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Calculations of the Thermal Conductivity of $Si_{1-x}Ge_x$ Films with Nonuniform Composition

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SiGe films have attracted much attention recently due to experimental demonstrations of improved thermoelectric properties over those of the corresponding bulk material. However, despite this increasing attention, available information on the thermoelectric properties of $Si_{1-x}Ge_x$ films is quite limited, especially for nonuniform composition in wide temperature interval. In this paper we have used the Boltzmann equation under the relaxation-time approximation to calculate the thermal conductivity of $Si_{1-x}Ge_x$ films with nonuniform composition. It is confirmed that SiGe films with nonuniform composition has significantly lower thermal conductivity than its uniform counterpart. This suggests that an improvement in thermoelectric properties is possible by using the SiGe films with nonuniform distribution of germanium.

Keywords: thermal conductivity, film, silicon, germanium, Boltzmann equation.

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Introduction

The semiconductor structures $Si_{1-x}Ge_x$ are widely used in the development of elements of microprocessor technology [1], optoelectronics [2] and infrared photodetectors [3] due to their comparative low cost and compatibility with the methods of obtaining silicon technology for making devices and schemes. The possibilities of silicon-germanium nanostructures with quantum dots or quantum wires are also intensively studied to create memory cells [4], lasers [5], and photovoltaic cells [6] on their basis. In recent years, the powerful direction of research has been formed in solid state physics, where structures, in particular $Si_{1-x}Ge_x$ films, are considered as one of the promising materials for improving the energy conversion efficiency of semiconductor thermoelectric elements [7]. At the same time, great attention is paid to the search of methods of influence on the processes of thermoelectric conversion in a material by changing its structural, electrical or thermal characteristics.

It is known that the efficiency of semiconductor thermoelectric elements is proportional to the dimensionless value of ZT, which is called the thermoelectric figure-of-merit, and depends on the electrical conductivity σ of the material, its thermal conductivity k and the Zeebeck coefficient S.

$$ZT = \frac{S^2 \sigma T}{k}, \qquad (1)$$

where T is the temperature. So reducing the thermal conductivity of the working material is one of the effective ways to increase the efficiency of energy conversion in thermoelectric elements. Different ways of reducing the heat conductivity of $Si_{1-x}Ge_x$ structures were proposed, including nanostructuring of the material, usage of Si/Ge superlattices, changes in their composition compound [8]. The usage of structures with a nonuniform distribution of doping impurities i.e. the modulated SiGe alloying films is considered an alternative way of increasing the thermoelectric figure-of-merit of $Si_{1-x}Ge_x$ [9]. Scattering of phonons on nonuniformly distributed doping impurities, for example, phosphorus or boron, leads to a decrease in the thermal conductivity of the working material, which results an increase of thermoelectric figure-of-merit.

In this paper we study the possibility of tuning the thermal conductivity of $Si_{1-x}Ge_x$ films by the nonuniform distribution of germanium atoms on film thickness. Using the Boltzmann equation, the thermal conductivity k of $Si_{1-x}Ge_x$ films is calculated in both - in film plane and in the perpendicular direction. The temperature dependences $k(T)$ of films with different types of

distribution of the content of germanium on the thickness of the film are analyzed.

I. Research Methods

$Si_{1-x}Ge_x$ films with nonuniform content x of germanium atoms on the thickness d of the film were studied (Fig.1). The calculation of thermal conductivity was done by using the Boltzmann equation in the framework of the approximation of relaxation time using the model proposed in [10] and improved in [11]. To calculate the thermal conductivity of inhomogeneous films at the initial stage, the breakdown of the

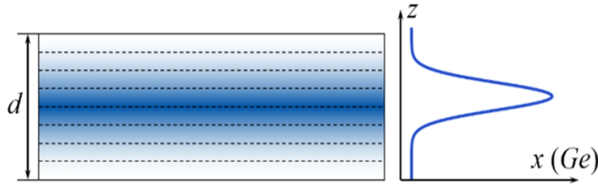

Fig. 1. Scheme of the investigated structure (on the left) and distribution of the atoms of germanium in it (on the right).

investigated structure into thin layers was performed (the dashed lines in the Fig. 1) and in each layer the Ge content x was constant. According to our calculations, the thickness of the films was chosen equal to 1 micron.

The thermal conductivity k_n of each layer with the number n was determined as the sum of the phonon thermal conductivity of one longitudinal k_L and two transverse k_T modes:

$$k_n = \frac{k_L + 2k_T}{3} . \quad (2)$$

Each of the contributions k_L and k_T was calculated according to the relation:

$$k_i = \frac{4\pi k_B^4 T^3}{h^3 v_i}\left(I_{i1} + \frac{I_{i2}^2}{I_{i3}} \right), \quad (3)$$

where $I = L$ (longitudinal mode) or T (transverse mode), k_B is the Boltzmann constant, h is the Planck constant, v_i is the speed of i-th phonon mode. The integrals I_{i1}, I_{i1}, I_{i3} in (2) were defined as:

$$I_{i1} = \int_0^{\theta_i/T} \frac{\tau_i \xi^4 e^\xi}{\left(e^\xi - 1\right)^2} d\xi , \quad (4)$$

$$I_{i2} = \int_0^{\theta_i/T} \frac{\tau_i \xi^4 e^\xi}{\tau_{N,i}\left(e^\xi - 1\right)^2} d\xi , \quad (5)$$

$$I_{i3} = \int_0^{\theta_i/T} \frac{\tau_i \xi^4 e^\xi}{\tau_{N,i}\tau_{R,i}\left(e^\xi - 1\right)^2} d\xi , \quad (6)$$

where θ_i is the Debye temperature, ξ is is the reduced energy for phonon, $\xi=\hbar\omega/k_BT$. The total relaxation time of phonons was determined by the Matisson rule, taking into account the possible scattering mechanisms:

$$\frac{1}{\tau_i} = \frac{1}{\tau_{N,i}} + \frac{1}{\tau_{R,i}} , \quad (7)$$

where $\tau_{N,i}$ is the phonon relaxation time due to normal phonon scattering, $\tau_{R,i}$ is the phonon relaxation time which takes into account the Umklapp-scattering $\tau_{U,i}$, alloy scattering $\tau_{A,i}$, phonon scattering at the boundary (surface) of a film $\tau_{B,i}$ and phonon-electron scattering $\tau_{E,i}$:

$$\frac{1}{\tau_{R,i}} = \frac{1}{\tau_{U,i}} + \frac{1}{\tau_{A,i}} + \frac{1}{\tau_{B,i}} + \frac{1}{\tau_{E,i}} , \quad (8)$$

The relaxation time for the normal scattering can be written as:

$$\frac{1}{\tau_{N,L}} = \frac{k_B^5 \gamma_L^2 T^5 \xi^2 \left[V_{Si}(1-x) + V_{Ge}x\right]}{v_L^5 \hbar^4 \left[M_{Si}(1-x) + M_{Ge}x\right]} , \quad (9)$$

$$\frac{1}{\tau_{N,T}} = \frac{k_B^5 \gamma_T^2 T^5 \xi^2 \left[V_{Si}(1-x) + V_{Ge}x\right]}{v_T^5 \hbar^4 \left[M_{Si}(1-x) + M_{Ge}x\right]} , \quad (10)$$

where γ is the Grüneisen parameter, M_{Si}, M_{Ge} is the mass of a Si and Ge atoms, V_{Si}, V_{Ge} is the volume of a Si and Ge atoms respectively. The relaxation time for the Umklapp scattering can be expressed as

$$\frac{1}{\tau_{U,i}} = \frac{\gamma_i^2 k_B^2 \xi^2 T^3}{\left[M_{Si}(1-x) + M_{Ge}x\right]\hbar v_i^2 \theta_i} e^{-\theta_i/3T} , \quad (11)$$

Finally, the relaxation times for scattering on stoichiometric inhomogeneities, film surfaces, and phonon-electron scattering were calculated as:

$$\frac{1}{\tau_{A,i}} = \Gamma \frac{\left[V_{Si}(1-x) + V_{Ge}x\right]}{4\pi v_i^3} \left(\frac{k_B T}{\hbar}\right)^4 \xi^4 , \quad (12)$$

$$\frac{1}{\tau_{B,i}} = \frac{v_i}{d}\left(\frac{1-\alpha}{1+\alpha}\right), \quad (13)$$

$$\frac{1}{\tau_{E,i}} = \frac{E_e^2 m^3 v_i}{4\pi \hbar^4 \rho \beta_i} \left\{ \xi - \ln\left[\frac{1 + e^{\beta_i - \mu + \xi^2/(16\beta_i) + \xi/2}}{1 + e^{\beta_i - \mu + \xi^2/(16\beta_i) - \xi/2}} \right] \right\} , \quad (14)$$

where α is the coefficient of surface specularity, E_e is the deformation potential, m is the electron effective mass, ρ is the density of crystal, μ is the chemical potential, $\beta_i = mv^2/(2k_BT)$.

Further in the work the integral thermal conductivity of the investigated film was determined and calculated in accordance with (2) the thermal conductivity of each layer. In this case, the thermal conductivity in the plane of the film is:

$$k_{\parallel} = \sum_n k_n , \quad (15)$$

while the thermal conductivity in the direction perpendicular to the area of the film:

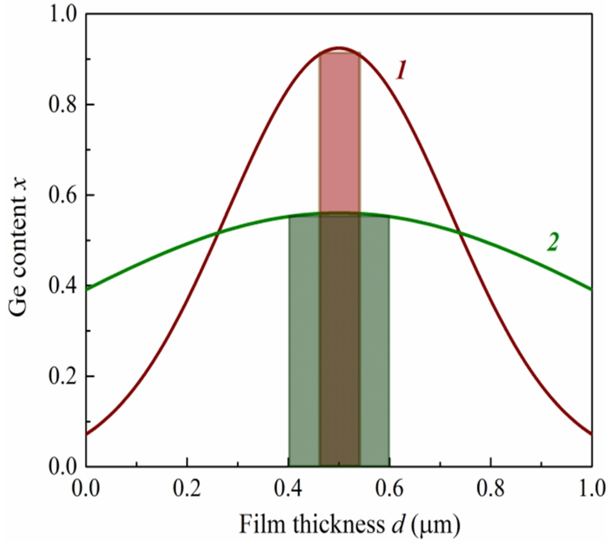

Fig. 2. Distributions of the germanium atoms content in the studied film: *1* – $\sigma = d/5$; *2* – $\sigma = d/2$. Rectangles schematically show the thickness of layers with a nonuniform content of germanium.

$$k_{\perp} = \left(\sum_n \frac{1}{k_n} \right)^{-1}, \qquad (16)$$

II. Results and discussion

It is known that the thermal conductivity of $Si_{1-x}Ge_x$ depends on the germanium content: with an increase in the Ge fraction x in the Si matrix, a monotonous decrease in the coefficient of thermal conductivity is observed, at $x \approx 0.5$ the value of k reaches a minimum, and with the subsequent growth of the fraction x, the thermal conductivity of the compound gradually increases and goes to the value of the thermal conductivity of the pure Ge. Taking into account the described $k(x)$ dependence we selected $Si_{1-x}Ge_x$ films with a average content of germanium $\bar{x} = 0.5$ which corresponds to the minimum on the curve $k(x)$ for further research. At the same time, for the films with a nonuniform distribution of germanium $x(z)$ in thickness, the condition was fulfilled:

$$\bar{x} = \frac{1}{d} \int_0^d x(z) dz, \qquad (17)$$

In this work, we studied the thermal conductivity of $Si_{1-x}Ge_x$ films with a distribution of germanium, whose profile is approximated by the functions of the form:

$$x(z) = A e^{-\left(\frac{(x-d/2)^2}{2s^2} \right)}, \qquad (18)$$

where A, σ are constants. In Fig. 2 it is shown the $x(z)$ distributions, described by the relation (18) for two different values of σ. Each distribution which is shown above can be characterized by a different degree of nonuniformity δx:

$$dx = \frac{x_{\max} - x_{\min}}{x_{\max}}, \qquad (19)$$

where $x_{\max}$ and $x_{\min}$ is the maximal and minimal content of germanium in the film, respectively. In Fig. 2 distribution *1* is characterized by a higher degree of nonuniformity in comparison with Ge distribution *2*. Each of these distributions has different thicknesses of layers with the same content of germanium: the value of

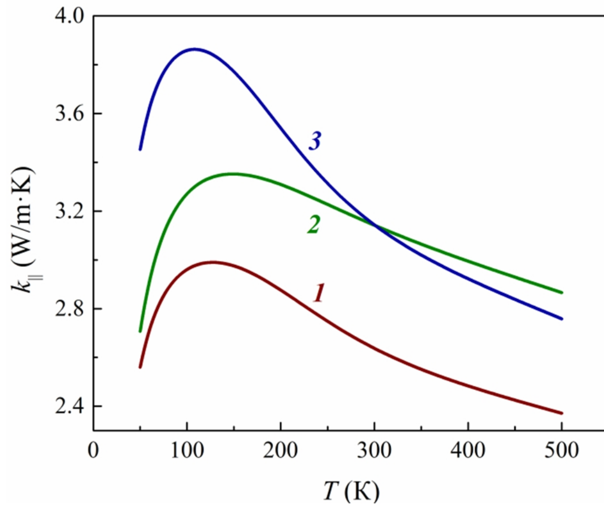

Fig. 3. Calculated the temperature dependence $k_{\parallel}(T)$ of the thermal conductivity in the plane of $Si_{1-x}Ge_x$ film with nonuniform distribution of germanium. The curves *1*, *2* correspond to the distributions *1* and *2* in Fig. 2. The curve *3* corresponds to a uniform distribution of germanium.

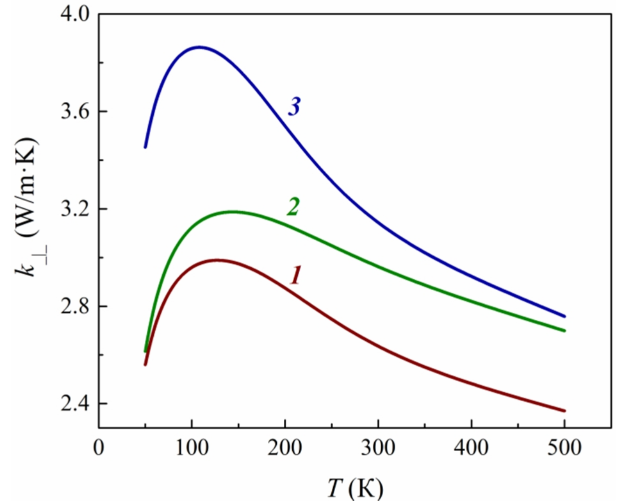

Fig. 4. Calculated the temperature dependence $k_{\perp}(T)$ of the thermal conductivity in the perpendicular direction to the area of the $Si_{1-x}Ge_x$ film with nonuniform distribution of germanium. The curves *1*, *2* correspond to the distributions *1* and *2* in Fig. 2. The curve *3* corresponds to a uniform distribution of germanium.

σ increases when the layers thickness of the same component composition $Si_{1-x}Ge_x$ is also increased.

Fig. 3 and Fig. 4 show the temperature dependences $k_{\|}(T)$ and $k_{\perp}(T)$ for films with different $x(z)$ distributions, which are represented in Fig. 2. These findings are compared with analogous dependences for $Si_{1-x}Ge_x$ films with homogeneous germanium contents $x = 0.5$ (curves *3* in Fig. 3 and Fig. 4). The thermal conductivity $k_{\|}$ in the plane of $Si_{1-x}Ge_x$ films shows a tendency for decreasing when the nonuniformity degree of the germanium distribution increases (curves *2* and *3* in Fig. 3). It is noteworthy that the thermal conductivity $k_{\|}$ in the region of low temperatures for a film with a lower degree of heterogeneity is smaller compared to a homogeneous film. But the inverse relations are observed in the region of high temperatures. Therefore, calculating the thermal conductivity $k_{\perp}$ in the perpendicular direction to the area of the $Si_{1-x}Ge_x$ films shows that the magnitude decreases with increasing degree of nonuniformity of the Ge distribution and is less than the thermal conductivity of the homogeneous film $Si_{0,5}Ge_{0,5}$ in the whole studied temperature range (Fig.4). In addition, comparing the thermal conductivities $k_{\|}$ and $k_{\perp}$ for films of the same nonuniformity degree, the value $k_{\perp}$ at any temperature is slightly lower than $k_{\|}$. It should be noted that our theoretical results are completely consistent with the experimental data of other authors [12], where the reduction of the thermal conductivity with the simultaneous growth of thermoelectric figure-of-merit in Si / Ge structures with nonuniform germanium distribution was confirmed.

Conclusions

Finally, in the presented paper we made the thermal conductivity calculations of the nonuniform $Si_{1-x}Ge_x$ films, using the Boltzmann equation in the approximation time of relaxation. It is shown that when the degree of film nonuniformity increases, the thermal conductivity decreases and turns out to be less than the thermal conductivity of films with uniform distribution of germanium. The obtained results may form the basis in the development of thermoelectric converters, using the heterogeneous film structures based on $Si_{1-x}Ge_x$.

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Розрахунок теплопровідності плівок $Si_{1-x}Ge_x$ з неоднорідним складом

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З використанням рівняння Больцмана в наближенні часу релаксації розраховано температурні залежності коефіцієнта теплопровідності кремній-германієвих плівок з неоднорідним розподілом германію по товщині структури. Показано, що теплопровідність плівок $Si_{1-x}Ge_x$ зменшується зі збільшенням ступеня їх неоднорідності. Проаналізовано механізми фононного розсіювання в досліджуваних плівках та встановлено домінуючі процеси, якими визначаються процеси теплоперенесення в області високих і низьких температур.

Ключові слова: коефіцієнт теплопровідності, плівка, кремній, германій, рівняння Больцмана.