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Low-Temperature Impurity Conduction in *n*-Type Silicon*

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Hall coefficients and electrical resistivities were measured down to liquid helium temperatures for silicon specimens containing about 10^{17} phosphorus impurities per cm^3 and about 10^{15} boron impurities per cm^3. The density of minority impurities was determined during the preparation of the ingots, rather than deduced from the electrical measurements themselves. The results are extremely sensitive to the density of minority impurities. They are discussed in relationship to the theories of Conwell, Mott, and Price.

I. INTRODUCTION

MEASUREMENTS on heavily doped samples of germanium[1–4] and silicon[5–7] have shown that, at very low temperatures, the Hall coefficient goes through a maximum and the conductivity varies less rapidly with temperature than it did at higher temperatures. When the impurity atoms are very close together their electronic wave functions overlap and the electrons can move freely from one impurity center to another.[8] The impurity level widens into a broad band in which conduction can take place, and the process is correctly described as "impurity band conduction." However, there is a range of intermediate impurity concentrations for which the overlap of the wave functions is insufficient for the above explanation to be adequate,[2,9] but which nevertheless shows an anomalous low-temperature behavior, and this is the phenomenon with which we are concerned in the present paper. Under these circumstances the conductivity is found to be sensitive to the degree of compensation, which is very readily explained by the theories advanced by Conwell[9] and Mott[10] and developed by Price.[11]

A satisfactory experimental verification of the Conwell-Mott theory is possible only if the density of minority impurities is known. This is normally deduced from the data on Hall coefficients and conductivities at higher temperatures, but there are several uncertainties in this procedure. In the present research an attempt was made to fabricate the silicon specimens in such a way that the density of minority impurities was known in advance.

II. PREPARATION OF SPECIMENS

Two silicon ingots, which we shall henceforth refer to as Si 215 and Si 216, were prepared for us by the Bell Telephone Laboratories. Each ingot was pulled to a length of $\frac{3}{8}$ inch from a separate melt containing only boron, which was to be the minority impurity. Phosphorus, which was to be the majority impurity, was then added in an amount calculated to give an impurity concentration of about 10^{17} cm^{-3}, the rest of the crystal was pulled and wafers were cut 1 inch beyond the point at which phosphorus was added in the case of Si 216 and $1\frac{1}{4}$ inch to $1\frac{1}{2}$ inch beyond this point in the case of Si 215. The room temperature resistivity of the first $\frac{3}{8}$-inch section, which contained only boron, was measured and the boron concentration deduced from the tables published by Prince.[12] Since the segregation coefficient of boron in silicon is just slightly less than one, it was assumed that the boron concentration was almost uniform throughout the entire ingot. This assumption implies that the addition of phosphorus to the melt in no way affected the value of the segregation coefficient; that is, the profile of boron concentration along the axis of crystal growth was not changed by the presence of the phosphorus.

One wafer from each ingot was cut by the technique described by Swartz[6] in such a way that the current flow was in the [110] direction. It was ground with aluminum oxide abrasive, cleaned with distilled water and acetone, rhodium plated and soldered as described by Swartz. Two other wafers, with the current flow in the [100] direction, were cut to a wider contact area shape by Philco Corporation, utilizing a Sheffield Cavitron, an ultrasonic cutter. The abrasive was boron carbide, 240 grit weight. These last two samples were then prepared for measurements in the same way as the first two. We therefore made measurements on four samples: Si 215*A* and Si 216*A* which were cut on the [110] direction, and Si 215*B* and Si 216*B* which were cut on the [100] direction. Their shapes and dimensions are shown in Fig. 1.

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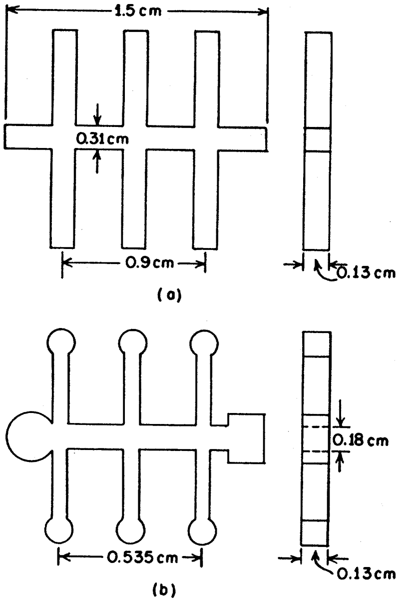

FIG. 1. Shapes and dimensions of silicon samples. (a) Si 215*A* and Si 216*A*. Thickness = 0.13 cm; (b) Si 215*B* and Si 216*B*. Thickness = 0.13 cm.

The oxygen content of the samples was determined from the infrared absorption at 9 μ[13] and was the same within experimental error for both ingots, being approximately 1.0×10^{18} atoms cm^{-3}.

III. EXPERIMENTAL DETAILS

The measuring apparatus was essentially the one built and described by Swartz,[6] but we made the following minor modifications. To achieve sufficient sensitivity in the temperature range of interest, where impedances of 10^9 to 10^{10} ohm were encountered, the galvanometer was replaced by an Applied Physics Corporation vibrating reed electrometer, Model 30*S*, borrowed from the Philco Corporation. To take full advantage of the electrometer, all the components of the measuring circuit were replaced by the highest resistance components available—the bakelite selector switch was replaced by a ceramic one, the two-position reversing switches were replaced by high-voltage copper knife edge switches to reduce contact potentials, the case of the *K*2 potentiometer was removed from the circuit and A.W.G. 36 teflon-covered wires were used for the leads into the cryostat. The leakage resistance was then of the order of 10^{11} ohm. To minimize ac pick up the sample container heater was converted to dc.

Although no attempt was made to measure departures from Ohm's law, all measurements were made with electric fields less than 3 volts cm^{-1}, which is sufficiently beneath the breakdown field to guarantee linear behavior. A magnetic field of 3500 oersteds was used for all Hall measurements.

IV. RESULTS AND DISCUSSION

The Hall coefficients are shown in Fig. 2 and the resistivities in Fig. 3. Because of the very high impedances of the specimens, it was difficult to make Hall coefficient measurements at the lowest temperatures. The difference in slope at the low-temperature end for Si 215*A* and Si 215*B* may not therefore be significant. Table I collects together various data for the four specimens. The density of majority impurities, N_D, was obtained from the room temperature resistivity using the table of Backenstoss.[14] The density of minority impurities, N_A, was measured while the specimens were being made, as explained previously.

The outstanding feature of our results is their extreme sensitivity to the density of minority impurities. The ratio of N_A for the two ingots is 4.4, but at 20°K the ratio of Hall coefficients is about 200, and below 20°K the ratio of resistivities is about 20.

Below 15°K the curves of Fig. 3 are very accurately straight lines, with no definite indication of the curvature found by Blakemore[4] for indium-doped germanium. An activation energy ϵ can be defined by the equation

$$\rho=Ae^{\epsilon/kT}. \tag{1}$$

The experimental values of ϵ are given in Table I.

Conwell[9] has proposed the following mechanism for low-temperature conduction in samples with these in-

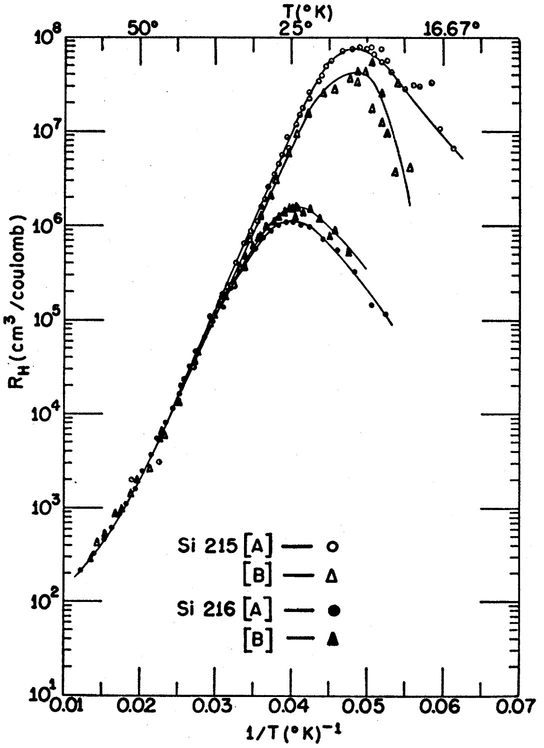

FIG. 2. Hall coefficients plotted against the reciprocal of the absolute temperature.

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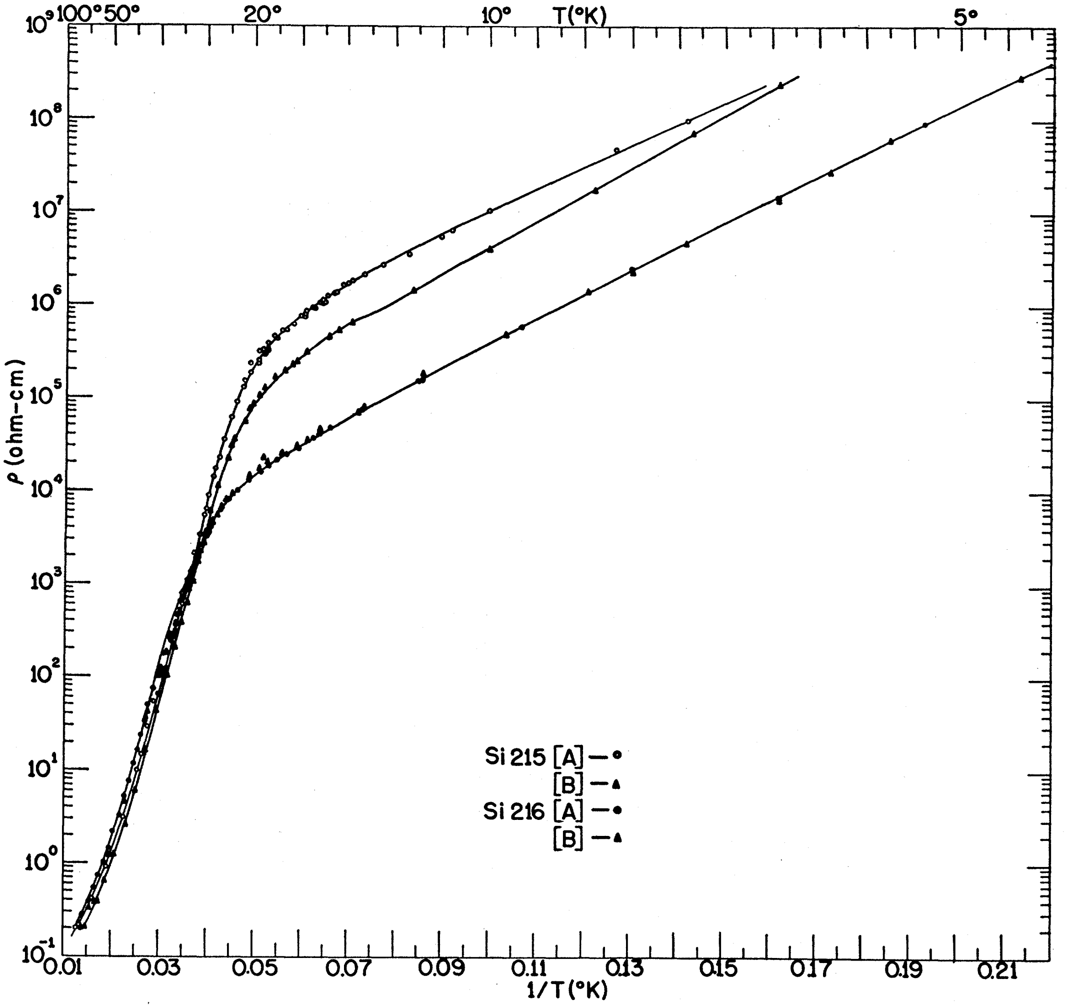

FIG. 3. Specific resistivities plotted against the reciprocal of the absolute temperature.

termediate impurity concentrations. Near 0°K N_A acceptors per cm^3 accept electrons from donor atoms, producing N_A positively charged donors and leaving $N_D - N_A \gg N_A$ neutral donors. The overlap of the donor atom wave functions is sufficient to enable the hole on an ionized donor to jump to a neighboring neutral donor and hence to diffuse throughout the whole material. This gives a mobility which can be calculated and is found to vary as $1/T$. Mott[10] has pointed out that a hole on a positively charged donor site adjacent to a negatively charged acceptor site has an electrostatic potential energy of the order of $-e^2N_D^{\frac{1}{3}}/K$ as compared with $-2e^2N_A^{\frac{1}{3}}/K$ when it is furthest away from an acceptor (K is the dielectric constant of the silicon lattice). Since $N_D \gg N_A$ the hole can become trapped in the vicinity of the acceptor. Taking into account the random arrangement of impurity sites and the nature of the statistics, Price[11] has derived from this model an activation energy

$$\epsilon_P = 0.45(4\pi/3)^{\frac{1}{3}}(N_D^{\frac{1}{3}} - 2N_A^{\frac{1}{3}})e^2/K. \qquad (2)$$

TABLE I. Collated data for all four specimens.

Specimen	Room temperature resistivity ohm-cm	Room temperature Hall coefficient cm^3 coulomb^{-1}	Density of majority impurities N_D cm^{-3}	Density of minority impurities N_A cm^{-3}	Activation energy ϵ (ev) Experimental	Activation energy ϵ_P (ev) Mott model
Si 215*A*	0.091		1.1×10^{17}	0.8×10^{15}	0.0050	0.0027
Si 215*B*	0.063	43	1.9×10^{17}	0.8×10^{15}	0.0058	0.0035
Si 216*A*	0.062	43	1.9×10^{17}	3.5×10^{15}	0.0051	0.0025
Si 216*B*	0.051		2.5×10^{17}	3.5×10^{15}	0.0051	0.0030

Values of ϵ_P are included in Table I and are seen to be smaller than the experimental activation energies by a factor of almost two. However, as Price was careful to point out, there are many uncertainties in the theoretical development of the Mott model.

Finally, we draw attention to the fact that our experimental activation energies are derived empirically from the specific resistivity, which depends upon both the density of carriers and the mobility, so that, if the mobility is a strong function of temperature, the activation energy relevant to the density of carriers is different. If, for example, the mobility were to vary as $1/T$, as suggested by Conwell,[9] then the activation energies for the density of carriers alone would be about 15% larger than the values we have quoted.

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Pulsed Nuclear Resonance Spectroscopy*

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A technique for the detection of weak nuclear resonance interactions in solids is carried out by a pulsed method which obtains nuclear double resonance. The resonance of the unknown species to be detected does not require a Boltzmann population difference in spin orientation, but must have a sufficient dipole-dipole interaction with a second spin species. At resonance, a single 180° pulse reorients the unknown spins at the time of the 180° pulse in the 90°–180° pulse sequence necessary to obtain the observed spin-echo signal of the second species. A reduction of the spin-echo signal signifies double resonance due to changes in local dipolar fields, coupled to the observed spins, which scrambles their precessional phases. Nuclear quadrupole coupling interactions of K, Cs, and Rb isotopes are measured in the chlorates of these ions, where the Cl^{35} nucleus provides the observed nuclear quadrupole echo. An analysis is presented for the case of low concentration of unknown spin species. Double quantum transitions and special properties of nuclear quadrupole spectra are observed.

A SENSITIVE method for the detection of weak nuclear resonance interactions is successful in solids where strong spin-echo signals can be observed. This is carried out by observing the change in spin-echo dipolar relaxation of a spin group A, due to the effect of the pulsed resonance of a nuclear neighbor (spin group B) obtained in the same crystal.[1] The particular experiments reported here deal with pure quadrupole resonance,[2] but the principles involved apply to any spin resonance system satisfying certain requirements. At all times, the relaxation of the A spins is observed in terms of the attenuation of a two-pulse 90°–180° spin-echo amplitude. The B spins are subjected to double resonance by the action of a single pulse. They may also undergo a continuous rf (radio-frequency) excitation,[3] which is less effective and hence has not been used for the purposes of spectroscopy reported here. The A spins are particularly sensitive to any disturbance of the Larmor frequency and phase relationships which are necessary for spin-echo formation. For a given time spacing τ between 90° and 180° pulses, the echo amplitude at time 2τ for the A spins will correspond to a certain degree of phase memory. If the A-B dipole-dipole coupling is modulated or suddenly changed by double resonance, phase relations are upset and the echo amplitude is modified. In the case of pulsed double resonance in solids, the echo is reduced in amplitude.

I. PULSED DOUBLE RESONANCE IN LIQUIDS

The effect of pulsed double resonance is clearly indicated by the study of proton (A-spin) echoes coupled to phosphorus nuclei (B spins) in an aqueous solution of phosphorous acid, $HPO(OH)_2$. The indirect spin-spin interaction occurs between H and P nuclei in the HPO group, described by $J\mathbf{I}_H\cdot\mathbf{I}_P$ in frequency units, where $\mathbf{I}$ is the spin operator, and $J/2\pi=708$ cps (cycles per

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