

## DETERMINATION OF THERMAL CONDUCTIVITY AND HEAT CAPACITY OF SILICON ELECTRON GAS

OLGA N. KOROLEVA<sup>1,2</sup>, ALEXANDER V. MAZHUKIN<sup>1,2</sup>

<sup>1</sup>M.V. Keldysh Institute of Applied Mathematics of RAS

<sup>2</sup>National Research Nuclear University MEPhI

**Summary.** Within the framework of quantum statistics, such properties of silicon with intrinsic conductivity as thermal conductivity and heat capacity of electron gas in an arbitrary degeneracy range in the temperature range from 300K to 2000K were determined. In the calculations, approximations of the Fermi-Dirac integrals were used. In modeling the heat capacity and thermal conductivity, the influence of bandgap narrowing in the conditions of a sufficiently strong heating of the intrinsic semiconductor and carrier degeneracy was taken into account. The results of the calculations are compared with the experimental data. Numerical and graphical information on the properties obtained and the results of comparison with experiment are presented.

### 1 INTRODUCTION

In connection with the development of technological applications based on laser processing of semiconductors with short pulses, the research of fundamental melting mechanisms [1] - [5] remains important, for which the properties of semiconductors, including heat capacity and thermal conductivity, are of great importance.

Determination of the heat capacity and thermal conductivity of semiconductors, like metals, is carried out in two ways, experimental or theoretical. The experimental approach is traditional. The data obtained by measurements are widely used for testing theoretical dependencies. The literature [6] - [10] presents experimental values of the equilibrium properties of silicon in temperature ranges that do not exceed the melting point. Basically, these data characterize the thermal conductivity and electrical conductivity.

The experimental approach has a number of limitations, primarily on the range of measurement conditions, especially in the melting region. As a rule, experimental data are obtained under conditions of thermodynamic equilibrium and give values of the equilibrium properties of silicon.

However, in the problems of laser action on semiconductors, the knowledge of equilibrium properties is insufficient. Laser heating of semiconductors (silicon), as well as metals, occurs at very short time and spatial scales and leads to a violation of the general local thermodynamic equilibrium. Therefore, in problems of laser action, silicon can be regarded as an object consisting of two interacting subsystems - electron and phonon subsystems [11] - [12]. At the same time, for each of the subsystems it is necessary to determine thermophysical, optical and thermodynamic characteristics that vary over a wide temperature range. In view of the limited possibilities of the experimental approach in determining the properties of silicon electron gas, in this paper, we propose to use a theoretical approach based

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on the application of quantum statistics of an electron gas, i.e. the distribution function and Fermi-Dirac integrals [13] - [15]. Of special interest in the problems of laser action is the behavior of electron subsystem of silicon under phase transition conditions. Numerous experiments [5], [7], [8] have shown that in silicon during the melting the covalent bonds are destroyed, with a change in the short-range order, accompanied by a sharp increase in the concentration of conduction electrons and leading to the transition of silicon to the metallic state. In order to determine the properties of electron subsystem under phase transition conditions, together with the temperature dependence of the carrier concentration, an important fundamental characteristic of the silicon phase transition, such as the width of bandgap is necessary, which narrows with increasing temperature, having a significant effect on the increase in carrier concentration reaching high  $N(T) \approx 10^{18} \text{ cm}^{-3}$  values and higher, which is confirmed by experimental studies [16], [17].

In the article, using the theoretical approach based on quantum statistics, such properties of the electron subsystem of silicon with intrinsic conductivity as the heat capacity  $C_e(T, N)$  and the thermal conductivity  $\kappa_e(T, N)$  are determined. The calculations were carried out taking into account the temperature and carrier-density dependences of the bandgap  $E_g(T, N)$ , Fermi energy  $E_F(T, N)$ , temperature dependences of the electron concentration  $N_e(T)$ , hole concentration  $N_h(t)$  in an arbitrary degeneracy range of the electron gas at temperature changes from 300K to 2000K. The results are compared with the experimental data.

## 2 THEORETICAL APPROACH TO DETERMINATION OF SILICON ELECTRON SUBSYSTEM PROPERTIES

To the most important thermophysical and thermodynamic characteristics of silicon electron gas within the framework of the heat transfer mechanism of energy transfer are the heat capacity  $C_e(T, N)$  and thermal conductivity  $\kappa_e(T, N)$ . For their determination, the statistics of the electron gas of semiconductors are used. The central place in this approach is occupied by the charge carrier distribution function over the energy states. Electrons in the conduction band and holes in the valence band of silicon can be regarded as an ideal Fermi gas. For an ideal Fermi gas, the probability of an electron filling a state  $k$  with energy  $E$  at a temperature  $T$  is found using the Fermi-Dirac distribution [13] - [15]:

$$f(E, T) = \frac{1}{\left(1 + \exp\left(\frac{E - E_F}{k_B T}\right)\right)} \quad (1)$$

where  $E_F$  – is Fermi energy, determined from the electroneutrality condition,  $k_B$  is Boltzmann constant.

For an electron gas, the value of the Fermi energy is defined as the amount of energy necessary to change the number of particles in the system per volume unit and coincides with the value of the chemical potential at  $T=0$  K.

### 2.1 Carrier concentration.

An important characteristic of semiconductors, necessary for determining the majority of thermophysical properties of silicon, is the concentration of charge carriers. In intrinsic semiconductors, unlike metals, the number of charge carriers and their mobility depend on temperature.

The electron  $N_e(T)$  and holes  $N_h(T)$  concentrations at the temperature  $T$  in the conduction band under thermodynamic equilibrium conditions are determined

$$N_e(T) = \int_{E_c}^{\infty} N_C f(E, T) dE \quad N_h(T) = \int_{-\infty}^{E_v} N_V f(E, T) dE \quad (2)$$

where  $N_C = 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2}$ ,  $N_V = 2 \left( \frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2}$  are effective densities of states in the conduction band  $E_C$  and the valence band  $E_V$ ,  $\hbar$  is the Planck constant,  $m_e = M^{2/3} (m_l \cdot m_t^2)^{1/3}$  is the effective mass of electron state density in the conduction band, taking into account the number of equivalent energy minima in the conduction band  $M$  (for silicon  $M = 6$ ) [13] - [15],  $m_l$ ,  $m_t$  are the longitudinal and transverse masses,  $m_h$  is the effective mass of the density of hole states in the valence band, and  $f(E, T)$  is the Fermi-Dirac distribution function (1). For an intrinsic semiconductor that does not contain impurities, equality of concentrations is observed

$$N_e(T) = N_h(T) = N(T). \quad (3)$$

The integrals in (2) can be represented in the form

$$N_e(T) = N_C \cdot \mathcal{F}_{1/2}(\eta_e) \quad N_h(T) = N_V \mathcal{F}_{1/2}(\eta_h) \quad (4)$$

where  $\mathcal{F}_{1/2}(x)$  is Fermi-Dirac integral of order  $j=1/2$ , is representative of the family of integrals that play an important role in determining the properties of semiconductors

$$\mathcal{F}_j(\eta_c) = \frac{1}{\Gamma(j+1)} \int_0^{\infty} \frac{\varepsilon^j}{1 + \exp(\varepsilon - \eta_c)} d\varepsilon \quad (5)$$

where  $\Gamma(x)$  is Gamma function,  $j$  is the index of the Fermi-Dirac integral,  $c=e$  for electrons and  $c=h$  for holes,  $\varepsilon$  is the reduced energy of the electron (hole),  $\eta_c$  is the reduced Fermi energy for electrons and holes

$$\eta_e(T, N_e) = \frac{E_F(T, N_e) - E_C(T, N_e)}{k_B T} \quad \eta_h(T, N_h) = \frac{E_V(T, N_h) - E_F(T, N_h)}{k_B T}. \quad (6)$$

where  $E_C(T, N)$  is energy of the bottom of the conduction band,  $E_V(T, N)$  is the energy of the top of the valence band.

At low temperatures in semiconductors, the concentration of conduction electrons is so small that they behave like a gas of noninteracting particles, the electron gas is nondegenerate. In this case, the Fermi level  $E_F(T, N)$  lies below the bottom of the conduction band ( $E_C - E_F > 0$ ) in bandgap  $E_g(T, N)$  and the distribution function (1) reduces easily to the classical Maxwell-Boltzmann distribution function, and the calculation of carrier concentration (4) reduces to

$$N_e(T) = N_C \exp\left(\frac{E_F(T, N_e) - E_C(T, N_e)}{k_B T}\right) \quad N_h(T) = N_V \exp\left(\frac{E_V(T, N_h) - E_F(T, N_h)}{k_B T}\right) \quad (7)$$

Taking into account the intrinsic conductivity  $N(T)$

$$N_e(T) = N_h(T) = N(T) = \frac{1}{4} \left( \frac{2k_B T}{\pi \hbar^2} \right)^{3/2} (m_e m_h)^{3/4} \exp\left(-\frac{E_g(T, N)}{2k_B T}\right), \quad (8)$$

where  $E_g = E_c - E_v$  is width of bandgap.

In the calculation view, the determination of carrier concentrations will not be difficult. As the temperature rises, the situation changes. Hot electrons give energy to the lattice, while the width of bandgap decreases and the concentration of free charge carriers in the conduction band increases. The Fermi level penetrates either to the conduction band ( $E_c - E_f < 0$ ) or to the valence band ( $E_f - E_v < 0$ ), the electron gas degenerates and the classical statistics become unjust, and (7) is not valid. Therefore, it becomes necessary to use quantum statistics and expressions (4) for carrier concentrations. This immediately leads to computational difficulties, since the integral (5), except for the integral with order  $j=0$ , can not be calculated analytically. The computational difficulties associated with the use of Fermi-Dirac integrals arise not only in determining the carrier concentrations, but also in determining the properties of electron gas such as heat capacity, thermal conductivity, and others [39], where Fermi-Dirac integrals with integer and half-integer indices, as a rule not high, are used  $-1/2 \leq j \leq 7/2$  и  $-1 \leq j \leq 3$ . In [18], [19] for Fermi-Dirac integrals of orders  $j = -1/2, 1/2, 1, 3/2, 2, 5/2, 3$  and  $7/2$  continuous analytical expressions single of each order have been obtained in a wide range of degeneracy

$$\mathcal{F}_j(\eta_c) = \exp\left(\sum_{i=0}^m a_i \eta_c^i\right), \quad c = e, h, \quad m = 5 \div 7, \quad (9)$$

which in this paper were used to calculate the properties of an electron gas. To calculate integrals with order  $j = 1/2$ , an approximating function (9) with  $m=7$  is used.

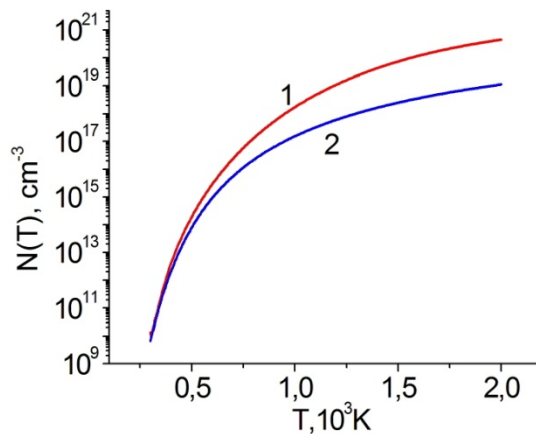


Figure 1. Temperature dependences of carrier concentrations calculated using (1) Fermi-Dirac statistics, (2) Maxwell-Boltzmann,  $E_g=1.12$  eV.

As the temperature in the semiconductor increases, the process of thermal excitation of electrons from the valence band to the conduction band proceeds continuously, electrons recombine from the conduction band to the valence band. In the intrinsic semiconductor these processes are balanced, and electron and hole concentrations are the same. From the

electroneutrality condition, we can find the temperature dependence of Fermi energy  $E_F$ , using (4) and (9) for  $j=1/2$ , we obtain

$$N_C \cdot \exp\left(\sum_{i=0}^7 a_i n_e^i(T, N)\right) = N_V \cdot \exp\left(\sum_{i=0}^7 a_i n_h^i(T, N)\right) \quad (10)$$

Figure 1 shows the temperature dependences of the carrier concentration calculated with quantum statistics and the bandgap (12) and the classical Maxwell-Boltzmann statistics and the constant value of the bandgap  $E_g=1.12$  eV at 300K.

## 2.2 Bandgap

The bandgap of silicon  $E_g$  with increasing temperature and increasing concentration of charge carriers tends to narrow [13] - [17].

Three basic mechanisms cause the narrowing of the bandgap: thermal expansion of the lattice, electron-lattice interaction and collective interactions of carriers. The thermal expansion with increasing temperature together with the enhancement of the electron-lattice interaction causes a displacement of the relative position of the conduction and valence bands. The total manifestation of the first two mechanisms of narrowing of the bandgap is described by a semiempirical relationship [20]

$$E_g(T, N) = E_{g,0} - \alpha T^2 / (T + \beta), \quad (11)$$

where  $E_{g,0} = 1.169$  eV is the bandgap at temperature 0°K,  $\alpha$  and  $\beta$  are constants, whose experimental estimates for silicon are  $\alpha = 7.021 \times 10^{-4}$  eV/T,  $\beta = 1108$ K.

The third mechanism of narrowing the bandgap is associated with the effects of collective interactions of carriers, which become dominant at sufficiently high concentrations. The effect of quantum effects becomes noticeable at a carrier concentration of  $N \approx 10^{18}$  cm<sup>-3</sup> and is formulated in a complex manner [21]. The most significant contribution to the narrowing of the bandgap is made by the exchange interaction estimated by the empirical dependence of the form  $\Delta E_g(N) \sim \gamma \times N^{1/3}(T)$  [22], where  $\gamma$  is the fitting parameter used for combining theoretical estimates with experimentally determined values of the narrowing of bandgap in various semiconductors. For silicon at a temperature of  $T \approx 300$ K and carrier concentration  $N = 10^{17} \div 10^{19}$  cm<sup>-3</sup>, the value of the parameter  $\gamma$  is in the range of values  $(1.0 \div 3.6)10^{-8}$  eV×cm [21],[23].

The influence of all mechanisms on narrowing the width of Si bandgap at high temperatures and carrier concentrations  $N \approx 10^{18} \div 10^{21}$  cm<sup>-3</sup> is taken into account in the semiempirical dependence [12], [24]

$$E_g(T, N) = E_{g,0} - \alpha T^2 / (T + \beta) - \gamma N^{1/3}(T), \quad (12)$$

where the value  $\gamma = 8.35 \times 10^{-8}$  eV×cm – was chosen from the condition that the width of bandgap should be zero at the equilibrium melting point  $E_g(T_m, N) = 0$  [24]. Figure 2 shows the temperature dependences of the narrowing of the bandgap  $E_g(T, N)$  and the position of Fermi energy level  $E_F(T, N)$ , calculated with quantum statistics, relative to the edges of the valence  $E_V(T, N)$  and conduction  $E_C(T, N)$  bands and intrinsic Fermi level in the middle of the bandgap. With increasing temperature, the Fermi energy  $E_F(T, N)$  deviates from its own level toward the edge of the valence band  $E_V(T, N)$ , which is determined by the lower effective mass of the

density of states of the valence band (for silicon,  $m_{de}/m_{dh}=1.89$ ). Because of this, the degeneracy of the hole gas ( $E_V-E_F < k_b T$ ,  $\eta_h \approx -4$ ) occurs at a temperature below the equilibrium melting point ( $T=1000\text{K}$ ), before the degeneracy of the electron gas.

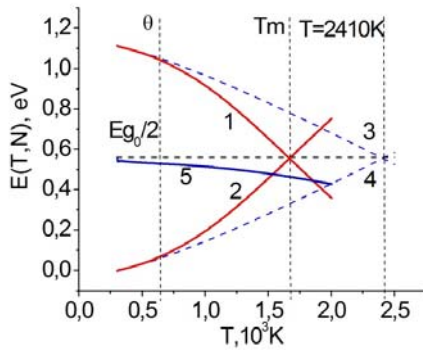


Figure 2. Temperature dependences of the edges of conduction  $E_C(T, N)$  and valence  $E_V(T, N)$  bands with allowance for: thermal and quantum effects (1), (2); thermal effects (3), (4). The Fermi energy is  $E_F(T, N)$  (5).

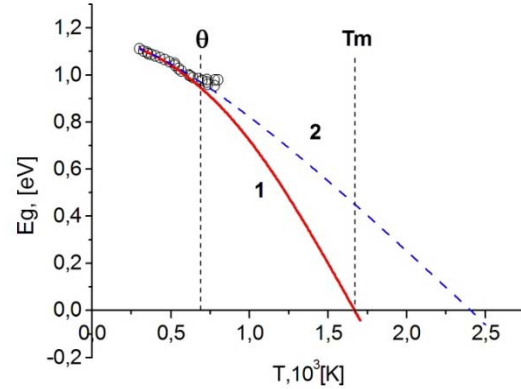


Figure 3. Temperature dependences of the bandgap with allowance for: thermal and quantum effects (1); thermal effects (2). Markers show the experimental data [25].

Dependences of the bandgap are shown in Fig. 3. Dependence (1) takes into account the quantum and thermal (12) effects, in dependence (2) - only thermal (11). In the temperature range from  $300^\circ\text{K}$  to  $\theta$ , where the influence of quantum mechanisms is weak, the width of bandgap is equally well approximated by both dependences and completely coincide with the experiment [25]. Above the Debye temperature, the contribution of collective interaction mechanisms to the width of bandgap becomes appreciable, which causes a stronger narrowing.

### 2.3 Thermal conductivity of electron gas

Thermal conductivity refers to the most important thermophysical properties of silicon. For laser action problems, properties for the electron and phonon subsystems are often necessary, and experimental data for thermal conductivity are usually obtained under thermodynamic equilibrium conditions and give the values of the total thermal conductivity of silicon. Therefore, to determine the thermal conductivity of electrons, we will use the theoretical approach.

Since the transfer of thermal energy is carried out by free charge carriers and phonons, the total thermal conductivity  $\kappa(T, N)$  is determined by the lattice thermal conductivity  $\kappa_{lat}(T)$  and the thermal conductivity of free carriers  $\kappa_e(T, N)$  (electrons and holes)

$$\kappa(T, N) = \kappa_{lat}(T) + \kappa_e(T, N) \quad (13)$$

The thermal conductivity of solid-state semiconductors, unlike metals, is determined by the lattice (phonon) thermal conductivity  $\kappa_{lat}(T) > \kappa_e(T, N)$ . The determination of the properties of phonon subsystem is an object of molecular dynamics modeling. However, in the framework of the problem in question, for comparison with the experimental data, the temperature dependence of  $\kappa_{lat}(T)$  (Fig.5) was estimated in accordance with the semiempirical dependence from [12]

$$\kappa_{lat}(T) = 1585 \cdot T^{-1,23} \text{ W/cmK} \quad (14)$$

The thermal conductivity of electrons with allowance for quantum statistics was determined

$$\kappa_c(T, N) = N(T) \mu_c(T, N) \frac{k_B^2 T}{e} \left[ 6 \frac{\mathcal{F}_2(\eta_c)}{\mathcal{F}_0(\eta_c)} - 4 \left( \frac{\mathcal{F}_1(\eta_c)}{\mathcal{F}_0(\eta_c)} \right)^2 \right]_{c=e,h} \quad (15)$$

where  $e$  is electron charge,  $N(T)$  is intrinsic concentration of charge carriers (3),  $\mathcal{F}_2(\eta_c)$ ,  $\mathcal{F}_1(\eta_c)$ ,  $\mathcal{F}_0(\eta_c)$ , are Fermi-Dirac integrals of orders  $j=0,1,2$  for electrons and holes, for calculation of

which were used approximating functions from [18],[19].  $\mu_c(T, N) = \mu_c^0(T) \frac{\mathcal{F}_0(\eta_c)}{\mathcal{F}_{1/2}(\eta_c)} \Big|_{c=e,h}$  is

charge carriers mobility [26], where  $\mu_c^0(T, N)$  is carriers mobility for nondegenerate semiconductor,  $\mathcal{F}_{1/2}(\eta_c)$ , is Fermi-Dirac integral of order  $j=1/2$ .

Figures 4-6 show the temperature dependences of the thermal conductivity of silicon: electron (15) and phonon (14) subsystems and total (13). Figure 7 shows the temperature dependence of the electronic contribution to the total thermal conductivity as a percentage.

As the temperature increases, the thermal conductivity of electrons increases (Fig. 4), and the lattice one decreases (Fig. 5). The obtained dependence of total thermal conductivity (13) in the temperature range  $300\text{K} < T < T_m$  shows good agreement with experimental data (Fig. 6). Because of the low electrical conductivity of silicon, electron fraction of thermal conductivity in the solid state is small and before melting does not exceed 4.7% of the total thermal conductivity (blue line in Fig. 7). At a temperature exceeding the melting point, the equilibrium thermal conductivity abruptly increases (Fig. 6). We have only experimental data on the equilibrium thermal conductivity of molten silicon [7]. The fraction of electron thermal conductivity in the experimental value of the thermal conductivity at  $T = 2000\text{K}$  is 4%.

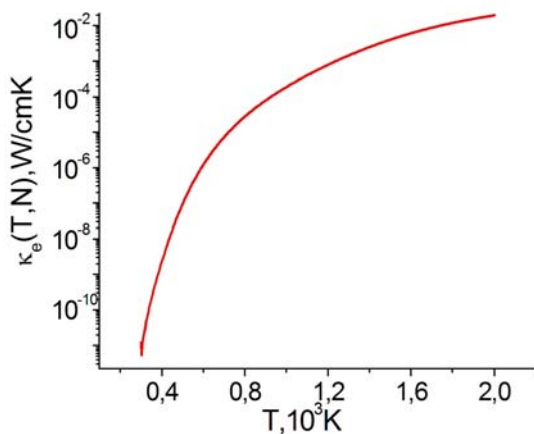


Figure 4. Temperature dependence of thermal conductivity of electrons.

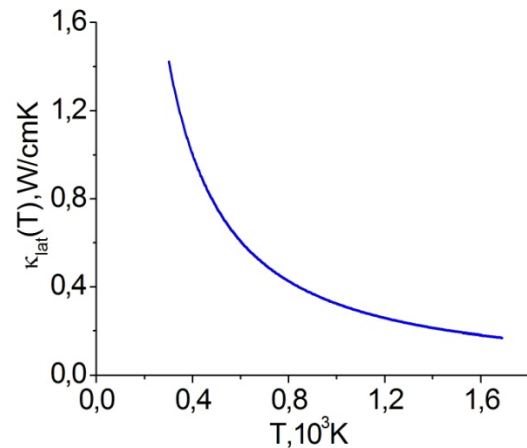


Figure 5. Temperature dependence of phonon thermal conductivity.

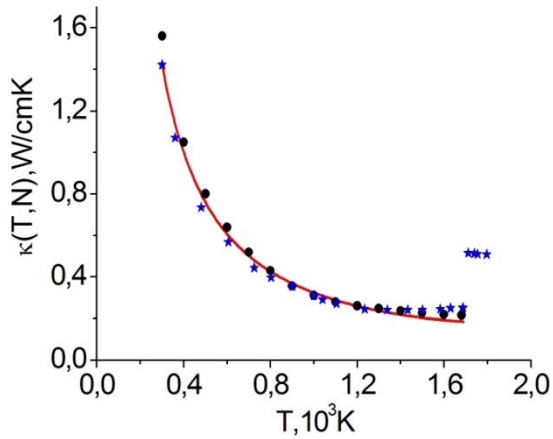


Figure 6. Temperature dependence of the total thermal conductivity (solid line). The markers are experimental data: blue [7], black [8].

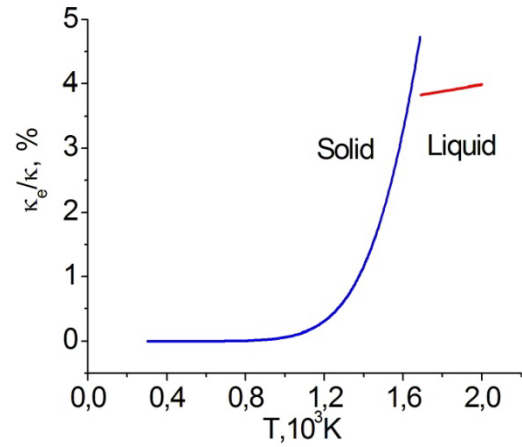


Figure 7. Temperature dependence of the percentage ratio of electron and total thermal conductivities.

## 2.4 Heat capacity of electron gas

The total heat capacity of electron gas is defined as the amount of energy needed to raise the temperature by one degree Kelvin in the system per volume unit. Since the transfer of thermal energy in a solid is carried out by free charge carriers and phonons, the total heat capacity  $C(T, N)$  as well as the thermal conductivity, is determined by the heat capacity of the lattice  $C_{lat}(T)$  and the heat capacity of free carriers  $C_e(T, N)$  (electrons and holes).

$$C(T, N) = C_{lat}(T) + C_e(T, N) \quad (16)$$

The determination of the phonon heat capacity is an object of molecular dynamics modeling, but for comparison with the experimental data the temperature dependence of  $C_{lat}(T)$  was estimated in accordance with the Einstein heat capacity formula [15]

$$C_{lat}(T) = 3R \left( \frac{\theta}{T} \right)^2 e^{\frac{\theta}{T}} / \left( e^{\frac{\theta}{T}} - 1 \right)^2, \quad (17)$$

where  $\theta$  – Debye temperature (for silicon  $\theta = 640\text{K}$ ),  $R$  - universal gas constant.

The heat capacity of the electron gas was determined as the temperature derivative of the energy density of electron-hole pairs in the system.

$$C_e(T, N) = \partial U(T, N) / \partial T \quad (18)$$

The total energy density  $U(T, N)$  of electron-hole pairs consists of kinetic energy and energy of the bandgap per volume unit [12]

$$U(T, N) = N(T)E_g(T, N) + \frac{3}{2}N(T)k_B T \left[ \frac{\mathcal{F}_{3/2}(\eta_e)}{\mathcal{F}_{1/2}(\eta_e)} + \frac{\mathcal{F}_{3/2}(\eta_h)}{\mathcal{F}_{1/2}(\eta_h)} \right] \quad (19)$$



where  $E_g(T,N)$  is bandgap (12),  $N(T)$  is intrinsic charge carrier concentration (3),  $\mathcal{F}_{3/2}(\eta_e)$ ,  $\mathcal{F}_{1/2}(\eta_e)$ ,  $\mathcal{F}_{3/2}(\eta_h)$ ,  $\mathcal{F}_{1/2}(\eta_h)$  are Fermi-Dirac integrals of orders  $j=1/2$  and  $j=3/2$  for electrons and holes. In the modeling, approximating functions for these integrals from [18],[19] were used.

Figure 8 shows the temperature dependences of the heat capacity of electrons (18) and of the lattice (17). It is seen that with increasing temperature the electronic component of the heat capacity approaches the phonon component, the magnitude of which determines the total heat capacity of silicon.

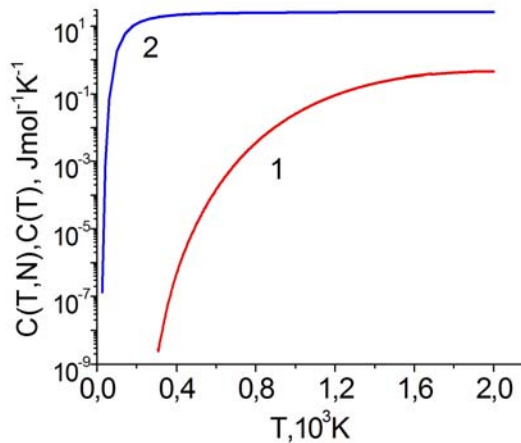


Figure 8. Temperature dependences of the heat capacity of electrons (1) and of the lattice (2).

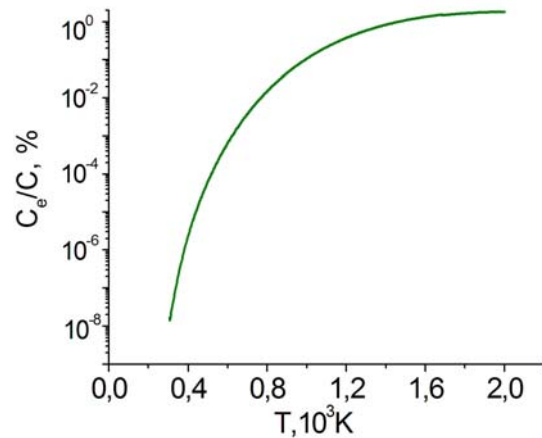


Figure 9. Temperature dependence of the percentage ratio of electron and total heat capacity of silicon.

The contribution of the electronic component to the total heat capacity is small, but increases with increasing temperature and at an equilibrium melting temperature is of 1.4% and at  $T=2000\text{K}$  is 1.72% (Fig. 9).

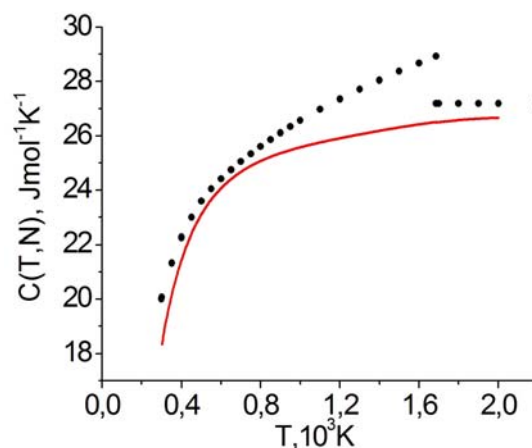


Figure 10. Temperature dependence of the total heat capacity (solid line). Markers indicate the experimental data [10].

Figure 10 shows temperature dependence of the total heat capacity and experimental data. The obtained temperature dependence agrees well with the experimental data in the temperature ranges  $300\text{K} < T < 1000\text{K}$  and  $T_m < T < 2000\text{K}$ .

#### 4 CONCLUSION

The thermal conductivity and heat capacity of the electron subsystem of silicon are calculated in the framework of the continuum approach, which uses quantum statistics and Fermi-Dirac integrals in an arbitrary range of degeneracy of an electron gas with a temperature change from 300K to 2000K. In the simulation of electron thermal conductivity and heat capacity, the influence of narrowing of the bandgap under conditions of sufficiently strong heating of the intrinsic semiconductor and carrier degeneracy is taken into account. The results of the calculations are compared with the results of the experiments. Comparison of the calculated characteristics of silicon with the experimental data showed an acceptable quantitative coincidence of the width of the bandgap, thermal conductivity and heat capacity. Numerical and graphical information on obtained properties and comparison results with experimental data are presented.

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