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EFFECT OF P DONORS ON THERMAL PHONON SCATTERING IN SI

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Résumé. — Les résultats de mesure, entre 1,5 et 50 K, de la conductivité thermique du silicium dopé au phosphore sont présentés pour des concentrations en dopant variant entre $2.5 \times 10^{14}$ et $1.1 \times 10^{18}$ cm$^{-3}$. Pour les faibles concentrations $n \leq 4 \times 10^{17}$ la conductivité thermique $K(T)$ aux basses températures est analysée sur la base d'une diffusion additionnelle des phonons par des impuretés isolées. Cette diffusion électron-phonon est très faible en comparaison avec celle qui est due aux impuretés du Groupe V dans le germanium et du lithium dans le silicium. Ceci est dû à la valeur élevée de l'intervalle orbite-vallée de l'état fondamental du P dans le Si. Pour les échantillons dont la concentration en impuretés est supérieure à $4 \times 10^{17}$ cm$^{-3}$, la résistance thermique devient plus importante que celle prévue par le modèle simple ci-dessus. Dans cette gamme de concentration, la conductivité thermique a une dépendance en température $T^n$ ($n \approx 2$) pour $T \lesssim 10$ K.

Abstract. — Experimental results are presented for the thermal conductivity of P-doped Si over the concentration range $2.5 \times 10^{14}$ to $1.1 \times 10^{18}$ cm$^{-3}$ in the temperature region 1.5-50 K. In the low concentration range, phonon scattering by isolated P donors is very weak in contrast with that by Group-V donors in Ge and Li donor in Si. This is due to the large valley orbit splitting of the P donor ground state. For samples with donor concentrations higher than $4.7 \times 10^{17}$ cm$^{-3}$, thermal resistance becomes larger than that predicted by a simple theory on the basis of phonon scattering by a single donor center. In this concentration range, thermal conductivity has the temperature dependence $T^n$ ($n \approx 2$) at low temperatures ($T \lesssim 10$ K).

1. Introduction. — It is well known that Group-V donors in Ge give rise to large thermal resistance. The thermal conductivity, $K(T)$, of n-Ge has been investigated experimentally [1-6] and theoretically [7-10] in detail. On the other hand, no detailed investigation of $K(T)$ of n-Si doped with Group-V donors has been carried out as long as we know, though very recently we have studied the phonon scattering in Li-doped Si in detail [11].

In the low impurity concentration region, the strong scattering of thermal phonons and coherent microwave phonons [12, 13] by neutral donors in Ge is arisen from the peculiar structure of the donor ground state, that is, the IS like excited states with a small energy difference [7, 8] [12], [14, 15]. (This energy difference is called the valley-orbit splitting [16].) In Si, the phonon scattering by a single neutral donor center at low temperature might be expected to be weak due to the large valley-orbit splitting [8]. Pomerantz [12] observed no attenuation of microwave by neutral donors in lightly doped Si at $T \lesssim 30$ K.

In this paper, we have investigated the thermal conductivity of P-doped Si over the concentration range $2.5 \times 10^{14}$ to $1.1 \times 10^{18}$ cm$^{-3}$. It is shown that, in the low concentration region, the phonon scattering by P donors is weak and a theory can fairly explain the experimental data of $K(T)$, while in the concentration region higher than $4.7 \times 10^{17}$ cm$^{-3}$, the thermal resistance becomes larger than that predicted by the theory. It is suggested that this stronger scattering of phonons might be due to the ground state modified by the interaction among donors or due to clusters.

2. Experimental. — The thermal conductivity was measured between 1.5 and 50 K using the usual longitudinal steady-state heat flow technique, as has been described elsewhere [17]. Allen Bradley carbon resistors were used as thermometers and attached at two points along the long dimension of the samples. The samples were cut from commercial crystals grown by floating zone technique, in the shape of rectangular parallelepipeds with a cross-
section of about 6 mm$^2$ and a length of 35 mm along \( \langle 111 \rangle \) direction. The uncertainty of the measurements was estimated to be 10\% in the temperature range 1.5–20 K and less than 15\% at higher temperatures. The carrier concentrations were evaluated by means of resistivity measurements at room temperature. The donor concentrations and Casimir's lengths \( (L = 2 \pi^{-1/2} \frac{s^1}{2}) \) of samples are given in table I.

### Table I

<table>
<thead>
<tr>
<th>Samples and Symbols</th>
<th>Number of donors (cm$^{-3}$)</th>
<th>( T = 300 ) K</th>
<th>Casimir's length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2.5 \times 10^{14} )</td>
<td>---</td>
<td>0.301</td>
</tr>
<tr>
<td>2</td>
<td>( 3.7 \times 10^{15} )</td>
<td>---</td>
<td>0.303</td>
</tr>
<tr>
<td>3</td>
<td>( 6.5 \times 10^{15} )</td>
<td>---</td>
<td>0.284</td>
</tr>
<tr>
<td>4</td>
<td>( 7.5 \times 10^{15} )</td>
<td>---</td>
<td>0.277</td>
</tr>
<tr>
<td>5</td>
<td>( 2.5 \times 10^{16} )</td>
<td>---</td>
<td>0.302</td>
</tr>
<tr>
<td>6</td>
<td>( 4.7 \times 10^{17} )</td>
<td>---</td>
<td>0.308</td>
</tr>
<tr>
<td>7</td>
<td>( 1 \times 10^{18} )</td>
<td>---</td>
<td>0.261</td>
</tr>
</tbody>
</table>

The measured thermal conductivity is shown in figure 1.

![Thermal conductivity K of P-doped Si as function of temperature.](https://example.com/figure.png)

3. Analysis and discussion. — In the effective mass approximation [16], the ground state of a shallow donor in Si is 6-fold degenerate, reflecting the six equivalent conduction band minima. This degeneracy of the ground state is partially split into a singlet \((A_1)\), a doublet \((E_2)\) and a triplet \((T_2)\) by the valley-orbit interaction and the central cell correction. The singlet is the lowest state and the triplet is higher by 11.7 meV and the doublet lies above the triplet [18] by 1.35 meV.

Hasegawa calculated the matrix elements of the donor electron-phonon interaction between the \( A_1 \) and \( E \) states and between the \( A_1 \) and \( T_2 \) states [19]. He found that the matrix elements for the latter are zero as long as we consider the intravalley process of the electron-phonon interaction. Thus we need consider only the matrix elements of the donor-phonon interaction among the \( A_1 \) and \( E \) states. Furthermore we have found that, for P donor (also for Sb and As donors), the relaxation rates of phonons by the inelastic scattering and thermally-assisted phonon absorption [15] hardly contribute to the total relaxation rate. As a consequence we need only consider the elastic phonon scattering by P donors.

The relaxation rate for this process is given by [11]

\[
\tau_{e-p}^{-1}(t) = \frac{\omega^4 (\frac{1}{\pi})^2 \frac{E_0}{a^4}}{10 \pi \rho^2 \frac{v_1}{v_1}} f^2 \left( \frac{\omega}{v_1} \right) \times \frac{2}{\Delta^2} \left( \frac{\omega}{\Delta} \right)^2
\]

\[
\times w_1 \left( \frac{\omega}{\Delta} \right)^2 \left( \frac{\omega}{\Delta} \right)^2
\]

\[
\times \left[ 2(N_0 + N_1) + N_1 \left( 1 + \Delta^2 \right) \right], \quad (1)
\]

with

\[
f(q) = \left( 1 + \frac{1}{2} a^* q^2 \right)^{-1}, \quad (2)
\]

\[
\Delta = E_{(0)} - E_{(A)} , \quad (3)
\]

and

\[
w_1 = \frac{1}{4} , \quad w_2 = \frac{1}{10} , \quad w_3 = \frac{1}{2}. \quad (4)
\]

Here \( a^* \) is the effective Bohr radius, \( \rho \) is the density of mass, \( \vec{v_1} \) and \( \vec{v_2} (= \vec{v_3}) \) are the average velocities of sound for the longitudinal and transverse modes, respectively, \( N_0 \) and \( N_1 \) are the number of electrons per unit volume in the \( A_1 \) state and one of the \( E \) states, respectively. \( \Delta \) is the energy difference between the \( A_1 \) and \( E \) states.

In the temperature region of interest \( (T \leq 50 \) K), the value of \( N_1 \) is very small because of the large value of \( \Delta (\approx 152 \) K) and we may put \( N_1 = 0 \). Eq. (1) is then identical to that obtained by Griffin and Carruthers [8].

We shall calculate \( K(T) \) by using the usual semi-phenomenological expression for the lattice thermal conductivity [20]

\[
K(T) = \frac{k^4 T^3}{6 \pi^2 h^2} \sum \frac{1}{v_i} \int_0^{\infty} \frac{X^4 e^X}{(e^X - 1)^2} \tau \, dx , \quad (5)
\]

\[
\tau^{-1} = \tau_{\text{fr}}^{-1} + \tau_{\text{i}}^{-1} + \tau_{\text{N}}^{-1} + \tau_{\text{c}}^{-1} + \tau_{\text{e-p}}^{-1}, \quad (6)
\]
where
\[ \tau_B = \frac{\tau_i}{L}, \quad \tau_1 = A \omega^4, \quad \tau_u = B \omega^2 T^3, \]
\[ \tau_N = 1, \quad \tau_{2-p} = 1, \quad \tau_{2-p}^1, \quad \tau_{2-p}^2 \]
represent the phonon relaxation rate due to boundary scattering, isotopic scattering, Umklapp process and normal process of phonon-phonon interaction, and electron-phonon interaction, respectively. \( \theta_D \) is the Debye temperature and \( L \) the Casimir length.

The values of physical parameters used in the calculation of \( K(T) \) are as follows: \( \rho = 2.33 \text{ g cm}^{-3}; \)
\[ v_1 = 9.33 \times 10^5 \text{ cm s}^{-1}; \]
\[ v_2 = 5.42 \times 10^5 \text{ cm s}^{-1}; \]
\[ A = 1.32 \times 10^{-45} \text{ s}^3; \]
\[ a^* = 17 \text{ Å, } E_a = 10 \text{ eV (ref. [21])} \]
\[ B_1 + B_2 \approx 3.8 \times 10^{-24} \text{ s deg}^3 \text{(ref. [22])}; \]
\[ \theta_D = 658 \text{ K}. \]

Figures 2, 3 and 4 show comparisons of the calculated thermal conductivity with the experimental data for samples 4, 5 and 6, respectively. As can be seen from figures 2 and 3 the theory is in reasonable agreement with the experimental results in the low concentration range where impurities are isolated.

It is noted that since the isotope scattering is strong for phonons with frequency at which the resonant scattering becomes effective, the latter is not important (see Fig. 5).

Figures 2 and 3 show that in samples with donor concentrations lower than 2.7 \( \times \) 10^{17} \text{ cm}^{-3}, the phonon scattering at lower temperatures is very weak in contrast with Group-V donors in Ge. This was also seen from ultrasonic attenuation by neutral donors: Pomerantz [12] observed large attenuation of microwave phonons in lightly doped n-Ge at low temperature, while in P-doped Si no attenuation was found at \( T \approx 30 \text{ K} \). The strong scattering of thermal phonons observed in Li-doped Si is caused by the degenerate lowest state and the small valley-orbit splitting of the ground state [11]. The weak scattering of phonons by P donor (also Sb and As donors) in Si is chiefly due to the large valley-orbit splitting.

In sample 6, phonon scattering is strong even at low temperature and the calculated \( K(T) \) can no longer reproduce the experimental data which exhibit a temperature dependence given approximately by \( K \propto T^{2.2} \) for 1.1 \( \text{ K} \leq T \leq 4 \text{ K} \) and \( K \propto T^2 \) for 4 \( \text{ K} \leq T \leq 12 \text{ K} \). Phonon scattering by electrons in an electronic state different from that of an isolated donor may therefore become effective around this concentration. The existence of an interaction among donors [23] would give rise to a modification of the donor ground state, and therefore one should expect a phonon scattering behaviour different from that of an isolated donor center. Furthermore, if some compensation exists, phonon scattering by homopolar pair or polar pair might be expected. At the present time, it is not clear whether the above-mentioned
scattering mechanisms give the temperature dependence observed experimentally. Thermal conductivity of sample no 7 also shows the temperature dependence $T^2$ for $6 \text{ K} \leq T \leq 12 \text{ K}$. On the other hand it is to be noted that the measured thermal conductivity for samples no 6 and 7 tends to merge for $T \gtrsim 30 \text{ K}$. This is expected to be due to the existence of a certain amount of oxygen [24] in these samples.

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**References**


