The Optical Properties of Semiconductors. I. The Reflectivity of Germanium Semiconductors

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In recent years it has been possible to prepare semiconducting alloys of germanium with known number of carriers of predictable sign.[1] The electrical behavior of these semiconductors is determined by the number and type of impurity centers and it was therefore of great interest to investigate also the optical properties of such materials. The reflectivity of silicon of indeterminate origin has been investigated before.[2]

Germanium alloys, both of the *N* type (electron conductor) and *P* type (hole conductor) have been selected. Two of these samples had a small number of carriers ($\sim 10^{16}/cm^3$) whereas the other two samples had high impurity content ($\sim 5.10^{18}/cm^3$) and form a degenerate electron gas at low temperatures.[3]

In the range from 0.6μ to 12μ a rock salt spectrometer was used. A Nernst filament held in a water jacket provided with a suitable window was the radition source. The radiation was focused by a concave aluminum mirror onto the sample from which it was reflected to another concave aluminum mirror which finally focused it on the entrance slit of the spectrometer. The semiconductor sample was mounted in exactly the same plane as a comparison aluminum mirror. The reflectivity was determined for various settings of the spectrograph by the intensity measured with a sensitive thermocouple and galvanometer, expressed in terms of the reflectivity of the aluminum mirror[4] (deposited by evaporation on an optical flat). The semiconductor samples were optically polished and their flatness determined by interference methods. Between 0.6μ and 0.8μ the reflectivity of all the samples is between 47 percent and 51 percent.[5] The reflectivity then decreases and remains almost constant about 35 percent up to about 40μ. From this reflectivity value the dielectric constant was calculated to be about 16 in agreement with the value necessary to calculate[6] resistivity due to impurity scattering in the material.

In the range from 8.7μ to 152μ the method of residual rays was used in a form similar to the one described by J. Strong.[7] The radiation source was a globar heating element enclosed in a water-cooled jacket and specially prepared thermocouples with sensitive galvanometers were used for the measurements of radiation intensities. The samples were held on a rotating disk provided with 12 circular openings. One of these openings holds an aluminum mirror for relative reflection measurements. In the residual ray apparatus it was possible to select radiations from the incident continuous radiation at 8.7μ, 20μ, 30μ, 41μ, 52μ, 117μ, and 152μ.

Table I. Reflectivity of germanium semiconductors in the infra-red in percent.

Sample type	Resistivity at ~20°C	8.7μ	20μ	30μ	41μ	52μ	117μ	152μ
1 *P* type	0.005Λcm	35.4	33.8	33.2	40.3	53	79	46
2 *P* type	0.5Λcm	37.3	41.0	36.7	38.5	38	41	36
3 *N* type	0.006Λcm	36.5	34.5	30.6	29.0	29	81	50
4 *N*-type	~3Λcm	37.2	37.2	37.2	38.5	38	34	39

Table I gives a summary of the results obtained for the various wave-length for the different samples.

It can be seen that the highly conducting samples 1 and 3 show a high reflectivity at 117μ which decreases again at 152μ, but is still considerably higher than the reflectivity of the high resistance samples which remains essentially constant through the whole wave-length range. Systematic investigation of low resistance samples also as a function of temperature is under way now.

Experiments have also been carried out with silicon samples of various impurity content and the results agree with earlier investigations. Of particular interest is the reflectivity of silicon samples which have been heat-treated and which show a definite indication of the formation of a silicate layer on the surface. This investigation will be discussed in detail somewhere else.

[1] K. Lark-Horovitz, "Preparation of semiconductors," NDRC report 14-585 (1945).
[2] Forsterling and S. Freedericksz, Ann. d. Physik **40**, 201 (1913); Ingersoll, Astrophys. J. **32**, 286 (1910); Pfesdorf, Ann. d. Physik **81**, 906 (1926).
[3] V. Johnson and K. Lark-Horovitz, Phys. Rev. **71**, 374, 909 (1947).
[4] The reflectivity for such aluminum mirrors is 90 percent at 0.6μ and increases between 2μ and 91μ regularly from 97 percent to 99 percent as verified by measurements of K. B. Hunt in this laboratory (M.S. thesis, Purdue (1945)).
[5] For a germanium film H. M. O'Bryan (I.O.S. **26**, 122 (1936)) has found in the visible a reflectivity of about 36 percent. This checks with recent observations by V. Bottom in this laboratory who found for a film deposited on a plate of optically polished fused silica 37 percent whereas the reflectivity as determined from the optical constants for bulk material was found to be 45 percent using sodium light. However, measurements by J. Thornhill in this laboratory indicate that germanium films may show the ordinary structure of the bulk material, but their mobility as determined from Hall effect and conductivity is too small by a factor of 1000, indicating the presence of electron traps.
[6] K. Lark-Horovitz and V. A. Johnson, Phys. Rev. **69**, 258 (1946).
[7] J. Strong, Phys. Rev. **37**, 1565 (1931); K. W. Meissner and K. B. Hunt, Research Report OPRD-WPB-74 (1945).

Optical Properties of Semiconductors. II. Infra-Red Transmission of Germanium*

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The extinction coefficient k of germanium for infra-red light has been determined by previous measurements[1] up to about 1.2μ. For silicon, values of k are given by Ingersoll's[2] measurements up to 2.25μ. All previous measurements on the optical constants of these materials were made either using reflected light or using light transmitted through a thin film of the material. Properties of thin films are often not the same as those of the bulk material. (See I.) Light reflection depends upon the surface condition. It is therefore preferable, wherever possible, to use light transmitted through bulk samples for the determination of optical constants of the material.

We have found that bulk material of germanium as thick as several cm gives appreciable transmission over broad regions of the infra-red spectrum.

Transmission measurements on bulk germanium samples were made with a Gaertner rocksalt monochromator using a Western

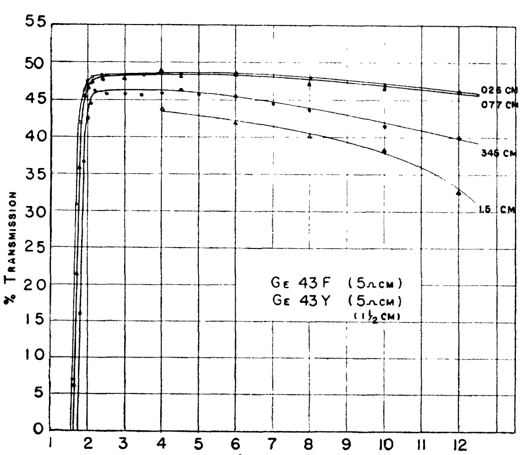

Fig. 1. Percentage transmission of high resistivity Ge as a function of wave-length for various thicknesses. The 1.5-cm sample is from melt 43 Y; the others are from melt 43 F.

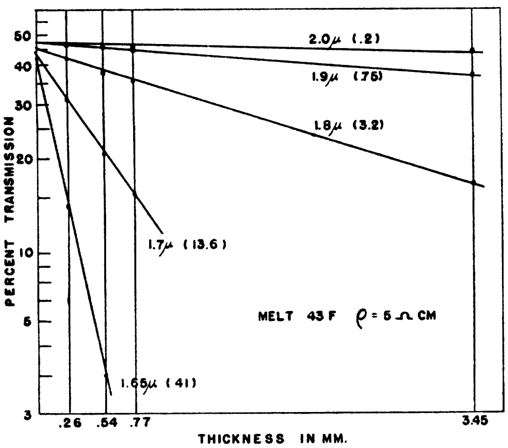

FIG. 2. Percentage transmission of germanium as a function of thickness for various wave-lengths. The figures in the parentheses give the absorption coefficient in cm^{-1} for each wave-length.

Union concentrated arc, or a Nernst glower as light sources, and a vacuum thermopile as detector. Curves for three samples of different thicknesses, 0.26 mm, 0.77 mm, and 3.45 mm, of N-type germanium from the same melt are shown in Fig. 1. The samples are single crystals with reistivity of about 5 ohm cm.[3] Figure 2 gives the logarithm of percentage transmission plotted against sample thickness for different wave-lengths. To determine the absorption coefficient from transmission measurements it is necessary for the samples to have the same reflecting power R. To insure this both surfaces of the samples were optically polished. It is seen from Fig. 2 that at wave-lengths where the absorption is small and the transmission is determined primarily by surface reflections, there is no irregular variation of transmission for the different samples. This shows that the surfaces of the samples as prepared do have nearly the same reflecting power.

If the transmitted light is given by

$$I/I_0=(1-R)^2e^{-\epsilon l},\quad l=\text{thickness of material},$$

then ϵ and R are determined from the slope and intercepts of the straight lines in Fig. 2. However, when the transmission is high, multiple reflections ot both surfaces have to be taken into account. Starting from known formulas[4] and taking into account the finite

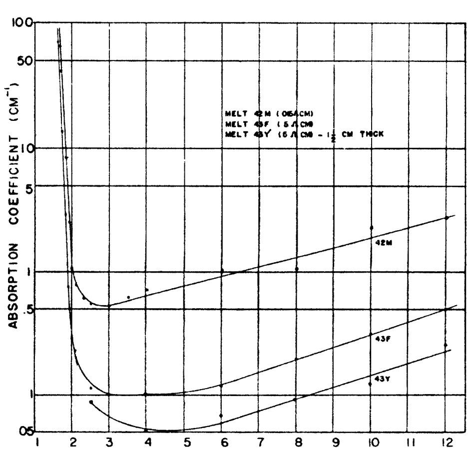

FIG. 3. Absorptivity of germanium as a function of wave-length for different resistivities. The curve for 43 Y is drawn assuming the same reflectivity as the other melts since only one thick piece was available.

width of the spectrum used in the measurement of each point, it can be shown that

$$I/I_0=[(1-R)^2+4R\sin^2x]/(e^{\epsilon l}-R^2e^{-\epsilon l}),$$

where $x=\tan^{-1}[2k/(n^2+k^2-1)]$, n being the index of refraction. The term involving x is negligible in the range of our measurements. Using this expression to analyze the experimental data we find that the reflecting power $R=0.35$ (in agreement with results in I), is constant within the spectrum covered by our measurements. The absorption coefficient, $\epsilon=4\pi k\nu/c$, is plotted in Fig. 3.

The absorption increases rapidly for wave-lengths below 2μ. For measurements below 1.6 much thinner samples have to be used. For wave-lengths above 2 the absorption is so small that much thicker samples, i.e., several cm, should be used for accurate measurement. A single crystal 15 mm thick was cut from a melt of about the same resistivity, 5 ohm cm. The transmission curve for this sample is included in Fig. 1 and the absorption coefficient, calculated using $R=0.35$, is given in Fig. 3. The absorption coefficient curves for the two similar melts agree in shape and in order of magnitude. The discrepancy may be due to inaccuracy on account of insufficient thickness of samples used.

Similar measurements were made on samples from a melt of much lower resistivity, 0.015 ohm cm. These samples are polycrystalline with 2 or 3 grain boundaries in the light beam. The curve of absorption coefficient is also shown in Fig. 3. The absorption is seen to be higher than that of high resistivity single crystal samples. The reflecting power is constant for the spectrum covered and is the same, $R=0.35$, as for the high resistivity samples.

* Signal Corps Contract W36-039-sc-38151; Progress Report (February, May, 1949). A summary of this work was presented at the Ad Hoc Crystal Meeting at M.I.T. (June, 1949).

[1] W. H. Brattain and H. B. Briggs, Phys. Rev. **75**, 1705 (1949).
[2] L. R. Ingersoll, Astrophys. J. **32**, 286 (1910).
[3] The authors wish to thank Mr. W. E. Taylor for preparing the single crystal, high resistivity melts.
[4] R. B. Barnes and M. Czerny, Phys. Rev. **38**, 338 (1931).

Optical Properties of Semiconductors. III. Infra-Red Transmission of Silicon*

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LIKE germanium, bulk silicon also shows appreciable transmission in the infra-red. This can be directly demonstrated photographically since high transmission begins at 1.0μ. Type I-Z photographic plates are sensitive to 1.3μ. Spot images of a parallel light beam can be photographed on such plates through a piece of silicon 0.3 mm thick in a few seconds of exposure. (In the case of germanium, high transmission begins at 1.6μ, beyond the sensitivity of the plates. Thirty-six hours of exposure through germanium does not affect the plate at all.)

Using basically the same experimental arrangement described in the companion letter on germanium, transmission measurements were made on low resistivity ($\rho=0.03$ ohm cm) P-type silicon from liquid air temperature to 380°C. The reflecting power deduced from these measurements is constant for the spectral region covered: $R=0.27$, in agreement with earlier measurements by K. Lark-Horovitz and K. W. Meissner. Figure 1 shows the absorption curves for different temperatures. The absorption is seen to decrease with decreasing temperature over the entire spectrum covered by the measurements. The values of extinction coefficient obtained by Ingersoll[1] are several orders of magnitude higher than our results. This may very well be due to the fact that the material used in these early experiments was very impure. For instance, germanium strongly doped with aluminum (~0.005 ohm cm) shows absorptions at least several orders of magnitude higher than the data presented in the companion letter.