Thermal Conductivity Measurements of Silicon from 30° to 425°C*†

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Measurements on single-crystal silicon show that the thermal conductivity varies nearly as T^{-1}, from 1.26±0.19 w/cm C° at 30°C, to 0.46±0.07 w/cm C° at 425°C. The series comparative method employed reduces errors due to radiation, thermocouple calibration, and contacts. The charged-carrier contribution to the conductivity is less than 1% at 425°C. The lattice conductivity is discussed in terms of phonon-phonon scattering at 425°C and in terms of isotope and phonon-phonon scattering at 30°C.

INTRODUCTION

THERMAL conductivity measurements in silicon and germanium[1] below room temperature have been reported. Recently values above room temperature have been given by Abeles,[2] Kettel,[3] Stuckes,[4] and Slack and Glassbrenner[5] for germanium, and by Stuckes[4] to 300°C for silicon. The present paper reports results of thermal conductivity measurements from 30°C to 425°C for single-crystal silicon[6] and discusses the findings.

MEASUREMENTS

Five measurement runs were made on two different samples of single-crystal p-type silicon (acceptor concentrations $\approx 6\times10^{14}$ and 3×10^{15} cm^{-3}). The crystals were supplied through the courtesy of F. J. Reid, Battelle Memorial Institute, Columbus, Ohio. The measurements extended from 30° to 425°C and utilized a series comparative method and analysis developed by Morris and Steigmeier.[7] This method, based in part on earlier work by Stuckes and Chasmar[8] and by others,[9] provides nearly the same heat flow Q through both a sample of unknown conductivity K_u and a standard of known conductivity K_s placed in series as shown in Fig. 1. Then we have ideally for Q, when the temperature in the specimens is independent of the time,

$$Q=K_uA_u(\Delta T/\Delta X)_u=K_sA_s(\Delta T/\Delta X)_s, \quad (1)$$

where A is the cross section and ΔT is the temperature difference between two planar isothermal surfaces separated by distance ΔX. In practice it is difficult to determine the heat flow Q *through* the sample in terms of heat delivered to some source at one end of the sample, in order to solve the left-hand side of Eq. (1) for K_u. This is especially true at high temperatures and for low-conductivity samples, where radiated heat may be large in comparison with conducted heat. The comparative method does not require knowledge of Q and so eliminates this experimental difficulty. Morris[10] has discussed errors inherent in absolute and comparative methods of different geometries.

For the experiment the sample was mounted between two standard materials as shown in Fig. 1. The second standard is used as a check. Sample and standards were

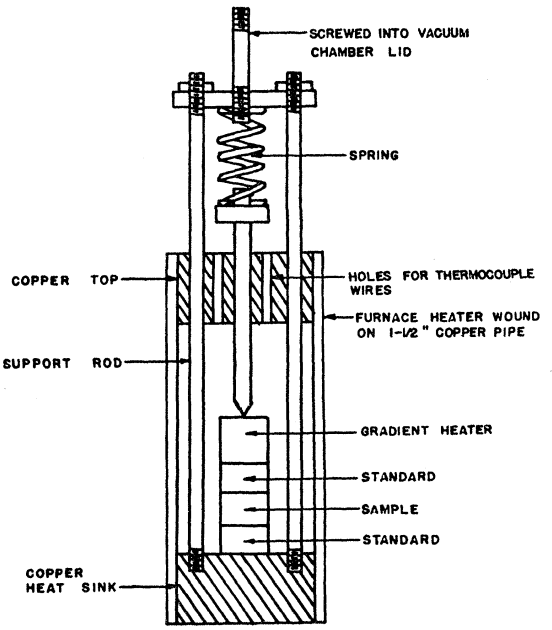

FIG. 1. Sample holder for thermal conductivity measurements (1½ in. diam×4 in. long). Lava radiation shield around "sandwich" not shown.

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about 12 mm in diameter and 7 mm thick. Armco iron (99.9+% Fe) was used for both standards, and values of the thermal conductivity were taken from Armstrong and Dauphinee[11] and from Powell.[12] The copper sample holder was operated in a vacuum chamber under pressures less than 10^{-5} mm Hg to reduce convection and conduction losses.

The temperatures were measured with 36-gauge butt-welded chromel-*p*-alumel thermocouples fastened to the sample and standards with Insalute (Sauereisen) cement thinned with water. This gave a strong bond, and the thermocouples were in thermal and electrical contact with the specimens. The thermocouple leads were clamped in a Lava[13] (fired talc) heat sink on the sample holder support rods to reduce conduction along the leads from the specimens. The thermocouples were led without a break from the specimens to the reference junction. They were fed out of the vacuum chamber through slits cut in the undrilled neoprene sealants of Conax[14] thermocouple glands mounted in the chamber lid. They terminated in tubes of mercury placed in holes drilled around the rim of a four-inch copper cylinder kept in a covered Dewar flask. The flask was about half-full of water and the water temperature was measured with a mercury thermometer. A circuit containing low-thermal-emf Leeds and Northrup[15] type 31-3 switches provided for selection and combination of thermocouples.

A modified back-to-back thermocouple connection was used to measure the small temperature differences ($\Delta T < 0.75$C°) across sample and standards. Separate temperature measurements taken at slightly different times and then subtracted may give an erroneous result if some drift is present. The ambient heater was regulated and maximum sample temperature drift was 0.05C°/min. A simple back-to-back connection of the thermocouples will not give a difference emf corresponding to ΔT because of shorting through the sample. A circuit due to Dauphinee[16] was utilized in measuring these difference emf's. This is shown in Fig. 2. Dauphinee's original circuit utilized motor-driven switches; we used Stevens-Arnold[17] BA-12-12-50 50-cps *dpdt* choppers, break-before-make type. The chopper alternately connects a 40-μf Mylar-dielectric capacitor to one thermocouple, and then switches the capacitor across the second thermocouple in series with a Leeds and Northrup K3 potentiometer. When the potentiometer is balanced it reads the difference emf although the thermocouples are never directly connected together. Two choppers 180° out of phase were used to double the sensitivity.

A Lava radiation shield composed of three segments, one for each part of the standard-sample-standard sandwich, surrounded the sandwich almost completely. A copper bridge was placed across the top of the shield and between the top standard and the gradient heater so that the temperature distribution along the shield was similar to that along the sandwich. During the last run the temperature at the midpoint of the radiation shield was monitored and it was found that the temperature was usually near the temperature of the midpoint of the sandwich and was at all times between the highest and lowest temperatures along the sandwich.

Equation (1) is based on the assumption that isothermal surfaces are planes perpendicular to the direction of heat flow; radiation losses will be minimized if the temperature of the sandwich overall is not much different from the temperature of the surroundings. Both these conditions require that thermal contacts between sample, standards, heater, and sink be homogeneous and of low contact resistance. Even high-pressure contacts between polished surfaces are poorly conducting[18]; and these pressure contacts conduct even less in a vacuum. This indicates that most of the conduction is through the air between the surfaces. For making measurements in a vacuum it is thus advisable to bridge the contact with some material which intimately bonds to each surface. The best junction material of many tried was powdered graphite in sodium silicate solution. Plated or soldered contacts were not used on the samples so as to eliminate any possibility of diffusion into the semiconductor. When the apparatus failed at elevated temperatures it was usually due to deterioration of the contacts.

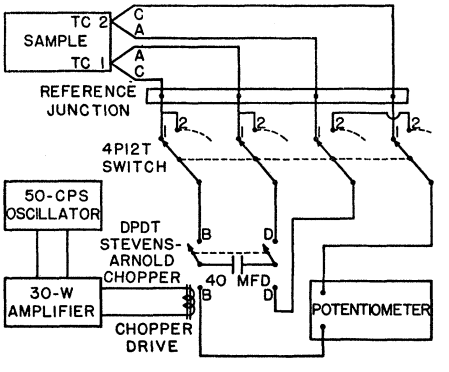

FIG. 2. Schematic design of comparator circuit. When 4-pole switch is in position shown, circuit measures difference emf between thermocouples TC1 and TC2 without connecting them together. Two break-before-make *dpdt* choppers 180° out of phase are used to double the sensitivity. When 4-pole switch is in position 2, circuit measures emf of thermocouple TC1 alone. For this measurement, points $B-B$ and $D-D$ may be shorted with another switch but it is not necessary.

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RESULTS

When ΔT_u is plotted vs ΔT_s for different values of gradient heater input at the same ambient temperature a straight line usually results, as would be expected from Eq. (1). But this line does not pass through the origin. Thus a heat flow appears to exist in one specimen under conditions of no heat flow in another. This behavior could be due to heat losses, small differences in thermocouples, or reference junction temperature drift. The fact that the plot is linear, however, means that Eq. (1) need be modified only by the addition of an error term Q_0 constant at a given ambient:

$$K_u A_u(\Delta T/\Delta X)_u = K_s A_s(\Delta T/\Delta X)_s + Q_0. \quad (2)$$

The slope of the plot of ΔT_u vs ΔT_s contains the unknown conductivity K_u along with known factors: Slope$=(K_s A_s \Delta X_u)/(K_u A_u \Delta X_s)$. A_u and A_s are made equal. An experimental plot for silicon is shown in Fig. 3. ΔV_{34} is the measured difference emf between the sample thermocouples, and ΔV_{12} and ΔV_{56} are the difference emf's of the thermocouples on the lower and upper standards, respectively. Each ΔT is given by the corresponding ΔV divided by the thermoelectric power of the thermocouple. The values of thermal conductivity obtained from the slopes of the two curves are averaged. Each value of thermal conductivity was computed from the slopes of curves like those shown in Fig. 3. The resulting values for five runs on two samples are shown in Fig. 4. The excellent agreement with the measurements of Stuckes[4] to 300°C is shown; also given in Fig. 4 are some of the low-temperature results of Carruthers *et al.*[1] Our value at 30°C differs from that of Carruthers *et al.*, by 0.19 w/cm C°, a value just equal to our maximum experimental error.

Because the heat radiated by a body of temperature T°K varies at T^4, radiation error has plagued measurements of thermal conductivity, especially in poorer conductors. The approximate ratio of radiated to conducted heat may be computed,[8,10] and the ratio decreases, the shorter a sample is with respect to its diameter. The ratio varies in proportion with the sample temperature gradient, and with the average difference in temperature between the sandwich and the radiation shield. We used samples 7 mm thick and 12 mm in diameter and small temperature differences across the specimens (<0.75C°). A radiation shield was used and low-resistance homogeneous contacts reduced the average temperature difference between the sandwich and the shield. The temperature of the shield was monitored. The result for this computed error due to radiation for our experiment was about 1% at 425°C.

Uncertainties in the reported values for the conductivity in the Armco iron standards is 2%. Error due to differences between thermocouples is less than 1%. This small error is due to our method of obtaining K_u from the slope of curves such as those in Fig. 3. This method depends only on small increases in thermocouple voltage and not on any voltage magnitude. This means two thermocouples may be considered identical if their voltage-vs-temperature characteristics have identical slopes, a far less stringent condition than that the characteristics coincide. The error in ambient temperature determination is less than 2%. Greatest error is in determination of the thermocouple separation and this is judged to be within 10%. This error of 10% is nearly constant for any one run, however, changing only about 0.1% due to thermal expansion. We shall attempt to reduce this maximum 10% uncertainty in future work.

The total calculated maximum error for the experiment is $\leqslant 15\%$, but the relative error for any run is $\leqslant 5\%$. The experimental difference between conductivity values at the same temperature on different runs appears less than 10%. The data from all five runs on both samples merged. This seems to show good reproducibility and to indicate that for these two samples, differing in impurity concentration by a factor of five, the thermal conductivity does not vary with impurity content.

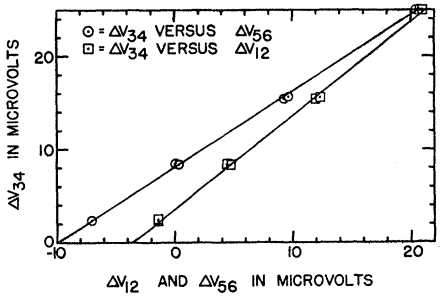

FIG. 3. Typical plot of thermocouple difference emf for sample (ΔV_{34}) *vs* difference emf's for lower and upper standards (ΔV_{12} and ΔV_{56}). Sample thermal conductivity is obtained from the two slopes. Negative values of ΔV_{12} and ΔV_{56} often occur for high ambient temperatures and low gradient-heater inputs. Ambient temperature here is 195°C.

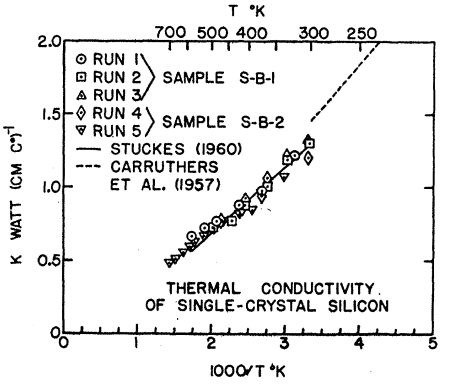

FIG. 4. Results of five measurement runs for the thermal conductivity of silicon. Results of other workers are shown for comparison.

DISCUSSION

Charged-Carrier Contribution

It is customary to consider the thermal conductivity K as being composed of two parts:

$$K=K_e+K_g. \tag{3}$$

K_e is the contribution of charged carriers and K_g is the contribution of the lattice vibrations. Writing Eq. (3) implies K_g and K_e are essentially independent. K_e depends on the number of carriers present, which is in turn proportional to $\exp(-\Delta E/2kT)$, where ΔE is the energy gap, k Boltzmann's constant, and T the absolute temperature. Thus any dominant contribution made to K by K_e will be seen as a turning up of the conductivity curve at higher temperatures. This turning up is not observed in Fig. 4.

A calculation of K_e was based on an equation of Price[19] which includes kinetic energy transport and bipolar diffusion (transport of electron-hole pair formation energy):

$$K_e=2\left(\frac{k}{e}\right)^2\sigma T\left[1+\frac{\sigma_n\sigma_p}{2\sigma^2}\left(\frac{\Delta E}{kT}+4\right)^2\right]. \tag{4}$$

e is the electronic charge, σ the total conductivity, σ_n and σ_p the electron and hole conductivities, $ne\mu_n$ and $pe\mu_p$, respectively. n and p are the electron and hole concentrations, μ_n and μ_p the electron and hole mobilities.

Equation (4) is derived under the assumptions the carriers obey Maxwell statistics and that the scattering of the carriers is by lattice acoustic modes. We obtain intrinsic values of n, p, μ_n and μ_p at 698°K from the work of Morin and Maita,[20] which we may use since our samples are so pure as to be intrinsic at that temperature. The result is $K_e=5.3\times10^{-4}$ w/cm C°, or only about 0.1% of the experimental value of K. Thus K_e plays no essential role in conductivity to 425°C.

Lattice Contribution, $T>\theta$

The discussion of K_g may be taken up at temperatures above and below the Debye temperature θ, which is given by different observers for silicon as 658°,[21] 636°,[22] and 645°K[23] from specific heat measurements. Our measurements extend to 698°K, just above the Debye temperature. At temperatures above θ, phonon transport of energy is limited by scattering with other phonons, giving rise to a conductivity treated by Leibfried and Schlömann[24]:

$$K_g=\frac{3(4)^{\frac{1}{2}}}{10\pi^3}\frac{k^3}{\hbar^3N}\frac{A\delta\theta^2}{\gamma^2}\frac{\theta}{T}. \tag{5}$$

In Eq. (5), A is the gram-atomic weight, N is Avogadro's number, δ^3 is the volume per atom, γ is the Grüneisen constant and $\hbar$ is Planck's constant divided by 2π. With an average $\theta=646$°K and $\gamma=2$, we obtain at 425°C

$$K_g=0.42 \text{ w/cm C°}.$$

The experimental value is 0.46 ± 0.07 w/cm C°.

It is customary to use $\gamma=2$ if no better value is known. Calculations of γ for silicon, germanium, and indium antimonide lead to values less than 2 (White and Woods[1]; Gibbons[25]). Busch and Steigmeier[26] find close agreement between the experimental value of K_g in InSb at 400°K and that predicted by Eq. (5) using $\gamma=2.0$. Our own calculations for silicon, with $\gamma=2$, give $K_g=0.42$ w/cm C°, compared with the experimental value of 0.46 ± 0.07 w/cm C°. It seems possible that the Leibfried-Schlömann result could have a wrong numerical factor which is corrected by the use of a too-large value of γ. However, Toxen[27] also had to use a Grüneisen constant of 1.42 for germanium, considerably larger than the calculated value,[25] to fit experimental data on Ge-Si alloys to a different theoretical model (that of Berman *et al.*,[28] for low-temperature conductivity).

Point-imperfection scattering of phonons above the Debye temperature would lead to a temperature-independent contribution to the limitation of K,[29] and must therefore be fairly small since our observed conductivity goes nearly as T^{-1}.

Although our measurements extend only a little way above the Debye temperature, both the observed temperature dependence of the conductivity and its value at $T=698$°K are consistent with the theory of Leibfried and Schlömann. We admit, of course, an uncertainty in the value of the Grüneisen γ and the possibility of a small temperature-independent contribution due to point imperfections. But phonon-phonon scattering is indicated as the dominant mechanism limiting thermal conductivity just above the Debye temperature.

Lattice Contribution, $T<\theta$

For $T<\theta$, if phonon-phonon scattering alone continued to limit the conductivity it would give rise to

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$K_g \propto \exp(\theta/\beta T)$,[30] where β is of the order of unity. Phonon scattering by point imperfections would lead to $K_g \propto T^{-1}$.[31] Our results (Fig. 4) indicate K is nearly proportional to T^{-1} over the entire range studied (303°K–698°K). This leads us to investigate point imperfections present in the samples.

Common point imperfections are substitutional or interstitial foreign atoms (chemical impurities) and isotopes. The expression for K_g limited by these imperfections and with no other scattering present is given by Klemens[31]:

$$K_g = \frac{hv^2(0.90)}{3(2\pi)^2 a^3} \frac{G}{S^2} \frac{1}{T}, \tag{7}$$

where a^3 is the atomic volume, S^2 a parameter of order unity, v the average phonon velocity, and G the number of atoms in a volume containing one point imperfection. We use the relationship[32] between the phonon velocity v, the Debye temperature θ, and the number of atoms per unit volume N to find $v = k\theta/(6\pi^2 N)^{\frac{1}{3}}\hbar = 5.9\times10^5$ cm/sec. If we substitute our acceptor impurity concentration of 3×10^{15} cm^{-3} for Klemens's $(a^3G)^{-1}$ and take $S^2 \approx 1$, we estimate that the ionized impurities limit the thermal conductivity only to a value about 5×10^3 w/cm C°, far greater than the observed value.

Berman *et al.*[33] and others have pointed out the possibility that phonons may be effectively scattered because not all lattice points in silicon are occupied by atoms of the same mass. Normal silicon consists of 92.27% Si^{28}, 4.68% Si^{29}, and 3.05% Si^{30}.[30,33] This is termed isotope scattering.

Equation (7), according to Klemens,[31] serves to describe the thermal conductivity limited by isotope scattering if S^2G^{-1} is replaced by $\epsilon/12$, where $\epsilon = \sum_a f_a \times[(M_a - M)/M]^2$. f_a is the relative concentration of each mass M_a, and M is the average mass. Using the abundances and masses listed by Bainbridge,[34] we find[35] for silicon $\epsilon = 1.98\times10^{-4}$. Equation 7 now gives a value of $K_g = 17.6$ w/cm C° at 303°K; the experimental value is about a factor of 14 smaller: 1.26 w/cm C°.

Any phonon-phonon scattering present must be treated not only for its own limitation of K_g but also for its effect on K_g as limited by point imperfections.[36] And one needs to consider also, in general, the relative amount of scattering by normal (momentum-conserving) processes and by Umklapp (momentum-nonconserving) processes,[26,36,37] although only the latter limit K_g acting alone. We now estimate whether phonon-phonon scattering may be appreciable at 303°K.

Ziman[37] estimates that the relative importance of Umklapp to isotope scattering in silicon is about five to one[35] at $T=\theta$ by obtaining the mean free paths. If we assume the Umklapp scattering effect varies as $\exp(\theta/\beta T)$ (obtaining β from Slack[38]), and that the isotope scattering varies at T^{-1}, we find at $T = 303$°K the relative importance is virtually the same as at $T=\theta$.

For our case, then, Callaway and von Baeyer's[36] treatment for the additional limitation of K_g due to small isotope scattering in the presence of phonon-phonon scattering dominated by Umklapp processes is preferable to that leading to Eq. (7). The difference in the result is a factor of 0.464 in front of Eq. (7), giving a numerical value of 8.2 w/cm C°. This corresponds to a resistivity of about 0.12 cm C°/w, or roughly one-sixth of the experimental resistivity of 0.79 cm C°/w, in agreement with our estimate of the relative importance of Umklapp and isotope scattering at 303°K.

The experimental results at 303°K are in rough agreement with the idea of a thermal conductivity limited by both Umklapp processes and scattering of phonons by isotopes.

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