Infrared Absorption in n-Type Silicon*

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The absorption by free carriers in n-type silicon has been studied in a spectral region from 1 to 45 microns for samples of various impurity and carrier concentrations. In all samples measured the absorption consists of a band between 1.5 and 5 microns in addition to an absorption which rises smoothly with wavelength. The absorption band is found to be proportional to the carrier concentration in samples doped with different donor impurities. It is suggested that the band is associated with the excitation of carriers to a higher lying energy band. The behavior of the smoothly rising portion of the absorption curve is in agreement with the Fan and Fröhlich theory of free-carrier absorption. Quantitative agreement is obtained with a value of $0.3m$ for the effective mass.

INTRODUCTION

IT has been shown previously that in n-type germanium[1] the spectral dependence and magnitude of the absorption on the long-wavelength side of the intrinsic absorption edge depend upon temperature, carrier concentration and impurity concentration of the specimen. This absorption is associated with the conduction property of carriers and is called "free-carrier absorption." At room temperature no absorption bands were found beyond the absorption edge, up to 45 microns, except those due to the germanium lattice.

The present measurements were made by using a number of n-type single-crystal silicon samples in a wavelength region between 1.0 and 45 microns. In all samples measured, a pronounced absorption band is observed between 1.5 and 5.0 microns. The experimental evidence indicates that this absorption band is due to the excitation of electrons from the conduction-band minima to a higher lying energy band. The normal free-carrier absorption is observed at longer wavelengths and is compared with the theory of Fan and Fröhlich.[2]

EXPERIMENTAL RESULTS

Table I is a list of the samples which were used for the optical measurements. The room-temperature

TABLE I. A list of the samples used with their donor impurities, room-temperature carrier concentrations, and impurity concentrations.

Sample No.	Donor impurity	$N_{297°K}$ (cm^{-3})	N_i (cm^{-3})
1	arsenic	1.4×10^{16}	
2	antimony	8.0×10^{16}	0.95×10^{17}
3	antimony	1.7×10^{17}	5.5×10^{17}
4	phosphorus	3.2×10^{17}	1.26×10^{18}
5	arsenic tin alloy	6.1×10^{18}	4.6×10^{19}
6	arsenic	1.0×10^{19}	6.6×10^{19}

carrier concentrations, N, were determined from electrical measurements of resistivity and Hall effect. The second column indicates the chemical donor impurity in the crystal. The values of the impurity concentrations, N_i, given in the last column were estimated from the Brooks-Herring formula[3] for the impurity-scattering mobility.

Figure 1 is a plot of the room-temperature absorption coefficient as a function of wavelength for the six samples of Table I. The absorption bands starting at approximately six microns, seen in the samples of small carrier concentrations, are due to absorption by the silicon lattice and have been reported previously.[4] It is apparent that the absorption in the 1.5- to 5-micron
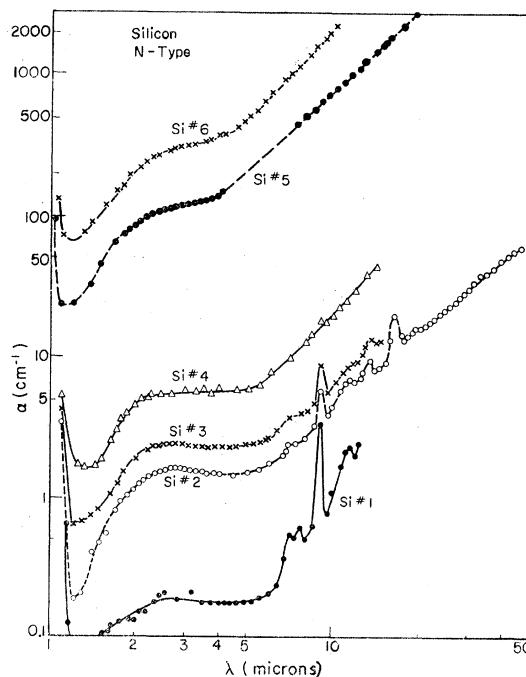

Fig. 1. Room-temperature absorption coefficient as a function of wavelength for six different silicon samples.

[1] Fan, Spitzer, and Collins, Phys. Rev. 101, 566 (1956).
[2] H. Y. Fan and M. Becker, "The Infrared Optical Properties of Silicon and Germanium," *Symposium Volume of the Reading Conference* (Butterworths Scientific Publications, Ltd., London, 1951). Also see reference 1.
[3] See P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954).
[4] R. J. Collins and H. Y. Fan, Phys. Rev. 93, 674 (1954).

region is the superposition of an absorption band and the normal free-carrier absorption which increases smoothly with wavelength. This absorption band varies with the concentration of conduction electrons and is not observed in p-type samples. The band may be isolated by extrapolating back the free-carrier absorption from beyond 5 microns and subtracting it from the measured curve. The peak of the band obtained in this way corresponds to approximately 2.3 microns. The peak absorption coefficient is plotted in Fig. 2 as a function of the carrier concentration. The points lie close to a straight line of slope one, indicating that the height of the absorption band is proportional to the carrier concentration.

The temperature dependence of the absorption is illustrated in Fig. 3 for sample Siilicon—3. The absorption band for this sample is shown in Fig. 4 for three different temperatures.
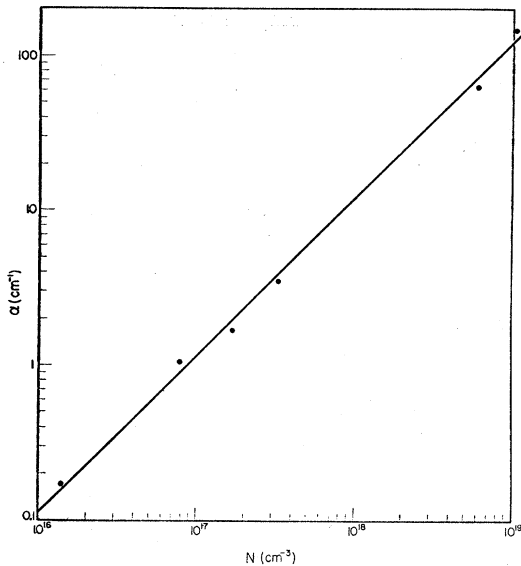

FIG. 2. Height of the absorption band as a function of carrier concentration for the different samples.

For $\lambda > 6$ microns, the absorption increases smoothly with wavelength and is evidently the effect of free carriers. As in n-type germanium, the absorption shows a larger spectral dependence for samples of higher carrier concentration. Figure 5 shows the absorption coefficient at 10 microns as a function of the carrier concentration for the different samples. It will be noted in this log-log plot that the absorption increases more rapidly than the carrier concentration.

DISCUSSION

The absorption band between 1.5 and 5 microns is present in all samples and is proportional to the carrier concentration. The samples have different donor impurities and were made in five different laboratories.
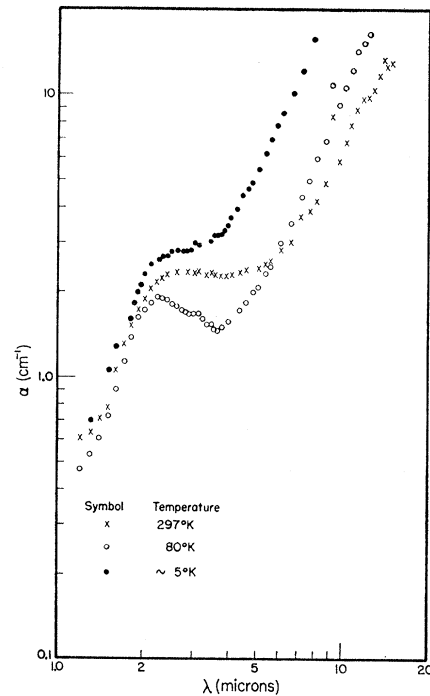

FIG. 3. Absorption coefficient vs wavelength for Silicon—3 at three temperatures.

Hence it is very unlikely that the band is an accidental result of a particular condition of crystal growth.

Two possible explanations may be offered for the existence of the absorption band. One possibility is that the band is associated with the excitation of carriers from the conduction-band minima or, at low temperatures, from the impurity levels to a higher
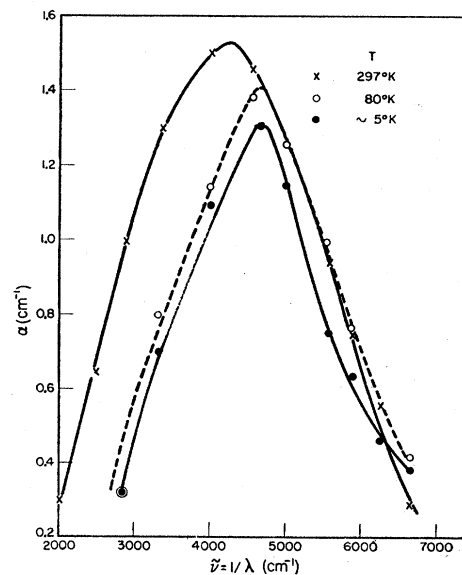

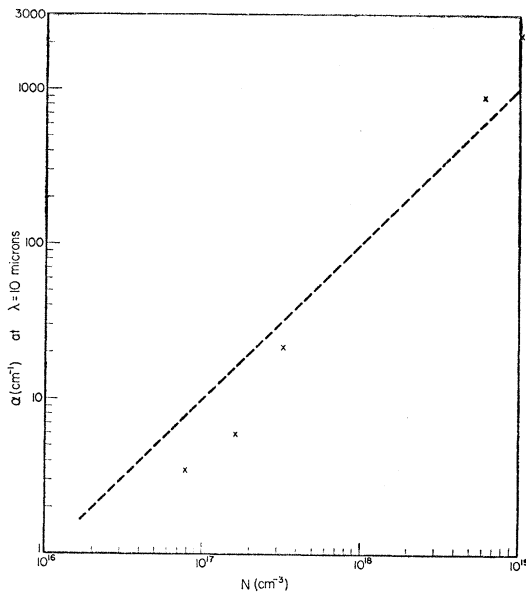FIG. 4. The absorption band of Silicon—3 obtained from the data in Fig. 3.

FIG. 5. Room-temperature absorption coefficient at 10 microns wavelength as a function of carrier concentration. The dash line has a slope equal to 1.

lying energy band. A second possibility is that the absorption band is produced by the excitation of electrons from deep lying levels in the forbidden energy gap to the conduction band. The latter explanation is unlikely since the concentration of such levels would have to be proportional to the conduction-electron concentration. Also, the location of the levels in the energy gap would have to be independent of the type of donor impurity used.

It may be noted in Fig. 4 that the center of the absorption band shifted to a higher energy in going from 297°K to 80°K. The value of the shift is 0.04±0.01 ev. Electrical measurements made on the sample showed that approximately $\frac{4}{5}$ of the free carriers at room temperature were in the impurity levels at liquid-nitrogen temperature. If the interband excitation is the correct interpretation for the absorption band, then the shift in energy should be approximately the ionization energy of antimony in silicon which is 0.039 ev.[5] The close agreement between the expected and observed shifts supports the interpretation.

If direct interband transitions were involved, then the expected half-width of the absorption band in Fig. 4 would be $\sim kT$, unless the higher lying energy band should have a steep slope at the same points in **k** space where the conduction-band minima are situated. The observed half-width is an order of magnitude larger. The oscillator strength of the absorption band calculated from the area under the curve in Fig. 4 is ~ 0.1. Therefore, indirect transitions are indicated. The absorption band extends from approximately 0.25 to

[5] Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833 (1954).

0.85 ev. It is possible that the low-energy threshold corresponds to carrier excitations to the higher lying minima in the $\langle 111 \rangle$ directions.

One method of proving that the absorption band is produced by the excitation of conduction electrons is to measure a pure specimen at an elevated temperature. The band, being too small to be observed at room temperature, should grow in magnitude as the electron concentration rises in the intrinsic range. Transmission measurements at 670°K and 726°K did not clearly show the band. However, the cross section of holes for absorption is larger than that of electrons and may well mask the absorption band.

This interpretation of the room-temperature absorption for $\lambda > 6$ microns is the same as was used by the authors for n-type germanium[1] in a previous paper. The absorption is treated as composed of two parts which are associated with lattice scattering and impurity scattering, respectively. The theoretical expressions for the absorption may be written as[6]

$$\alpha = N(m/m^*)^2 L(\bar{\nu}, T) \quad \text{for lattice scattering}$$

and

$$\alpha = N N_i (m/m^*)^{\frac{3}{2}} I(\bar{\nu}, T) \quad \text{for impurity scattering,}$$

where $L(\bar{\nu}, T)$ and $I(\bar{\nu}, T)$ are functions of wave number, $\bar{\nu}$, and temperature, T. These functions may be calculated for silicon in the same manner as was done for germanium.

The absorption, at $\lambda = 10$ microns, per unit carrier concentration for the different samples is plotted against impurity concentration in Fig. 6. A straight line of best fit is drawn through the points. The slope of the line should be equal to $(m/m^*)^{\frac{3}{2}} I(\bar{\nu}, T)$ and the intercept at $N_i = 0$ should be given by $(m/m^*)^2 L(\bar{\nu}, T)$. In view of inaccuracy involved in the experimental values of α/N and N_i, the obtained intercept at $N_i = 0$ is not sufficiently reliable to be used. However, the slope of the line agrees with the value predicted by the
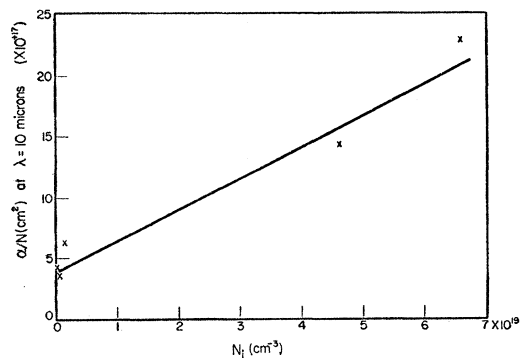

FIG. 6. Ratio of room-temperature absorption coefficient at 10 microns to carrier concentration as a function of impurity concentration for the different samples.

[6] See reference 1 for definition of terms.

theoretical expression with $m^* \sim 0.3m$. This value of m^* is in reasonable agreement with the value of conductivity effective mass obtained from other measurements.[7]

[7] W. Spitzer and H. Y. Fan, Phys. Rev. 106, 882 (1957).

Magnetic Annealing Effect in Cobalt-Substituted Magnetite Single Crystals*

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The effect of magnetic annealing at 375°K on the room-temperature anisotropy of a series of six single crystals in the composition series $Co_xFe_{3-x}O_4$, in the range of x values between 0.0 and 0.15, is investigated. The anneal-induced anisotropy is shown to be represented by the equation $W_U = -F\Sigma_i \alpha_i^2\beta_i^2 - G\Sigma_{i>j} \alpha_i\alpha_j\beta_i\beta_j$, where α_i and β_i are direction cosines of the magnetization during measurement and during the annealing process, respectively. F and G are shown to vary with x in a regular fashion: $F \approx 10.1 \times 10^6 x^2$ erg/cc and $G \approx 9.25 \times 10^6 x$ erg/cc. These results cannot be explained by the Néel orientation-ordering model or by the precipitate model of magnetic annealing. A new model, involving cobalt ions individually rather than in pairs or larger agglomerates, is introduced.

1. INTRODUCTION

DURING the course of an investigation of the temperature dependence of the cubic anisotropy constants of some cobalt-substituted magnetite single crystals[1] it was found that measurements above about 400°K were greatly affected by magnetic annealing. The magnetic field applied during the torque measurements induced continuous changes in the anisotropy of the specimen, and thus masked the cubic anisotropy. This paper is a report of a systematic study of the anneal-induced anisotropy in these crystals and in others of the same composition series.

The effect of magnetic annealing on the anisotropy of ferrites containing large concentrations of cobalt has been investigated by Bozorth, Tilden, and Williams.[2] These authors found that the anisotropy of their crystals could be expressed by the equation

$$W_A = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_U \sin^2(\theta - \theta_U), \quad (1)$$

in which the α's are the direction cosines of the saturation magnetization (M_s) with respect to the crystal axes; θ is the angle between M_s and [001]; θ_U is the angle between the uniaxial preferred direction and [001]; and K_U is the uniaxial anisotropy constant. This equation was shown to be valid by experiments performed on (100) and (110) disks of $Co_{0.32}Zn_{0.24}Fe_{2.18}O_4$. Two characteristic features of their results were as follows: (1) The magnitude of K_U was the same for all

* A preliminary account of this work was presented at the 1957 Annual Meeting of the American Physical Society [Bull. Am. Phys. Soc. Ser. II, 2, 21 (1957)].
[1] Bickford, Brownlow, and Penoyer, Proc. Inst. Elec. Engrs. (London) 104, Part B, Suppl. 5, 238 (1957).
[2] Bozorth, Tilden, and Williams, Phys. Rev. 99, 1788 (1955).

values of θ_A, the angle between the annealing magnetic field and [001]; (2) The direction of the annealing field became the uniaxial preferred direction (θ_U coincided with θ_A).

In this paper we report the results of similar experiments performed on crystals in the composition range from Fe_3O_4 to $Co_{0.15}Fe_{2.85}O_4$ and show that neither of the characteristic features referred to in the foregoing paragraph were observed. The magnitude of K_U and the deviation of θ_U from θ_A are both shown to be strongly dependent on θ_A. The strength and symmetry of this dependence change systematically with increasing cobalt concentration. We discuss our experiments in the light of existing theories of magnetic annealing and show that our results are not entirely consistent with the predictions of these theories. Finally, we introduce a new model which is consistent with our experimental observations.

2. EXPERIMENTAL PROCEDURE

The six crystals studied in this investigation belong to the composition series $Co_xFe_{3-x}O_4$, and have the following values of x: 0.005, 0.01, 0.04, 0.07, 0.10, and 0.15. Details concerning the method of crystal growth (from the melt) have been published elsewhere.[1]

A spherical sample shape was chosen in order to minimize errors introduced by the fact that the cobalt concentration is not uniform throughout a given crystal growth. By using one and the same sample, measurements could then be carried out with the magnetization in each of the three crystal planes. The spheres were shaped by the abrasion technique of Bond[3] to a diameter

[3] W. L. Bond, Rev. Sci. Instr. 22, 344 (1951).