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Ab initio molecular dynamics calculations of heat conductivity for silicon related materials

Abstract. Results of the ab initio molecular dynamics for pure silicon and phosphorus doped silicon crystals have been presented. The relation between the phonon lifetime τ and the root mean square deviation δ of atoms based on the condition of the interferometric minimum has been proposed. The relation approximates adequately the temperature dependence of the heat conductivity of pure silicon. However, that relation has not reproduced properly the reference experimental magnitude of the phonon conductivity coefficient of silicon for the phosphorus content $n_P = 5 \cdot 10^{20}$ cm^{-3}. This result indicates that the additional kind of the phonon scattering on the local phosphorus stimulated defects should be taken into consideration.

*Streszczenie. Przedstawiono wyniki obliczeń z pierwszych zasad dynamiki molekularnej niedomieszkowanych i domieszkowanych fosforem kryształów krzemu i zaproponowano wzór relacji między czasem życia fononów τ i odchyleniem standardowym atomów δ, bazujący na interferencyjnym warunku minimum fal fononowych. Zaproponowany wzór adekwatnie opisuje temperaturową zależność współczynnika przewodnictwa cieplnego niedomieszkowanego krzemu. Jednak zaproponowany wzór nie odtwarza zadowalająco referencyjnej doświadczalnej wartości przewodności cieplnej krzemu dla koncentracji fosforu $n_P = 5 \cdot 10^{20}$ cm^{-3}. Ten wynik wskazuje na to, że dla adekwatnego odtwarzania wartości doświadczalnych należy uwzględnić dodatkowy kanał rozpraszania fononów, związany z lokalnymi około fosforowymi defektami. (**Obliczenia z pierwszych zasad przewodności cieplnej materiałów na bazie krzemu metodą dynamiki molekularnej**).*

Słowa kluczowe: krzem, dynamika molekularna, współczynnik przewodności cieplnej, czas życia fononów
Keywords: silicon, molecular dynamics, thermal conductivity coefficient, phonon lifetime

Introduction
Thermal effects occurring in the active electronic elements and devices lead to their temperature increase and may change their functional characteristics. To keep these characteristics within the determined frameworks, one has to construct the corresponding devices taking into account the heat conductivity characteristics of the corresponding active and neighboring materials. Because of the large variety of these materials in modern electronics the problem of their heat characteristics determination is extremely important [1].

There are several theoretical techniques reported in the literature [2], which are used for determination of the phonon thermal conductivity. One of the often applied techniques is the molecular dynamics (MD), which can be separated into two main groups: (1) equilibrium and (2) non-equilibrium methods. In an equilibrium MD simulation, the system under investigation has a constant average temperature and an average heat flux of zero [2]. However, at each instant of time a finite heat flux exists due to instantaneous fluctuations of temperature. The popular Green-Kubo method [3, 4], based on the general fluctuation-dissipation theorem [5], relates the lattice thermal conductivity of the system to the time required for such fluctuations to dissipate. The corresponding algorithms however are not implemented in the more popular *ab initio* packages, for example in VASP code [6].

In the present study, we propose a new approach for the theoretical first-principles calculations of the phonon lifetime τ and thermal diffusivity D of a material on the basis of the standard *ab initio* molecular dynamics (AMD) study. This approach has been applied to the study of heat conductivity in pure silicon and phosphorus doped silicon crystals. Some subsidiary calculations of this type were performed with diamond, sapphire (Al$_2$O$_3$) and silver. On the basis of the calculated thermal diffusivity D one can obtain the corresponding data for the coefficient of thermal conductivity κ, if the information on the heat capacity C_p of the material studied is available. This approach uses the relation for the thermal conductivity κ derived from the kinetic theory of phonons propagation [7],

$$(1) \qquad \kappa = (1/3)\rho C_p V^2 \tau,$$

where ρ is a density, V is the velocity of acoustic waves, and τ is the phonon lifetime.

Method and calculation details
The equilibrium-type *ab initio* molecular dynamics (AMD) calculations of the crystal have been performed in the framework of the density functional theory (DFT) using the VASP package [6]. The projector augmented-wave (PAW) method with a cutoff energy of 400 eV for the plane waves was employed [6, 8] together with the corresponding pseudopotentials. For the exchange and correlation terms, the gradient corrected Perdew-Burke-Ernzerhof (PBE) functional was used. The AMD calculations of silicon related crystals were performed at the macro-canonical NVT ensemble for different temperatures at the optimized crystal structure of the super cell 3×3×3. Most results of AMD calculations have been obtained for the simulation time up to 15 ps with the time steps of 1.5 fs. For the post MD analysis the nMoldyn 3.0 program was used [9].

From the relation (1), the value of heat diffusivity D is determined as,

$$(2) \qquad D = (1/3)V^2\tau = (1/3)LV,$$

where L is the phonon mean free path. The values V, τ and L are interrelated according to the known relation $L = V\tau$.

Analysis of the reference data of the temperature dependences of the values from the relations (1) and (2) in the range near $T = 293$ K has revealed that the dependence $\tau(T)$ determines mainly the dependence of the thermal conductivity $\kappa(T)$. Relative temperature changes of the values ρ, C, and V are about one order of magnitude smaller.

It is known that the phonon lifetime τ and the corresponding phonon mean free path L are determined by the phonon scattering in solids, caused by the thermal atomic vibrations and crystal structure defects.

Here, we propose the method of the phonon lifetime τ estimation based on the results of the molecular dynamics calculations. We demonstrate that the root-mean-square deviation of atoms obtained from the molecular dynamics calculations determines the phonon lifetime τ and its

temperature dependence. This value τ together with the reference data of the longitudinal acoustic velocity V allows to obtain the heat diffusivity D of a material using the relation (2).

The proposed method is based on the supposition that the phonon mean free path L is equal to the interferometric coherence length L_{coher}. This coherence length L_{coher} in turn is determined from the condition of the interferometric minimum, $\Delta = \lambda/2$, for two phonons of the wavelength λ and path difference Δ. This coherence length L_{coher} may be presented in term of the smallest interatomic distance d in the direction of the acoustic waves propagation,

(3) $$L = L_{\text{coher}} = N \cdot d \,,$$

where the number N is determined from the condition of the interferometric minimum,

(4) $$\Delta = (1/3)\delta \cdot N = \lambda/2 \,.$$

Here, δ is a root-mean-square deviation of atoms obtained from the MD calculation at certain temperature T and λ is an acoustic wavelength. The coefficient $(1/3)$ originates from the fact that the root-mean-square deviation of atoms is a spatial characteristic, whereas the condition of the interferometric minimum (4) relates to one certain direction of acoustic wave propagation.

By combining relations (3) and (4) and taking into account the relation between the wavelength λ, velocity V and frequency ν of the acoustic wave, $\lambda = V/\nu$, the phonon mean free path L may be presented in the form,

(5) $$L = N \cdot d = (3/2)\lambda d/\delta = (3/2)Vd/(\nu\delta) \,,$$

Using the latter result and the relation (2), the phonon lifetime τ may be presented in the form,

(6) $$\tau = (3/2)d/(\nu\delta) \,.$$

Taking into account the following relation between the frequency and temperature,

(7) $$h\nu = k_{\text{B}}T \,,$$

(here, h and k_{B} are the Planck and Boltzmann constants respectively), the phonon lifetime τ (6) may be presented in the form

(8) $$\tau = (3/2)dh/(k_{\text{B}}T\delta) \,.$$

The latter relation has been used for the study of dependences of the phonon lifetime τ on the temperature and crystal unit cell content of materials.

Results and discussion

Results of our MD calculations reveal that the proposed relation (8) is a good approximation of the real phonon lifetime τ in silicon. According to that calculations performed for the temperature $T = 300$ K, corresponding to the frequency $\nu = 6.25$ THz (7), the root-mean-square deviation is equal to $\delta = 1.3 \cdot 10^{-11}$ m. These values together with the shortest interatomic distance $d = 0.22$ nm in silicon lead, according to (8), to the phonon lifetime $\tau = 4.05$ ps. The corresponding thermal diffusivity D, calculated by formula (2), is then equal to $D = 95.9$ mm^{2}s^{-1}, when the velocity $V = 8430$ ms^{-1} of longitudinal acoustic waves is taken for

silicon [10]. The corresponding experimental magnitude of the heat diffusivity of silicon is equal to $D_{\text{e}} = 88$ mm^{2}s^{-1} [11].

Our results of AMD calculations for undoped silicon reveal almost perfect linear dependence $\delta^2(T)$, that is expected because the harmonic vibration changes of the potential energy of atoms are proportional to the thermal energy $k_{\text{B}}T$. Taking this into account one may expect that, in the considered approximation (8), the temperature dependence of the phonon lifetime will be close to $\tau \sim T^{-1.5}$. According to the reference data on the temperature dependence of the thermal conductivity of silicon [12] the relation $\kappa \sim T^{-1.35}$ takes place in the wide temperature range 300 K - 1000 K, that is in a satisfactory agreement with the dependence $\tau \sim T^{-1.5}$ proposed in the present model.

To check the correctness of the relation (8) one may compare the calculated value of the phonon lifetime τ (or the corresponding thermal conductivity κ) for some anisotropic crystal with corresponding experimental data to see whether the order of these anisotropic values agree.

For sapphire, Al_2O_3, the anisotropy of the crystal has been taken into account, so the value of the interatomic distance d in (8) was taken different for the crystallographic plane xy and for z- direction because of the different unit cell dimensions ($a = 1.43$ nm, $b = 1.43$ nm, $c = 1.30$ nm). The corresponding anisotropic values $d_x = d_y$ and d_z have been calculated on the basis of known unit cell volume and dimensions a and c: $d_x = d_y = 0.221$ nm, $d_z = 0.201$ nm. Then the MD calculations were performed for Al_2O_3 crystal at the supercell $3 \times 3 \times 1$, containing 270 atoms, at the temperature 300 K of NVT ensemble. The mean square displacements were found to be $\delta^2_x = 4.982 \cdot 10^{-5}$ nm^2, $\delta^2_y = 5.083 \cdot 10^{-5}$ nm^2 and $\delta^2_z = 5.565 \cdot 10^{-5}$ nm^2. The corresponding root mean square deviations $\delta_x \approx \delta_y = 0.709 \cdot 10^{-2}$ nm, $\delta_z = 0.746 \cdot 10^{-2}$ nm. The latter values $\delta_x \approx \delta_y$ and δ_z and the values $d_x = d_y = 0.221$ nm, $d_z = 0.201$ nm correspond according to relation (8) to the phonon lifetimes $\tau_x = \tau_y = 7.47$ ps and $\tau_z = 6.46$ ps. These phonon lifetimes correspond, according to the relation (2), to the phonon mean free paths $L_x = 82.9$ nm and $L_z = 71.7$ nm if the value of acoustic velocity $V_{\text{sapphire}} = 1.11 \cdot 10^4$ m/s is taken for both x- and z-directions of the crystal. The values obtained are in a satisfactory agreement with the reference data for sapphire [13], which is one of the widely used materials in electronics.

The relative difference of the calculated value τ, $2(\tau_x - \tau_z)/(\tau_x + \tau_z) = 0.145$, is of the same sign and is not far from to the relative difference of the reference data of the thermal conductivity $2(\kappa_x - \kappa_z)/(\kappa_x + \kappa_z) = 0.087$. For sapphire, $\kappa_x = \kappa_x = 25.2$ Wm^{-1}K^{-1}, $\kappa_z = 23.1$ Wm^{-1}K^{-1} [14]. These results indicate that relation (8) can reproduce properly the anisotropy of the phonon lifetime in crystals, that in turn may serve as a proof for its correctness.

The proposed method was applied also to silicon, diamond and silver to compare the corresponding calculated and reference data (Table 1). Much smaller value of the estimated phonon thermal conductivity $\kappa^{(\text{ph})}$ than the experimental data κ_{ref} for silver originates from the fact that the phonon thermal conductivity is not dominant.

Table 1. Calculated and reference (ref) data related to heat conductivity of silicon, diamond and silver

	T K	d nm	δ Pm	τ ps	V kms^{-1}	D mm^{2}s^{-1}	κ Wm^{1}K^{-1}	C_p Jkg^{1}K^{-1}	ρ kgm^{-3}	D_{ref} mm^{2}s^{-1}	κ_{ref} Wm^{-1}K^{-1}
Si	300	0.235	19.6	2.88	8.43	68.3	111	700	2329	80	130
C	300	0.155	8.41	4.44	17.5	454	830	520	3515	300	600
Ag	300	0.293	33.5	2.10	3.65	9.33	23.5	240	10490	166	418

The value $\kappa^{(ph)} = 23.5$ Wm^{-1}K^{-1} for silver, obtained by us on the basis of the phonon lifetime τ (Table 1) and reference data for the acoustic velocity, specific thermal heat and density, is however larger than the similar reference value for the room temperature $\kappa^{(ph)}_{ref} \approx 5$ Wm^{-1}K^{-1} obtained by using the *ab initio* theoretical calculations [15]. One of the reasons of this discrepancy is probably the reference experimental value of the silver specific heat used ($C_p = 240$ Jkg^{-1}K^{-1}), which relates to both corresponding inputs, from phonons and electrons. For silicon and diamond, the calculated values of phonon thermal conductivity $\kappa^{(ph)}$ and the corresponding experimental data κ_{ref} differ not very much (Table 1), if taking into account the complexity of the problem for theoretical estimation of the phonon thermal conductivity.

In the framework of the proposed relation (8), we have also studied the influence of the phosphorus doping of silicon crystals on the corresponding phonon lifetime. The phosphorus doping of silicon was realized by means of replacement of 1 to 27 silicon atoms among 216 ones of the crystal super cell $3\times3\times3$, that corresponds to the atom density range of $(2.26\cdot10^{20} - 6.12\cdot10^{21})$ cm^{-3}. We have found a clear decrease of the phonon lifetime τ, from 4.0 ps to 3.4 ps, with the increase of the phosphorus doping n_P (Fig. 1). The largest decrease of the phonon lifetime τ from 4.0 ps to 3.4 ps occurs just in the beginning part $(0 - 2.26\cdot10^{20}$ cm$^{-3})$ of the whole range $0 - 6.12\cdot10^{21}$ cm^{-3} of phosphorus atom density n_P. This decrease of the phonon lifetime τ is however insufficient to be comparable with the experimental data [16], where the decrease of the thermal conductivity from $\kappa(n_P = 0) = 130$ Wm^{-1}K^{-1} to $\kappa(n_P = 5\cdot10^{20}$ cm$^{-3}) = 57$ Wm^{-1}K^{-1} has been found (the relation $\kappa/\kappa_{nP=0} \approx \tau/\tau_{nP=0}$ takes place). This indicates that the simple model of the phonon lifetime calculation, resulting in relations (6) or (8), is not sufficiently good for the case of the doped silicon. The phosphorus doped atoms cause centers of local defects in silicon matrix, which interact more strongly with phonons than it could be expected on the basis of relations (6) or (8) due to the different values of δ.
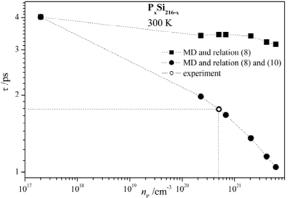

Fig.1. Dependences of the phonon lifetime τ on the phosphorus content n_P of the doped silicon P$_x$Si$_{216-x}$ at the temperature 300 K obtained using relation (8) (squares) and relation (8) and (10) (circles). The latter dependence has been normalized taking into account the experimental data [16]

To take this into account one can use the fact that, in the case of phonons scattering at the heat reservoir (crystal super cell), two sources of scattering should be taken into account; (1) phonon-phonon scattering and (2) scattering on the boundaries of defects in the super cell. These both types of phonon scattering decrease the total thermal conductivity. Taking into account the proportionality $\kappa \sim L$ (see relation (2)), the corresponding total mean free path L may be presented as the following,

$$(9) \qquad L^{-1} = L_{ph\text{-}ph}^{-1} + L_d^{-1} \;,$$

where $L_{ph\text{-}ph}$ denotes phonon-phonon scattering length and L_d is proportional to the averaged distance between phosphorus scattering centers (defects) in silicon matrix. On the basis of this relation, the total thermal conductivity κ fulfills the relation

$$(10) \qquad \kappa^{-1} \sim L^{-1} = (V\tau)^{-1} = (V\tau_{ph\text{-}ph})^{-1} + L_d^{-1} \;.$$

Conclusions

The relation (8), based on the interference model of the phonon mean free path, satisfactorily reproduces the absolute value and the temperature dependence of the phonon mean lifetime $\tau(T)$ in silicon. Due to generality of the interference model the proposed method seems to be useful for other materials. One of the strong features of the method is that the only one necessary value (root mean square deviation δ) should be obtained from the standard *ab initio* molecular dynamics run to use it for the estimation of the phonon mean lifetime τ.

An increase of the root mean square deviation δ for the phosphorus doped silicon crystals has been detected as a function of the phosphorus atom concentration. However, for the adequate quantitative description of the experimental dependence $\tau(\delta)$ the additional kind of phonon scattering on the phosphorus defects should be taken into account.

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