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ULTRASONIC ATTENUATION AND VELOCITY CHANGES IN DOPED *n*-TYPE GERMANIUM AND *p*-TYPE SILICON AND THEIR USE IN DETERMINING AN INTRINSIC ELECTRON AND HOLE SCATTERING TIME

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Recent measurements of the acoustoelectric effect[1] and the absence of acoustic propagation in certain crystalline directions[2] at frequencies of 8.9 kilomegacycles per second and temperatures of 4.2°K, both for doped *n*-type germanium, have shown that there is an acoustic attenuation connected with the exchange of electrons between the $\langle 111\rangle$ valleys of the Fermi energy surface caused by the deformation potential. Quantitative measurements of the attenuation of shear waves in *n* germanium presented here have been used to show that the intervally relaxation time for highly doped materials is in the order of 2×10^{-13} second.

Measurements have also been made for *p*-type silicon doped with 2.5×10^{18} boron atoms per cc which show that similar attenuations occur with the addition of smaller attenuations in directions for which there was no electronic damping for *n* germanium. Corresponding velocity changes have been measured which can be used to evaluate the time τ required for holes to change from one energy surface to the other. Since both processes are relaxation effects, the attenuation in nepers per cm and the internal friction Q^{-1} are given by equations of the form–valid when $\omega\tau \ll 1$ and $(\omega/V)\lambda < 1$, where λ is the mean free electron path–

$$Q^{-1} = \Delta E\omega\tau/E_0; \quad A = Q^{-1}\omega/2V = \Delta E\omega^2\tau/2\rho V^3, \quad (1)$$

where ΔE is the change in the appropriate elastic modulus caused by the strain-produced changes in the energy surfaces, and V is the sound velocity $(E/\rho)^{1/2}$.

Attenuation measurements were made at 480 Mc/sec for two longitudinal waves along $\langle 100\rangle$ and $\langle 110\rangle$, respectively, with the results shown by Fig. 1 for *p*-type silicon. This figure also shows measurements for 300 Mc/sec and measurements of pure samples (doping less than 10^{14} boron atoms per cc) for the same conditions. From the difference between the doped and pure specimens it is obvious that there is a large at-

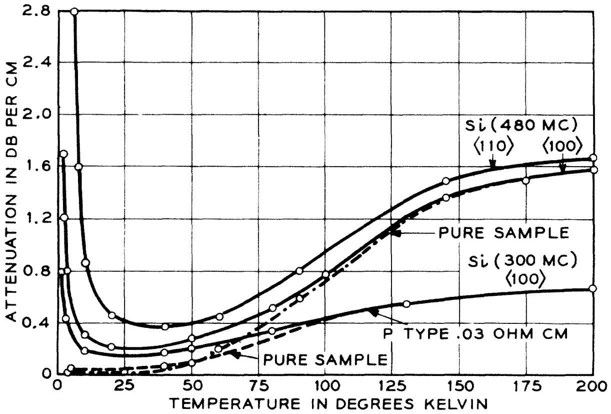

FIG. 1. Attenuation at 300 Mc/sec and 480 Mc/sec for longitudinal waves in *p*-type silicon (doping 2.5 $\times 10^{18}$ boron atoms per cc). Dashed curves show attenuation for pure samples.

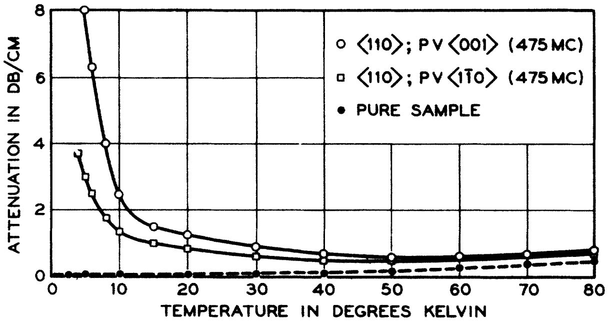

FIG. 2. Attenuation at 475 Mc/sec for two shear waves in doped p-type silicon. PV is the direction of the particle velocity.

tenuation at low temperatures caused by the impurity doping. This loss increases, within the experimental error, proportionally to the square of the frequency. An even larger loss occurs when shear waves are propagated along the ⟨110⟩ direction. Figure 2 shows measurements for the 001 shear polarization and the $1\bar{1}0$ shear polarization. It should be pointed out that the results differ from n germanium, in that there are effects for longitudinal waves along ⟨100⟩ and shear waves along ⟨110⟩ with a polarization along ⟨$1\bar{1}0$⟩, whereas no such effects[2] were observed for germanium.

From the measurements of Figs. 1 and 2, values of $\Delta E\tau$ can be calculated. The values of Table I are for 5°K. A_d is the measured attenuation of the doped material in nepers per cm, and A_p the attenuation of the pure material.

An analysis of the table shows that

$$\Delta c_{11}\tau = 0.0218, \quad \Delta c_{12}\tau = -0.0119 \cong -\tfrac{1}{2}\Delta c_{11}\tau,$$
$$\Delta c_{44}\tau = 0.0895. \tag{2}$$

The last measurement gives a check value,

$$\tfrac{1}{2}(0.0218 - 0.0119) + 0.0895 = 0.0994, \tag{3}$$

compared to the measured value of 0.1.

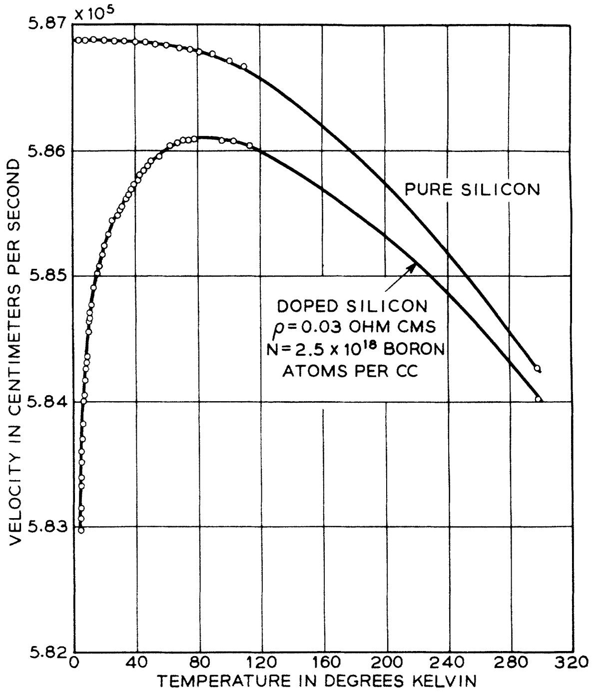

FIG. 3. Velocity of shear waves along ⟨110⟩, polarization ⟨100⟩, for pure and doped (2.5×10^{18} boron atoms per cc) silicon. Velocity measured at 20 Mc/sec.

By using a pulse superposition method,[3] velocity measurements of a sufficient accuracy have been made to determine the difference Δc_{44} between the pure and the doped samples. Figure 3 shows the velocity measurements for a shear wave along the ⟨100⟩ direction. From these measurements the values of Δc_{44} are directly determined. Table II shows values measured from 5°K to 100°K. The second column shows the measured attenuation difference in nepers per cm between the pure and doped samples, while the last column shows the corresponding relaxation time.

For most of the temperature range, the relaxation time is approximately constant. At low temperatures, the relaxation time τ increases

Table I. Values for the three possible modulus changes, times the relaxation time τ, for p-type silicon doped with 2.5×10^{18} boron atoms per cc.

Propagation direction	Particle direction	Elastic modulus	Velocity (cm/sec)	$A_d - A_p$ (Np/cm)	$\Delta E\tau$
100	100	c_{11}	8.49×10^5	0.068	$\Delta c_{11}\tau = 0.0218$
110	001	c_{44}	5.86×10^5	0.86	$\Delta c_{44}\tau = 0.0895$
110	$1\bar{1}0$	$\frac{1}{2}(c_{11}-c_{12})$	4.69×10^5	0.317	$(\Delta c_{11}-\Delta c_{12})\tau = 0.0337$
110	110	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	9.175×10^5	0.25	$[\frac{1}{2}(\Delta c_{11}+\Delta c_{12})+\Delta c_{44}]\tau = 0.1$

Table II. Modulus change, attenuation difference, and relaxation time for *p*-type silicon doped with 2.5 × 10^{18} boron atoms per cc.

Temp (°K)	Δc_{44} (10^9 dyn/cm^2)	$A_d - A_p$	τ (10^{-12} sec)
5	10.5	0.84	8.5
10	6.47	0.23	3.7
20	4.54	0.12	2.8
30	3.8	0.075	2.3
50	2.56	0.046	1.8
80	2.02	0.035	1.8
100	1.8	0.029	1.7
300	0.74	0.014	2

approximately according to an equation of the form

$$\tau = 1.6 \times 10^{-12} \exp(\Phi/kT) \text{ sec},$$

where Φ is about 0.00075 eV = 17 cal/mole.

The interpretation of the modulus and attenuation effect is much simpler in *n*-type material for which the multivalley energy surfaces apply. For *n* germanium, Keyes[4] has shown that the change in modulus Δc_{44} is given in the degenerate and normal regions by the equations

$$\Delta c_{44_0} = -\tfrac{4}{3}(\tfrac{4}{3}\pi)^{2/3} m^* \Xi_u{}^2 N^{1/3}/h^2,$$

$$\Delta c_{44} = \Delta c_{44_0}(\tfrac{2}{3}T_D/T) = N\Xi_u{}^2/9kT, \tag{5}$$

where T_D, the degeneracy temperature, is

$$T_D = (3/32\pi)^{2/3} h^2 N^{2/3}/2m^*k. \tag{6}$$

In these equations, m^* is the effective mass ($0.12\, m_0$ for Ge), Ξ_u is the deformation potential, N the number of impurity atoms per cc, h is Planck's constant, k Boltzmann's constant, and T the absolute temperature. If the deformation potential is determined from the related piezoresistance effect

$$m_{44} = \frac{1}{9}\frac{\Xi_u}{kT}\left(\frac{\mu_\parallel - \mu_\perp}{\mu_0}\right) = \frac{1}{9}\left(\frac{\Xi_u}{kT}\right)(-1.39) \text{ for Ge}, \tag{7}$$

we find from[5] $m_{44} = -93$ at 300°K that $\Xi_u = 16$ eV. For lower temperatures, $\Xi_u = 20$ eV appears to be more probable. Hence for a doping of 3.5 $\times 10^{19}$ arsenic atoms per cc, the calculated value of Δc_{44} at absolute zero is -2.9×10^{10} dyn/cm^2 compared to a measured value[6] of -3.76×10^{10} dyn/cm^2.

Since no measurements have been made of the relaxation time in germanium for such high doping, attenuation measurements were made at 480 Mc/sec for a germanium sample doped with 3×10^{19} arsenic atoms per cc. The difference between the measured attenuation of the doped and a pure sample is shown by the second column of Table III. The measured modulus change[6] is shown by the third column, while the last column shows the corresponding relaxation time τ. The relaxation time appears to be nearly constant with a value $\tau \cong 2 \times 10^{-13}$ second. A measurement was also made for a specimen with a doping of 10^{18} arsenic atoms per cc, yielding a $\tau \cong 4 \times 10^{-13}$ second.

Table III. Attenuation difference, modulus change, and relaxation time for *n*-type germanium doped with 3×10^{19} arsenic atoms per cc.

Temp (°K)	$A_d - A_p$ (Np/cm)	Δc_{44} (10^{10} dyn/cm^2)	τ (10^{-13} sec)
4.2	0.165	3.76	2.2
10	0.165	3.76	2.2
40	0.16	3.75	2.15
77	0.16	3.7	2.1

The relaxation time τ is the average time between collisions with phonons or impurity atoms of a sufficient strength to cause a change in valleys. At low temperatures, where impurity collisions dominate, it requires a near contact to produce an intervalley collision. In the low doping range, acoustoelectric voltages[1] have shown that the scattering rate S.R. (which is the inverse of the relaxation time τ) is given by the equation

$$\text{S.R.} = 1/\tau \cong 4 \times 10^{-6} N \text{ sec}^{-1}, \tag{8}$$

where N is the number of doping atoms per cc. As the doping increases, the ratio of the intervalley collisions to total collisions increases. For a doping of 10^{18} arsenic atoms per cc, if we compare 4×10^{-13} second with the total scattering time

$$\tau_0 = \sigma m^*/Ne^2 \cong 6 \times 10^{-14} \text{ second}, \tag{9}$$

it is found that one in about seven collisions results in a transfer between energy surfaces. For a larger doping, it appears that the scattering rate $(1/\tau)$ approaches a constant limit. Since τ_0 has not been measured in this range, it is not certain whether the ratio of intervalley to intravalley collisions remains constant.

p-type silicon has three energy surfaces and three types of holes.[7] Two of the energy surfaces in the valence band are degenerate, in that they make contact at the central zone point. Cyclotron resonance experiments show that the average mass of a hole in the V_1 band is $0.49\,m_0$, while that in the V_2 band is $0.16\,m_0$, where m_0 is the mass of the electron. The third band is spherical but lower in energy by 0.035 eV, so that at the low temperatures involved in these measurements, almost all the holes will be in the V_1 and V_2 bands. The relative numbers of holes in the two bands is proportional to $(m_1/m_2)^{3/2} = 5.4$. Hence, about 85% of the holes are in the V_1 band and 15% in the V_2 band.

It was first pointed out by Adams[8] that a piezoresistance would result due to the separation of the energy surfaces by the two types of shearing strains that actuate the $\langle 111\rangle$ and $\langle 100\rangle$ valleys of the n-type materials. The most complete calculations are those of Pikus and Bir,[9] who derive a formula for the piezoresistance effect:

$$m_{11} = -2m_{12} = -\frac{3}{5}\frac{Bb}{\overline{B}kT}\left(\frac{\sigma_{02}-\sigma_{01}}{\sigma_0}\right),$$

$$m_{44} = -\frac{3}{20}\frac{Dd}{\overline{B}kT}\left(\frac{\sigma_{02}-\sigma_{01}}{\sigma_0}\right), \tag{10}$$

where B and C are values determining the curvature[7] of the energy surfaces, $\overline{B} = (B^2 + \frac{1}{5}C^2)^{1/2}$, $D = (3B^2 + C^2)^{1/2}$, b and d are deformation potential values, and $(\sigma_{02} - \sigma_{01})/\sigma_0 = [1 - (m_1/m_2)^{1/2}]/[1 + (m_1/m_2)^{1/2}] = -0.272$ is the difference in conductivities produced by the two types of holes divided by their sum. With the values[7] of $B = 1.4$, $C = 3.7$, and $m_{44} = 110$ at 300°K,[5] it requires a deformation potential value of $d = 34$ eV.

The only calculation of the change in modulus in p-type material is that by Keyes[4] using a simplified model. In the low-temperature degenerate limit, this results in a value

$$\Delta c_{44} = -\tfrac{1}{5}(\tfrac{8}{3}\pi)^{2/3} m^* \Xi^2 N^{1/3}/h^2. \tag{11}$$

The value obtained by using $\Xi = 34$ eV is 2.4 larger than the largest measured value of Fig. 3. The activation energy and the larger relaxation time indicate that the scattering process in p-type material is different from the scattering (bumping) process for n germanium. It appears likely that the hole is captured by the impurity and has to change energy levels in changing energy surfaces. The tunneling frequency for such a process is

$$f_0 = \frac{\epsilon_2 - \epsilon_1}{h} = \frac{1.20\times10^{-15}}{6.62\times10^{-27}} = 1.83\times10^{11}\ \text{cycles/sec.} \tag{12}$$

The time of a cycle is 5.6×10^{-12} second, and the measured scattering time $\tau \cong 1.6\times10^{-12}$ second indicates that at high temperatures the time between capture and release is a quarter of a cycle.

On account of the large deformation potential, the separation of the energy surfaces may be due to the residual shearing strain produced by the substitution of boron for silicon. Boron has a smaller radius than silicon, and moreover is bonded strongly to only three of the adjacent silicons. Hence a shearing strain of the type producing the largest effect of Table I will be induced in the region of the impurity atom. Since the deformation potential is 34 eV, it requires a strain of only 2.2×10^{-5} to produce the separation of $\Phi = 0.00075$ eV observed. With this permanent separation, a hole will require the activation energy Φ to change surfaces.

Since all four positions of the hole in the unit cell are equally probable, the average shear strain is zero. The shape of the elastic-constant–temperature curve of Fig. 3 indicates that the light-hole surface is displaced a larger amount below the resulting Fermi surface than is the heavy-hole surface. At very low temperatures, the holes tend to congregate in the light-hole surface, and the modulus change, due to strain, increases.

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