

Electrical Properties of Near-Degenerate Boron-Doped Silicon

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Measurements of extrinsic resistivity and Hall effect have been carried out for a group of single crystals of silicon containing a wide range of boron concentration, with particular stress on samples in the near-degenerate range, 10^{18} to 10^{19} boron atoms per cm^3 . The anomalous Hall mobility effect previously observed by Morin and Maita in silicon was studied in finer detail over the temperature range 25°K to 300°K. For degenerate samples the 300°K Hall mobility is approximately 46 $\text{cm}^2/\text{volt sec}$.

INTRODUCTION

AN extensive study of the electrical properties of single-crystal silicon containing a wide range of boron and arsenic impurities has been made by Morin and Maita,¹ yielding values of the forbidden band gap, the ionization energies of these impurities, the lattice scattering mobility dependence on temperature, and the Hall mobility dependence on impurity concentration. An anomalous low-temperature behavior of the Hall mobility of several of the boron- and arsenic-doped samples suggested that impurity band conduction might be occurring at low temperatures with low-mobility charge carriers. Impurity band conduction has been experimentally observed in germanium² at temperatures of less than 10°K. The temperature at which impurity band conduction becomes experimentally observable shifts toward room temperature with increasing impurity concentration. The data reported in this paper were principally taken on samples in the near-degenerate range of silicon with impurity concentrations of 10^{18} to 10^{19} per cm^3 . Measurements to 25°K were sufficient to observe the Hall mobility anomaly.

METHOD

The single crystals used in this experiment were prepared by the Czochralski technique. A highly concentrated boron-silicon zone melt was used as the doping material³ and added to the melt in weighed quantities before each crystal was pulled. Samples were cut transverse to the crystal axis with approximate dimensions $2.5 \times 2.0 \times 10$ mm. Phosphor bronze springs were used in the sample holder to make contact to rhodium-plated areas on the etched samples. The sample holder was glued to a thin mica sheet held against a copper backing strip, the latter in turn being coupled through a heater strip and stainless steel heat leak to a liquid nitrogen or liquid hydrogen reservoir in a cryostat. The Hall field was provided by a 900-gauss permanent magnet which could be rotated through 360° about the sample. Voltages were measured with a vibrating reed

electrometer, and the temperature with a potentiometer and calibrated copper constantan thermocouple.

DATA AND RESULTS

Figures 1 and 2 are plots of the extrinsic resistivity and Hall coefficient as a function of the reciprocal of the Kelvin temperature. Note the rapid change in electrical properties between samples 51D and 120H. Their impurity concentrations differ by less than a factor of four at room temperature. Hole concentrations shown in Fig. 3 were calculated from the Hall data using the relation $p = 1/R_H e$ throughout the concentration range.

Hall mobility, taken as R_H/ρ , is given as a function of temperature in Fig. 4. Curves obtained by Morin and Maita¹ are plotted in the same figure for comparison.⁴ For the purer samples, the data in this report give steeper slopes, but lower room temperature mobilities⁵; for sample RR48A, $\mu_H \propto T^{-2.9}$. The data reported here were taken at a constant field of 900 gauss; a possible dependence of Hall coefficient, and hence Hall mobility, on magnetic field was not investigated.⁶ The positive slopes in the Hall mobility curves for crystal sample 51D and Morin and Maita's sample 141 indicate a mobility temperature dependence greater than the $\frac{3}{2}$ power characteristic of ionized-impurity-scattering mobility.⁷ Neutral-impurity scattering⁸ could not give rise to such a rapid drop in mobility at low temperatures.

The model of impurity-band conduction described by Hung and Gliessman² can be characterized as follows. Conduction in a p -type semiconductor can take place not only in a valence band but also in an acceptor impurity band. At extremely low impurity concentrations, there is essentially no overlap of impurity-atom wave functions and hence no impurity banding. With increasing concentrations, the larger overlap of wave functions will cause a broadening of the impurity band. For large impurity concentrations, the conductivity in

⁴ Net carrier concentrations given by Morin and Maita for their samples are: $M 127 - 7.0 \times 10^{14}$; $M 117 - 2.4 \times 10^{16}$; $M 119 - 2.0 \times 10^{17}$; $M 141 - 1 \times 10^{18}$; $M 125 - 1.5 \times 10^{19}$.

⁵ P. P. Debye and T. Kohane, *Phys. Rev.* **94**, 724 (1954).

⁶ Willardson, Harman, and Beer, *Phys. Rev.* **96**, 1512 (1954).

¹ F. J. Morin and J. P. Maita, *Phys. Rev.* **96**, 28 (1954); see also G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

² H. Fritzsche and K. Lark-Horowitz, *Physica* **20**, 834 (1954); C. S. Hung and J. R. Gliessman, *Phys. Rev.* **96**, 1226 (1954).

³ F. H. Horn, *Phys. Rev.* **97**, 1521 (1955).

⁷ E. Conwell and V. F. Weisskopf, *Phys. Rev.* **77**, 388 (1950); H. Brooks, *Phys. Rev.* **83**, 879 (1951); P. P. Debye and E. M. Conwell, *Phys. Rev.* **93**, 693 (1954).

⁸ C. Erginsoy, *Phys. Rev.* **79**, 1013 (1950).

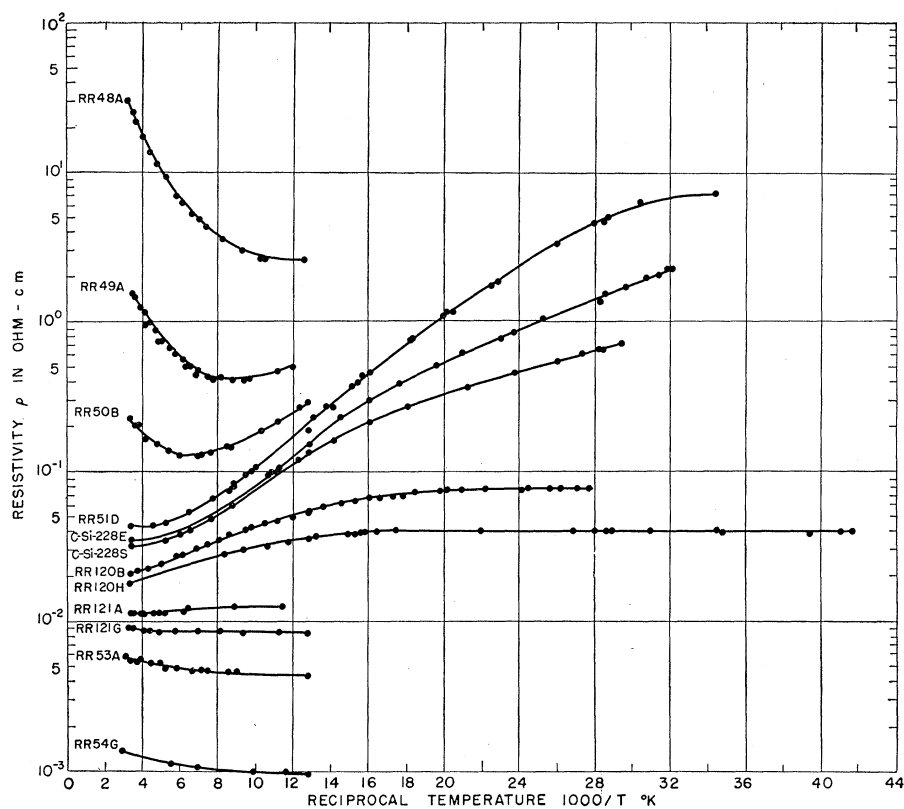


FIG. 1. Extrinsic resistivity of boron-doped silicon samples as a function of reciprocal temperature. The curve for sample RR51I almost overlaps that for C-Si-228E and is omitted for clarity.

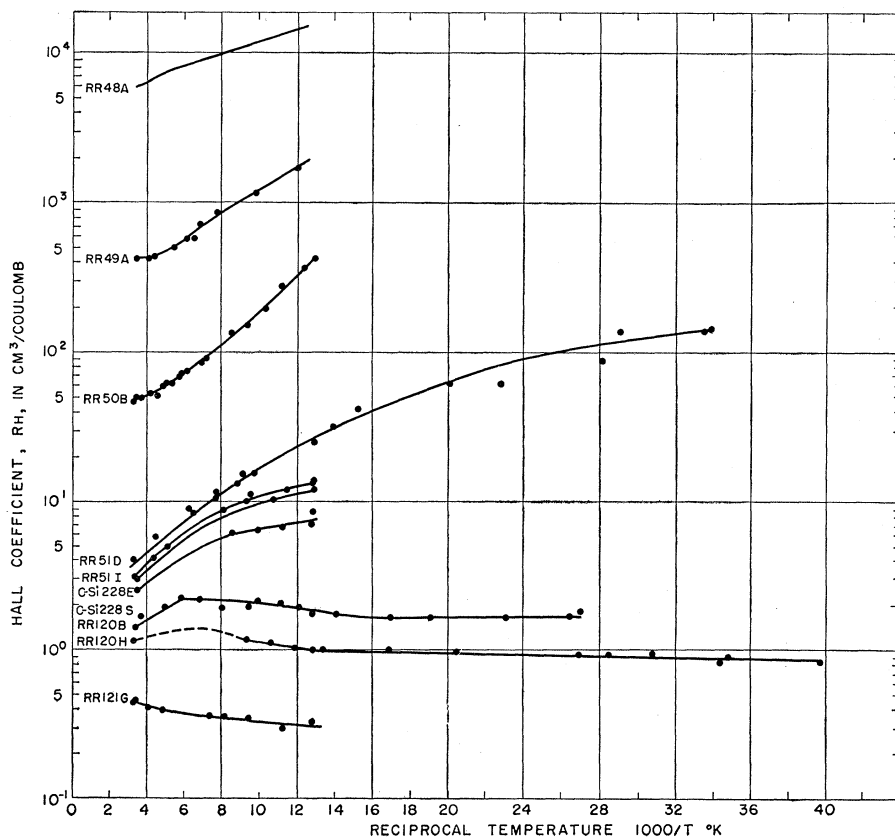


FIG. 2. Hall coefficient of boron-doped silicon samples as a function of reciprocal temperature.

the impurity band can become comparable to that in the valence band at sufficiently low temperatures. When the impurity concentration becomes great enough, the impurity band formed will overlap the valence band and a simple model of two parallel conducting bands will not be valid.

The question of the sign of the charge carrier in the impurity band is not fully settled. In germanium,² no change in the sign of the Hall coefficient is observed over the temperature range in which impurity band conduction dominates the conductivity process, leading to the conclusion that in an acceptor impurity band the charge carriers are holes. The present data and that of Morin and Maita¹ for silicon also indicate no change in Hall coefficient. For samples *RR120B* and *RR120H*, resistivity and Hall coefficient are nearly temperature independent from 70°K to ~30°K, indicating Fermi degeneracy and conduction by holes in the acceptor

TABLE I. Room-temperature data for boron-doped silicon samples

Crystal	Sample ^a	Cryostat data 300°K				Conductivity ^b cm ² /volt sec
		Resistivity ohm-cm	Hall coefficient cm ³ /Coulomb	Hall mobility cm ² /volt sec	Net hole concentration cm ⁻³	
<i>RR55</i>	<i>G</i>	0.0014				46
<i>RR54</i>	<i>A</i>	0.0053				47
<i>RR53</i>	<i>A</i>	0.0092				46
<i>RR52</i>	<i>A</i>	0.0090	0.44	49	1.4×10^{19}	53
<i>RR121</i>	<i>A</i>	0.013	0.55	49	1.1×10^{19}	
<i>RR120</i>	<i>H</i>	0.018	1.16	65	5.4×10^{18}	
	<i>B</i>	0.020	1.43	72	4.4×10^{18}	
	<i>A</i>	0.020	1.48	74	4.2×10^{18}	
<i>C-Si-228</i>	<i>S</i>	0.033	2.57	78	2.4×10^{18}	
	<i>E</i>	0.035	3.12	89	2.0×10^{18}	
	<i>I</i>	0.037	3.07	82	2.0×10^{18}	
<i>RR51</i>	<i>D</i>	0.043	3.7	86	1.7×10^{18}	
	<i>B</i>	0.049	3.3	78	1.6×10^{18}	101
	<i>A</i>	0.225	48	213	1.3×10^{17}	202
<i>RR49</i>	<i>A</i>	1.65	430	260	1.45×10^{16}	288
<i>RR48</i>	<i>A</i>	26	6000	230	1.0×10^{15}	

^a Samples marked *A* are taken from transverse cross sections approximately one-third way down the crystal; other samples are from cross sections further down the crystal.

^b Computed from data of Horn. See references 3 and 10.

impurity bands. The crossover of mobility curves for these samples may perhaps be accounted for by an increase in hole mobility in the impurity band with increasing acceptor concentration. For samples *RR51D* and *M141*, the data point to the possibility that the Hall mobility will become zero between 10 to 20°K due to a sign change in Hall coefficient. This possibility is supported by the Seebeck effect data of Geballe and Hull⁹ which shows a sign change in the thermoelectric power of sample *M141* at 19°K. Their data indicate that electrons are the charge carriers in the acceptor impurity band.

The ionization energy for the boron impurity level has been computed for sample *RR50B* (impurity concentration $\sim 10^{17}$ cm⁻³) from the Hall data with best fit for $E = 0.044$ eV and hole mass $= 0.8M_e$, in agreement with previous work.¹ Since the slope of the Hall curve for sample *RR51D* (impurity concentration $\sim 10^{18}$ cm⁻³)

⁹ T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

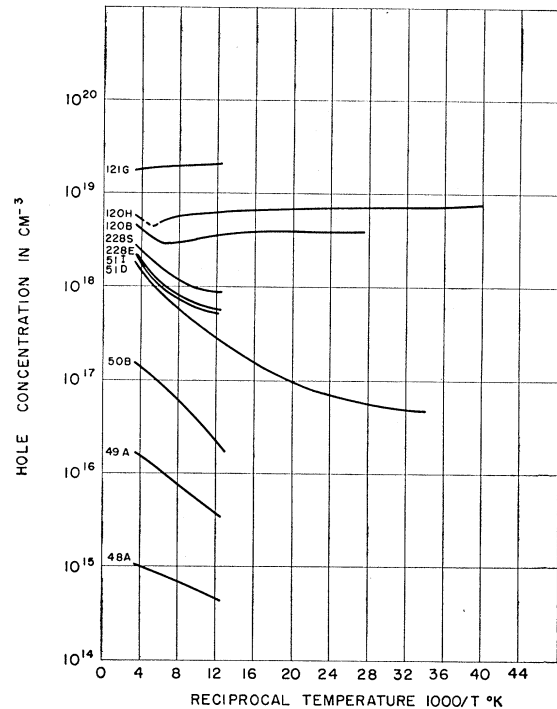


FIG. 3. Charge carrier concentration of boron-doped silicon samples as a function of reciprocal temperature.

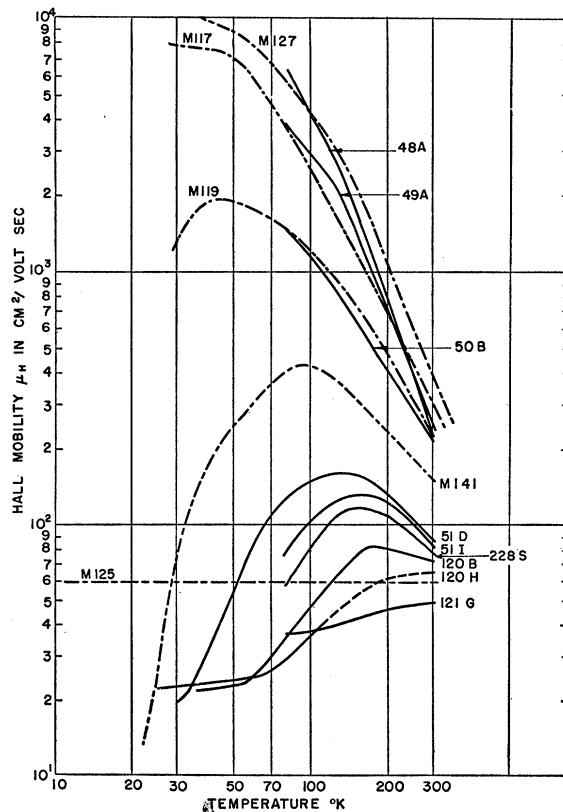


FIG. 4. Hall mobility for boron-doped samples as a function of temperature. Dashed lines refer to samples (composition given in footnote 4) previously measured by Morin and Maita.

in Fig. 2 is changing with temperature, a unique ionization energy cannot be determined. For the temperature range 50°K to 150°K, best fit is given by $E=0.020$ ev with a hole mass $=0.5M_e$. For more heavily doped crystals, degeneracy sets in at higher temperatures and the ionization energy becomes zero.

Table I gives the room-temperature cryostat data with mobility and net hole concentration calculated for each sample. Also given are conductivity mobilities computed from the data of Horn.¹⁰ Carrier mobility

¹⁰ The mobilities tabulated in Table III of reference 3 were recomputed from resistivities as listed there but assuming different boron atom concentrations, based on chemical analysis of crystal RR55 grown directly from the boron-silicon doping material. Chemical analyses of the boron content of crystals RR54 and RR55 are not consistent with the weights of doping material

appears to be constant in the degenerate range at $46 \text{ cm}^2/\text{volt sec}$.

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used in growing these crystals. The concentrations given by Horn were based on the analysis of crystal RR54, but better agreement of net hole concentration computed from Hall effect data and the boron atom concentration is obtained when crystal RR55 is used as the standard.

Mean Free Path for Discrete Electron Energy Losses in Metallic Foils*

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The discrete energy losses observed when a beam of electrons passes through a thin foil have been studied as a function of incident energy. Foils of Al, Mg, and Cu ranging in thickness from 14 to $85 \mu\text{g}/\text{cm}^2$ have been bombarded with electrons of energies 25 to 115 kev. Losses appear at multiples of 14.9 ev and 10.7 ev respectively for Al and Mg whereas only one loss is found in Cu at 22.6 ev. Mean free paths for the losses lie in the range $25 \pm 10 \mu\text{g}/\text{cm}^2$, $165 \pm 55 \mu\text{g}/\text{cm}^2$, and $90 \pm 30 \mu\text{g}/\text{cm}^2$ for the three metals. The magnitudes of the losses agree with the plasma oscillation theory of Pines and Bohm for Al and Mg if the number of free electrons per atom is chosen about equal to the valence. In addition the mean free path as a function of energy for Al agrees closely with the theoretical curve.

INTRODUCTION

THE first extensive study of the discrete energy losses suffered by electrons passing through absorbers originated in the experiments of Rudberg¹ on several metals and metallic oxides at rather low bombarding energies of several hundred electron volts. Much experimental work has been performed since, resulting in the accumulation of data on a wide variety of metals, metallic oxides and sulfides, organic and inorganic gases, and various plastics,² totaling over fifty substances in all and at incident electron energies ranging from a few tens of electron volts to 115 kev. Emphasis in the experimental work has been on the achievement of extremely high resolution in order that electron beams of high energy may be employed to minimize scattering effects and so that losses of only a few electron volts may be investigated. The magnetic deflection method of energy analysis appears to have

been exploited most successfully by Ruthemann³ in his work on Al_2O_3 , Be, Al, and Ag, and by Lang⁴ in his investigation of Al, Cu, and Ni. Electrostatic deflection for the determination of electron energy has been used by Reichertz and Farnsworth⁵ in the study of the electrons reflected from the (100) face of a copper single crystal and by Lander⁶ in his study of Auger peaks in Al and Be wherein he noticed in the energy distribution of his primary beam additional peaks displaced from the incident beam energy by amounts corresponding to the losses reported by Ruthemann.

More recent work has utilized the chromatic aberration present in off-axis rays of certain electrostatic lenses for the separation of the energy components of an electron beam after it has traversed a thin foil, when such components differ only slightly in energy. This technique, originated by Mollenstedt⁷ in his work on a dozen or more different materials, has been carried on

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⁴ W. Lang, Optik **3**, 233 (1948).

⁵ P. P. Reichertz and H. E. Farnsworth, Phys. Rev. **75**, 1902 (1949).

⁶ J. J. Lander, Phys. Rev. **91**, 1382 (1953).

⁷ G. Mollenstedt, Optik **5**, 499 (1949).