

Seebeck Coefficient in N-Type Germanium-Silicon Alloys: "Competition" Region

A. AMITH

RCA Laboratories, Princeton, New Jersey

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The Seebeck coefficient Q of arsenic-doped germanium-silicon alloys was measured as a function of silicon content from 0 to 20 at.%. The values of Q were found to go through a maximum at the alloy $\text{Ge}_{85}\text{Si}_{15}$; furthermore, they were smaller on the germanium side of that composition than they were on the silicon side. The behavior of Q as a function of alloy composition, in the case of lightly doped samples, can be accounted for in terms of the changes in the density-of-states: at $\text{Ge}_{85}\text{Si}_{15}$ the structure of the conduction-band minima passes from that of germanium, with four valleys along the $\langle 111 \rangle$ directions, to that of silicon, with six valleys along the $\langle 100 \rangle$ directions; and at $\text{Ge}_{85}\text{Si}_{15}$ all ten valleys are equi-energetic. In the case of the heavily doped samples, there is also a contributory effect due to the decrease in the relative strength of the ionized-impurity scattering ($\tau \sim E^{3/2}$) as alloy-disorder scattering ($\tau \sim E^{-1/2}$) increases with the addition of silicon.

I. INTRODUCTION

THIS work relates the Seebeck coefficient in n -type germanium-silicon alloys to changes in the structure of the conduction-band with alloying. Measurements have been performed at 295°K on alloys, both lightly and heavily doped with arsenic, in which the silicon content varied from 0 to 20 at.%. Of particular interest was the behavior near the alloy composition $\text{Ge}_{85}\text{Si}_{15}$, where the conduction band passes from a structure characteristic of germanium to one characteristic of silicon. The conduction-band minima in germanium consist of four equivalent valleys along the $\langle 111 \rangle$ axes, and those of silicon consist of six equivalent valleys along the $\langle 100 \rangle$ axes in reciprocal lattice space.¹ The conduction-band structure changes gradually as silicon is alloyed with germanium; it retains the germanium-like structure until the silicon nears 15 at.%, past which it assumes the silicon-like structure. This behavior of the conduction band had been postulated² to explain the measurements of the optical band gap as a function of composition³ and it was substantiated subsequently by detailed galvanomagnetic⁴⁻⁶ as well as optical measurements.^{7,8}

The present investigation of the Seebeck coefficient of arsenic-doped germanium-silicon alloys is related to the changes in the conduction band with alloying—both in terms of the effective mass and in terms of the number of valleys. The behavior near the composition $\text{Ge}_{85}\text{Si}_{15}$ reflects the fact that there are ten equi-energetic valleys, four along the $\langle 111 \rangle$ axes and six along the $\langle 100 \rangle$ axes, resulting in a very large density of states. The effects of changes in electron scattering with alloying are also taken into account.

¹ G. Dresselhaus, A. F. Kip, and C. Kittel, *Phys. Rev.* **98**, 368 (1955).

² F. Herman, *Phys. Rev.* **95**, 847 (1954).

³ E. R. Johnson and S. M. Christian, *Phys. Rev.* **95**, 560 (1954).

⁴ M. Glicksman, *Phys. Rev.* **100**, 1146 (1955).

⁵ M. Glicksman and S. M. Christian, *Phys. Rev.* **104**, 1278 (1956).

⁶ M. Glicksman, *Phys. Rev.* **111**, 125 (1958).

⁷ R. Braunstein, A. R. Moore, and F. Herman, *Phys. Rev.* **109**, 695 (1956).

⁸ J. Tauc and A. Abraham, *J. Phys. Chem. Solids* **20**, 140 (1961).

II. MEASUREMENTS

Measurements of resistivity, Hall and Seebeck coefficients, were performed on two sets of samples. The first was cut from a graded germanium-silicon ingot of low arsenic content (about 10^{15} cm^{-3}), the second was cut from a heavily doped ingot (about 10^{19} cm^{-3}). The lightly doped samples were all single crystals. The heavily doped ones contained two or three large crystals. The samples were all bridge-shaped of over-all dimensions 0.25×0.50 in. and 0.03 in. thick. The resistivities and Hall voltages were measured by standard dc potentiometric methods (the samples were not in vacuum). The Seebeck coefficients were measured by soldering 0.003-in. copper-constantan thermocouples to three of the arms, and using the copper leads as the potential probes. A small heater was soldered to one end of the sample while the other end was soldered to a copper block. The temperature gradients were varied between 3 and 6°K.

The carrier densities were deduced from the Hall coefficients through the relation⁹ $R = 1/nec$. We thus neglect the effects of the scattering on the ratio of the Hall to the conductivity mobility, as well as the anisotropy factor which is related to the ratio of the transverse and longitudinal effective masses.¹⁰ The latter is different for silicon and for germanium, and would have to be changed as we cross the $\text{Ge}_{85}\text{Si}_{15}$ alloy from the germanium-rich side to the silicon-rich side.¹¹ The effects of this are rather small, and would cause but a slight shift of the data on the two sides of $\text{Ge}_{85}\text{Si}_{15}$ with respect to each other.

The average carrier density of all samples in the lightly doped series was thus determined to be $1.3 \times 10^{15} \text{ cm}^{-3}$, and the variations of the individual samples from this average did not exceed 20% either way. The Seebeck coefficient depends rather weakly upon the carrier concentration (see below), and would be almost insensitive to such fluctuations. Figure 1 depicts the values of the Seebeck coefficients measured in the series

⁹ E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths Scientific Publications Ltd., London, 1960).

¹⁰ C. Herring, *Bell System Tech. J.* **34**, 277 (1955).

¹¹ M. Glicksman, *Phys. Rev.* **102**, 1496 (1956).

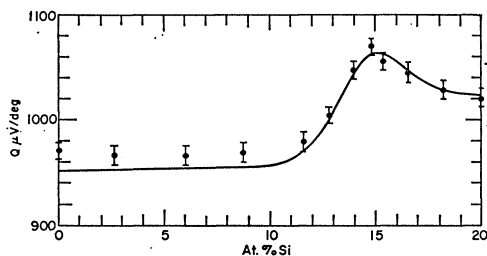


FIG. 1. Seebeck coefficients of lightly doped Ge-Si samples ($n \sim 1.3 \times 10^{18} \text{ cm}^{-3}$). \bullet : experimental points. Solid curve is calculated on the basis of conduction in two sets of valleys, taking into account lattice, alloy disorder and intervalley scattering of electrons.

of alloys with an average carrier density of $1.3 \times 10^{18} \text{ cm}^{-3}$. Figure 2 depicts the Hall mobilities $R\sigma$ measured in the same series of alloys. The effects of ionized impurities were subtracted from the measured values, in the same manner as had been done by Glicksman.⁶

In the samples of the heavily doped series, the carrier densities were deduced from the measured Hall coefficients in the same manner as for the lightly doped samples. The average carrier density of all samples was $1.1 \times 10^{19} \text{ cm}^{-3}$, and the maximum deviation of any sample from that average was 30%. The measured Seebeck coefficients are shown in Fig. 3. The measured Hall mobilities are shown in Fig. 4.

III. DISCUSSION

The Seebeck coefficients which have been measured in the two sets of samples, the lightly doped and the

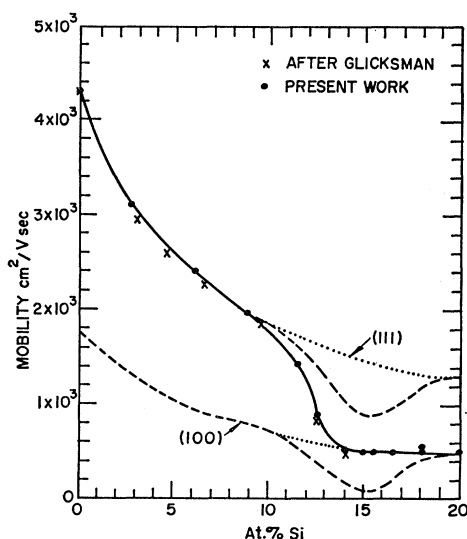


FIG. 2. Experimental values of Hall mobilities, from which effects of ionized-impurity scattering were subtracted. The crosses are from the work of Glicksman (Ref. 6). The dashed curves refer to mobilities in the $\langle 111 \rangle$ and in the $\langle 100 \rangle$ sets of valleys alone: lattice scattering was assumed to be independent of alloying, while alloy disorder and intervalley scattering were determined by fitting to the data (Ref. 6). The dotted portions neglect the intervalley scattering.

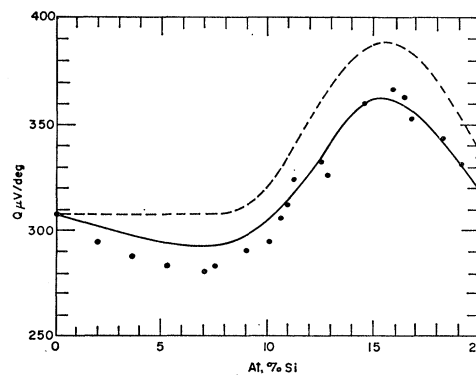


FIG. 3. Seebeck coefficients of heavily doped Ge-Si alloys ($n \sim 1.1 \times 10^{19} \text{ cm}^{-3}$). \bullet : experimental points. Solid curve is calculated on the basis of conduction in two sets of valleys, taking into account lattice, alloy disorder, intervalley and ionized-impurity scattering of electrons. Dashed curve neglects the decrease in the relative importance of ionized-impurity scattering with increase in alloying.

heavily doped ones, show pronounced maxima in the region of $\text{Ge}_{85}\text{Si}_{15}$. We shall discuss the data from a phenomenological point of view and, after justifying a set of simplifying assumptions, show how the experimental results conform to our understanding of the behavior of the conduction band in the alloy region under investigation.

The conduction in n -type germanium takes place in a set of four prolate spheroids along the $\langle 111 \rangle$ directions. The longitudinal and transverse effective masses are $m_l = 1.58m_0$ and $m_t = 0.08m_0$, respectively,¹² where m_0 is the free-electron mass. In n -type silicon, the conduction takes place in a set of six prolate spheroids along the $\langle 100 \rangle$ directions, and the corresponding effective masses are¹² $m_l = 0.92m_0$ and $m_t = 0.19m_0$. As silicon is alloyed with germanium, conduction still takes place in the $\langle 111 \rangle$ valleys, yet at the same time their energy increases until, at $\text{Ge}_{85}\text{Si}_{15}$, they have become equienergetic with the set of $\langle 100 \rangle$ valleys—whose energy has not been affected by the alloying. The set of the $\langle 111 \rangle$ minima moves at the rate of $17 \times 10^{-3} \text{ eV}$ ($0.66kT$ units at 295°K) per one atomic percent of silicon.⁸ In a

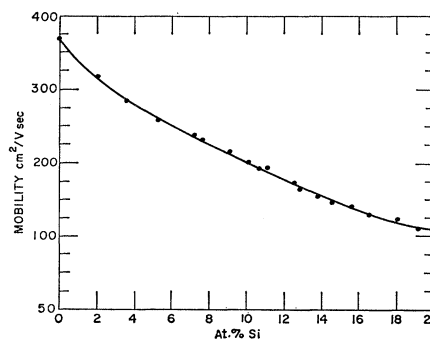


FIG. 4. Experimental values of Hall mobilities for the heavily doped Ge-Si samples ($n \sim 1.1 \times 10^{19} \text{ cm}^{-3}$).

¹² D. M. S. Bagguley, R. A. Stradling, and J. S. S. Whiting, Proc. Roy. Soc. (London) A262, 340, 365 (1961).

range of six or seven atomic percents of silicon, centered about $\text{Ge}_{85}\text{Si}_{15}$, the conduction takes place in both the $\langle 111 \rangle$ and the $\langle 100 \rangle$ sets of valleys, so that the total Seebeck coefficient is

$$Q = \frac{Q_{(111)}n_{(111)}\mu_{(111)} + Q_{(100)}n_{(100)}\mu_{(100)}}{n_{(111)}\mu_{(111)} + n_{(100)}\mu_{(100)}}, \quad (1)$$

where Q , n , and μ are the Seebeck coefficient, the electron concentration and the conductivity mobility in the particular set of spheroids designated by the subscript. In each of the two sets of valleys we have

$$Q = -\frac{k}{e}(-\eta^* + \delta), \quad (2)$$

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi kT}{h^2} \right)^{3/2} m_D^{3/2} F_{1/2}(\eta^*), \quad (3)$$

and

$$\mu = \frac{e}{m_I} \langle \tau \rangle. \quad (4)$$

All parameters refer to a single set of valleys¹⁰; η^* is the reduced Fermi level in units of kT , δ is a parameter which is a function of η^* and of the energy dependence of the scattering relaxation time, $F_{1/2}$ is a Fermi integral and $\langle \tau \rangle$ is the relaxation time averaged over the energy distribution of the carriers. The total density-of-states effective mass is

$$m_D = N_v^{2/3} m_v = N_v^{2/3} (m_l^{1/2} m_t)^{2/3}, \quad (5)$$

where N_v is the number of equivalent valleys (four in the case of the $\langle 111 \rangle$ set, and six in the case of the $\langle 100 \rangle$ set), and m_v is the density-of-states effective mass in a single valley. The inertial effective mass is

$$m_I = 3 \left/ \left(\frac{1}{m_l} + \frac{2}{m_t} \right) \right. \quad (6)$$

Let the energy separation between the $\langle 100 \rangle$ and the $\langle 111 \rangle$ minima be Δ , in kT units (Δ is positive on the germanium side of $\text{Ge}_{85}\text{Si}_{15}$). Then

$$\eta^*_{(111)} - \eta^*_{(100)} = \Delta, \quad (7)$$

and

$$\frac{n_{(111)}}{n_{(100)}} = \frac{m^{3/2}_{D(111)} F_{1/2}(\eta^*_{(111)})}{m^{3/2}_{D(100)} F_{1/2}(\eta^*_{(100)})}. \quad (8)$$

In the range where classical statistics apply Eq. (8) becomes

$$\frac{n_{(111)}}{n_{(100)}} = \frac{m^{3/2}_{D(111)}}{m^{3/2}_{D(100)}} e^{\Delta}. \quad (9)$$

Of particular pertinence to our analysis of the data is the behavior of the effective masses and of the scattering mechanisms, in the $\langle 111 \rangle$ and the $\langle 100 \rangle$ sets of valleys, as functions of alloying. Glicksman^{6,11}

studied the mobilities and the galvanomagnetic effects in the alloy range 0–30 at. % silicon, and concluded that the effective masses in each set of valleys are independent of alloying or of the proximity of the other set of valleys. The values of $m_{l(111)}$ and $m_{t(111)}$ retain the values they have in germanium, while $m_{l(100)}$ and $m_{t(100)}$ retain the values they have in silicon. Equation (8) thus becomes

$$\frac{n_{(111)}}{n_{(100)}} = 0.37 \frac{F_{1/2}(\eta^*_{(111)})}{F_{1/2}(\eta^*_{(111)} - \Delta)}; \quad (10)$$

and the total density-of-states effective mass at the alloy composition where the $\langle 111 \rangle$ and the $\langle 100 \rangle$ minima are equi-energetic, which is given by

$$m_{D(\text{Ge}_{85}\text{Si}_{15})}^{3/2} = m_{D(111)}^{3/2} + m_{D(100)}^{3/2}, \quad (11)$$

assumes the value $m_{D(\text{Ge}_{85}\text{Si}_{15})} = 1.33m_0$. Busch and Vogt¹³ measured the magnetic susceptibilities in a series of germanium-silicon alloys and deduced that a certain average m_v , which they defined, increased slightly as silicon was alloyed with germanium. In the alloy range with which we are concerned, their results are not at variance with Glicksman's conclusion that the effective masses do not change, when the average m_v which they define is recalculated in terms of our Eq. (11).

We turn next to consider the scattering mechanisms which are operative in the alloys. There are four electron-scattering mechanisms which we have to consider: (a) scattering by acoustical phonons,¹⁴ represented by a relaxation time τ_{ph} ; (b) scattering by alloy disorder,^{15,16} represented by τ_{dis} ; (c) scattering by ionized impurities,¹⁴ represented by τ_{ii} ; and (d) intervalley scattering,^{10,14} represented by τ_{iv} .

The mobility data in the ranges 0–10 and above 20 at. % silicon conform to the existence of two scattering mechanisms in each set of valleys: acoustical phonon scattering which is independent of alloying, and alloy disorder scattering which increases with increased alloying. In the case of the lightly doped samples, scattering by ionized impurities is quite small and may be neglected. Both τ_{ph} and τ_{dis} are proportional to $E^{-1/2}$ where E is the electrons' energy. The parameter δ in Eq. (2) for the Seebeck coefficient is a function of the energy dependence of τ , but not of its absolute value. Consequently, although in each set of valleys τ_{ph} is constant while τ_{dis} is proportional to $[x(x-1)]^{-1}$, where x is the atomic fraction of one alloy component, the parameters δ will remain constant with a value of 2 so long as τ_{ph} and τ_{dis} are the two main scattering mechanisms.¹⁷

¹³ G. Busch and O. Vogt, *Helv. Phys. Acta* **33**, 889 (1961).

¹⁴ F. J. Blatt in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 199.

¹⁵ L. Nordheim, *Ann. Physik* **9**, 607, 641 (1931).

¹⁶ A. Amith, *Proceedings of the 7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 393.

¹⁷ V. A. Johnson and K. Lark-Horovitz, *Phys. Rev.* **92**, 226 (1953).

On the basis of the conclusion that $m_{l(111)}$ and $m_{i(111)}$ are independent of alloy concentration, and that the electron scattering in the lightly doped alloys is represented by τ_{ph} and τ_{dis} , so long as the conductivity takes place only in the $\langle 111 \rangle$ set of valleys, we would expect that the Seebeck coefficient Q would be constant in that region, since the electron concentration is fairly constant. The solid curve in Fig. 1 is calculated on this basis and it is in rather good accord with the data. As we enter the region of competition between the $\langle 111 \rangle$ and the $\langle 100 \rangle$ sets of valleys, where Eq. (1) has to be employed, intervalley scattering has to be taken into account. The probability of intervalley scattering is directly proportional to the number of valleys into which a particular electron could be scattered, and that number increases to 9 at $\text{Ge}_{85}\text{Si}_{15}$. Intervalley scattering was discussed by Herring,¹⁰ who showed that τ_{iv} is proportional to $(E-h\nu)^{-1/2}$ or to $(E+h\nu)^{-1/2}$ for emission or absorption of a phonon of frequency ν . This scattering process is strongest where the electron can be scattered from one valley to the next with a small change in energy—i.e., accompanied by the emission or absorption of a low-frequency phonon. In these cases τ_{iv} will have an energy dependence similar to that of τ_{ph} and of τ_{dis} . Glicksman¹¹ showed that although the presence of this type scattering in the competition region was required in order to fit the measured values of the mobilities, the energy dependence of the total τ was approximately $\tau \sim E^{-0.4}$. We conclude, then, that the addition of this mode of scattering in the competition region will not have a significant effect on $\delta_{(111)}$ and $\delta_{(100)}$, and thus on $Q_{(111)}$ and on $Q_{(100)}$. Intervalley scattering will, however, lower $\mu_{(111)}$ and $\mu_{(100)}$. Glicksman expressed the relaxation time τ_{iv} by a trial function with two adjustable parameters which were determined by fitting to the data. The resulting modifications in $\mu_{(111)}$ and in $\mu_{(100)}$ are shown in Fig. 2.

The Seebeck coefficient of Eq. (1) can be calculated now from our knowledge of the carrier concentration ($1.3 \times 10^{15} \text{ cm}^{-3}$), the effective masses, the mobilities $\mu_{(111)}$ and $\mu_{(100)}$ and Eq. (10). The result is the solid curve in Fig. 1. The agreement between the measured values and the calculated one is quite good, especially in view of the many simplifying assumptions which were postulated.

We now turn to consider the case of the series of the heavily doped samples. The noticeable difference between the data in Fig. 3 and the data in Fig. 1 is the tendency of the measured values of Q to decrease as silicon is added to germanium, before they start increasing again in the competition region. Here the scattering by ionized impurities is quite strong, and has to be added to those discussed earlier in the case of the lightly doped samples. We may still assume τ_{ii} , like τ_{ph} and τ_{dis} , is operating independently in the two sets of valleys; and that τ_{iv} is the only relaxation time which connects electrons between the two sets. However, the

energy dependence of ionized-impurity scattering is $\tau_{ii} \sim E^{3/2}$, and, furthermore, it is a relaxation time which is extremely anisotropic.^{18,19} A detailed analysis in this region is unwarranted; it will be very complicated and require many more parameters than are available. However, a qualitative interpretation is quite feasible. In germanium, with an electron concentration of $1.1 \times 10^{19} \text{ cm}^{-3}$, it is possible to derive the Fermi level as well as the ratio of τ_{ii}/τ_{ph} from measurements of the Hall and Seebeck coefficients.¹⁶ The parameter δ will be larger, the larger the relative contribution of τ_{ii} to the total relaxation time,¹⁷ because $\tau_{ii} \sim E^{3/2}$, which means that the more energetic electrons are scattered less. In germanium with this carrier concentration, $\mu_{ph}/\mu_{ii} = 1.36$. In conformity with our assumptions above, τ_{ph} and τ_{ii} remain constant as we alloy silicon with the germanium. However, the alloy disorder mechanism is brought in, and since τ_{dis} has the same energy dependence as τ_{ph} , the relative weight of $\tau_{ii} \sim E^{3/2}$ will decrease as silicon is being added. Consequently, Q will go down even though the effective masses and the carrier concentrations remain unchanged. Since $\mu_{ph,dis}$ is given in Fig. 2 for each set of valleys, we can estimate how the ratio $\mu_{ph,dis}/\mu_{ii}$ changes with alloying and from this how δ and thus Q change. We have adopted this procedure for the transport in the $\langle 111 \rangle$ and the $\langle 100 \rangle$ valleys, independently. The calculated Q is shown by the solid line in Fig. 3. If we had ignored the change in the relative weight of the $\tau_{ii} \sim E^{3/2}$ relaxation time with respect to the combined τ_{ph} and τ_{dis} , then the calculated Q would have been that depicted by the dashed curve in Fig. 3.

IV. CONCLUSION

The measurements of the Seebeck coefficients in n -type Ge-Si alloys have been related to changes of the band structure in terms of effective masses and multi-valley structure and to changes in the relative weights of lattice, alloy, and ionized impurity scattering. The data were explained in terms of the change of the conduction band structure from a set of four valleys along the $\langle 111 \rangle$ directions in reciprocal lattice space to a set of six valleys along the $\langle 100 \rangle$ directions in reciprocal lattice space. Near the alloy composition $\text{Ge}_{85}\text{Si}_{15}$, all ten valleys are equi-energetic, and the Seebeck coefficient showed a peak which corresponded to that maximum in the total density of states. For the very heavily doped samples, the effects of the increase in the importance of lattice and alloy scattering as compared to ionized-impurity scattering were invoked in order to explain why the Seebeck coefficient did not show the increase which was to be expected on the basis of density-of-states considerations alone.

¹⁸ F. S. Ham, Phys. Rev. **100**, 1251 (1955).

¹⁹ V. I. Fistal, E. M. Omelyanovsky, D. G. Andvianov, and I. V. Dahovsky, *Proceedings of the 7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 371, and references therein.