small. The vibronic structure recently reported by Kiss[26] for the transitions $7T_1^{(2)} \rightarrow 8E^{(2)}$ and $7T_1^{(1)} \rightarrow 8T_2^{(2)}$ of Dy^{2+} in CaF_2 and SrF_2 may be an indication, however, that α_κ need not always be small.

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Thermal Conductivity of Electron-Irradiated Silicon*

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Changes in the low-temperature thermal conductivity of single-crystal Si were investigated upon 2-MeV electron irradiation and annealing. The additive thermal resistivity of high-purity p-type Si irradiated below 60°K to maximum time-integrated fluxes Φ of 8.0×10^{18} 2-MeV e/cm^2 increases as $1/K-1/K_0 = 3.75\times10^{-13}\,\Phi^{0.61}$ cm-deg/W at 47°K. The $\Phi^{0.61}$ dependence of the additive thermal resistivity of Si on bombardment is very similar to the $\Phi^{0.58}$ dependence previously observed for Ge. The magnitude of the increase is, however, much smaller than previously observed for either Ge, InSb, or GaAs. The linear concentration dependence of GaAs has been related to mass-difference strain-field scattering, whereas the nonlinear concentration dependencies of InSb, Ge, and Si suggest phonon-electron scattering. For the high-purity Si, annealing begins near 80°K, and exhibits a single dominant annealing stage near 140°K corresponding to the annealing temperature of vacancies in p-type Si. Measurements of the temperature dependence of the thermal conductivity indicate that the defects anneal primarily as point defects, although evidence exists for a small amount of precipitation of point defects in the annealing-temperature interval between 80 and 135°K. Sharp minima observed in the temperature dependence of the thermal conductivity of Si are similar to those previously observed in Ge and attributed to resonant scattering.

I. INTRODUCTION

ALTHOUGH electron spin resonance measurements by Watkins[1] have established that vacancies move and interact with impurities[1–3] at low temperature in silicon, there have been very few investigations of the effects on other physical properties of the low-temperature introduction and annealing of lattice defects. Such investigations must be conducted with the realization that the motion of the vacancy at 65°K in n-type Si[1] and near 140°K in p-type Si,[2] leads to interactions with chemical impurities well below room temperature[3] and greatly complicates measurements at higher temperatures.[4] Primary defects must therefore be studied in high-purity silicon irradiated at low temperature.

Electrical measurements are difficult to perform in irradiated high-purity Si at low temperature, and therefore very few exist.[5,6] However, low-temperature thermal conductivity has been shown to be highly sensitive to lattice defects introduced into high-purity GaAs,[7] InSb,[8] and Ge,[9] by electron irradiation. It has also been shown that measurements of the temperature dependence of the low-temperature thermal conductivity on annealing are related to changes in the structural properties of the defects and are therefore useful in distinguishing between the annealing behavior of radiation-induced defects in different semiconductors. Precipitation in GaAs[7] of point defects introduced by electron irradiation is in contrast to the almost complete recovery and annihilation of similar point defects introduced in Ge.[9] In addition, the increase in low-temperature thermal resistivity on electron irradiation can be related to theories of phonon scattering, and the magnitude and kind of such scattering can differ greatly from one semiconductor to another. For these reasons, changes in the thermal conductivity of Si upon electron irradiation were investigated.

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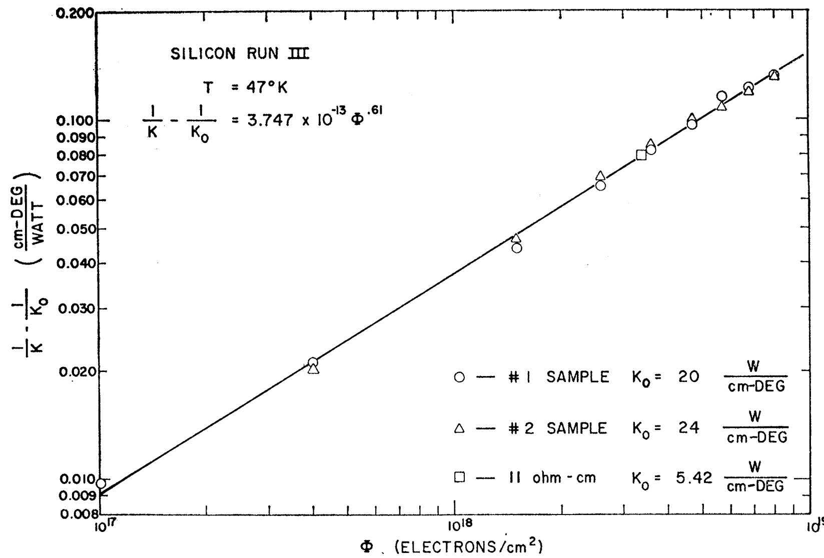

FIG. 1. Increase in the additive thermal resistivity of silicon as a function of the number of 2-MeV e/cm^2 passed through the sample.

Following a description of the experiments and presentation of the results, the phonon scattering of the defects introduced by electron irradiation in Si is compared both with previous measurements of the phonon scattering of chemical impurities introduced in Si and with the phonon scattering of defects introduced by electron irradiation in other semiconductors. In addition, the annealing measurements of the thermal conductivity are compared with other measurements of annealing in electron-irradiated silicon.

II. EXPERIMENTAL

Measurements of the change in thermal conductivity of high-purity p-type silicon were made *in situ* without warmup at a base temperature of 47°K. The experimental arrangement and measuring apparatus were similar to those reported in preceding papers,[7–9] except that Chromel-p–versus–Constantan thermocouples were used for the temperature measurements. Each sample was soldered at one end to a sample block which in turn was conduction-cooled in an irradiation cryostat. Measurements of the change in thermal conductivity were made on 2-MeV electron irradiation using either the heat of small wire heaters attached to the ends of the samples or, in some cases, the ionization heat of the electron beam.

Two essentially equivalent samples Si-1 and Si-2 were prepared from high-purity vacuum-floating-zone single-crystal material obtained from Merck and Company. The samples were initially 5000 Ω-cm p type (residual boron) with a carrier concentration of $\sim 3\times 10^{12}$ cm^{-3}. Both samples, Si-1 and Si-2, were bar shaped and were, respectively, 0.152 and 0.153 cm wide, 0.046 and 0.048 cm thick, with irradiated lengths of 1.0 cm. The samples were irradiated in the ⟨110⟩ direction, and the long dimension was the ⟨111⟩ direction.

Heater measurements were made both on bombardment and annealing. The fraction of the heater power which flowed through a sample was obtained by calibrating the heater using the thermal-conductivity data of unirradiated silicon above 50°K given by Holland,[10] and Glassbrenner and Slack.[11] The increase in thermal resistivity on bombardment obtained using the heaters calibrated in this way agreed very well with the measurements using the beam-heating method which depends only on the loss of energy of electrons passing through matter.[12]

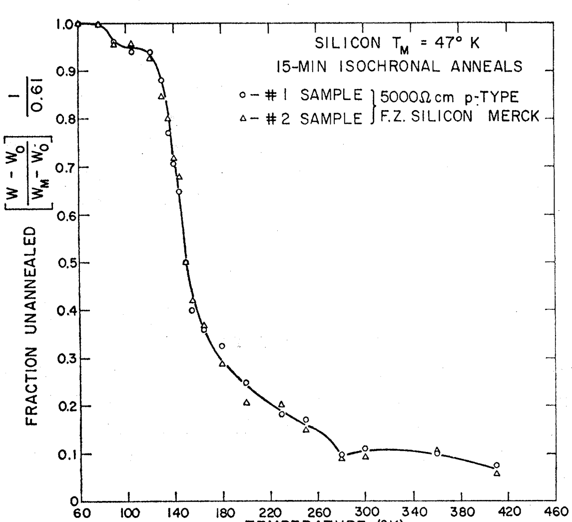

FIG. 2. Normalized 15-min isochronal anneals of thermal resistivity. All measurements made at 47°K.

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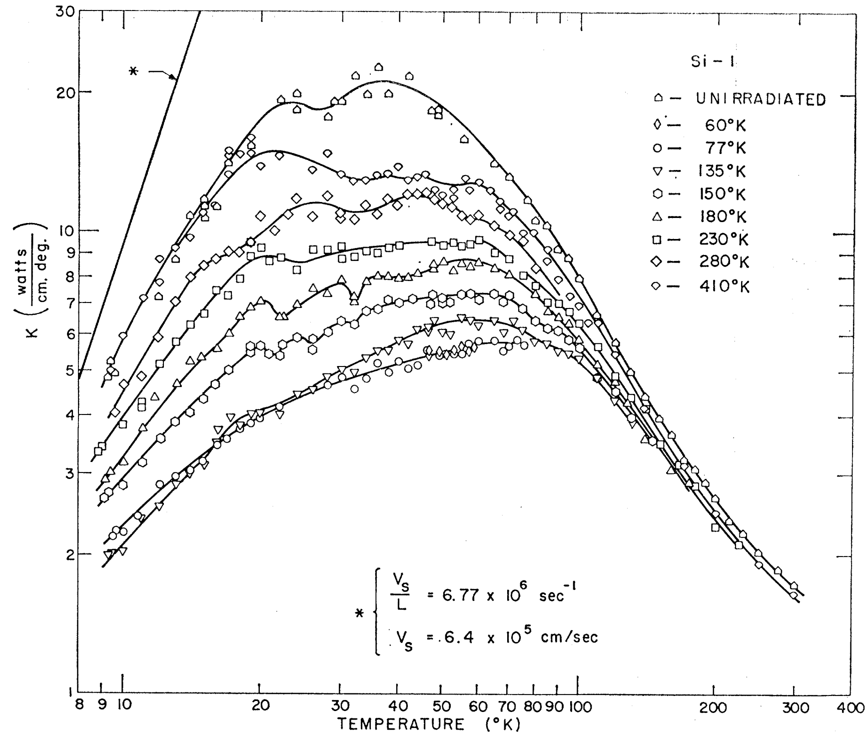

FIG. 3. Temperature dependence of the thermal conductivity of Si-1 before irradiation and after annealing below each of the indicated 15-min anneal temperatures.

During the irradiations of the high-purity Si samples, the base temperature of the samples was near 47°K. The samples were irradiated with such a flux that the maximum temperature of the sample tips was never more than 60°K. Measurements of the increase in thermal resistivity were made periodically on irradiation using the sample heater. After a total time-integrated flux of 8.0×10^{18} 2-MeV e/cm^2 was reached, 15-min isochronal anneals were performed in steps to 410°K. In addition, the temperature dependence of the thermal conductivity was measured below the anneal temperatures for selected anneal temperatures. The influence of tungsten light illumination on the thermal conductivity of the irradiated samples was also investigated.

III. RESULTS

The data from Si-1 and Si-2 agree very well with each other both on bombardment and annealing. The increase in thermal resistivity on bombardment is shown in Fig. 1. The thermal resistivity increase is a nonlinear function of the integrated electron flux Φ and is nearly proportional to the 0.61 power. The data can be fitted closely by the following expression

$$1/K-1/K_0=3.75\times10^{-13}\Phi^{0.61}\ \text{cm-deg/W} \quad \text{at} \quad 47°\text{K}.$$

Data from a preliminary investigation of 11 Ω-cm p-type Si are in agreement with these results and are also shown in Fig. 1.

If it is assumed that the annealing proceeds such that the thermal resistivity $W=1/K$ maintains the concentration dependence observed on bombardment, then

$$([W-W_0]/[W_m-W_0])^{1/0.61}$$

gives the fraction of the damage which is unannealed. Here W_m is the maximum thermal resistivity observed at the end of the bombardment and the start of annealing. The low-temperature annealing of the additive thermal resistivity in silicon is shown in Fig. 2 for 15-min isochronal anneals between 60 and 410°K, with all measurements made at 47°K. The thermal resistivity exhibits annealing beginning near 80°K in high-purity p-type Si with a large annealing stage near 140°K.

Figure 3 shows the temperature dependence of the thermal conductivity of Si-1 before irradiation and after irradiation below the indicated anneal temperatures. Figure 4 shows the corresponding results for Si-2. No effects of illumination on the thermal conductivity were observed.[13] The thermal conductivity shows a shift in the maximum to higher temperatures following bombardment and a return to lower temperatures on annealing. In the annealing interval between 80 and 135°K a *reverse annealing* is exhibited in which the thermal conductivity at low temperatures has decreased upon annealing rather than increased. Above 135°K the thermal conductivity recovers in a normal manner as the annealing temperature is increased. Fairly sharp resonance scattering minima are observed in the temperature dependence of the thermal conductivity of both samples.

[13] This is in contrast to results for Ge reported in Ref. 9.

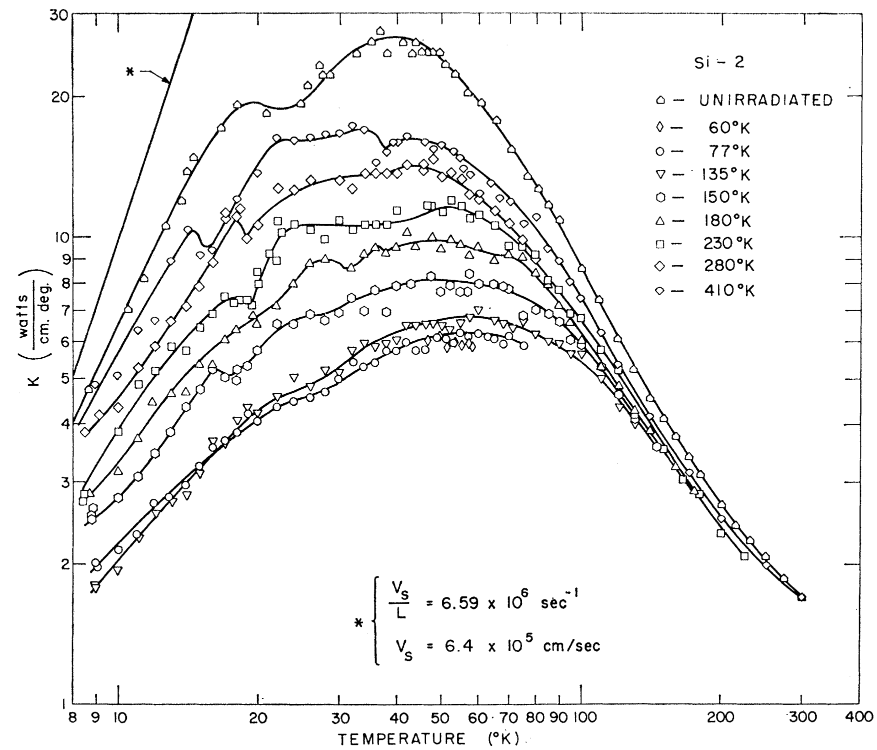

FIG. 4. Temperature dependence of the thermal conductivity of Si-2 before irradiation and after irradiation below each of the indicated 15-min anneal temperatures.

IV. DISCUSSION

A. Bombardment

The samples studied here were high-purity, high-resistivity, *p* type before irradiation and remained high-resistivity on bombardment. The additive thermal resistivity is approximately proportional to the 0.61 power of the integrated flux of 2-MeV electrons, and therefore the same dependence on defect concentration is also implied. This conclusion is valid assuming a constant introduction rate of defects, which is consistent with the very low, chemical impurity concentration relative to radiation-induced defect concentration and the lack of any indication of a saturable effect such as radiation annealing.[14]

The defect-concentration dependence of the irradiation-induced additive thermal resistivity of Si at 47°K is equal to the corresponding boron-concentration dependence for chemically doped Si.[15] The 0.58 power dependence of $1/K-1/K_0$ observed for electron-irradiated Ge[9] is also very similar. Figure 5 compares the present results for Si with the previously reported results for 2-MeV electron-irradiated Ge[9], GaAs,[7] and InSb.[8] The strong similarities in the concentration dependencies of InSb, Ge, and Si suggest a common scattering mechanism.

Theoretical studies to explain the magnitude and concentration dependence of mass-difference and strain-field scattering have been made by several authors and previously reviewed.[7,9] Most theories predict that the additive thermal resistivity is directly proportional to the concentration of defects for small concentrations. It has been shown that the observed linear increase in low-temperature thermal resistivity of GaAs upon electron irradiation[7] can be adequately related to the measured linear increase in lattice strain[16] through the theories of mass-difference and strain-field scattering of Klemens[17] and Ziman.[18] On the other hand, the very different nonlinear increase in thermal resistivity of InSb and Ge cannot be related to the measurements of lattice strain[16] and are attributed instead to a phonon-electron scattering mechanism, such as proposed by Keyes,[19] which is based upon the large effect of strain on impurity-electron wave functions. The close similarity of the nonlinear concentration dependencies of InSb, Ge, and Si suggests that the scattering in Si also results from a similar phonon-electron scattering mechanism. This would not be surprising since silicon and germanium are similar in many ways. In particular, the electronic effect in the elastic constants predicted by the

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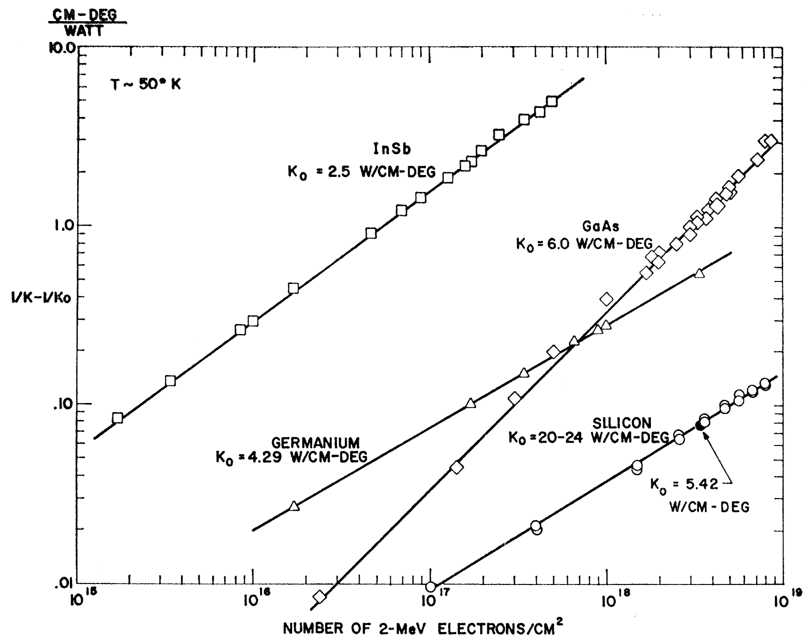

FIG. 5. Comparison of the additive thermal resistivity $1/K-1/K_0$ measured at ~50°K, for InSb, GaAs, Ge, and Si as a function of the number of 2-MeV e/cm^2 passed through the samples. The maximum temperatures on bombardment are 80, 80, 70, and 60°K, respectively, for InSb, GaAs, Ge, and Si.

Keyes' theory has been observed for both silicon[20] and germanium.[21]

Considering the fact that the magnitude of the additive thermal resistivity of doped p-type Ge at 47°K as a function of impurity concentration[22] is comparable to the magnitude of the additive thermal resistivity of doped p-type Si at 47°K,[15] the question remains why the magnitude of the irradiation-induced scattering at 47°K is so much smaller for electron-irradiated Si than for Ge even though the number of defects produced per cm^3 per 2-MeV e/cm^2 should be comparable.[23,24] The probable answer to this question is that on bombardment the limiting Fermi level for Si is near the center of the band gap whereas for Ge (and InSb) the samples are rapidly driven p-type before measurements are begun, and the limiting Fermi level is near the valence band. In the Keyes' theory, the scattering is proportional to the number of un-ionized donors. Goff[25] has confirmed this fact and has shown that compensated n-type Ge samples scatter like the net *difference* of donors and acceptors rather than as the total impurity concentration. Since there is good evidence that intrinsic defects, presumably Frenkel pairs, introduced into Si tend to compensate each other,[5,6,26] a similar behavior would explain the smallness of the scattering observed in Si.

B. Annealing

The isochronal annealing data in Fig. 2 show that a prominent annealing stage occurs near 140°K in the recovery of the additive thermal resistivity. This stage appears to be associated with the annealing of the lattice vacancy. Watkins has identified the lattice vacancy in Si and has determined the activation energy of motion to be 0.33±0.03 eV for the neutral vacancy in p-type material consistent with annealing in this temperature range.[1,2] (This annealing stage also agrees quite well with recent results of Stein[27] on the annealing of electrical properties of electron-irradiated p-type Si.) Watkins has shown that as the vacancy spectra disappear, new spectra appear which are associated with defect-impurity interactions. The same conclusions are reached by Vavilov[6] in low-temperature studies of the monochromatic photoconductivity of electron-irradiated p-type Si. Indeed, preliminary thermal-conductivity measurements on less-pure p-type boron-doped Si have shown that although the additive resistivity is approximately the same on bombardment (Fig. 1), the fraction of the thermal resistivity that anneals in this stage is much smaller. This behavior apparently also reflects the low-temperature formation of defect-impurity complexes.

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Figures 3 and 4 show a shift in the maximum of the thermal conductivity to higher temperatures on irradiation and a general return to lower temperatures on annealing. This is consistent with the previously observed behavior of irradiated semiconductors[7,9] and also with the behavior of p-type Si as a function of the boron concentration.[15] The lines giving the limiting theoretical[28] boundary scattering curves for the respective sample sizes are also shown. The velocity v_s is the average of the transverse and acoustical mode velocities derived from elastic-constant data, and L is defined as the diameter of a circle having the same cross-sectional area as the sample.

The "reverse annealing" observed in the temperature dependence of the thermal conductivity for annealing temperatures between 77 and 135°K suggests that point defects are precipitating to form clusters which scatter phonons more nearly like boundary scattering. A similar but more pronounced behavior was observed in the annealing of electron-irradiated GaAs.[7] Although the precipitation may indirectly involve interstitials,[1] boron impurity atoms seem to be directly involved since the reverse annealing was greately enhanced in measurements on 11 Ω cm boron-doped Si crystals.[29]

A detailed study of the temperature dependence of the thermal conductivity on annealing reveals reproducible local inflections or minima. These minima are very similar to the minima observed upon annealing of electron-irradiated Ge.[9] They are different from the relatively broad minima seen before irradiation and also observed in many other crystals.[7,30–32] Walker and Pohl,[32] and Wagner[33] have attributed the minima seen in ionic crystals to resonant scattering from localized modes. Broad minima seen in silicon[30] and electron-irradiated GaAs [7] have been attributed to similar processes. The narrow minima seen in irradiated Si and Ge and in unirradiated n-type Ge by Goff[25] probably involve a different process. Griffin and Carruthers[34] attempted, but were not able, to explain the minima seen by Goff in terms of the resonance-fluorescence scattering of phonons by donor electrons. Additional theoretical and experimental investigations are clearly necessary for an understanding of the actual mechanisms.

ACKNOWLEDGMENT

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