JOURNAL OF SOLID STATE CHEMISTRY 73, 92–97 (1988)

Three-Phonon Scattering Processes and Their Role in Phonon Thermal Conductivity of Silicon

P. C. SHARMA

Department of Physics, Tuskegee University, Tuskegee, Alabama 36088

AND M. FRANK ROSE

Space Power Institute, Auburn University, Auburn, Alabama 36849

Received March 12, 1987; in revised form June 22, 1987

The true temperature exponents of three-phonon scattering processes for silicon in the temperature range 5–1200°K have been calculated. These values have been used to explain the temperature dependence of phonon thermal conductivity. The theoretically obtained values agree very well with the experimental values. The contributions of transverse and longitudinal phonons toward thermal conductivity of undoped silicon have been investigated, both in high as well as low temperature regions. It is observed that the transverse phonons make a major contribution toward phonon thermal conductivity in the entire temperature range. © 1988 Academic Press, Inc.

Introduction

The low temperature phonon thermal conductivity can be explained well by taking into account the scattering of phonons by the boundary of the crystals and the defects present in it. But above the conductivity maximum temperature, the decrease of phonon conductivity with temperature is mainly due to phonon–phonon scattering. The phonon conductivity of solids at low temperatures has been satisfactorily explained by the formulation given by Callaway (*1*), based on the concept of making no distinction between different phonon polarizations. However, to explain the high temperature thermal conductivity values, distinction between longitudinal and transverse phonon polarization branches has been made by Holland (*2*) and the model was applied to explain the temperature phonon conductivity of germanium and silicon. In the analysis of phonon conductivity at high temperatures there is no exact theory which gives the expressions for the relaxation rates to the three-phonon scattering processes, which depend both on phonon frequency and temperature. In the low temperature range Herring (*3*) gave the relaxation rates for three-phonon scattering processes as

$$\tau^{-1} \propto \omega^2 T^3 \quad \text{for longitudinal phonons}$$

and

$$\tau^{-1} \propto \omega T^4 \quad \text{for transverse phonons.}$$

In the high temperature region, the three-phonon scattering relaxation rate has a T dependence, which explains the T^{-1} variation of lattice thermal conductivity.

The three-phonon relaxation rates can be written as

0022-4596/88 $3.00

$$\tau_{3\,\mathrm{ph}}^{-1} \propto g(\omega) f(T)$$

where

$$g(\omega) = \omega \quad \text{for transverse phonons}$$
$$= \omega^2 \quad \text{for longitudinal phonons}$$
$$f(T) = T^m.$$

The value of exponent m varied between 1 and 4 for transverse and 1 and 3 for longitudinal phonons. This situation was modified by Klemens (*4*, *5*) by including three-phonon Umklapp processes as $\tau_{3\,\mathrm{ph}}^{-1} \propto g(\omega) T^m e^{-\theta/\alpha T}$, where θ is the Debye temperature. Guthrie (*6*) studied the temperature dependence of three-phonon relaxation rates, distinguishing three-phonon scattering events as (i) Class I events, in which the carrier phonon is annihilated by combination with the other phonon, and (ii) Class II events, in which the carrier phonon is annihilated by splitting. Guthrie proposed the idea that the temperature exponent m is a continuous function of temperature, i.e., $m = m(T)$. Hence the modified three-phonon relaxation rate can be written as $\tau_{3\,\mathrm{ph}}^{-1} \propto g(\omega) T^{m(T)} e^{-\theta/\alpha T}$. Guthrie (*6*) quoted in his paper the expression for the upper and lower bounds for $m(T)$. Sharma *et al.* (*7*) have proposed the model to determine the true values of $m(T)$ from the average values given by Guthrie (*6*). By this model (*7*), the exact values of temperature dependence of three-phonon relaxation rates for both transverse and longitudinal branches, as well as Class I and Class II events, can be calculated. It has been applied to study the conductivity of germanium (*7*).

In the present work, we analyze the phonon conductivity of silicon by using the more realistic three-phonon scattering rates. We will use more accurate approximation for the value of V_g/V_p^2 instead of crude approximation of $V_g/V_p^2 = 1/V_p$; it has been used by earlier workers. We have used an empirical relation $\mathbf{q} = \omega/\mathbf{v}\,(1 + \beta\omega^2)$ to describe the realistic dispersion curve. This expression has been used to calculate V_g/V_p^2 in order to have a more realistic approach.

Three-Phonon Relaxation Rates

The three-phonon scattering relaxation rate can be written as

$$\tau_{3\,\mathrm{ph}}^{-1} = (\tau_{3\,\mathrm{ph}}^{-1})_{\mathrm{I}} + (\tau_{3\,\mathrm{ph}}^{-1})_{\mathrm{II}}, \tag{1}$$

where subscripts I and II represent Class I and Class II events. Class I events for three-phonon interaction, in which the carrier phonon $\mathbf{q}$ combines with $\mathbf{q}'$ into a phonon $\mathbf{q}''$, can be represented as

$$\begin{aligned} \mathbf{q} + \mathbf{q}' &= \mathbf{q}'' \\ \mathbf{q} + \mathbf{q}' &= \mathbf{q}'' + \mathbf{b}, \end{aligned} \tag{2}$$

where $\mathbf{b}$ is the reciprocal lattice vector. The process in which $\mathbf{b} = 0$, is called the three-phonon normal process, which others are Umklapp processes. Class II events in which the phonon $\mathbf{q}$ splits into $\mathbf{q}'$ and $\mathbf{q}''$ are represented as

$$\begin{aligned} \mathbf{q} &= \mathbf{q}' + \mathbf{q}'' \\ \mathbf{q} &= \mathbf{q}' + \mathbf{q}'' + \mathbf{b}. \end{aligned} \tag{3}$$

The three-phonon scattering events satisfy energy and momentum conservation conditions. The momentum conservation conditions for Class I and Class II events are given in Eqs. (2) and (3). The energy conservation conditions for Class I and Class II events are

$$\omega + \omega' = \omega'' \quad \text{or} \quad vq + v'q' = v''q'' \tag{4}$$

$$\omega = \omega' + \omega'' \quad \text{or} \quad vq = v'q' + v''q''. \tag{5}$$

The possible three-phonon processes are

$$t + t \rightleftharpoons L \tag{6}$$

$$t + L \rightleftharpoons L \tag{7}$$

$$L + L \rightleftharpoons L \tag{8}$$

$$t + t \rightleftharpoons t \tag{9}$$

$$t + L \rightleftharpoons t \tag{10}$$

$$L + L \rightleftharpoons t, \tag{11}$$

where "t" represents transverse and "L" represents longitudinal phonons. Since the longitudinal phonons have the highest phase velocity, the energy and momentum conservation conditions forbid the processes represented in Eqs. (8) to (11) and the only allowed three-phonon processes are given (*8–10*) by Eqs. (6) and (7). In Class I events both longitudinal and transverse phonons can participate, as given by

$$\begin{aligned} t + t &\rightarrow L \\ t + L &\rightarrow L. \end{aligned} \tag{12}$$

In Class II events only longitudinal phonons can take part as given by

$$\begin{aligned} L &\rightarrow t + t \\ L &\rightarrow t + L. \end{aligned} \tag{13}$$

The three-phonon relaxation rates for transverse and longitudinal phonons can be written as

$$(\tau_{3\,\mathrm{ph}}^{-1})_t = B_{tI}\omega T^{m_{tI}(T)} e^{-\theta/\alpha T} \tag{14}$$

and

$$(\tau_{3\,\mathrm{ph}}^{-1})_L = B_{LI}\omega^2 T^{m_{LI}(T)} e^{-\theta/\alpha T} + B_{LII}\omega^2 T^{m_{LII}(T)} e^{-\theta/\alpha T}, \tag{15}$$

where B_{tI}, B_{LI}, and B_{LII} are the three-phonon scattering parameters for transverse Class I events and longitudinal Class I and Class II events, respectively; $m_{tI}(t)$, $m_{LI}(T)$, and $m_{LII}(T)$ are the corresponding m values.

The upper and lower bounds of $m(T)$ for Class I and Class II events can be calculated and the average value of $m(T)$ is $m_{av}(T) = (m_{max} + m_{min})/2$. But $m_{av}(T)$ is not the true value of $m(T)$ in the entire temperature range. The true value of $m(T)$ can be written by phenomenological considerations using the SDV model (*7*) as $T^{m(T)} = T^{m_{av}(T)}(1 + \theta/\alpha T)$. Hence

$$m(T) = m_{av}(T) + \frac{\ln(1 + \theta/\alpha T)}{\ln T}. \tag{16}$$

At high temperatures $T \gg \theta$; $m(T) = m_{av}(T) = 1$, while at low temperatures $T \ll \theta$, $m(T) \neq m_{av}(T)$. Using Eq. (16), true values of $m(T)$ can be ascertained for both longitudinal and transverse branches from the values of $m_{av}(T)$ given by Guthrie (*6*). The average values of $m(T)$ obtained by taking the average of lower and upper bonds for $m(T)$ are given for Class I and Class II even as

$$m_{avI} = x_{max}(e^{x_{max}} - 1)^{-1} + 0.5x_{max}$$

$$m_{avII} = 0.5x_{max}(e^{x_{max}} - 1)^{-1} + 0.5,$$

where

$$x_{max} = \hbar\omega_{max}/k_B T.$$

The true values of $m(T)$ are given as

$$m_{tI}(T) = x_{maxt}(e^{x_{maxt}} - 1)^{-1} + 0.5x_{maxt} + \frac{\ln(1 + \theta/\alpha T)}{\ln T} \tag{17}$$

$$m_{LI}(T) = x_{maxL}(e^{x_{maxL}} - 1)^{-1} + 0.5x_{maxL} + \frac{\ln(1 + \theta/\alpha T)}{\ln T} \tag{18}$$

$$m_{LII} = x_{maxL}e^{0.5x_{maxL}}(e^{x_{maxL}} - 1)^{-1} + 0.5 + \frac{\ln(1 + \theta/\alpha T)}{\ln T}, \tag{19}$$

where $x_{maxL} = \hbar\omega_{maxL}/k_B T$, $x_{maxt} = \hbar\omega_{maxt}/k_B T$, and ω_{maxL} and ω_{maxt} are zone boundary frequencies for longitudinal and transverse phonon branches. Using the values of $m_{tI}(T)$, $m_{LI}(T)$, and $m_{LII}(T)$ in Eqs. (14) and (15), the exact three-phonon relaxation rates for longitudinal and transverse phonon branches can be determined.

Lattice Thermal Conductivity

In the calculation of phonon conductivity, the phonon velocity given by acoustic approximation, $\omega = qV$, is not realistic provided the dispersion effects of different po-

larizations are taken into consideration. The acoustic approximation is modified as

$$q = \frac{\omega}{\mathbf{v}}(1 + \beta\omega^2), \tag{20}$$

where β is the parameter given by

$$\beta = \frac{1}{\omega^2}\left(\frac{qV}{\omega}\right)^{-1}.$$

The value of V_g/V_p^2 becomes

$$(V_g/V_p^2) = \frac{1}{V_p} \cdot \frac{(1 + \beta\omega^2)^2}{(1 + 3\beta\omega^2)}, \tag{21}$$

where V_g is the phonon group velocity ($d\omega/dq$) and V_p is the phase velocity ω/q. Using the value of V_g/V_p^2 in the expressions for thermal conductivity due to longitudinal and transverse phonon branches (*2*), we get

$$K_t = \frac{2k_B}{3.2\pi^2}\left(\frac{k_BT}{\hbar}\right)^3 \left[(V_{tI})_{0<\omega<\omega_1} \int_0^{\theta_1/T} \frac{(1 + \beta_1\omega^2)^2}{(1 + 3\beta_1\omega^2)} \frac{x^4e^x dx}{(\tau_c^{-1})_t(e^x - 1)^2} + (V_{tII})_{\omega_1<\omega<\omega_2} \int_{\theta_1/T}^{\theta_2/T} \frac{(1 + \beta_2\omega^2)^2}{(1 + 3\beta_2\omega^2)} \frac{1x^4e^x dx}{(\tau_c^{-1})_t(e^x - 1)^2}\right] \tag{22}$$

and

$$K_L = \frac{1}{3}\frac{k_B}{2\pi^2}\left(\frac{k_BT}{\hbar}\right)^3 \left[(V_{LI})_{0<\omega<\omega_4} \int_0^{\theta_4/T} \frac{(1 + \beta_3\omega^2)^2}{(1 + 3\beta_3\omega^2)} \frac{1}{(\tau_c^{-1})_L} \frac{x^4e^x dx}{(e^x - 1)^2} + (V_{LII})_{\omega_4<\omega<\omega_3} \int_{\theta_4/T}^{\theta_3/T} \frac{(1 + \beta_4\omega^2)^2}{(1 + 3\beta_4\omega^2)} \frac{1}{(\tau_c^{-1})_L} \frac{x^4e^x dx}{(e^x - 1)^2}\right]. \tag{23}$$

The total phonon thermal conductivity can be expressed as

$$K = K_t + K_L.$$

ω_1 and ω_2 are the phonon frequencies corresponding to the wave vectors ($q_{max}/2$) and q_{max} for transverse phonons, and ω_4 and ω_3 for that of longitudinal phonons. These values are calculated from the phonon velocities in the frequency regions $0 < \omega < \omega_1$ and $\omega_1 < \omega < \omega_2$, respectively, for transverse phonons. V_{LI} and V_{LII} are the velocities for longitudinal phonons in the frequency regions $0 < \omega < \omega_4$ and $\omega_4 < \omega < \omega_3$, respectively. $(\tau_c^{-1})_t$ and $(\tau_c^{-1})_L$, the combined relaxation rates for transverse and longitudinal phonons, are given as

$$(\tau_c^{-1})_t = \tau_B^{-1} + \tau_{pt.}^{-1} + B_{tI}\omega/T^{m_{tI}(T)}e^{-\theta/\alpha T}$$

$$(\tau_c^{-1})_L = \tau_B^{-1} + \tau_{pt.}^{-1} + B_{LI}\omega^2T^{m_{LI}(T)}e^{-\theta/\alpha T} + B_{LII}\omega^2T^{m_{LII}(T)}e^{-\theta/\alpha T}.$$

Here B_{tI}, B_{LI}, and B_{LII} are the three-phonon scattering parameters for transverse Class I events and longitudinal Class I and Class II events, respectively. τ_B^{-1} is the relaxation rate for boundary scattering of phonons and τ_{pt}^{-1} is the relaxation rate for phonon-point defect scattering.

Results and Discussion

It is observed from our calculations that the contribution of transverse phonons dominates over the longitudinal phonon contribution toward lattice thermal conductivity. The ratio of $K_t : K_L$ at low temperatures is approximately 6 : 1. At low temperatures, the boundary scattering of phonons dominates over other scattering processes. Since the longitudinal phonon velocity is considerably higher than the transverse phonon velocity, therefore, the thermal conductivity due to longitudinal phonons K_L is less than the conductivity due to transverse phonons, K_t, as the phonon velocity term appears in the denominator of conductivity expression. Further, as there exist two transverse polarized phonon modes corresponding to each longitudinal phonon mode, the larger thermal conduction is due to transverse phonons rather than to longitudinal ones. This results is also supported by other work (*11*).

The total thermal conductivity, K, is due to the acoustic and optic phonons. However, in silicon, the optic phonons have much smaller group velocities than the acoustic phonons. Since K varies as the square of the group velocity, we totally ig-

TABLE I

AVERAGE, MAXIMUM, AND TRUE VALUES OF $m(T)$ USED IN THE CALCULATION OF THE PHONON THERMAL CONDUCTIVITY OF SILICON

	Longitudinal phonons						Transverse phonons		
	Class I			Class II			Class I		
T (°K)	m_{max}	m_{av}	m_{true}	m_{max}	m_{av}	m_{true}	m_{max}	m_{av}	m_{true}
100	—	—	—	2.00	0.50	1.8	3.50	1.60	3.80
150	4.00	2.20	2.80	2.00	0.55	0.75	1.90	1.35	1.90
200	2.90	2.30	1.80	2.00	0.58	0.75	1.30	1.35	1.80
250	2.50	1.90	1.70	2.00	0.59	0.76	1.20	1.34	1.65
300	1.80	1.30	1.50	2.00	0.60	0.76	1.20	1.30	1.40
400	1.75	1.25	1.45	2.00	0.63	0.77	1.15	1.26	1.38
500	1.60	1.20	1.40	2.00	0.65	0.77	1.15	1.20	1.35
700	1.50	1.10	1.35	2.00	0.68	0.78	1.10	1.15	1.30
900	1.30	1.00	1.20	2.00	0.70	0.78	1.10	1.10	1.25
1000	1.25	1.00	1.10	2.00	0.72	0.78	1.10	1.10	1.20
1200	1.20	1.00	1.00	2.00	0.75	0.78	1.10	1.10	1.20

nore the optic phonons as thermal energy carriers. The optic phonons influence thermal conduction in two ways: (a) they enhance conductivity by transporting heat and (b) they reduce the conductivity by interacting with the acoustic phonons. It was concluded (*12*) that the net effect of optic phonons on lattice conductivity will be negligibly small. Therefore, the acoustic mode will be the dominant mode for heat conduction. The lattice thermal conductivity of silicon has been described by Joshi and Verma (*13*). Singh and Verma (*14*) studied the influence of internal stress in germanium and silicon at low temperatures.

The equations $\tau^{-1} \propto \omega^2 T^3$ and $\tau^{-1} \propto \omega T^4$ are valid at low temperatures for longitudinal and transverse phonons, respectively. At high temperatures it would lead to T dependence but relaxation rates would remain ω^2 and ω dependent for longitudinal and transverse phonons, respectively, in entire temperature regions. This was shown by Herring earlier. Klemens had modified this as $\tau_{3\,ph}^{-1} \propto g(\omega) T^m e^{-\theta/\alpha T}$.

He has taken the temperature exponent, m as 1 and 3 in the low and high temperature regions, respectively. Our main concern is about the temperature exponent m and its temperature dependence. It should be a continuous function of temperature; i.e., $m = m(T)$. In the present work, we have given a method to calculate this exponent m as a function of temperature and, therefore, our equations are the most realistic equations in the entire temperature region for the calculation of three-phonon relaxation rates.

The average, maximum, and true values of $m(T)$ for both longitudinal and transverse phonons for Class I and Class II events, used in performing the present calculations, are displayed in Table I. m_{max} is the maximum value obtained by Guthrie (*6*), m_{av} is the mean value of upper and lower bounds, and m_{true} (T) is the value of the exponent used in our calculations. Table II shows the theoretically computed values of the longitudinal, transverse and the total phonon conductivity and their comparison with the experimental value in the temperature range 5–1200°K. It is observed that the theoretically computed values agree very well with the experimental values. The values of other parameters used in making these calculations are shown in Table III.

TABLE II

THEORETICAL VALUES ($K_{theo} = K_t + K_L$) OF THE PHONON CONDUCTIVITY OF SILICON COMPARED WITH EXPERIMENTAL VALUES (K_{exp}) IN THE TEMPERATURE RANGE 5–1200°K

T (°K)	K_{exp} (W cm^{-1} deg^{-1})	K_t (W cm^{-1} deg^{-1})	K_L (W cm^{-1} deg^{-1})
5	3.2	2.7	0.5
10	12.2	10.2	2.0
20	24.1	17.1	7.0
40	40.2	25.0	12.0
80	19.4	16.2	3.1
100	13.6	12.2	1.3
200	4.1	4.1	—
300	2.2	2.2	—
400	1.8	1.7	—
600	0.7	0.7	—
1000	0.35	0.38	—
1200	0.3	0.3	—

Note. K_t and K_L are the contributions of transverse and longitudinal phonons, respectively.

TABLE III

PARAMETERS USED IN THE CALCULATIONS OF THERMAL CONDUCTIVITY OF Si IN THE TEMPERATURE RANGE 5–1200 K

τ_B^{-1}	$= 1.3 \times 10^6$ sec^{-1}
$(V_{tI})_{0<\omega<\omega_1}$	$= 5.86 \times 10^5$ cm sec^{-1}
$(V_{tII})_{\omega_1<\omega<\omega_2}$	$= 2.0 \times 10^5$ cm sec^{-1}
$(V_{LI})_{0<\omega<\omega_4}$	$= 8.5 \times 10^5$ cm sec^{-1}
$(V_{LII})_{\omega_4<\omega<\omega_3}$	$= 4.0 \times 10^5$ cm sec^{-1}
B_{tI}	$= 1.43 \times 10^{-6}$ deg^{-m}
B_{LI}	$= 3.9 \times 10^{-17}$ deg^{-m} sec
B_{LII}	$= 3.9 \times 10^{-17}$ deg^{-m} sec
A	$= 0.25 \times 10^{-44}$ sec^3
θ_1	$= 180$°K, $\theta_4 = 350$°K
θ_2	$= 210$°K, $\theta_3 = 570$°K

Acknowledgments

We thank the Innovative Science and Technology Office of SDIO for providing the financial support to carry out this work. One of us (P.C.S.) thankfully acknowledges Dr. Anthony K. Hyder, Associate Vice President for Research, Auburn University, Auburn, and Dr. O. C. Williamson, Dean, College of Arts and Sciences, Tuskegee University, for their interest, help, and constant inspiration. This work has been done under NSWC Contract N60921-86-C-A226, Subcontract No. 86-206.

References

1. J. CALLAWAY, *Phys. Rev.* **113,** 1046 (1959).
2. M. G. HOLLAND, *Phys. Rev.* **132,** 2461 (1963).
3. C. HERRING, *Phys. Rev.* **95,** 954 (1954).
4. P. G. KLEMENS, "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 7, p. 1, Academic Press, New York (1958).
5. P. G. KLEMENS, *Proc. Roy. Soc. (London)* **208,** 108 (1951).
6. G. L. GUTHRIE, *Phys. Rev.* **152,** 801 (1966).
7. P. C. SHARMA, K. S. DUBEY, AND G. S. VERMA, *Phys. Rev. B* **4,** 1306 (1971).
8. A. HERPIN, *Ann. Phys.* **7,** 91 (1951).
9. P. G. KLEMENS, "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 7, p. 27, Academic Press, New York (1958).
10. J. M. ZIMAN, "Electrons and Phonons," p. 137, Oxford Univ. Press, London/New York (1960).
11. R. A. H. HAMILTON AND J. E. PARROTT, *Phys. Rev.* **178,** 1284 (1969).
12. R. G. ROSS, P. ANDERSON, AND G. BACKSTROM, *Int. J. Thermophys.* **2,** 289 (1981).
13. Y. P. JOSHI AND G. S. VERMA, *Phys. Rev. B* **1,** 750 (1970).
14. M. SINGH AND G. S. VERMA, *Phys. Rev. B* **18,** 5625 (1979).