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Thermal Conductivity of Silicon from 300 to 1400°K*

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The thermal diffusivity of pure silicon has been measured from 300 to 1400°K. The specific heat of the same material over the same temperature range has been measured by Dennison. The thermal conductivity was obtained from the product of the thermal diffusivity, specific heat, and density. At 1400°K about two-thirds of the thermal conductivity was caused by lattice vibrations and one-third by bipolar diffusion. Wiedemann-Franz type diffusion accounted for less than one percent of the total thermal conductivity at 1400°K. Thermal transport by direct transmission of radiation appeared to be negligible up to 1400°K. The Grüneisen constant for silicon from these high-temperature thermal conductivity measurements was 1.96, if the Debye temperature is taken as 636°K.

INTRODUCTION

KNOWLEDGE of the relative contributions of lattice vibrations, electron diffusion, electron-hole (bipolar) diffusion, and radiation to the thermal conductivity of silicon at high temperatures has been handicapped by the unavailability of experimental data at sufficiently high temperatures. Kuprovsky and Gel'd[1] in 1956 reported four values of the thermal conductivity of silicon between 300 and 1150°K. Morris and Martin[2] and Abeles *et al.*[3] have recently reported more complete data up to 1000°K. At temperatures up to 1000°K, their thermal conductivity measurements indicate that the lattice (phonon) conductivity is completely dominant. At higher temperatures, however, one would expect to find a significantly increasing contribution from electron-hole diffusion. The purpose of this work is to extend the experimental temperature range upward to 1400°K and to discover whether the phonon and electron contributions can account quantitatively for the entire thermal conductivity of silicon up to 1400°K or whether a radiation contribution is also present.

THERMAL DIFFUSIVITY MEASUREMENTS

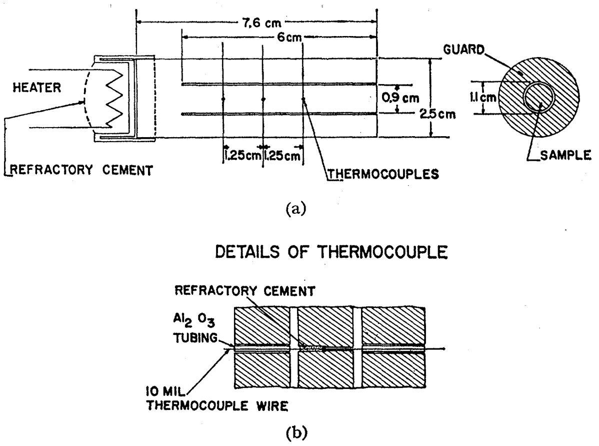
It is difficult to obtain reliable experimental data on the thermal conductivity of any material above 1000°K because of radiation losses and thermocouple problems. As suggested previously by Sidles and Danielson,[4] these difficulties can be minimized if one measures the thermal diffusivity instead of the thermal conductivity directly.

The particular thermal diffusivity method used in this investigation has been described by Kennedy *et al.*[5] The most critical aspect of the experiment was the preparation of the sample. The construction of the sample and the details of the thermocouple mounting are shown in Fig. 1.

The cylindrical sample was constructed from a single crystal of silicon 7.6 cm long and 2.5 cm in diameter. An inner cylinder was cut ultrasonically from one end to a depth of 6 cm. This inner cylinder 6 cm long and 0.9 cm in diameter was the sample; the outer cylinder, which remained joined to the sample at the heater end of the rod, was the guard cylinder. The thickness of the cut (the difference between the radius of the sample and the inner radius of the guard cylinder) was less than 1 mm.

The purpose of this sample construction was to eliminate radiative heat transfer from the sample. The temperatures along the guard shield and along the sample were extremely closely matched because (1) the heater was placed a relatively large distance of 1.6 cm from the end of the sample, (2) the guard and sample were both part of the same crystal of silicon, and (3) the heat capacity of the guard cylinder was large compared to the heat capacity of the sample.

Devyatkova *et al.*[6] have shown that it is possible to



(a)

(b)

FIG. 1. Sample construction for thermal diffusivity measurements.

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TABLE I. Resistivity and orientation of silicon samples.

Sample number	Type	Resistivity at 300°K (Ω-cm)	Orientation
1F	*n*	33	111
3C	*n*	1010	100
4A	*p*	107	111

have heat flux in the annular region between the sample and the guard even when the temperatures of the sample and guard are perfectly matched. They calculate the longitudinal flux of radiation energy between a sample and a mirror. The equivalent thermal conductivity of the gap varies directly as the thickness of the gap and as the cube of the absolute temperature. In our experiment, this effect on our measurements was less than one percent at 1400°K owing to the very small separation (less than 1 mm) between the sample and the guard cylinder.

An equally important problem was the mounting of the three thermocouples which were located 1.25 cm apart. As shown in Fig. 1, the thermocouple head was pulled against a shoulder in the center of the sample and cemented in place with refractory cement. Good electrical contact was confirmed by measurement of the electrical resistance between thermocouples. The small heat capacities of the thermocouples resulted in sufficiently short response times.

A problem peculiar to these measurements was the chemical reaction of standard thermocouple materials with silicon at high temperatures. Tungsten and niobium, however, were found to be sufficiently inert up to 1400°K. The sensitivity of the tungsten-niobium thermocouples at elevated temperatures was about the same as that of platinum-platinum rhodium thermocouples, although the sensitivity at room temperature was considerably lower. An advantage of measuring thermal diffusivity rather than thermal conductivity is the absence of any need to calibrate the thermocouples to read temperature. Only the slopes of the curves of thermocouple emf vs temperature are required to be the same for the different thermocouples. A separate chromel-alumel thermocouple was used to measure the ambient furnace temperature.

After the sample had been placed in a vacuum furnace, the heater was turned on and the temperature change (maximum of 2°K) at each thermocouple was recorded as a function of time. The temperatures at the first and third thermocouples determined the empirical boundary conditions for the heat-flow equation. For various values of the thermal diffusivity, this equation could then be solved with a high-speed computer to give the temperature as a function of time at the middle thermocouple. The computer compared these solutions with the experimental readings of the middle thermocouple in order to obtain the best value of the thermal diffusivity at the ambient temperature of the furnace.

Measurements were made on three single crystals of silicon. The type, resistivity, and orientation are given in Table I.

The thermal diffusivity of silicon from 300 to 1400°K is shown in Fig. 2. The decrease in thermal diffusivity from 300 to 1400°K is caused by phonon-phonon scattering.

THERMAL CONDUCTIVITY RESULTS

The thermal conductivity, K, was obtained from the thermal diffusivity, k, by the relation $K=kcd$ where c is the specific heat and d is the density. For the specific

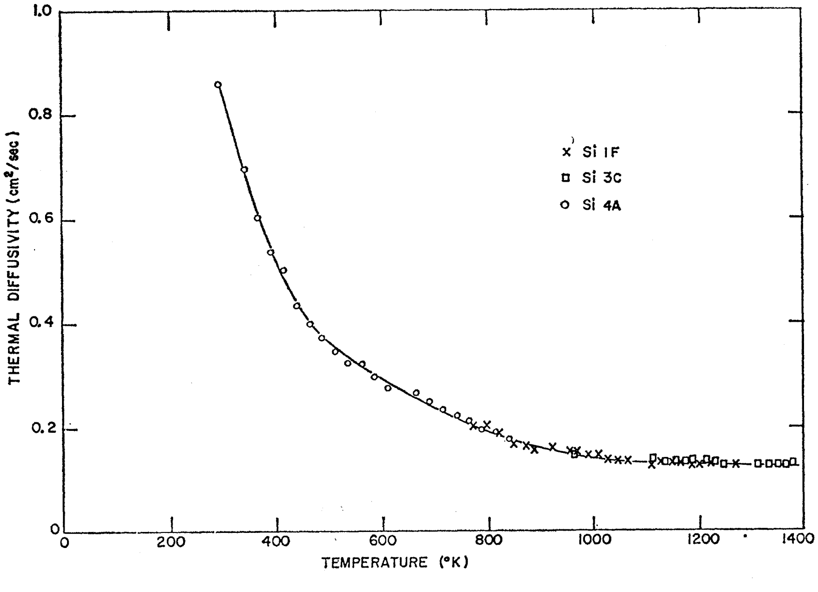

FIG. 2. Thermal diffusivity of silicon from 300 to 1400°K.

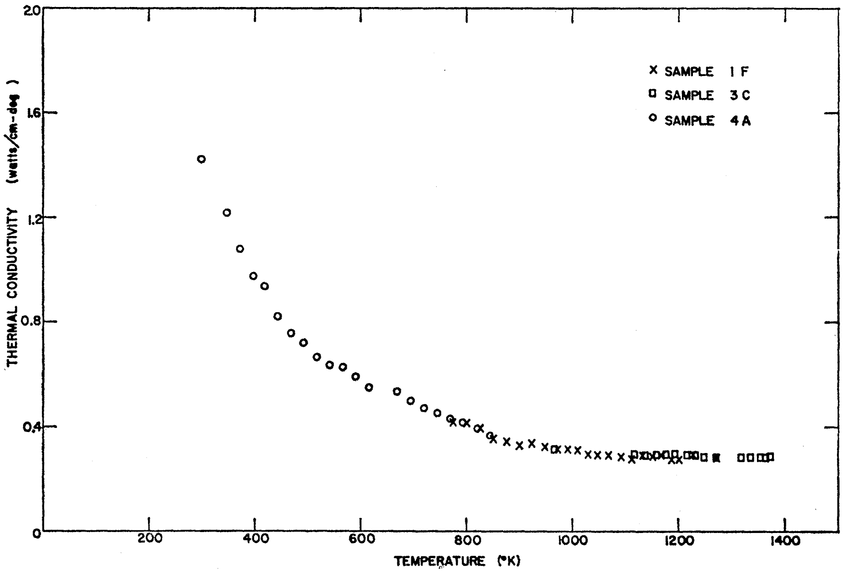

FIG. 3. Thermal conductivity of silicon from 300 to 1400°K.

heat we used the recent measurements by Dennison,[7] who used a high-temperature Bunsen type calorimeter. His results, as given in Table II, were taken on our sample 4A and are estimated to be accurate to within 0.5%.

For the density we used the value determined by Smakula and Sils,[8] $d=2.32902\pm3\times10^{-5}$ g/cm^3, for single-crystal silicon at 25°C. The expansion with temperature was almost a negligible correction of about 1% maximum. Nevertheless, the density was corrected for the temperature coefficient of expansion as given by the x-ray diffraction data of Mauer and Bolz.[9]

The thermal conductivity of silicon from 300 to 1400°K is shown in Fig. 3. The values at 100-deg intervals are tabulated in Table III.

The thermal resistivity, reciprocal of the thermal conductivity, from 300 to 1400°K is shown in Fig. 4 along with the results by Morris and Martin,[2] Morris and Hust,[10] Stuckes,[11] Kuprovsky and Gel'd,[1] and Abeles *et al.*[3] Up to 1000°K our results are in good agreement with the recent results of Morris and Martin[2] and Abeles *et al.*[3] Above 1000°K, however, our results show that the thermal resistivity of silicon does not continue to increase at the rapid rate observed below 1000°K. On the contrary, the thermal resistivity levels off to an almost constant value.

ELECTRON THERMAL CONDUCTIVITY

From Fig. 4, the very slow increase in thermal resistance above 1000°K indicates that the entire thermal conductivity above 1000°K cannot be caused by lattice vibrations alone. We shall assume that the total thermal conductivity, K, can be represented as the sum of an electronic term, K_e, a lattice or phonon term, K_g, and a radiation or photon term, K_r.

$$K=K_e+K_g+K_r. \tag{1}$$

The electronic conductivity is given by Joffe[12] and

TABLE II. Specific heat of silicon.[a]

Temperature (°K)	Specific heat (cal/g-°K)	Temperature (°K)	Specific heat (cal/g-°K)
273	0.1650	873	0.2145
373	0.1840	973	0.2180
473	0.1970	1073	0.2215
573	0.2025	1173	0.2250
673	0.2065	1273	0.2290
773	0.2105	1373	0.2345

[a] See reference 7.

TABLE III. Thermal conductivity of silicon.

Temperature (°K)	Thermal conductivity (W/cm-°K)	Temperature (°K)	Thermal conductivity (W/cm-°K)
300	1.422	900	0.337
400	0.974	1000	0.298
500	0.692	1100	0.290
600	0.577	1200	0.289
700	0.483	1300	0.288
800	0.400	1400	0.287

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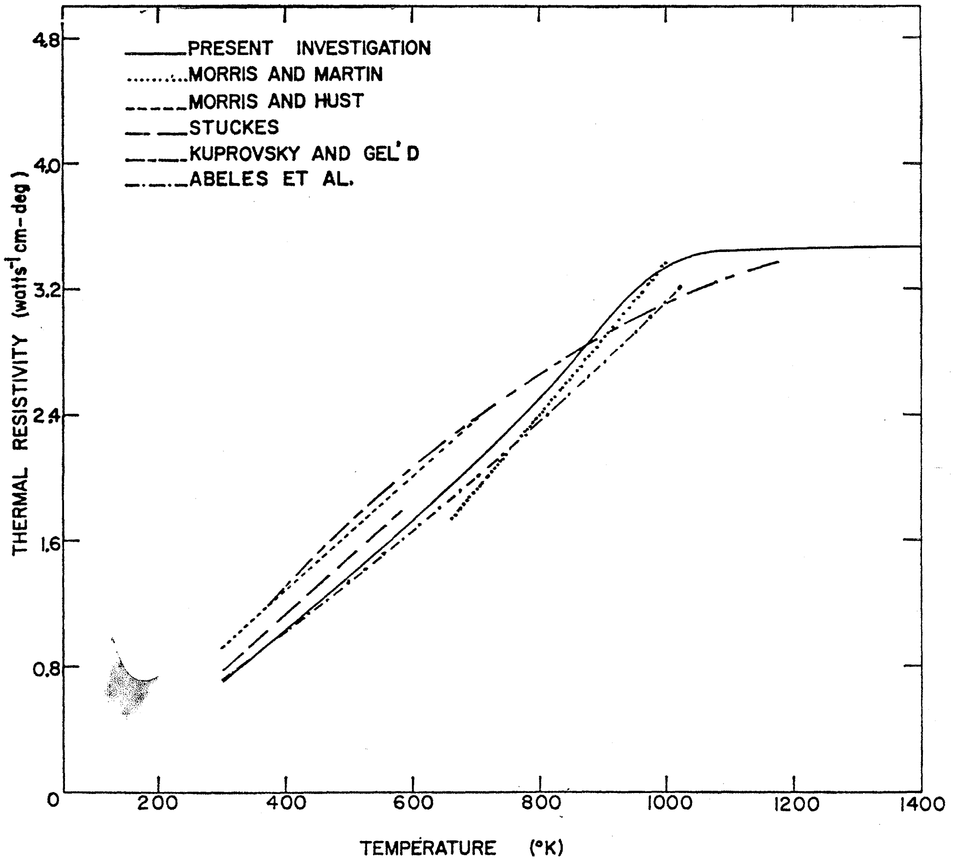

FIG. 4. Thermal resistivity of silicon. The present investigation shows that the thermal resistivity of silicon is almost constant from 1000 to 1400°K.

can be evaluated from the known electrical properties of silicon.

$$K_e=2(k/e)^2T\{\sigma+(2\sigma_n\sigma_p/\sigma)[(\Delta E/2kT)+2]^2\},\quad (2)$$

where k is Boltzmann's constant, e is the charge on an electron, T is the absolute temperature, ΔE is the energy gap, and σ, σ_n, σ_p are the total, intrinsic electron, and intrinsic hole electrical conductivities, respectively.

The first term of Eq. (2) expresses the Wiedemann-Franz law which gives the unipolar contribution to the thermal conductivity owing to transport of kinetic energy by diffusion of charge carriers. The magnitude of this contribution depends upon the number of charge carriers which can be obtained from our resistivities and the known carrier mobilities of pure silicon. The resistivities of our samples up to 1000°K are shown in Fig. 5 and the resistivities may be extrapolated with confidence up to 1400°K. The Wiedemann-Franz contribution was found to be completely negligible up to 1000°K and only 1% of the total thermal conductivity at 1400°K.

TABLE IV. Electronic contribution to thermal conductivity.

Temperature (°K)	Electronic thermal conductivity (W/cm-°K)
600	0.0000
700	0.0017
800	0.0060
900	0.0134
1000	0.0241
1100	0.0385
1200	0.0540
1300	0.0702
1400	0.0866

The second term in Eq. (2) represents the bipolar contribution to the thermal conductivity owing to the formation and annihilation of electron hole pairs as they diffuse down the temperature gradient. We shall not attempt to distinguish between complete separation of the electron-hole pairs (bipolar diffusion) and incomplete separation (exciton diffusion). It should be pointed out that all the excitons are probably ionized at temperatures above 1000°K, since the exciton binding energy in silicon is very small. Excitons should, therefore, have no appreciable effect on the thermal conductivity of silicon at high temperatures. This bipolar diffusion is clearly a very efficient mechanism for the transport of heat, and may contribute significantly for a relatively small number of electron-hole pairs. Calculations showed that for pure silicon the effect would be barely noticeable at 1000°K, but might represent nearly one-third of the total thermal conductivity at 1400°K.

The bipolar contribution was calculated from data given by Morin and Maita.[13] The product $\sigma_p\sigma_n = (pe\mu_p) \times (ne\mu_n)$ can be obtained from their values for p, n, μ_p, and μ_n. The total conductivity, σ, was measured up to 1000°K, as shown in Fig. 5, and extrapolated to 1400°K. The values for the energy gap were obtained from the equation given by Morin and Maita,[13] $\Delta E = (1.21 - 3.6 \times 10^{-4}T)$ eV. The total electronic contribution to the thermal conductivity as given by Eq. (2) is shown in Table IV.

PHONON THERMAL CONDUCTIVITY

According to Leibfried and Schlömann,[14] with only Umklapp processes taken into account, the lattice conductivity at high temperatures is

$$K_g = [3(4)^{1/3}k^3 A\delta/10\pi^3\hbar^3 N](\theta^3/\gamma^2)(1/T), \qquad (3)$$

where A is the gram-atomic weight, N is Avogadro's number, δ^3 is the volume per atom, θ is the Debye temperature, and γ is the Grüneisen constant.

We note that the lattice thermal resistivity, $1/K_g$, varies directly as the temperature. The radiation thermal resistance, $1/K_r$, on the other hand, varies as T^{-3} according to Genzel.[15] If we subtract the values in Table IV from the values in Table III, we obtain values for $K_g + K_r$. The reciprocal of these values is plotted in Fig. 6. At temperatures well above the Debye temperature (about 636°K) the thermal resistivity $1/(K_g+K_r)$ varies linearly with temperature. There is no evidence of a T^{-3} dependence, as would be expected if K_r were appreciable. We conclude from Fig. 6 that the thermal conductivity due to radiation, K_r, is negligible in comparison with K_g up to 1400°K.

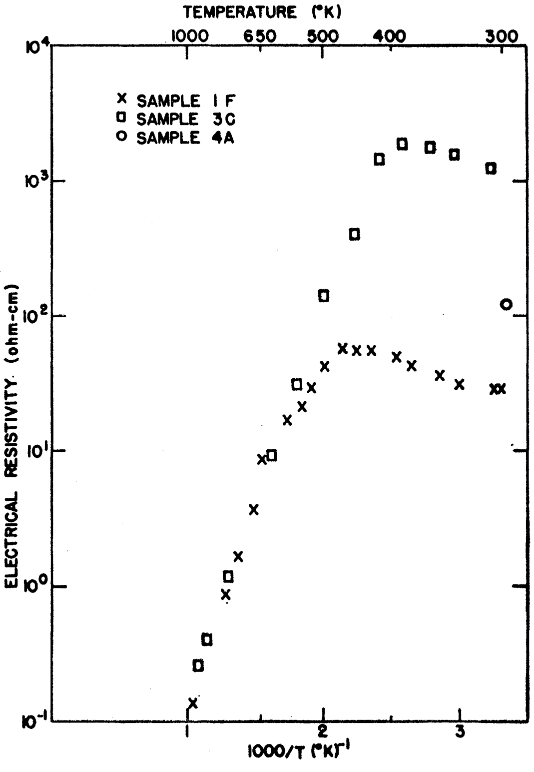

FIG. 5. Electrical resistivity of the silicon samples used for thermal diffusivity measurements.

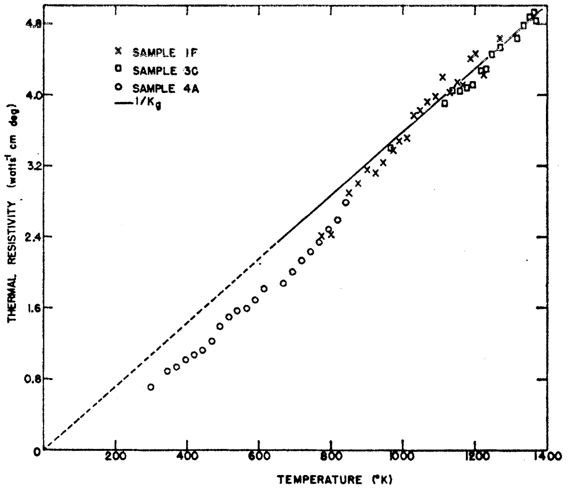

FIG. 6. Residual thermal resistivity of silicon after the electronic contribution to the thermal conductivity has been subtracted from the total thermal conductivity. The linear dependence on temperature well above the Debye temperature (636°K) indicates that thermal conductivity by radiation was negligible compared to thermal conductivity by lattice vibrations, K_g.

In Fig. 6 the solid line represents the best least-squares fit to the data above 1000°K. The line passes through the origin, since imperfection scattering is negligible in comparison to phonon-phonon scattering. From the slope of this line and Eq. (3), we can evaluate the quantity θ^3/γ^2. We obtained a value of $\theta^3/\gamma^2 = 6.69 \times 10^7$ $(°\mathrm{K})^3$. If we take for the Debye temperature the value given by Keesom and Seidel,[16] $\theta = 636$°K, we obtain a Grüneisen constant $\gamma = 1.96$.

The value $\gamma = 1.96$ is about three times as large as one obtains from data at 300°K on the atomic volume V, compressibility χ, specific heat at constant volume c_v, and coefficient of volume expansion β. $\gamma' = (V/\chi)/(c_v/\beta)$. There is good reason to believe, however, that γ and γ' are not equal. This point has been emphasized by Barron[17] and by White and Woods.[18] Morris and Martin[2] assumed for their investigation a value of $\gamma = 2.0$; Abeles *et al.*[3] obtained a value of $\gamma = 1.90$ from their thermal conductivity measurements.

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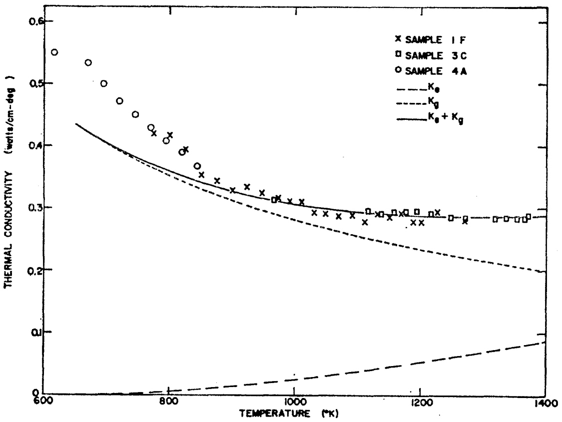

FIG. 7. Thermal conductivity of silicon from 600 to 1400°K. The total thermal conductivity well above the Debye temperature (636°K) is the sum of the electronic contribution (bipolar diffusion) K_e and the lattice contribution K_g.

The total thermal conductivity of silicon from 600 to 1400°K is shown in Fig. 7. The electronic and lattice contributions are also shown. Although small at 1000°K, the electronic contribution is nearly half the lattice contribution at 1400°K and would presumably equal the lattice contribution at about 1650°K.

PHOTON THERMAL CONDUCTIVITY

It is not surprising that the contribution to the thermal conductivity by radiation is negligible in comparison to the contribution by lattice vibrations. The photon contribution for germanium has been calculated by Slack and Glassbrenner.[19] The photon contribution for silicon is probably not very different from that in germanium. The number of charge carriers is less for silicon, which would make the infrared absorption by free carriers smaller, but this reduction is largely offset by the larger cross section for absorption by silicon, the smaller emissivity and smaller dielectric constant.

Slack and Glassbrenner[19] give for germanium an approximate photon contribution $K_r=3.5\times10^{-3}$ W/cm-°K at 600°K, which is only 0.6% of the lattice contribution K_g for silicon. At 1000°K, they give $K_r=0.8\times10^{-3}$ W/cm-°K, which is only 0.3% of K_g for silicon. At higher temperatures, the percentage contribution of K_r is even smaller since K_r varies inversely as the number of free carriers which increases exponentially with temperature.

CONCLUSION

Up to 1000°K the thermal conductivity of pure silicon is almost entirely due to transmission of lattice vibrations. From 1000 to 1400°K the contribution by electron-hole pairs increases significantly and is about one-third the total thermal conductivity at 1400°K. The contribution of kinetic energy transfer by the charge carriers according to the Wiedemann-Franz law is completely negligible at 1000°K and less than 1% of the total thermal conductivity at 1400°K. The contribution by direct transmission of radiation is negligible (less than 1%) for pure silicon up to 1400°K and is probably negligible at all temperatures up to the melting temperature.

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