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*Abstract.* The electrical conductivity and Hall effect have been measured over the temperature range 20°K to 500°K on single crystals of silicon with extrinsic carrier concentrations between 2 and $5 \times 10^{12}$ cm$^{-3}$. The Hall mobility for electrons and holes can be represented between 100° and 300°K by the expression $1{\cdot}2 \times 10^{8} T^{-2}$ and $2{\cdot}9 \times 10^{9} T^{-2{\cdot}7}$ respectively. Both these results indicate a higher Hall mobility than has been previously reported, and the result for holes is greater than values reported for the drift mobility. From the results between 350° and 500°K the expression $n_i = 3{\cdot}10 \times 10^{16} T^{3/2} \exp -0{\cdot}603/kT$ was obtained for the intrinsic concentration. Attempts were made to estimate the total impurity concentration in these specimens. The variation of extrinsic carrier concentration with temperature and the effect of impurity scattering at 20°K both indicate that the total concentration of impurities is less than $10^{14}$ cm$^{-3}$.

## § 1. Introduction

Recent improvements in the techniques for preparing silicon (Wilson 1957) have made it possible to extend measurements on the intrinsic conductivity to a lower temperature than has been previously reported (Morin and Maita 1954). In addition, measurements have been made down to 20°K in order to estimate the purity of the material and to study the behaviour of the Hall mobility. Mobilities of both electrons and holes are found to be greater than previously observed. In particular, on comparing the Hall mobility of holes with recent measurements of drift mobility (Ludwig and Watters 1956, Cronemeyer 1957), it is found that the ratio of Hall to drift mobility is not less than unity and is practically independent of temperature. The impurity in the p-type specimens used is believed to be boron, and in the n-type specimen phosphorus.

## § 2. Experimental Details

Samples of the shape shown in figure 1 and about 1 mm thick were cut from plates of silicon using an ultrasonic drill. The material had been prepared in single crystal form as described elsewhere (Wilson 1957). Contacts were made to them by fusing spots of aluminium to the p-type specimens and antimony–gold alloy to the n-type specimen. The samples were mounted in a cryostat for measurements below room temperature and in an oil bath for measurements up to 500°K. Measurements were made using either an Applied Physics Corporation vibrating reed electrometer, or, where the resistance was sufficiently low, a potentiometer and galvanometer. The electric fields used were not allowed to exceed 1v cm$^{-1}$ because it was found that some departure from Ohm's law

could be observed for fields between 1 and 10 v cm$^{-1}$ both at 20°K and room temperature. A magnetic induction of 2300 gauss was used except where stated.

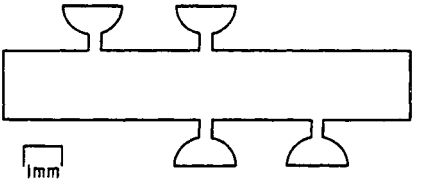


Figure 1. Plan of specimen.

It was found that with both the p-type specimens the nature of the surface was important. If an etched surface were used, then surface conductance appeared to be present above 300°K, causing a rapid rise in the conductance of the specimen before the intrinsic range was entered and causing the Hall coefficient to change sign at a lower temperature than would be expected. These effects disappeared if the surface of the specimen were lightly sandblasted. Between 20°K and 300°K the results were independent of the nature of the surface. In figure 2 the results obtained with an etched and a sandblasted surface are compared. These effects were not found in n-type specimens.

The accuracy of the results is estimated to be to between 5 and 10%. For the conductivity measurements this is determined by the accuracy with which the dimensions of the samples could be determined. For Hall effect measurements the largest source of error was measuring the Hall voltage.

## § 3. Results Below Room Temperature

Figure 3 shows a plot of log $\sigma$ and log $R$ against $1/T$ down to 20°K for two p- and one n-type specimen. Between 50° and 20°K the plots are approximately straight lines. If it is assumed that both donor and acceptor levels are present in all specimens, then the variation of the electron concentration $n$ in an n-type specimen is given by:

$$\frac{n(N_A+n)}{(N_D-N_A-n)} = \frac{(2\pi m^* \boldsymbol{k} T)^{3/2}}{h^3} \exp\left(-\frac{E_D}{\boldsymbol{k}T}\right). \qquad \ldots\ldots (1)$$

In deriving this expression it is assumed that each impurity level can accommodate one electron of either spin (Wilson 1953).

At low enough temperatures, $n \ll N_A$ and $N_D - N_A$, so that the expression becomes

$$n = \frac{N_D - N_A}{N_A} \frac{(2\pi m \boldsymbol{k} T)^{3/2}}{h^3} \left(\frac{m^*}{m}\right)^{3/2} \exp\left(-\frac{E_D}{\boldsymbol{k}T}\right) \qquad \ldots\ldots (2)$$

and a similar expression can be written down for $p$ the hole concentration in a p-type specimen.

To fit (2) to the experimental results, $n$ was obtained from the Hall coefficient:

$$R = -\frac{3\pi}{8}\left(\frac{1}{ne}\right). \qquad \ldots\ldots (3)$$

The value for $N_D - N_A$ was found from the Hall coefficient in the exhaustion region. Then from the slope of the plot of log $(nT^{-3/2})$ against $1/T$ the value of $E_D$ was found while the intercept of this plot gave the quantity $(m^*/m)^{3/2}/N_A$. In some cases it is possible to determine $N_A$ and $m^*/m$ independently by fitting

the results to equation (1), but in this case the behaviour was so insensitive to the value of $m^*/m$ that the calculation was not practicable. A similar difficulty was found when the method of analysis described by Lee (1957) was applied. Thus, in order to obtain a value for $N_A$ (or, for the p-type specimen, $N_D$) an assumption has to be made of the value $m^*/m$. According to the results given by Lax and Mavroides (1955) and assuming the six ellipsoid model for the conduction band, probable values for the density-of-states effective masses are:

$$\frac{m^*}{m} = 1{\cdot}0 \text{ (electrons)}; \quad \frac{m^*}{m} = 0{\cdot}6 \text{ (holes)}.$$

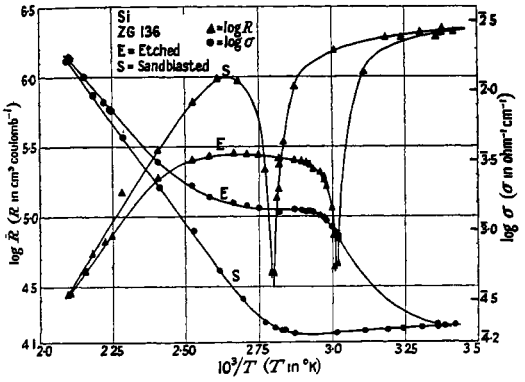


Figure 2. Influence of surface on behaviour above room temperature.

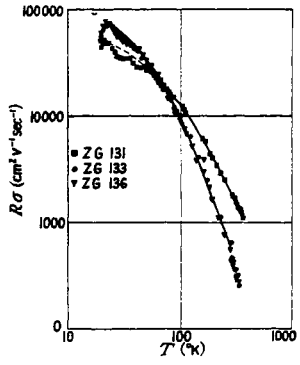


Figure 4. Hall mobility.

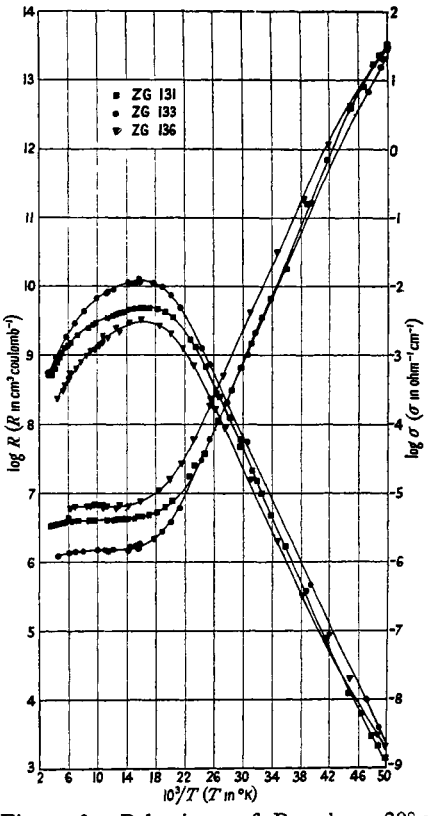


Figure 3. Behaviour of $R$ and $\sigma$: 20°K upwards.

Using these values, $N_A$ and $N_D$ were calculated. The results obtained and the values found for $E_D$ or $E_A$ are given in the table. This table also gives $N_I$ the concentration of impurity scattering centres required to account for the mobility at 20°K (see next section).

| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|
| ZG 131 | n | 0·045 | $2{\cdot}12\times10^{12}$ | $1{\cdot}8\times10^{13}$ | $2\times10^{13}$ | $6\times10^{13}$ |
| ZG 136 | p | 0·043 | $1{\cdot}31\times10^{12}$ | $3{\cdot}5\times10^{13}$ | $3{\cdot}3\times10^{13}$ | $4\times10^{13}$ |
| ZG 133 | p | 0·043 | $5{\cdot}84\times10^{12}$ | $5{\cdot}3\times10^{13}$ | $4{\cdot}7\times10^{13}$ | |

(1) specimen; (2) sign of excess carriers; (3) $E_D$ or $E_A$ (ev); (4) $N_A$–$N_D$ or $N_D$–$N_A$ (cm$^{-3}$); (5) $N_A$ (cm$^{-3}$); (6) $N_D$ (cm$^{-3}$); (7) $N_I$ (cm$^{-3}$).

The values found for $E_A$ and $E_D$ are in satisfactory agreement with those found by other workers for boron and phosphorus levels respectively. There was some difficulty in assigning a value for $N_A - N_D$ for ZG 136 because just below room temperature $R$ started to fall as the temperature rose, suggesting the presence of a deeper acceptor level. The value used was found by estimating from the results at 150°K for the value which would have been found at room temperature in the absence of the deeper level.

## § 4. Hall Mobility

Figure 4 is a logarithmic plot of $R\sigma$ against $T$. The results for the two p-type specimens are practically identical. Between 100° and 300°K the results can be fitted to expressions of the form $R\sigma = AT^{-\alpha}$ with $A = 1{\cdot}2 \times 10^8$, $\alpha = 2{\cdot}0$ for electrons and $A = 2{\cdot}9 \times 10^9$, $\alpha = 2{\cdot}7$ for holes. Below 100°K the mobility increases less rapidly as the temperature falls, passing through a maximum between 20° and 30°K. Below 60°K the mobility of the p-type specimens is greater than that of the n-type. The values given above for $A$ and $\alpha$ predict that below 63°K the hole mobility should be the greater. The fact that below 100°K the mobilities are not as large as the formulae predict, and in fact pass through maxima can be accounted for by ionized impurity scattering. If at 20°K the mobility is determined by ionized impurity scattering, then about $4 \times 10^{13}$ centres $cm^{-3}$ are required to account for the mobility of the p-type specimens, and $6 \times 10^{13}$ for the n-type one. These values are comparable with those given for the concentration of impurity centres in the table. The Hall mobility obtained here for holes is appreciably greater than values reported previously. Thus at 298°K Cronemeyer's (1957) results obtained on material of less than 1000 ohm cm resistivity indicate that $R\sigma$ is flattening out at about 410 $cm^2 v^{-1} sec^{-1}$, while our data indicate that the upper limit is not less than 500. Comparing this with Cronemeyer's values for drift mobility suggests that the ratio of Hall to drift mobility is not less than unity. Comparing our results with those obtained for the drift mobility by Ludwig and Watters (1956) indicates a ratio of Hall to drift mobility of about 1·26 which is independent of temperature. Previous results had indicated a ratio of Hall to drift mobility of less than unity. It appears that this ratio in silicon is rising as it did in germanium with improvements in the quality of the material.

The value of the Hall mobility of electrons at room temperature falls within the spread of values obtained by Cronemeyer for material of comparable resistivity. The variation with temperature ($\alpha T^{-2\cdot0}$) differs from that reported by Morin and Maita (1954) ($\alpha T^{-2\cdot5}$). It is seen (figure 3) that at temperatures where the variation of electron concentration is a constant, the conductivity shows a similar variation with temperature to that of the Hall mobility. Since the conductivity variation is determined by that of the drift mobility, the ratio of Hall to drift mobility must be independent of temperature. Hence the difference between the rate of variation of Hall mobility found here and the previously reported values for it and for the rate of variation of drift mobility with temperature (Ludwig and Watters 1956), cannot be accounted for by supposing that in our case the ratio of Hall to drift mobility is varying with temperature. It is possible that the rate of variation of the electron mobility given by Morin and Maita may be too high because their value was obtained after making a correction for impurity

scattering. Between 200 and 300°K the uncorrected Hall mobility of their purest specimen varies as more like $T^{-2\cdot0}$ and their values are only about 15% smaller than those found in this material. For an estimated concentration of scattering centres of about $6 \times 10^{13}$ impurity scattering in the material used here will be negligible above 200°K. An overestimate by Morin and Maita of the effect of impurity scattering in their material may account for this discrepancy between the rates of variation of the electron mobility.

## § 5. Results in the Intrinsic Range

Figures 5 and 6 show the behaviour of the conductivity and Hall coefficient from room temperature up to above 500°K. It is seen that the intrinsic properties become dominant above about 370°K. The p-type specimens were examined

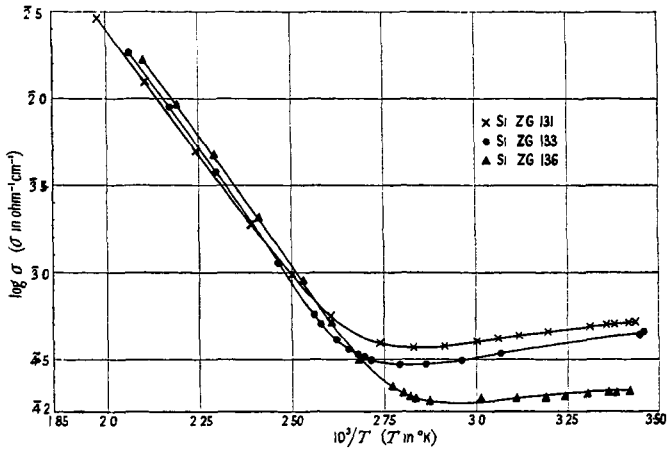


Figure 5. Conductivity above room temperature.

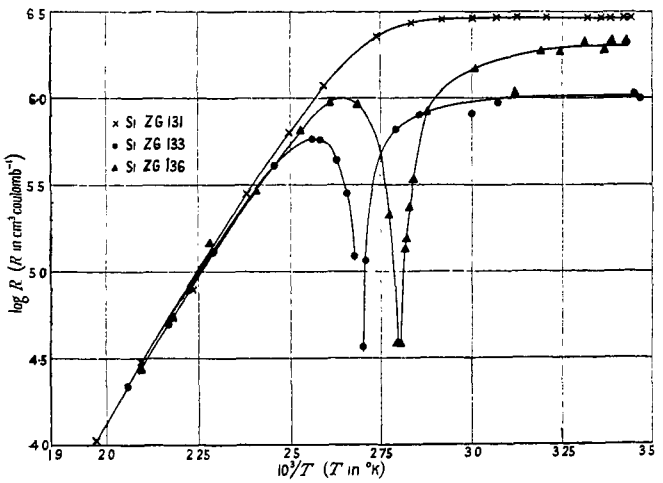


Figure 6. Hall coefficient above room temperature.

carefully near the temperatures at which the Hall coefficients change sign to see if the presence of light holes could be detected, as has been found in germanium (Willardson *et al.* 1954), but the Hall coefficient appeared independent of induction over the range 1000 to 10 000 gauss. The measurements of the conductivity of the n-type specimen were considered the most reliable of these results (accuracy to $\pm 5\%$). The conductivity can be written

$$\sigma = ne\mu_n + pe\mu_p \qquad \ldots\ldots (4)$$

where $n$ and $p$ are the concentration of electrons and holes and will be related to each other by

$$np = n_i^2, \quad n - p = m \qquad \ldots\ldots (5)$$

where $n_i$ is the intrinsic carrier concentration and $m$ the electron concentration, when all the impurity levels are ionized. $\mu_n$ and $\mu_p$ are the conductivity mobilities.

Hence, if $m$ is determined from the Hall coefficient at room temperature,

$$R_{ex} = -3\pi/8em \qquad \ldots\ldots (6)$$

and values for the mobilities are assumed, these equations can be solved for $n_i$. The values were obtained by writing $\mu = 8R\sigma/3\pi$ where $R\sigma$ is the Hall mobility and using for $R\sigma$ the values given in § 4. When this is done it is possible to calculate $n_i$ over the temperature range 370°K to 500°K and the results obtained (see figure 7) can be represented by the formula

$$n_i = 3{\cdot}10 \times 10^{16}\, T^{3/2} \exp(-0{\cdot}603/kT). \qquad \ldots\ldots (7)$$

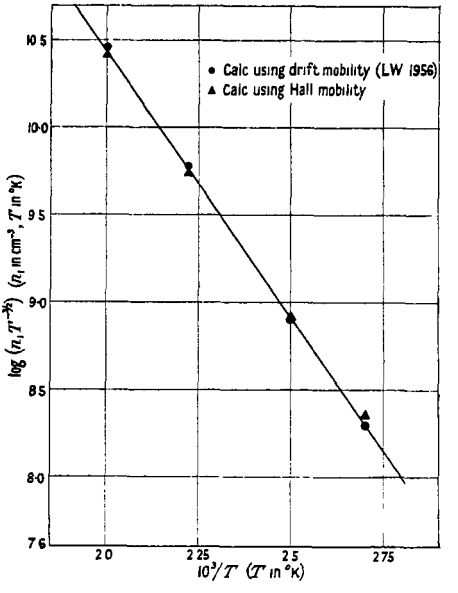


Figure 7. Intrinsic carrier concentration in silicon (LW = Ludwig and Watters 1956).

This can be compared with the results obtained by Morin and Maita, valid above 450°K

$$n_i = 3{\cdot}88 \times 10^{16}\, T^{3/2} \exp(-0{\cdot}605/kT). \qquad \ldots\ldots (8)$$

It is seen that the rates of variation with temperature are almost identical. The

values obtained here are about 25% smaller than those of Morin and Maita. This difference is somewhat larger than the probable error of the calculation. Our values for the intrinsic conductivity are in very close agreement with Morin and Maita's values, and therefore the lower values we obtain for $n_i$ are accounted for by the higher values we have used for the mobility.

Our results depend on the somewhat arbitrary assumption that the ratio of Hall to conductivity mobility is a constant, $3\pi/8$. As has already been pointed out, comparison of the Hall mobility with the conductivity in the exhaustion range leads to the conclusion that the ratio of the two mobilities is independent of the temperature. Comparison of our values for the Hall mobility of holes with recent measurements of drift mobility (Ludwig and Watters 1956) suggest that $3\pi/8$ is not an unreasonable value to take for the ratio, but a similar comparison for electrons leads to no definite conclusion. An alternative calculation of $n_i$ was made using Ludwig and Watter's results in place of our mobility data. This led to results which agreed to within 5% of expression (7). This suggests that

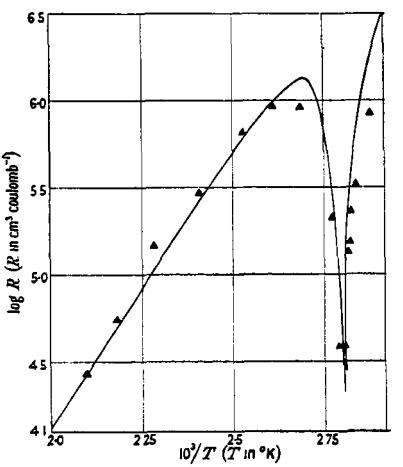


Figure 8. Hall coefficient for ZG 136—curve calculated, points experimental.

our assumptions do not lead to errors greater than the experimental error in the available data. Taking the values of $n_i$ given by expression (7) it is possible to calculate the variation of the Hall coefficient with temperature and to obtain a curve which fits the experimental results within the accuracy of measurement (10%). The curve drawn in figure 8 is that calculated for ZG136 using the expression

$$R = -\frac{3\pi}{8e}\frac{nc^2-p}{(nc+p)^2}$$

with $p-n=1{\cdot}4\times10^{12}$ and $np=n_i^2$; $c$ and $n_i$ are taken from the expression for the Hall mobilities and equation (7) for the intrinsic concentration. The points plotted are the measured ones. It is seen that above 400°K the agreement is good, but the fit near the Hall zero is not perfect. The position of the Hall zero agrees with what would be expected from the hole concentration at exhaustion (see table) and the mobility ratio calculated from the expressions for the electron and

hole mobilities. The measured Hall maximum is smaller than the calculated one and below the Hall zero temperature the Hall coefficient starts to fall at a much lower temperature than would be expected, but at a slower rate.

These discrepancies may be accounted for by the presence of deeper acceptor levels (as already suggested) or of light holes.

## § 6. Conclusion

Silicon can now be prepared in which the total concentration of impurities is less than $10^{14}$ cm$^{-3}$. In this material the Hall mobility of both holes and electrons is greater than the values found in less pure material. It now appears that the ratio of Hall to drift mobilities for holes is greater than unity.

The intrinsic carrier concentration has been calculated down to 370°K. The results are in good agreement with those found by Morin and Maita above 450°K.

One surprising feature of these results is that the calculations in § 3 indicate a high degree of compensation. If this is so it is difficult to explain the high values obtained for the mobilities and the uniform values obtained for the conductivity from samples cut from different parts of the crystals unless there is some interaction between the two types of impurity centre which eliminates the point-to-point fluctuation in the degree of compensation usually found in highly compensated material.

## Acknowledgments

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## References

Cronemeyer, D. C., 1957, *Phys. Rev.*, **105,** 522.
Lax, B., and Mavroides, J. G., 1955, *Phys. Rev.*, **100,** 1650.
Lee, P. A., 1957, *Brit. J. Appl. Phys.*, **8,** 340.
Ludwig, G. W., and Watters, R. L., 1956, *Phys. Rev.*, **101,** 1699.
Morin, F. J., and Maita, J. F., 1954, *Phys. Rev.*, **96,** 28.
Willardson, R. K., Harman, T. C., and Beer, A. C., 1954, *Phys. Rev.*, **96,** 1512.
Wilson, A. H., 1953, *Theory of Metals*, p. 115 (Cambridge: University Press).
Wilson, J. M., 1957, *Research*, **10,** 166.

*Note added in proof.* Recent studies of the nature of impurity levels in silicon (see Kohn, 1957, *Solid State Physics*, **5,** 257, Academic Press Inc., New York) indicate that equation (1) should be modified to take into account the four-fold degeneracy of the acceptor ground state and the proximity of excited states close to the ground state of the donor impurities. These modifications reduce the number of impurity centres given in the table to about half for the p-type specimens and to about 65% for the n-type specimen.