the polarization in the wall is determined by two factors: the elastic energy which tends to decrease the wall thickness, and the dipole interaction energy which is greatly increased by steep changes in P, since PP'' must be negative in the wall, and which therefore tends to increase the width of the wall.

The authors wish to thank Dr. A. von Hippel for his kindness in introducing their manuscript to the editors of *The Physical Review*. They also wish to express their gratitude to Dr. H. Kawai and Mr. M. Marutake for supplying many rochelle salt crystals, and to Dr. E. Kanda for his suggestion on design of the microscope stage for low temperature. They also are indebted to Mr. Y. Katsui for his valuable help at the beginning of this work, and to Mr. I. Ohmura and Mr. N. Nishida for their valuable help.

PHYSICAL REVIEW VOLUME 90, NUMBER 2 APRIL 15, 1953

The Infrared Absorption Characteristics of Thermiated Germanium*

D. H. RANK AND D. C. CRONEMEYER
General Electric Company, Electronics Laboratory, Syracuse, New York
(Received December 18, 1952)

The infrared absorption spectrum of thermiated germanium has been obtained. It is shown that this material in addition to its greatly changed electrical properties becomes strongly absorbing in the infrared. A 48-hour anneal in air at 500°C restores the infrared transmission to that identical with the untreated control sample. The absorption spectrum for chemically P-doped germanium has been obtained and the absorption cross section for the P-doped material compared with that of thermium.

IT is well known that thermal treatment and subsequent quenching of germanium produces the appearance of acceptor centers. The radically different electrical properties of heat-treated samples which have been quenched has resulted in the common application of the name "thermium" to germanium semiconductors which have been thus thermally processed.

We have investigated the infrared transmission of thermiated germanium and also examined the effect of annealing upon the absorption spectrum of a thermiated sample.

The study of thermium was undertaken in the following manner: A 5-ohm-cm homogeneous N type single crystal was sectioned into four pieces each 1 cm thick. The specimens were given treatments as follows:

(a) Control (5-ohm-cm N type).

(b) Light thermal shock (700°C quenched into air 5-ohm-cm N→8-ohm-cm N).

(c) Strong thermal shock (900°C quenched into air 5-ohm-cm N→1.55-ohm-cm P).

(d) Strong thermal shock (900°C quenched into air plus 48-hour anneal of 500°C in air. 5-ohm-cm N→1.6-ohm-cm P→6–9-ohm-cm N).

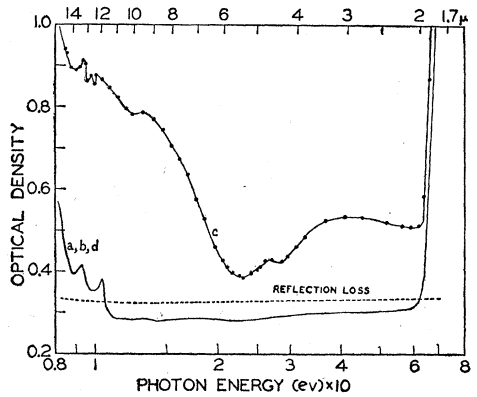

FIG. 1. Curve marked a, b, d represents the identical optical density *vs* wavelength curves obtained for germanium samples a, b, and d, respectively. Curve c represents the results obtained with the thermiated germanium sample c. The dotted curve was calculated from refractive index data.

The specimens described above were ground optically plane and parallel. A good optical polish was produced on the surfaces, care being taken to assure that the surface quality was sufficiently good so that surface defects could not influence the transmission measurements.

The infrared transmission of the germanium samples has been measured by the authors at the Pennsylvania State College and at the General Electric Electronics Laboratory, respectively. Both spectrophotometers were Perkin-Elmer model 112 double-pass high resolution instruments.

Briggs[1] has measured the index of refraction of bulk germanium in the 1.8- to 3-micron region making use of the method of minimum deviation. We have measured the index of refraction of bulk germanium in the 8–12 micron region by means of an interference method. A parallel plate of 0.5-mm thickness was used for this experiment, and the value obtained for the index of refraction was 3.96 ± 0.02, which is substantially in agreement with the value expected from an extrapola-

* This work was supported by the Air Materiel Command, the Bureau of Ships, and the U. S. Signal Corps.

[1] H. B. Briggs, Phys. Rev. **77**, 287 (1950).

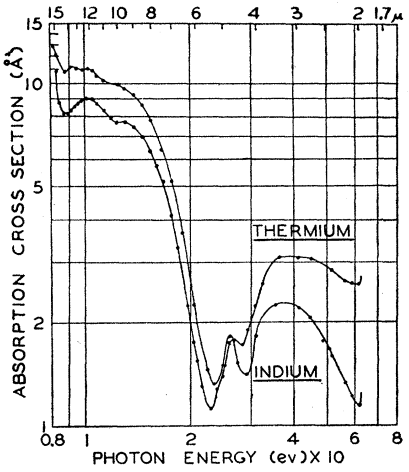

FIG. 2. Absorption cross section *vs* wavelength curves for chemically indium *P*-doped germanium and for strongly thermiated germanium.

tion of the measurements of Briggs. The details of the interference method used by us are in principle the same as the method described previously by one of us,[2] which was used in the first approximation for calibrating a Fabry and Perot etalon in the near infrared.

We have calculated the reflection loss making use of the measured values of the index of refraction, which result appears in the dotted curve Fig. 1.

The data obtained from samples *a*, *b*, and *d* are represented by a single curve given in Fig. 1. Since these three samples gave identical transmission curves, the multitude of experimental points making up this curve have been deleted from the figure. It will be noted that samples *a*, *b*, and *d* have a higher transmission in the 2- to 11-micron region than is to be expected from the measured value of the index of refraction. This slightly higher than "theoretical" transmission apparently is real and probably must find its explanation in surface films. It should be noted that the data given by Briggs[3] also show this transmission anomaly, but no discussion or mention of the anomalous transmission appears in his note.

Curve *a*, Fig. 1 shows the very strong absorption characteristics of thermiated germanium. The behavior of curve *d*, Fig. 1 shows that annealing restores the optical properties of thermiated germanium to their original condition.

The 1-cm thick thermiated sample *c* was sectioned into three pieces; the optical density curves for the different thickness specimens were used to derive the absorption coefficient *versus* photon energy characteristics. The results obtained from these measurements are displayed in Fig. 2, "Thermium." A rectangular bar cut from the center of one piece was utilized for a resistivity traverse measurement to test homogeneity (*ca* 10 percent). With an average resistivity of 1.55-ohm-cm and a Hall coefficient of 4350 cm³/coulomb, $\mu_p = 2400$ cm²/volt-sec, the number of free holes was calculated to be 1.70×10^{15}/cm³. This information on hole density permitted a calculation of the free hole cross section (see Fig. 2).

We have measured the infrared absorption spectrum of *N*- and *P*-type chemically doped germanium and find our results to be in general agreement with those reported by Briggs and Fletcher.[4] A comparison of the absorption cross section spectrum for thermium and chemical *P*-doping (indium doped, 1.17-ohm-cm *P*, $R = 4250$ cm³/coulomb, $\mu_p = 3100$ cm²/volt-sec, $p = 1.73 \times 10^{15}$/cm³) is shown in Fig. 2. It can be seen that near the absorption edge, the cross section for absorption is significantly higher for the thermium sample than it is for the chemically *P*-doped sample. It is surmised that two mechanisms are taking place simultaneously in the thermiated sample—one the ordinary mechanism of free hole absorption within the valence band, the second a trap ionization phenomena specific to thermium. This view is partially substantiated by the plot of the ratio of cross sections against photon energy shown in Fig. 3.

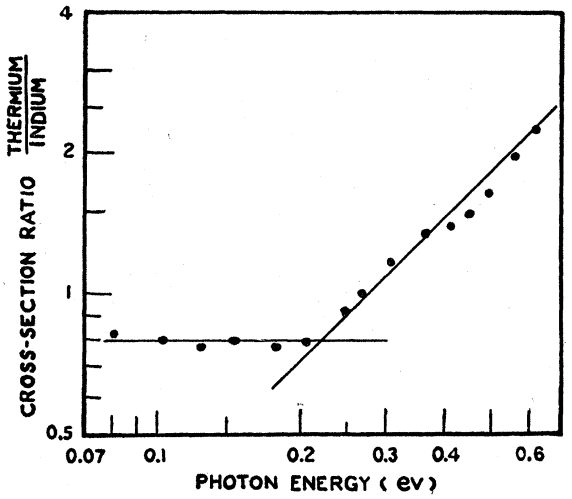

FIG. 3. Absorption cross-section ratio calculated from data of Fig. 2 plotted against photon energy in ev.

We are grateful to Mr. J. P. Jordan and Dr. J. S. Saby for helpful discussion, and are indebted to Dr. I. A. Lesk for the preparation of the thermiated samples.

[2] D. H. Rank and T. A. Wiggins, J. Opt. Soc. Am. (to be published).

[3] H. B. Briggs, J. Opt. Soc. Am. 42, 686 (1952).

[4] H. B. Briggs and R. C. Fletcher, Phys. Rev. 87, 1130 (1952).