF GRAPHENE

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INTRODUCTION

Graphene is a single two-dimensional structure whose surface is covered with regular hexagons of 0.142 nm side, with carbon atoms in hexagons' vertices. It can be considered as a structural part of graphite, whose 3D structure is composed of graphene planes located at a distance of 3 nm [1]. Graphene has unique properties such as anomalous high electrical and thermal conductivity, extremely high mobility of charge carriers, dependence of electronic properties from the presence of impurities on the surface, the ability to set the size of the band gap, quantum Hall effect, good electromechanical characteristics, which makes graphene a very promising material for nanoelectronics.

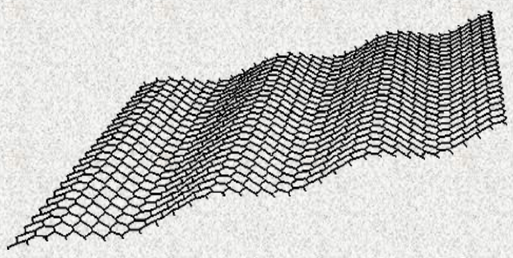

Figure 1. Wavy surface of graphene [7]

Ideal pristine two-dimensional structure cannot be obtained due to thermodynamic instability [2-6]. But, if this structure is strained or has defects, it can exist without contact with the wafer. It is experimentally established that there are free graphene sheets that constitute the complex wavy form, Fig. 1.

Analysis of the graphene thermal conductivity can help explaining the paradox of a solid-state physics, associated with a monotone growth of the coefficient of thermal conductivity of an ideal crystal with the increase of its size, due to enlarged number of phonon degrees of freedom [1]. By examining the coefficient of thermal conductivity of graphene it is possible to determine the reasons limiting the thermal conductivity of 2D structures, as well as the changes of the coefficient of thermal conductivity with increasing number of layers. It is assumed that an increase in the number of layers reduces the coefficient of thermal conductivity, because there is another channel for the scattering of phonons, associated with the interaction of layers. Ideal infinite graphene sheets do not differ mutually. But the real samples differ not only in size but also in the structure of boundaries, as shown in Fig. 2.

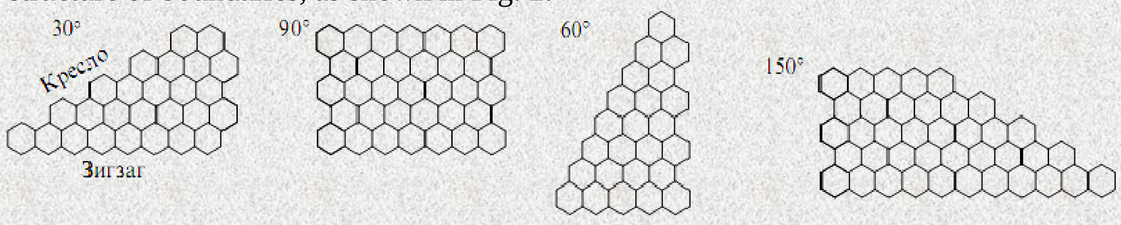

Figure 2 Graphenes with different structures of boundaries [1]

Graphene of sufficiently large size cannot have an ideal structure, because the graphene surface contains structural defects depending on the synthesis and external conditions, Fig. 3. These defects are the most common type vacancies or adsorption of some functional group on the surface, or Stone-Wales defect, isotopic defect, dislocations [1]. The existence of these defects and boundaries significantly affects the coefficient of thermal conductivity and other transport properties of graphene.

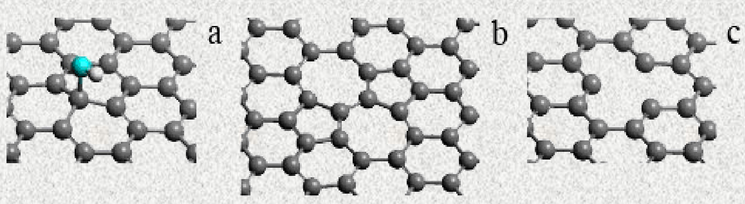

Figure 3 Graphene defects (a) adsorption on surface, (b) Stone-Wales defect, (c) vacancies

PHONON SPECTRUM OF GRAPHENE

Thermal properties of graphene (specific heat, thermal expansion coefficient, the coefficient of thermal conductivity) are significantly determined by phonon characteristics. Characteristics of phonon spectrum are determined by 2D structure of graphene. Graphene has a hexagonal structure with two carbon atoms in each cell. This determines the appearance of the six phonon branches in the dispersion spectrum: three acoustic (LA, TA and ZA) and three optical (LO, TO and ZO), Fig. 4. LA and TA modes correspond to longitudinal and transverse phonon oscillations in a graphene plane. Mode ZA corresponds to oscillations of phonons in the direction normal to the direction of oscillation modes LA and TA.

LA and TA modes have a linear dispersion law [9-10] determining the values of speed. For mode ZA there is no agreement related to the dispersion law. According to one source dispersion law is quadratic, and according to other sources dispersion law is linear.

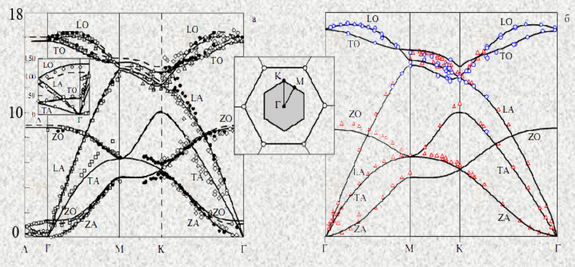

Figure 4 Dispersion law of phonons in graphene (theoretical and experimental results) [1]

THERMAL CONDUCTIVITY OF GRAPHENE

Finding the phonon thermal conductivity is determined by solving the Boltzmann transport equation:

$$\frac{\partial n_s(\vec{q})}{\partial t} + v \cdot \frac{\partial n_s(\vec{q})}{\partial x} = \left.\frac{\partial n_s(\vec{q})}{\partial t}\right|_{coll}$$

Eventually one can finally find an expression for the thermal conductivity of graphene:

$$\bar{\kappa} = \frac{1}{4\pi\hbar k_B T^2} \sum_s \int_{\omega_{\min}}^{\omega_{\max}} (\hbar\omega_s)^2 \frac{e^{\frac{\hbar\omega_s}{k_B T}}}{\left(e^{\frac{\hbar\omega_s}{k_B T}} - 1\right)^2} \tau(\omega_s) \frac{v_s}{u_s} \omega_s d\omega_s$$

The average time of relaxation of phonons, which exists in the last expression is determined by phonon scattering processes. The most common scattering processes are: scattering of phonons at boundaries, scattering of phonons at defects (isotopic impurities, vacancies), and phonon-phonon scattering. Relaxation time, which will be used for appropriate type of scattering, is the estimated time.

TEMPERATURE DEPENDENCE OF THE COEFFICIENT OF THERMAL CONDUCTIVITY

The main contribution to thermal conductivity of graphene is given by phonon branches LA and TA, in which the oscillations are going in the graphene plane. Contribution of other branches is ignored. Namely, the oscillations of branch ZA are in the direction normal to the graphene plane, and therefore they are not involved in the heat transport along the plane, while in the optical branch the group velocity is zero, so they also do not participate in the heat transport.

This paper analyzes various mechanisms of relaxation. Phonon–phonon scattering (U-scattering) and scattering at boundaries, taken together, provide high thermal conductivity values. If we take into account the scattering at defects, thermal conductivity is significantly reduced even for small concentration of defects. Calculations were carried out on the basis of relation:

$$\kappa = \frac{1}{4\pi\hbar k_B T^2} \sum_s \int_{\omega_{\min}}^{\omega_{\max}} (\hbar\omega_s)^2 e^{\frac{\hbar\omega_s}{k_B T}} \left(e^{\frac{\hbar\omega_s}{k_B T}} - 1\right)^{-2} (\tau_B^{-1} + \tau_U^{-1} + \tau_{pd}^{-1})^{-1} \omega_s d\omega_s$$

by taking into account certain derived relations from the paper.

Calculations were performed using the software package *Mathematica*. Index s has values $s \in (LA, TA)$ while relevant parameters are given in table below:

h	L	v_{LA}	v_{TA}	γ_{LA}	γ_{TA}
0.35 nm	100 μm	21.3 km/s	13.6 km/s	1.8	1.6
M	Γ	S_0	p	$\omega_{\max}$	$\omega_{\min}$
$2\cdot10^{-26}$ kg	0.1	$4.61\cdot10^{-20}$ m^2	0.9	$2.9\cdot10^{14}$ Hz	$f(\omega,T)$

On the basis of numerical calculations, when only scattering at boundaries and phonon-phonon interaction do contribute, temperature-dependence of the graphene thermal conductivity in wide temperature range is depicted in Fig. 5 (left). For the case when scattering on defects is accounted, the temperature dependence of the coefficient of thermal conductivity in the same range of temperature is depicted in Fig. 5 (right).

In Fig. 5 (left) it is shown that the coefficient of thermal conductivity reaches a value of around 4000 W/mK when there is no scattering at defects. Taking into account the scattering on defects, the coefficient of thermal conductivity abruptly drops to ten times smaller value for the value of the concentration of defects of about 1%, as shown in Fig. 5 (right).

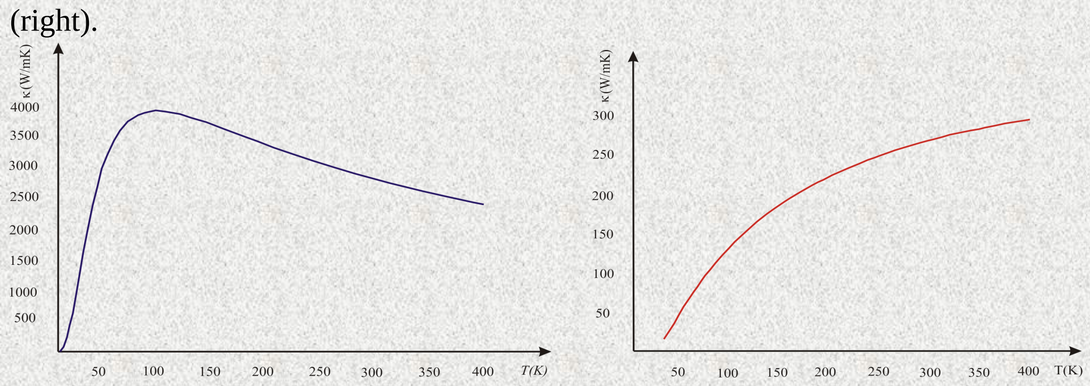

Figure 5 Temperature dependence of coefficient of thermal conductivity

Furthermore, we compared different values of thermal conductivity for different values of Grüneisen parameter:

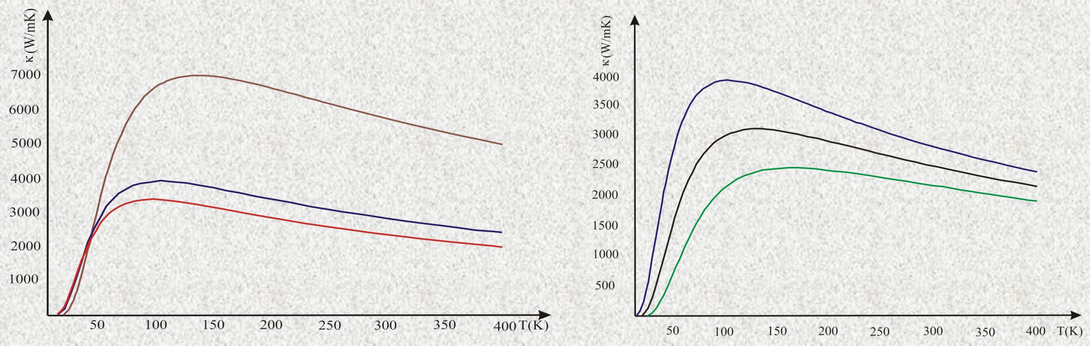

Figure 6. Thermal conductivity for different values of Grüneisen parameter
red line $\gamma_s(LA) = 2; \gamma_s(TA) = 1{,}8$
blue line $\gamma_s(LA) = 1{,}8; \gamma_s(TA) = 1{,}6$
brown line $\gamma_s(LA) = 1{,}2; \gamma_s(TA) = 1$

Figure 7. Thermal dependence of conductivity on the length of grapheme sheet
blue line $L = 100\,\mu m$
black line $L = 50\,\mu m$
green line $L = 25\,\mu m$

Also, the paper analyzes the dependence of the coefficient of thermal conductivity of graphene on the graphene sheet dimension, as shown in Fig. 7. It is clear that the coefficient of thermal conductivity of graphene increases with the size of graphene sheet. Obviously, the size reduction diminishes the role of graphene sheet three-phonon U-process, which causes reduction of the coefficient of thermal conductivity.

CONCLUSION

Studying of graphene is justified because of its extraordinary properties and potential significant applications. Thermal conductivity of graphene is essentially phonon-based. Graphene samples with dimensions exceeding average free path of phonons (800 nm [1]) were analyzed. Different results were obtained from different measurements of the coefficient of thermal conductivity of graphene, as well as from different theoretical studies. But it is evident that the low temperature coefficient of thermal conductivity is proportional to T^2, fully in agreement with the general theory for the coefficient of thermal conductivity in 2D structures. Also, absolute value of the coefficient of thermal conductivity increases with the size of graphene sheet.

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