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NRL REPORT 3880

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FR-3880

SILICON AS A FAR-INFRARED DETECTOR

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Date: 3 Feb 2017

Reviewer's name(s): A. THOMPSON,
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Declassification authority: NAVY DECLASS
GUIDE/NAVY DECLASS MANUAL, 11 DEC 2012

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INTRODUCTION

Infrared detectors having short time-constants and low equivalent-noise input values (ENI) are needed in various military applications for the detection of low-intensity radiation in the region of 8 to 12 microns. For such applications, photoconductors as quantum detectors would be preferable to thermocouples and other thermal elements since they generally have considerably greater sensitivity and much shorter time constants. The spectral response of previously available photoconductors does not, however, extend beyond 6 microns, the long-wavelength limit of lead telluride (PbTe) at liquid hydrogen temperatures.¹ A search for suitable materials which are photoconductive beyond 6 microns was therefore undertaken at this Laboratory.

Earlier efforts at other laboratories to find such photoconductors were primarily concerned with heteropolar substances such as heavy metal tellurides and arsenides and inter-metallic compounds.² A survey of such heteropolar materials was also carried out at this Laboratory but did not uncover any promising material. The investigation was then directed toward homopolar materials. Among these, silicon and germanium were of particular interest since available data on their electrical properties showed the existence of impurity levels having thermal-ionization energies corresponding to possible long-wavelength photoconductivity limits beyond 15 microns for silicon and 50 microns for germanium. In addition, the infrared properties of silicon and germanium associated with lattice vibrations were already under investigation as part of a study of the infrared properties of diamond structures.

The present investigation of the optical and photoconductive properties of homopolar substances, which has dealt primarily with silicon thus far, has successfully demonstrated the existence of impurity photoconductivity in silicon extending at least to 25 microns, having a time constant smaller than 10^{-4} sec, and an ENI of the order of 10^{-6} watts/cm². In addition, data from the optical and photoconductive properties of the impurity levels were shown to be in agreement with data from electrical studies. The present report deals with the results obtained thus far on both the fundamental and the applied aspects of the investigation, and includes an evaluation of silicon as a far-infrared detector.

¹ Moss, T. S., Proc. Phys. Soc. 62 B, 741-748 (1949)

² Moss, T. S., Proc. Phys. Soc. 63 B, 982-989 (1950); Braithwaite, J. G., Proc. Phys. Soc. 64 B, 274-275 (1951); Zhuze, V. P., Mochan, I. V., and Ryvkin, S. M., J. Tech. Phys. USSR 18, 1494 (1948); Morton, G., Infrared photoconductors. R.C.A. Interim Reports, Contract NR onr-23603 (1950 through 1951)

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BACKGROUND

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Semiconductor Properties

Silicon and germanium have diamond structures consisting of two identical interpenetrating face center cubic (f.c.c.) lattices with one lattice displaced relative to the other along a body diagonal by a distance equal to one-fourth of the length of the diagonal (Figure 1). Thus, each atom has four equivalent neighbors with which it forms "covalent" bonds in a tetrahedral arrangement. Near absolute zero, pure silicon and germanium are insulators with energy gaps between the valence band and the conduction band of 1.1 ev and 0.72 ev, respectively (Figure 2). At higher temperatures, electrons are transferred from the valence band to the conduction band by thermal ionization, leaving behind an equal number of mobile positive holes in the valence band. Under these conditions silicon and germanium behave as intrinsic semiconductors.

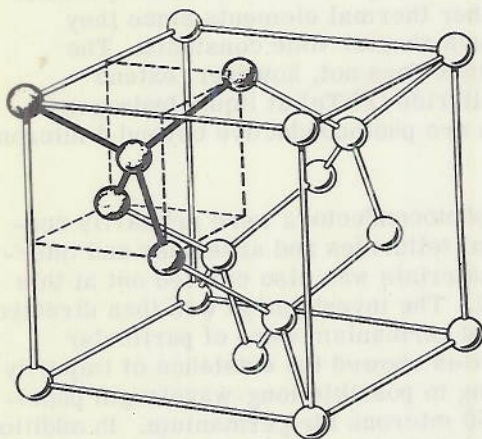


Figure 1 - The diamond structure

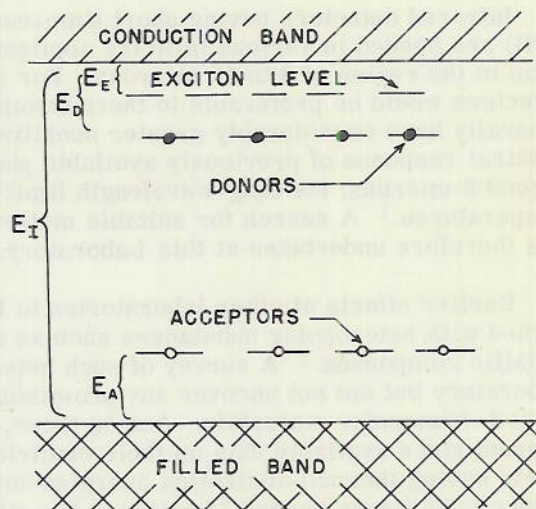


Figure 2 - Energy level diagram for semiconductors

The product of the electron and hole concentrations is a function of temperature only, and according to statistical theory,³ is given by

$$\begin{aligned}
 n_e n_h &= 4 \left(\frac{2\pi m k T}{h^2} \right)^3 \left(\frac{m_e m_h}{m^2} \right)^3 \exp(-E_I/kT) \\
 &= N^2 \left(\frac{m_e m_h}{m^2} \right)^3 \exp(-E_I/kT)
 \end{aligned} \quad (1)$$

³ Fowler, R. H., Statistical Mechanics. Cambridge University Press, London, Second Edition (1936) Chapter 11; Shockley, W., Electrons and Holes in Semiconductors. D. Van Nostrand Co., Inc. (1950) Chapter 10

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where $N = 4.82 \times 10^{15} T^{3/2} \text{ cm}^{-3}$, m_e is the mass of an electron and m_h the mass of a hole both of which differ from the mass of an electron in free space, m , because of interactions with the lattice, E_I is the thermal energy gap between the valence band and the conduction band, T is the absolute temperature, k is the Boltzman constant, h is Planck's constant, $N \left(\frac{m_e}{m} \right)^{3/2}$ is the effective density of states in the conduction band, and $N \left(\frac{m_h}{m} \right)^{3/2}$ is the effective density of states in the valence band.* The concentration of electrons in the conduction band is equal to that of holes in the valence band and is therefore given by

$$n_e = n_h = N \left(\frac{m_e m_h}{m^2} \right)^{3/2} \exp (- E_I / kT). \quad (2)$$

The value of the intrinsic energy gap has been determined from temperature dependence of the density of mobile charge carriers which is obtained most readily from measurements of the temperature dependence of the Hall coefficient.⁴ Data on the energy gap may also be obtained from optical measurements on the long-wavelength absorption edge of the intrinsic absorption band,⁵ and from the long-wavelength limit of intrinsic photoconductivity.⁶

The electrical conductivity of pure silicon and germanium is given by

$$\sigma_I = e (n_e \mu_e + n_h \mu_h) = en_e (\mu_e + \mu_h) \quad (3)$$

where μ_e and μ_h are the mobilities of the electrons and holes, and e is the electronic charge. The mobilities of the charge carriers vary considerably with temperature (4). At high temperatures, the mobilities are primarily determined by interactions of the charge carrier with lattice vibrations; at lower temperatures they are determined by interactions with impurities and lattice imperfections. Differences between the mobilities of electrons and holes which are observed at the higher temperatures may be attributed in part to differences in the effective masses of electrons and holes. According to theory, the mobility in the lattice-scattering range of temperature varies inversely as the 5/2 power of the effective mass. Available data on the mobilities of electrons and holes at relatively high temperature indicate that $m_e = 0.65 m_h$ in silicon, and that $m_e = m_h$ in germanium.

Silicon and germanium become impurity semiconductors when appropriate impurities are introduced. Elements in the fifth column of the periodic table, such as P and As, introduce donor levels into the forbidden zone and yield electrons on thermal ionization; elements in the third column of the periodic table, such as B and Al, introduce acceptor levels into the forbidden zone and yield holes on thermal ionization. When the concentration of free electrons

* The theoretical treatment of free holes in the valence band is essentially identical with that of free electrons in the conduction band. Thus, to the approximations which are generally employed, holes differ from electrons only in the magnitudes of their effective masses and mobilities.

⁴ Pearson, G. L., and Bardeen, J., Phys. Rev. 75, 865-883 (1949)

⁵ Briggs, H. B., Phys. Rev. 77, 727-728 (1950); Becker, M., and Fan, H. Y., Phys. Rev. 76, 1530-1532 (1949)

⁶ Teal, G. K., Fisher, J. R., and Treptow, A. W., Phys. Rev. 69, 686 (1946); Goucher, F. S., Phys. Rev. 78, 816 (1950)

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in a semiconductor exceeds that of free holes, the semiconductor is n-type. When the concentration of free holes exceeds that of free electrons, it is p-type. Heat treatment or bombardment with alpha particles, neutrons, or deuterons may also convert silicon and germanium into p-type semiconductors by displacing atoms from their normal positions into interstitial positions leaving behind vacant lattice points which act as acceptors.

The equilibrium concentration of electrons in n-type materials containing only donor impurities over the impurity range of temperatures, where the thermal ionization of the valence band may be neglected, is determined by a balance between the rate at which electrons are thermally excited from neutral donors to the conduction band and the rate at which electrons recombine with ionized donors. The equilibrium constant for the thermal ionization of donors, according to statistical theory, is given by

$$K = \frac{n_e n_d}{n_D} = N \left(\frac{m_e}{m} \right)^{3/2} \exp (-E_D/kT) \quad (4)$$

where n_d is the concentration of ionized donors, n_D is the concentration of neutral donors, and E_D is the thermal energy separation between the donor impurity level and the conduction band (Figure 2). The concentration of electrons which is equal to the concentration of ionized donors in the impurity range of temperature is correspondingly given by

$$n_e = n_d = n_D^{1/2} N^{1/2} \left(\frac{m_e}{m} \right)^{3/4} \exp (-E_D/kT) \quad (5)$$

and the electrical conductivity by

$$\sigma_e = n_e \mu_e e \quad (6)$$

The density of holes and the corresponding electrical conductivity in p-type materials containing only acceptor impurities are similarly given by

$$n_h = n_a = n_A^{1/2} N^{1/2} \left(\frac{m_h}{m} \right)^{3/4} \exp (-E_A/kT) \quad (7)$$

and

$$\sigma_h = n_h \mu_h e \quad (8)$$

where n_a is the concentration of ionized acceptors, n_A is the concentration of neutral acceptors, and E_A is the thermal energy separation between the acceptor impurity level and the valence band (Figure 2). The mobilities of the electrons and holes in n- and p-type materials at low temperature differ from those at higher temperature as a result of an additional scattering by impurities.

Information about the energy separation between the impurity levels and their corresponding conduction bands has been obtained experimentally only from resistivity and Hall coefficient measurements. The impurity ionization energy decreases rapidly with increasing impurity concentration, becoming zero at relatively low impurity concentrations (Figure 3). At the limit of zero impurity concentration, the thermal ionization energy of acceptor impurities in silicon is found experimentally to be 0.08 ev while the corresponding value for donor impurities is 0.05 ev (Table 1).

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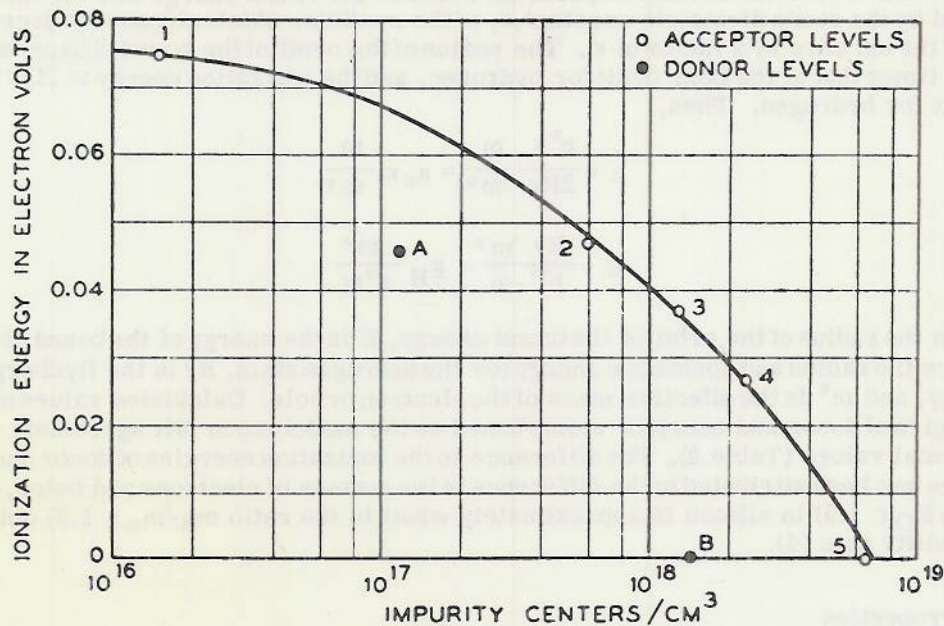


Figure 3 - Variation of the ionization energy of impurity centers with concentration in silicon (G. L. Pearson and J. Bardeen - Reference 4)

TABLE 1
Electrical and Optical Properties of Diamond Structures

	Intrinsic		n-type			p-type		
	E_L^* (ev)	λ_L (microns)	E_D (ev)	λ_o (microns)	μ_e^{***} (cm ² /volt sec)	E_A^* (ev)	λ_A (microns)	μ_h^{***} (cm ² /volt sec)
Diamond	7	0.23	—	0.3	900	—	0.3	>200
Silicon	1.12	1.2	0.05	(~25)**	300	0.08	(~15)**	100
Germanium	0.76	1.8	0.01	(~100)**	3500	0.01	(~100)**	1700
Tin	0.1	(12)	—	—	—	—	—	—

* From electrical conductivity and Hall coefficient data

** Estimated from energy gap data

*** From Table in J. Bardeen and W. Shockley, Phys. Rev. 80, 76 (1950)

Typical curves of resistivity and of charge carrier density plotted on a logarithmic scale as a function of the inverse absolute temperature for p-type silicon are given in Figures 4a and 4b. The slopes of the charge-carrier density curves are equal to E/k where E is the thermal activation energy which in the absence of complicating factors is equal to half the corresponding energy gap.

The small ionization energies of donor and acceptor impurities in silicon and germanium have been explained in terms of a hydrogen-like model in which the bound electron or hole moves in large orbits about the positively or negatively charged ion core of the impurity

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atom.⁷ In this model the attractive potential between the bound charge and the ion core is reduced by the static dielectric constant, κ , of the medium, which effectively decreases the charge of the ion core by a factor of κ . The radius of the orbit of the bound charge is therefore $\kappa (m/m^*)$ times that of the Bohr orbit for hydrogen, and the ionization energy is $(1/\kappa) (m^*/m)$ times that for hydrogen. Thus,

$$a = \frac{e^2 \kappa}{2Ry} \frac{m}{m^*} = a_0 \kappa \frac{m}{m^*} \quad (9)$$

and

$$E = \frac{Ry}{\kappa^2} \frac{m^*}{m} = E_H \frac{m^*}{\kappa^2 m} \quad (10)$$

where a is the radius of the orbit of the bound charge, E is the energy of the bound charge, a_0 and E_H are the radius and ionization energy for the hydrogen atom, Ry is the Rydberg constant for energy, and m^* is the effective mass of the electron or hole. Calculated values of the ionization energies of donor and acceptor atoms based on the model are in fair agreement with the experimental values (Table 2). The difference in the ionization energies of donor and acceptor impurities has been attributed to the difference in the masses of electrons and holes, since the ratio E_A/E_D (1.5) in silicon is approximately equal to the ratio m_h/m_e (1.5) obtained from mobility data (4).

Optical Properties

Optical absorption in pure silicon and germanium due to electronic transitions extends into the near infrared (5). The absorption is accompanied by photoconductivity whose long wavelength limit coincides closely with the optical absorption edge which occurs at 1.1 microns in silicon (Figure 5a) and at 1.8 microns in germanium (Figure 5b) (6). According to band theory, the long-wavelength absorption edge corresponds either to the excitation of an electron from the top of the valence band into the lowest level of an exciton band in which the electron remains bound to the positive hole or to the photoionization of an electron from the top of the valence band to the lowest level of the conduction band, leaving behind a mobile positive hole (Figure 6).

An exciton formed by light absorption moves freely through the lattice in the form of an excitation wave carrying momentum. It therefore has associated with it a quasi-continuous band of allowed energies similar to those in the conduction band for free electrons.⁸ Although there are no data on the separation between the lowest level of the exciton band and the conduction band, it can be estimated by treating the exciton as a hydrogen-like system in which the electron and hole revolve about one another in a bound orbit. The energy of the lowest exciton level, having zero momentum, is thus given by

$$E_E = \frac{Ry}{2\kappa_0} \left(\frac{m_e m_h}{m^2} \right)^{\frac{1}{2}} \quad (11)$$

where κ_0 is the optical dielectric constant. In homopolar substances where the optical and static dielectric constants are very nearly equal, as in the case of silicon and germanium, the energy gap between the lowest level of the exciton band and the conduction band is approximately one-half that of the impurity levels. This model leads to exciton ionization energies of 0.02 eV in silicon. Exciton states formed by optical absorption at room temperature in silicon and germanium will therefore be thermally dissociated into free electrons and holes. At room temperature, this absorption mechanism leads to the same final state as direct photoionization, and either mechanism may account for the observed photoconductivity. Because of small exciton energies, there should be relatively little difference in the long wavelength limit of absorption for the two processes.

⁷ Bethe, H., M.I.T., Radiation Laboratory Report No. 43-12 (1942)

⁸ Wannier, G.H., Phys. Rev. 52, 191-197 (1937); Seitz, F., Phys. Rev. 76, 1376-1393 (1949); Frohlich, H., and Seitz, F., Phys. Rev. 79, 526-527 (1950)

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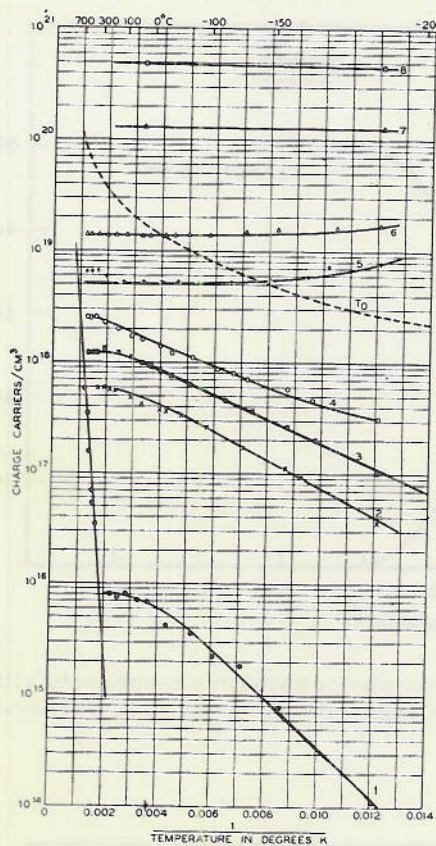


Figure 4a - Number of charge carriers per unit volume, in silicon samples containing boron, as a function of the inverse absolute temperature. Compositions correspond to those given in Figure 3. (G. L. Pearson and J. Bardeen - Reference 4)

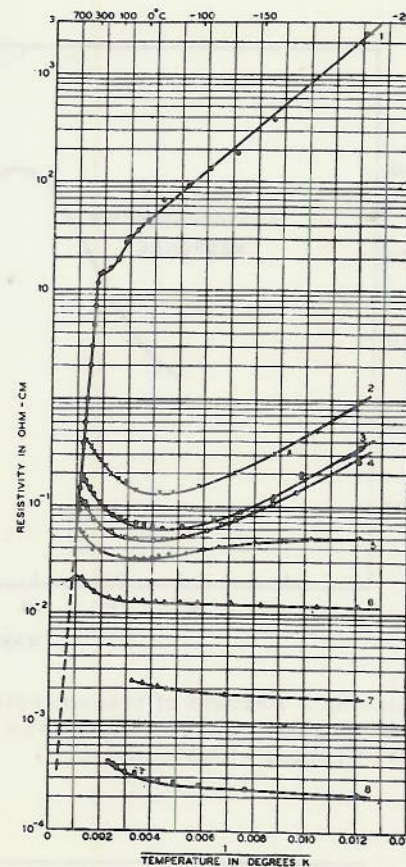


Figure 4b - Resistivity of silicon-boron alloys as a function of the inverse absolute temperature. Compositions correspond to those given in Figure 3. (G. L. Pearson and J. Bardeen - Reference 4)

TABLE 2
Calculated and Experimental Ionization Energies

	Dielectric Constant κ	E_0 Calc. $m = m^*$ ev	n-type E_D ev	p-type E_A ev
Diamond	5	0.43	---	---
Silicon	11.6	0.10	0.05	0.08
Germanium	16	0.05	0.01	0.01

$$* E_0 = \frac{Ry}{\kappa^2} \frac{m^*}{m}$$

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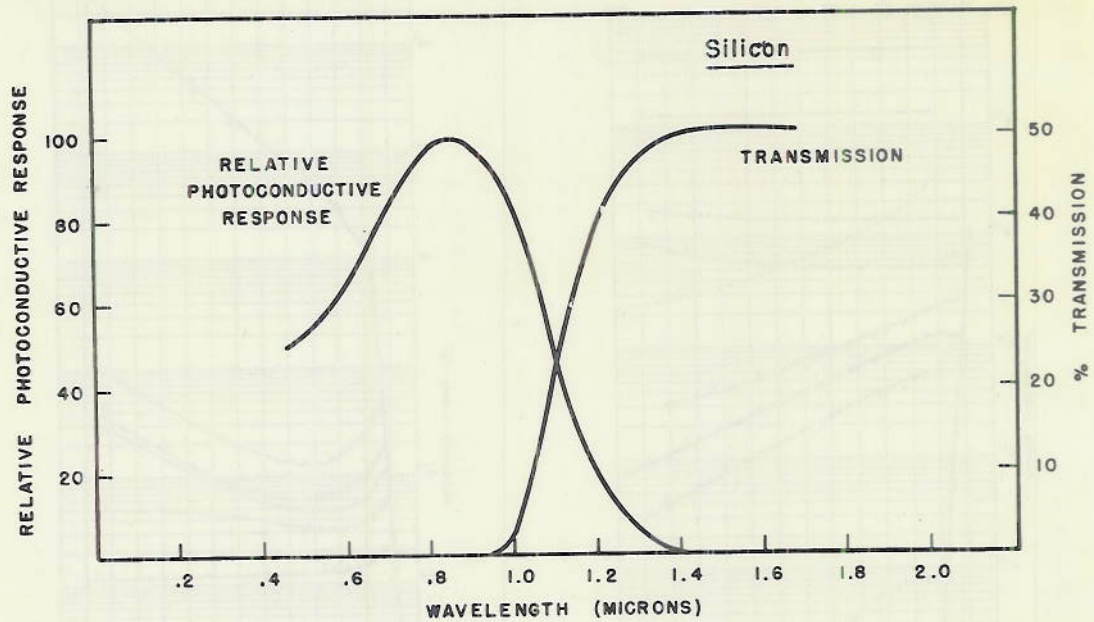


Figure 5a - Percent of transmission and relative photoconductive response of silicon in the region of the intrinsic absorption edge. (G. K. Teal, J. R. Fisher, and A. W. Treptow - Reference 6)

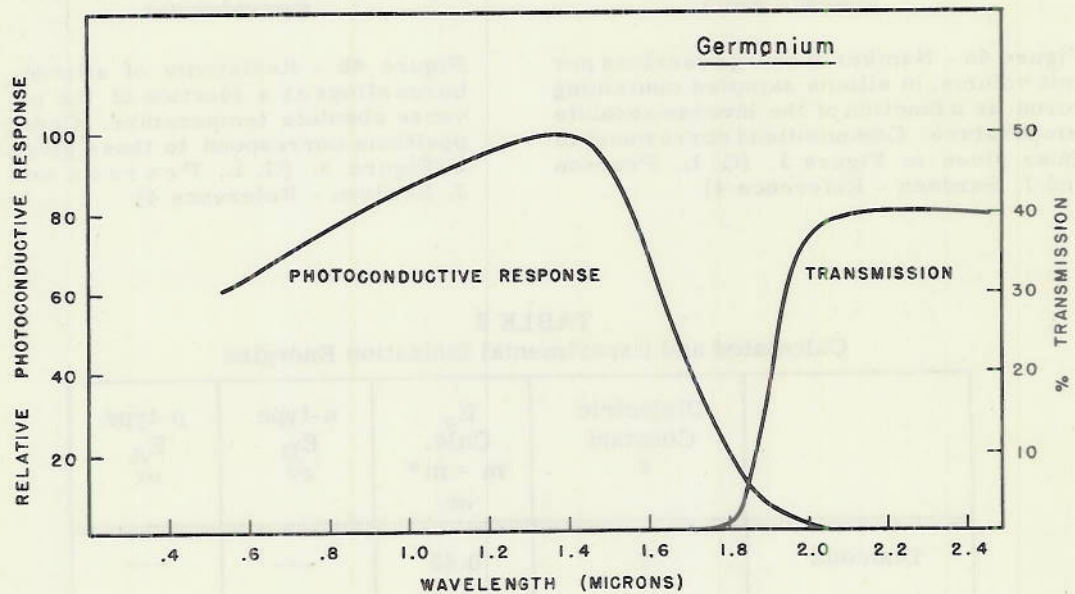


Figure 5b - Percent of transmission and relative photoconductive response of germanium in the region of the intrinsic absorption edge. (F. S. Goucher - Reference 6)

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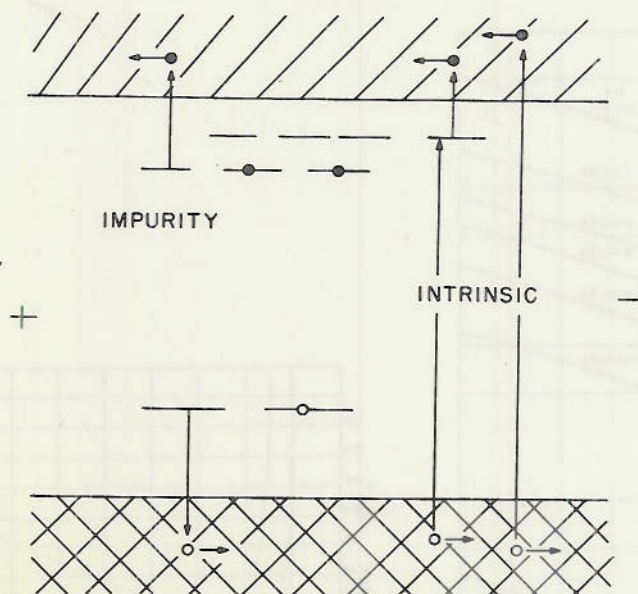


Figure 6 - Energy level diagram showing optical transitions corresponding to absorption in the intrinsic and impurity bands.

The energy gap between the valence band and the conduction band obtained from data on the absorption edge is in good agreement with that obtained from electrical measurements. This is in accordance with the qualitative theory that optical excitation energy will be approximately equal to thermal excitation energy in homopolar substances where the optical and low-frequency dielectric constants are equal. Similarly, the experimental shift in absorption edge with temperature is in good agreement with the change in the intrinsic energy gap with temperature.

At room temperature, the mobile charge carriers which are present in silicon and germanium containing donor and acceptor impurities also contribute to optical absorption, particularly at wavelengths beyond the intrinsic absorption edge (Figure 7). This absorption by the free charge-carriers involves the excitation of free electrons or holes to higher levels within the conduction band. Although the observed absorption coefficients vary as the square of the wavelength, in agreement with theory, their magnitudes are considerably larger than the theoretical values. Attempts to develop a more rigorous quantum mechanical theory for absorption by free charge-carriers have thus far been unsuccessful.⁹

At low temperatures, neutral impurities may be expected to contribute to the infrared absorption. Evidence for the existence of absorption by neutral impurities in silicon has thus far been limited to wavelengths in the vicinity of the absorption edge.¹⁰ Data obtained at liquid nitrogen temperature for silicon containing approximately 10^{18} impurities/cm³ shows, just beyond the intrinsic absorption band, increased absorption over that obtained at room temperature (Figure 8). Since the number of free-charge carriers at liquid nitrogen temperature is roughly one-tenth that at room temperature in silicon containing 10^{18} acceptor atoms/cm³, the increased absorption must be attributed to neutral donors.

⁹ Bardeen, J., Phys. Rev. 78, 315 (1950)

¹⁰ Fan, H.Y., and Becker, M., Phys. Rev. 78, 178-179 (1950)

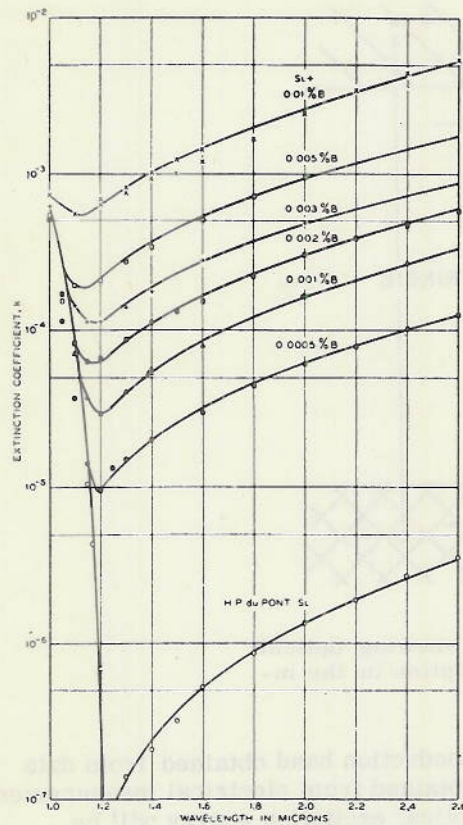


Figure 7 - Extinction coefficient of silicon containing varying amounts of boron in the region from 1.0 to 2.6 microns. (H. B. Briggs - Reference 5)

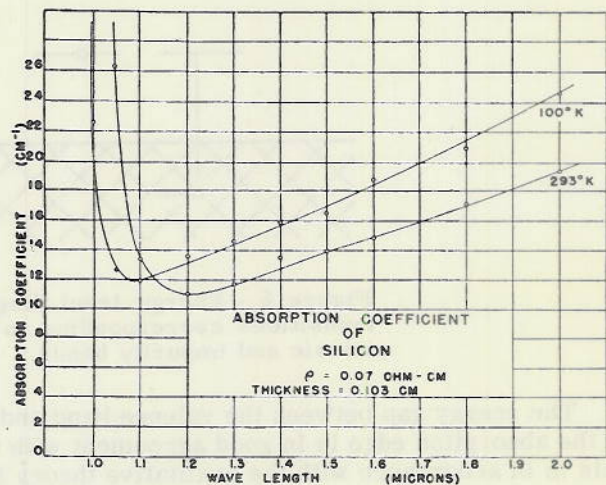


Figure 8 - Absorption coefficient of silicon at 100° K and 293° K in the region of 1.0 to 2.0 microns. (H. Y. Fan and M. Becker - Reference 10)

The position of the long-wavelength edge of the absorption band associated with photoionization can be estimated from the thermal ionization energies of the impurities, particularly for impurities present in homopolar substances where photoionization energies are approximately equal to thermal ionization energies. For low concentrations of donor impurities in silicon, the absorption edge should occur at 25 microns corresponding to a thermal energy of 0.05 ev, whereas for low concentrations of acceptor impurities the absorption edge should occur at approximately 15 microns, corresponding to thermal ionization energies of 0.08 ev. The absorption edge should occur at even longer wavelengths in germanium (Table 1) and also in silicon containing higher concentrations of impurities.

The optical properties of neutral impurities may be expected to resemble those of atomic hydrogen. Accordingly, optical absorption would involve the excitation of the bound charge from the ground state to higher levels, as well as its photoionization. In addition, the photoionization process should lead to relatively broad absorption bands, in contrast with the narrow bands expected with excitation. Since the excited states lie very close to the conduction band, they may, even at low temperatures, be thermally ionized though the unexcited impurity is thermally stable. As a result, both absorption processes should be accompanied by photoconductivity.

Silicon and germanium also exhibit weak absorption bands owing to lattice vibrations similar to those observed in diamond (Figure 9).¹¹ The bands in the region of the fundamental lattice vibration are probably due to the presence of impurities in the lattice as in the case of Type I diamonds; the bands at shorter wavelengths are probably combination bands which arise from the deformation of electron shells during vibration of the atoms.¹²

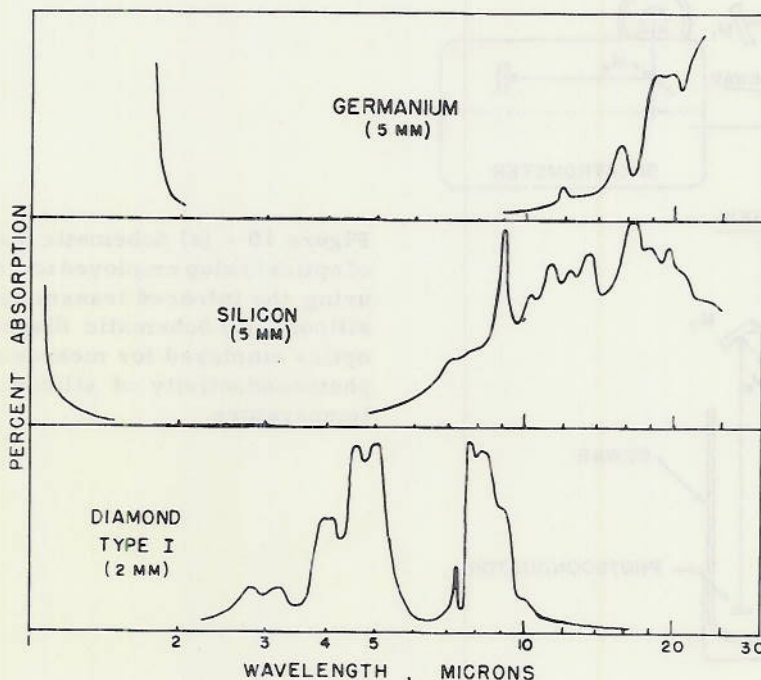


Figure 9 - Infrared absorption spectra of diamond (type I), silicon, and germanium (E. Burstein and J. J. Oberly - Reference 11)

OPTICAL PROPERTIES OF NEUTRAL IMPURITIES

Experimental Results

In order to obtain further data on the optical properties of neutral donor and acceptor impurities in silicon, infrared transmission was measured at liquid nitrogen temperature for two specimens (Si I 101, n-type hyperpure duPont silicon, B.T.L. melt #1335; and Si I 106, p-type, duPont silicon + 0.001% B by weight, B.T.L. melt #1276) which were kindly supplied to this Laboratory by Dr. J. Bardeen and Dr. H. L. Briggs of the Bell Telephone Laboratory. The measurements were carried out with a Perkin-Elmer spectrometer equipped with interchangeable NaCl and KBr prisms and automatic recording equipment. The usual techniques for reducing scattered radiation by means of appropriate transmission and reflection filters were employed. The optics in front of the entrance slit of the spectrometer were modified as shown in Figure 10a to permit the sample to be placed

¹¹ Burstein, E., and Oberly, J. J., Phys. Rev. 78, 642-643 (1950)

¹² Burstein, E., Oberly, J. J., and Plyler, E. K., Proc. Ind. Acad. Sci. 28, 388-400 (1948)

at a focus point. A demountable all-metal dewar with KBr windows (Figure 11) was used as the specimen holder. The specimen could be moved into and out of the optical path by rotating the inner part of the dewar 90°. The observed transmission spectra for the materials mentioned above are shown in Figure 12 and Figure 13, and the related data are given in Table 3.

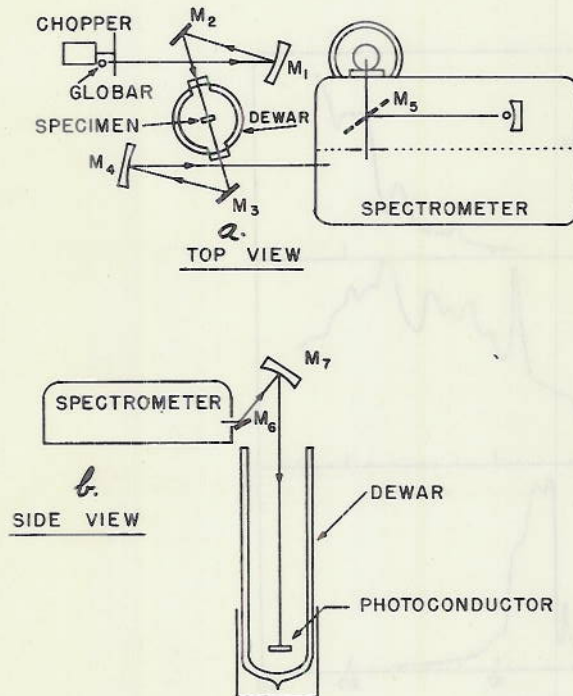
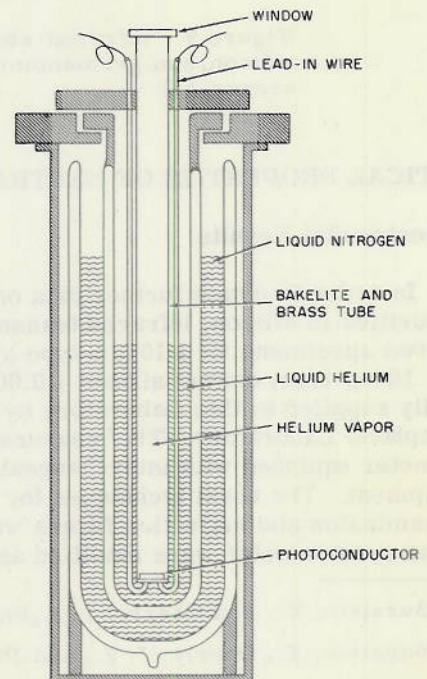


Figure 10 - (a) Schematic diagram of optical setup employed for measuring the infrared transmission of silicon. (b) Schematic diagram of optics employed for measuring the photoconductivity of silicon at low temperature.

Figure 11 - Schematic diagram of liquid helium dewar and specimen holder used in the photoconductivity measurements



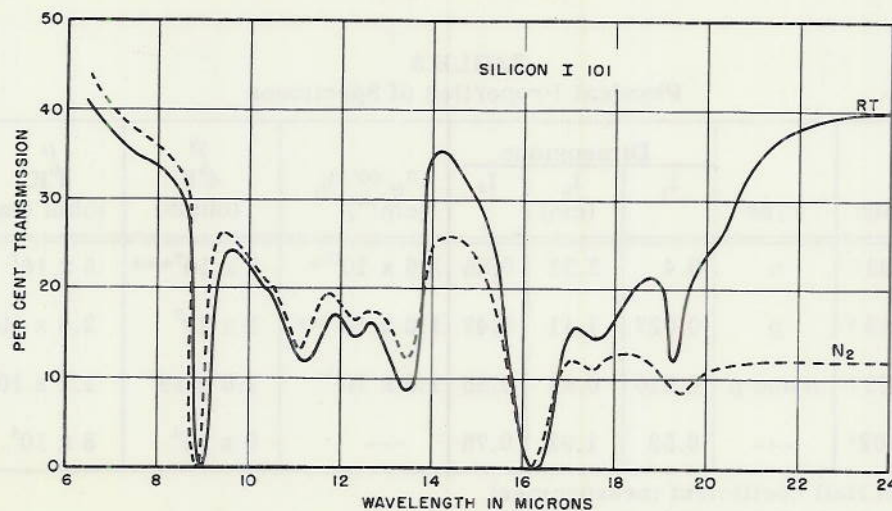


Figure 12 - Transmission curve of the "hyperpure" silicon (I 101) at room temperature and at liquid-nitrogen temperature

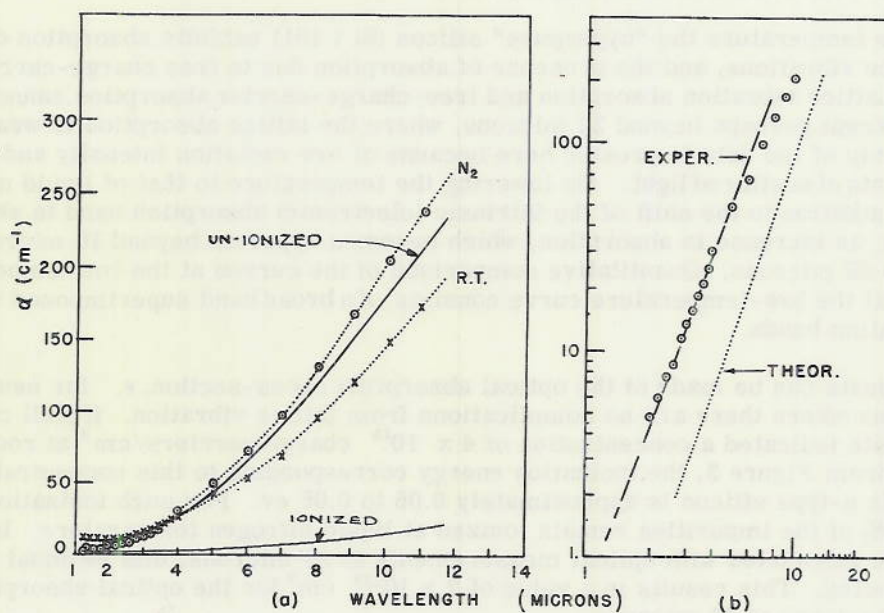


Figure 13 - (a) Absorption spectrum of silicon containing 0.001% B (I 106) at room temperature and at liquid-nitrogen temperature. (b) The experimental and theoretical absorption spectra of silicon (I 106), plotted on a logarithmic scale.

TABLE 3
Physical Properties of Specimens

Specimen	Type	Dimensions			n_e or n_h (cm^{-3})	R 4°K (ohms)	ρ 4°K (ohm cm)
		l_1	l_2 (cm)	l_3			
Si I 103†	n	0.4	2.22	0.55	$2.5 \times 10^{15}*$	$3 \times 10^7***$	5×10^7
Si I 119†	p	0.027	1.11	0.47	$1.0 \times 10^{18}**$	1×10^7	2.4×10^5
Si I 123†	n and p	0.036	0.65	0.55	1.6×10^{17}	2.6×10^9	1.1×10^8
Ge I 102†	---	0.52	1.92	0.75	---	6×10^4	8×10^4

* From Hall coefficient measurement

** From optical data at 2 microns

*** Measured in presence of background room temperature radiation
In absence of background radiation, R was greater than 10^{12} ohms.

† Si I 101 and I 103 are from B.T.L. melt #1335 ("hyperpure")

Si I 106 and I 119 are from B.T.L. melt #1276 (0.001% B)

Si I 123 N.R.L. melt

Ge I 102 B.T.L. melt #491 ("hyperpure")

At room temperature the "hyperpure" silicon (Si I 101) exhibits absorption due primarily to lattice vibrations, and the presence of absorption due to free charge-carriers is not apparent. Lattice vibration absorption and free-charge-carrier absorption cannot be readily separated except perhaps beyond 23 microns, where the lattice absorption is weak. However, the uncertainty of the data is greater here because of low radiation intensity and relatively larger amounts of scattered light. On lowering the temperature to that of liquid nitrogen, there is, in addition to the shift of the intrinsic (electronic) absorption band to shorter wavelengths, an increase in absorption, which becomes apparent beyond 10 microns and continues to 25 microns. Quantitative comparison of the curves at the two temperatures indicates that the low-temperature curve consists of a broadband superimposed upon the lattice vibration bands.

An estimate can be made of the optical absorption cross-section, ϵ , for neutral donors at 25 microns where there are no complications from lattice vibration. If Hall coefficient measurements indicated a concentration of 4×10^{15} charge carriers/ cm^3 at room temperature, then from Figure 3, the ionization energy corresponding to this concentration of impurities in n-type silicon is approximately 0.05 to 0.06 ev. For such ionization energies, less than 10% of the impurities remain ionized at liquid nitrogen temperature. In view of the other errors associated with optical measurements at 25 microns, this residual ionization can be neglected. This results in a value of $7 \times 10^{-16} \text{ cm}^2$ for the optical absorption cross-section of the donor at 25 microns.

The impure specimen (silicon I 119), on the other hand, clearly exhibits the typical absorption associated with free holes at room temperature. On lowering the temperature, there is, besides the shift of the intrinsic absorption edge to shorter wavelengths, a decrease in absorption at wavelengths below 4 microns, and an increase in absorption at wavelengths beyond 4 microns. The sample was opaque beyond 12 microns at both temperatures. The concentration of acceptor impurities in the impure silicon is 1×10^{18} atoms/ cm^3 .

This was obtained from the absorption coefficient at 2 microns and the known absorption cross-section for free holes. According to the data given in Figure 4a, 10^{17} acceptors remain ionized at liquid nitrogen temperature. The absorption at liquid nitrogen temperature due to neutral acceptor impurities was accordingly obtained by subtracting one-tenth of the absorption observed at room temperature from that observed at liquid nitrogen temperature. The remaining absorption is due to the nine-tenths of the acceptor atoms now un-ionized. The resulting curve for the absorption cross-section of neutral acceptors as a function of wavelength at liquid-nitrogen temperature is given in Figure 13a, together with the corresponding curve for the absorption cross-section of free holes included for purposes of comparison. The absorption cross-section of neutral donors increases approximately as $\lambda^{2.5}$ whereas that of the free holes is found to increase as λ^2 in agreement with the results of other investigators (5).

The absorption by neutral impurities may reasonably be attributed to a photoionization process, since the energies of the incident photons are greater than the ionization energies of the neutral impurity atoms. It is believed that these results represent the first conclusive evidence for the existence of optical absorption by neutral impurities in silicon.

Discussion

An estimate of the impurity ionization energy for the pure specimen, which contains roughly 4×10^{15} donor atoms/cm³, can be made from the dependence of the ionization energy of donors on concentration. This indicates an ionization energy of approximately 0.05 to 0.06 ev. On the assumption that the absorption is due to photoionization, one would expect to observe a rapid decrease in absorption at wavelengths greater than that of the ionization limit. Since this is not observed at the longest wavelength measured (25 microns), the optical ionization energy must be less than 0.05 ev. It is possible, of course, that there is a smearing of the long wavelength limit due either to the existence of a distribution of impurity levels with varying ionization energy or to temperature broadening.

A theoretical estimate of the absorption cross-section of bound charges in neutral impurities can be obtained by means of the theory of photoionization of K-shell electrons.¹³ According to this theory, the absorption cross-section ϵ is given by

$$\epsilon(\nu) = \frac{2^8 \pi e R y}{3 m c Z^2} \left(\frac{\nu_0}{\nu} \right)^4 f(n') \quad (12)$$

where Ze is the effective nuclear charge, ν_0 is the ionization frequency, ν is the frequency at which the absorption cross-section, $\epsilon(\nu)$, is being calculated, and $f(n')$ is given by

$$f(n') = \frac{\exp(-4n' \tan^{-1} n')}{1 - \exp(-2\pi n')} \quad (13)$$

and n' is given by

$$\left(\frac{\nu_0}{\nu - \nu_0} \right)^{\frac{1}{2}}$$

¹³ Bethe, H., Handbuch der Physik, 2nd Edition, vol 24/1, p. 477

The interaction potential between the ion core and the bound charge of the neutral impurity can be written

$$\nu = \frac{Ze}{r} \approx \frac{e}{\kappa r} \quad (14)$$

where the effective charge on the nucleus, Ze , is approximately equal to e/κ . In applying the theory to the present case, we will, however, make use of the empirical values for Ze obtained from the relation

$$E_0 = Z^2 Ry. \quad (15)$$

Equation (12) can then be written

$$\epsilon = \frac{463 \times 10^{-17}}{E_0} \left(\frac{\nu_0}{\nu} \right)^4 f(n') \quad (16)$$

and at the ionization limit becomes

$$\epsilon_0 = \frac{8.48 \times 10^{-17}}{E_0} \left(\frac{\nu_0}{\nu} \right)^{8/3} \quad (17)$$

Using this relation and assuming E_0 to be ≈ 0.05 ev for the pure silicon specimen, we obtain an absorption cross-section of 1.7×10^{-15} cm^2 at the ionization limit, which is somewhat larger than the value of 7×10^{-16} cm^2 obtained experimentally (Table 4). Similar calculations for the impure silicon ($E_0 = 0.04$ ev) also show rough agreement with the observed values shown in Figure 13b where the absorption cross-sections are plotted against wavelength on a log-log scale. Although the calculated values of ϵ_0 are smaller than the observed values by a factor of approximately 3, the observed dependence of on wavelength agrees roughly with the theoretical dependence given by Equation (16).

TABLE 4
Optical Absorption Cross-Section

Specimen	n (cm^{-3})	Wavelength (microns)	Absorption Cross-Section	
			$\epsilon_{\text{obs.}}$ (cm^2)	$\epsilon_{\text{calc.}}$ (cm^2)
Si I 103	2.5×10^{15}	25	7×10^{-16}	17×10^{-16}
Si I 119	1×10^{18}	10	2×10^{-16}	0.8×10^{-15}

Theoretical curves of ϵ versus wavelength for various ionization energies are given in Figure 14. It is interesting to note that the absorption cross-section of an impurity atom at a given wavelength decreases as the photoionization wavelength limit increases. Thus, impurities in germanium having ionization energies of the order of 0.01 ev (corresponding to a long-wavelength absorption edge of 120 microns) would have considerably lower ϵ values in the region of 2 to 25 microns than the corresponding impurities in silicon.

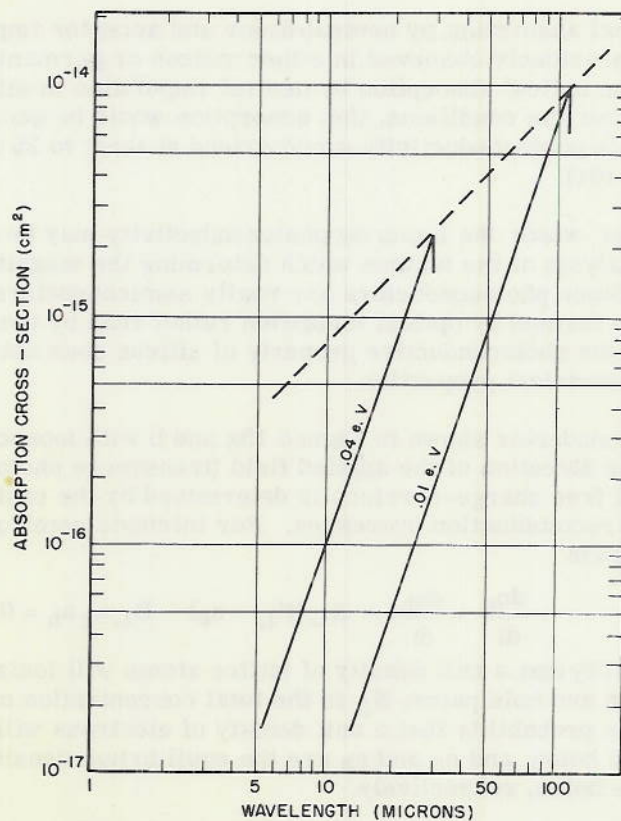


Figure 14 - Theoretical absorption cross-section of impurity centers having ionization energies of 0.01 eV and 0.04 eV as a function of wavelength

Although the agreement with theory is not exact, the results do confirm the usefulness of the hydrogen-like model for neutral impurities in silicon, and in particular for acceptor impurities where bound holes are the counterpart of the K-shell electrons. Further measurements on these specimens are now being carried out at longer wavelengths, in the hope that it will be possible to locate the long-wavelength absorption edge of the neutral impurities. Such information is of value in determining the relation between thermal and optical ionization energies, and in furnishing more detailed information about the distribution of impurity levels than do the corresponding electrical measurements.

PHOTOCONDUCTIVITY

Theory

As mentioned earlier, optical absorption in the intrinsic absorption bands of silicon and of germanium is accompanied by photoconductivity whose long-wavelength limit coincides with the optical absorption edge. The absorption process at the absorption edge may involve either the formation of excitons or the photoionization of the lattice in the vicinity of lattice defects. Since excitons would be thermally dissociated at room temperature, either process can account for the observed photoconductivity at room temperature.

In the case of optical absorption by neutral donor and acceptor impurities, photoconductivity has not been previously observed in either silicon or germanium. From the experimental data on the optical absorption by neutral impurities in silicon, it was fairly certain that under appropriate conditions, this absorption would be accompanied by photoconductivity and that this photoconductivity would extend at least to 25 microns in the hyperpure silicon (Si I 101).

The condition under which the impurity photoconductivity may be observed can be determined from an analysis of the factors which determine the magnitude of the photoconductive response. Since photoconductors are really semiconductors in which free electrons and holes are formed by optical ionization rather than by thermal ionization, the theoretical analysis of the photoconductive property of silicon does not differ greatly from that employed for the electrical properties.

Consider the semiconductor shown in Figure 15a and b with monochromatic radiation incident normally to the direction of the applied field (transverse photoconductivity). In the dark, the density of free charge-carriers is determined by the equilibrium between thermal ionization and recombination processes. For intrinsic semiconductors this equilibrium takes the form

$$\frac{dn_e}{dt} = \frac{dn_h}{dt} = A_L (N_L - n_e) - B_L n_e n_h = 0 \quad (18)$$

where A_L is the probability that a unit density of lattice atoms will ionize thermally in time dt to form free electron and hole pairs, N_L is the total concentration of ionized and unionized lattice atoms, B_L is the probability that a unit density of electrons will combine in time dt with a unit density of holes, and n_e and n_h are the equilibrium densities in the dark of free electrons and free holes, respectively.

Under steady-state monochromatic irradiation in the intrinsic absorption band, the densities of free electrons and holes are increased. The resulting distribution of free charge-carriers and ionized impurities is not uniform, however, since radiation is absorbed exponentially along the light path.¹⁴ Under these conditions (if we neglect the diffusion of charge carriers under a concentration gradient), the equilibrium condition in a thin layer, dx , of the photoconductor normal to the light path at a distance x from the front surface takes the form

$$\frac{dn'_e}{dt} = \frac{dn'_h}{dt} = A_L (N_L - n'_e) + Q_L I_0 \alpha_L \exp(-\alpha_L x) - B_L n'_e n'_h = 0 \quad (19)$$

where n'_e and n'_h are the equilibrium concentrations of electrons and holes in the layer under irradiation; Q_L is the number of electron-hole pairs formed by unit intensity of absorbed radiation, I_0 is the intensity of incident monochromatic radiation of wavelength λ , and α_L is the absorption coefficient of the lattice. The term $Q_L I_0 \alpha_L \exp(-\alpha_L x)$ represents the density of electron-hole pairs produced in the layer.

Combining the "dark" and "light" equilibrium equations (and noting that $n_e = n_h$ for intrinsic semiconductors), we obtain for the change in density of free charge-carriers in a layer of thickness dx

$$\Delta n_e = (n'_e - n_e) dx = n_e \left[\left(1 + \frac{Q_L I_0 \alpha_L \exp(-\alpha_L x)}{B_L n_e^2} \right)^{\frac{1}{2}} \right] dx \quad (20)$$

¹⁴ Gilleo, M.A. (M.I.T.) and Wannier, G. (B.T.L.), private communication

where the term $QE_0 \alpha_L \exp(-\alpha_L x)/B_L n_e^2$ represents the ratio of the density of free charge carriers produced by irradiation in the layer to that produced by thermal ionization alone. The fractional change in conductivity of the whole specimen produced by irradiation is obtained by integration over the thickness l and is given by

$$\frac{\Delta\sigma}{\sigma} = \frac{1}{\alpha_L l} \left[2 \left\{ (1 + \gamma_L)^{\frac{1}{2}} - (1 + \gamma_L \exp(-\alpha_L l))^{\frac{1}{2}} \right\} - \log \frac{\left\{ 1 + \gamma_L \exp(-\alpha_L l) - 1 \right\} \left\{ (1 + \gamma_L)^{\frac{1}{2}} + 1 \right\}}{\left\{ 1 + \gamma_L \exp(-\alpha_L l) + 1 \right\} \left\{ (1 + \gamma_L)^{\frac{1}{2}} - 1 \right\}} - 1 \right] \quad (21)$$

where σ is the dark conductivity and γ_L is $Q_L I_0 \alpha_L / B_L n_e^2$, the ratio of optical to thermal generation of charge carriers at $x = 0$. When α_L is considerably less than unity, the fractional change in conductivity is given by the approximate relation

$$\frac{\Delta\sigma}{\sigma} = \frac{\gamma_L}{2\alpha_L l} (1 - \exp(-\alpha_L l)) \quad (22)$$

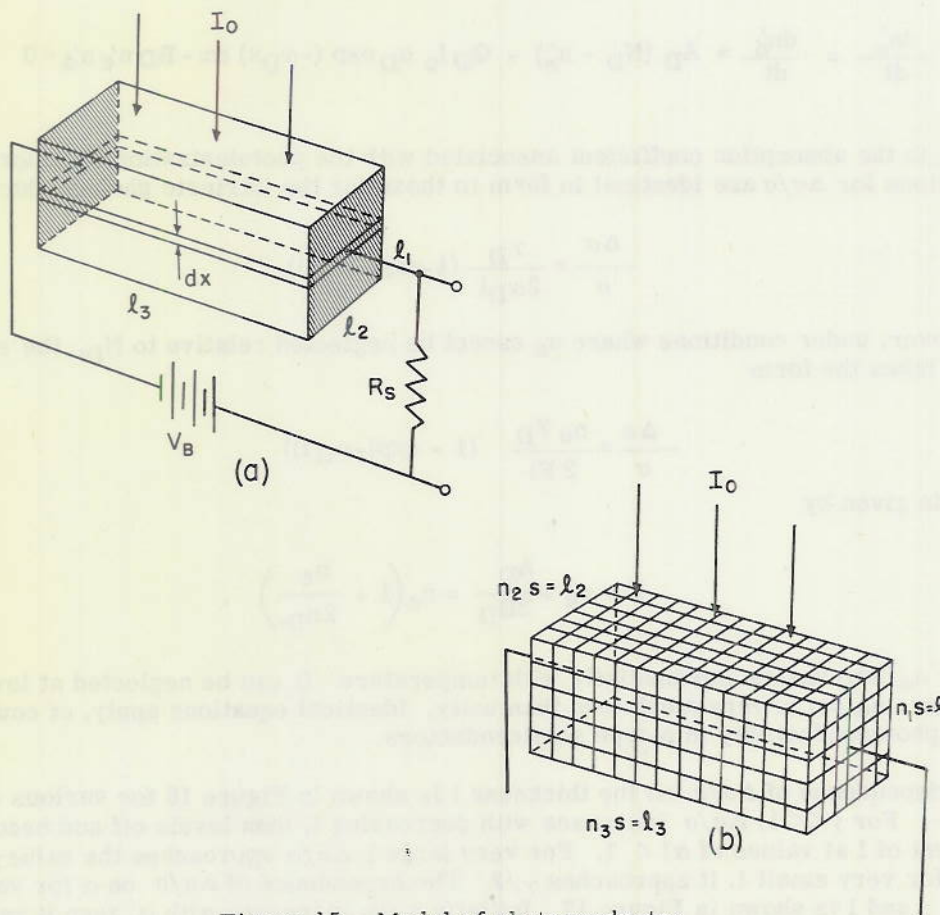


Figure 15 - Model of photoconductor and the photoconductor circuit

The above equation enables us to predict the dependence of $\Delta\sigma/\sigma$ on the various parameters, α, γ, l , etc. The dependence of $\Delta\sigma/\sigma$ on temperature is determined by the manner in which α and γ vary with temperature.

The above analysis can be readily extended to impurity photoconductors. Thus, the "dark" equilibrium equation for an n-type semiconductor in the impurity range of temperatures (where we can neglect the generation of electron-hole pairs by thermal ionization of the lattice) is given by

$$\frac{dn_e}{dt} = \frac{dn_d}{dt} = A_D (N_D - n_e) - B_D n_e n_d = 0 \quad (23)$$

where N_D is the total number of ionized and un-ionized donor atoms, n_e and n_d are the equilibrium concentrations in the dark of free electron and ionized donors; A_D is the probability that a unit density of donor atoms will be thermally ionized in time dt , and B_D is the probability that a unit density of electrons will combine with a unit density of ionized donors in time dt .

The corresponding equilibrium equation for a layer dx under constant monochromatic irradiation in the impurity absorption band takes the form

$$\frac{dn'_e}{dt} = \frac{dn'_d}{dt} = A_D (N_D - n'_e) + Q_D I_0 \alpha_D \exp(-\alpha_D x) dx - B_D n'_e n'_d = 0 \quad (24)$$

where α_D is the absorption coefficient associated with the photoionization of donor impurities. The equations for $\Delta\sigma/\sigma$ are identical in form to those for the intrinsic photoconductor

$$\frac{\Delta\sigma}{\sigma} = \frac{\gamma_D}{2\alpha_D l} (1 - \exp(-\alpha_D l)). \quad (25)$$

However, under conditions where n_e cannot be neglected relative to N_D , the equation for $\Delta\sigma/\sigma$ takes the form

$$\frac{\Delta\sigma}{\sigma} = \frac{n_e \gamma_D}{2 F l} (1 - \exp(-\alpha_D l)) \quad (26)$$

where F is given by

$$F = n_e + \frac{A_D}{2B_D} = n_e \left(1 + \frac{n_e}{2n_D} \right). \quad (27)$$

The term $n_e/2n_D$ varies exponentially with temperature. It can be neglected at low temperature, where n_e/n_D is very much less than unity. Identical equations apply, of course, to impurity photoconductivity in p-type semiconductors.

The dependence of $\Delta\sigma/\sigma$ on the thickness l is shown in Figure 16 for various values of α and γ . For $\gamma \ll 1$, $\Delta\sigma/\sigma$ increases with decreasing l , then levels off and becomes independent of l at values of $\alpha l < 1$. For very large l , $\Delta\sigma/\sigma$ approaches the value $\gamma/2l$, whereas for very small l , it approaches $\gamma/2$. The dependence of $\Delta\sigma/\sigma$ on α for various values of γ and l is shown in Figure 17. Initially $\Delta\sigma/\sigma$ increases with α , then it passes through a maximum and decreases. The decrease at large α results from the fact that the increase in absorptance with increasing α becomes relatively small, while the rate of recombination continues to increase as the radiation is absorbed in thinner layers. This

dependence of $\Delta\sigma/\sigma$ on α has been used to explain the existence of a maximum in the spectral response curves of intrinsic photoconductors.

Figure 16 - The photoconductive response $\Delta\sigma/\sigma$ plotted as a function of thickness for different values of α and γ

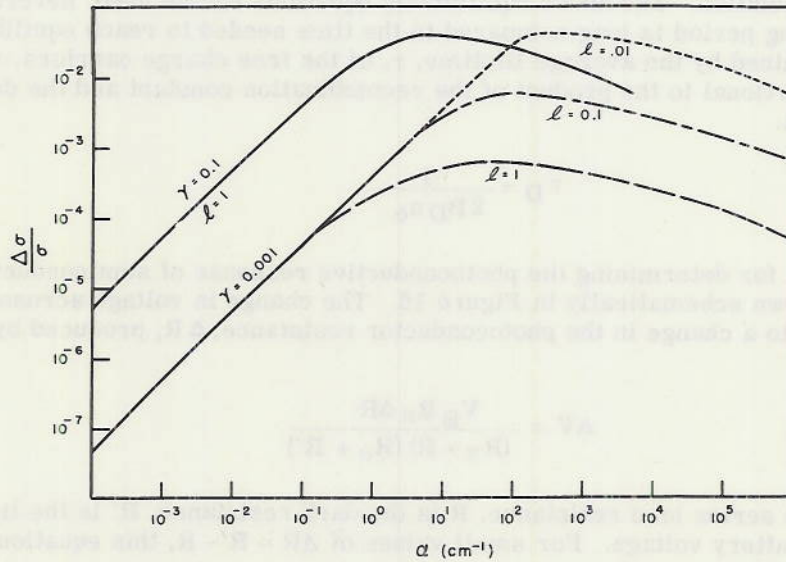
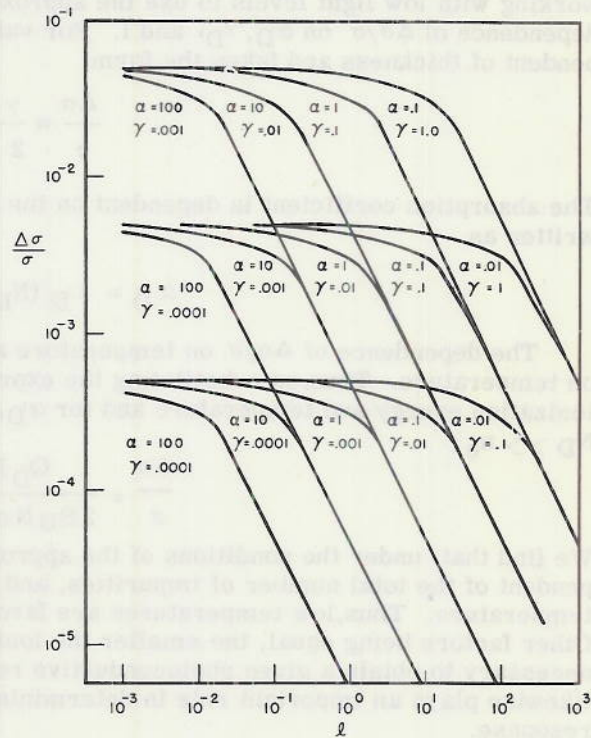


Figure 17 - The photoconductive response $\Delta\sigma/\sigma$ plotted as a function of the absorption coefficient, α , for different values of l and γ . The curves for $l = 1$ were calculated by A. Gilileo, M.I.T. (Private communication).

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The absorption coefficient in impurity photoconductors is generally considerably smaller than that encountered in intrinsic photoconductors. It is usually possible, therefore, when working with low light levels to use the approximate Equation (22) for $\gamma_D < 1$ to describe the dependence of $\Delta\sigma/\sigma$ on α_D , γ_D , and l . For values of l where $\alpha l < 1$, $\Delta\sigma/\sigma$ becomes independent of thickness and takes the form

$$\frac{\Delta\sigma}{\sigma} = \frac{\gamma}{2} = \frac{Q_D I_0 \alpha_D}{2 B_D n_e^2} \quad (28)$$

The absorption coefficient is dependent on the density of un-ionized impurity and can be written as

$$\alpha_D = \epsilon_D (N_D - n_e) \quad (29)$$

The dependence of $\Delta\sigma/\sigma$ on temperature arises primarily from the dependence of n_e on temperature. Thus, on substituting the expression for n_e in terms of the thermal ionization energy and temperature and for α_D , we obtain at low temperatures where $N_D \gg n_e$

$$\frac{\Delta\sigma}{\sigma} = \frac{Q_D I_0 \epsilon_D}{2 B_D N \exp(-E_D/kT)} \quad (30)$$

We find that, under the conditions of the approximation which is employed, $\Delta\sigma/\sigma$ is independent of the total number of impurities, and increases exponentially with decrease in temperature. Thus, low temperatures are favorable for the observation of photoconductivity. Other factors being equal, the smaller the ionization energy, the lower is the temperature necessary to obtain a given photoconductive response. The recombination constant, B , likewise plays an important role in determining the magnitude of the photoconductive response.

In actual practice, when making photoconductive response measurements one generally uses chopped radiation. The above equilibrium equations can be used, nevertheless, whenever the chopping period is long compared to the time needed to reach equilibrium. The latter is determined by the average lifetime, τ , of the free charge carriers, which is inversely proportional to the product of the recombination constant and the density of free charge carriers.

$$\tau_D = \frac{1}{2 B_D n_e} \quad (31)$$

The circuit for determining the photoconductive response of semiconductors to chopped radiation is shown schematically in Figure 18. The change in voltage across the load resistance due to a change in the photoconductor resistance, ΔR , produced by radiation is given by

$$\Delta V = \frac{V_B R_S \Delta R}{(R_S + R)(R_S + R')} \quad (32)$$

where R_S is the series load resistance, R is the dark resistance, R' is the light resistance, and V_B is the battery voltage. For small values of $\Delta R = R' - R$, this equation takes the approximate form

$$\Delta V = V_B \frac{R_S}{(R_S + R)^2} \Delta R \quad (33)$$

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and when R_S "matches" R , ($R_S = R$) this change in voltage across R_S will be a maximum given by

$$\Delta V = \frac{V_B}{4} \frac{\Delta R}{R} \quad (34)$$

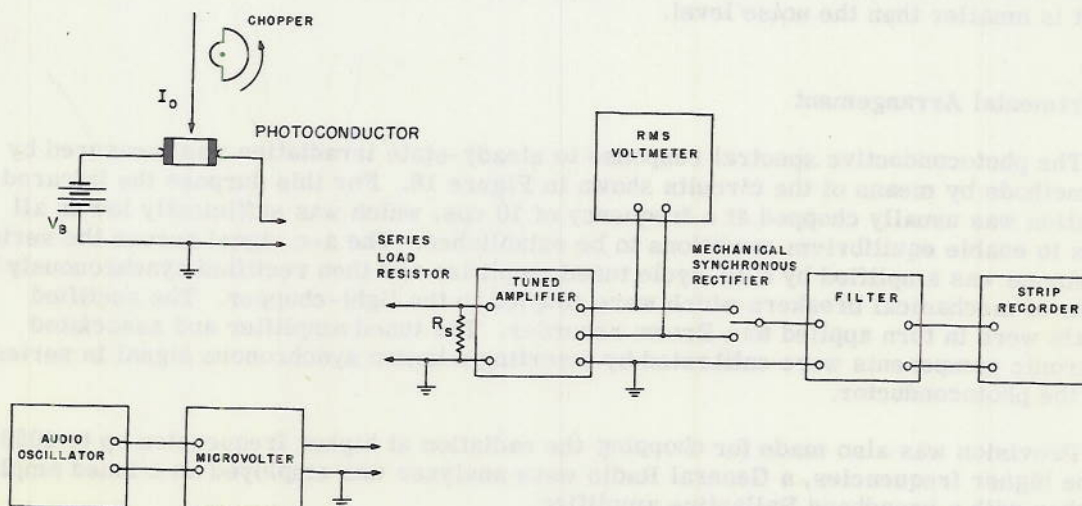


Figure 18 - Schematic diagram of circuits used to measure photoconductive signal and noise

Wherever feasible, measurements are made with matching load resistance. This requires the selection of a different load resistance at each temperature at which measurements are made. Frequently, however, when R is large, it is necessary to employ $R_S \ll R$, and the change in voltage is given by

$$\Delta V = V_B \frac{R_S}{R} \frac{\Delta R}{R} \quad (35)$$

To relate the change in voltage to the fractional change in conductivity is fairly simple whenever $\Delta R/R \ll 1$, since $\Delta\sigma/\sigma = -\Delta R/R$. Under these conditions Equations (34) and (35) can be written as

$$\Delta V = -\frac{V_B}{4} \frac{\Delta\sigma}{\sigma} \quad (36)$$

and

$$\Delta V = -V_B \frac{R_S}{R} \frac{\Delta\sigma}{\sigma} \quad (37)$$

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Thus far we have discussed only the magnitude of ΔV , which is proportional to $\Delta\sigma/\sigma$, without considering practical limitations to the photoconductivity measurements. The smallest photoconductive response which can be detected actually depends on the magnitude of the noise from various sources, such as thermal noise, current noise, and amplifier noise, as well as the photoconductive response. When the photoconductive effect is small, it may be completely masked by the noise. Thus, the absence of photoconductivity under given conditions may mean only that the change in voltage associated with the photoconductive effect is smaller than the noise level.

Experimental Arrangement

The photoconductive spectral response to steady-state irradiation was measured by a-c methods by means of the circuits shown in Figure 18. For this purpose the infrared radiation was usually chopped at a frequency of 10 cps, which was sufficiently low in all cases to enable equilibrium conditions to be established. The a-c signal across the series resistance was amplified by a 10-cycle tuned amplifier and then rectified synchronously by means of mechanical breakers which were coupled to the light-chopper. The rectified signals were in turn applied to a Brown recorder. The tuned amplifier and associated electronic components were calibrated by inserting a known synchronous signal in series with the photoconductor.

Provision was also made for chopping the radiation at higher frequencies up to 1080 cps. At the higher frequencies, a General Radio wave analyzer was employed as a tuned amplifier together with a broadband Ballantine amplifier.

Preliminary attempts to detect impurity photoconductivity in relatively pure silicon (Si I 101) at liquid nitrogen temperatures using a residual ray monochromator (Figure 19) to obtain high intensities of monochromatic radiation were unsuccessful, but the specimen did exhibit a weak intrinsic photoconductivity at this temperature. Similar results were obtained with silicon containing 0.001% boron (I 119). An appreciable photoconductive response was, however, observed at liquid helium temperatures when five LiF restrahlen plates and a LiF shutter were used. Since LiF reflects infrared radiation only beyond 15 microns, which could mean only that the photoconductivity was excited by radiation beyond 15 microns. With five SiO₂ restrahlen plates and a NaCl shutter it was possible to show that the photoconductive response extended at least as far out as 23 microns.

Spectral response curves were obtained by means of the Perkin-Elmer spectrometer for "pure" silicon (Si I 103), and a specimen of silicon was grown by Mr. J. Hino of the Electric and Magnetic Alloys Branch, Metallurgy Division, NRL, from hyperpure duPont silicon (Si I 123) which contained an intermediate concentration of impurities (Table 4).

A simple arrangement (Figure 10b) was used to hold the photoconductor for measurements at liquid nitrogen and liquid helium temperatures. The mirror just beyond the exit slit inside the spectrometer housing was arranged so that it could be rotated from its position to allow monochromatic radiation to pass through an appropriate "window" in the rear of the housing to a spherical mirror which then focussed the radiation downward to the photoconductor mounted in the dewar. Thus, with the mirror in its usual position, the radiation intensity could be measured by means of the thermocouple, and with the mirror turned aside, the photoconductor could be irradiated. Care was taken in all cases to eliminate or minimize scattered light by using appropriate reflection and transmission filters.

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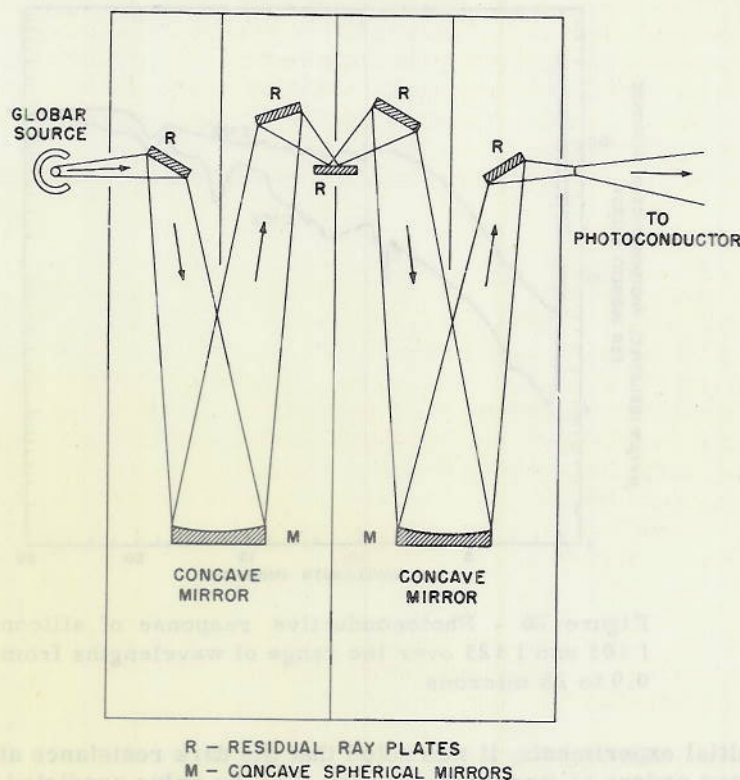


Figure 19 - Schematic diagram of residual ray monochromator employed in the photoconductivity measurements

Rhodium electrodes were applied to the specimen by electrodeposition from a standard rhodium plating bath. Before the electrodes were applied, the areas to be plated were cleaned by sandblasting, and the areas to be left unplated were covered with lacquer. Generally, the two large opposite surfaces of the photoconductor normal to the incident radiation were ground and polished; in the case of one specimen (Si I 119) the surfaces were fine ground but not polished.

The spectral response curves are plotted in Figure 20 as relative photocurrent per incident energy versus wavelength. The magnitudes of the spectral response, as well as the dark resistance are given in Table 4 as microvolts per microwatt at 10 microns for the various specimens. The various dips in the I 103 photoconductive response curve are due to nonphotoconductive absorption processes which compete with the photoionization process. A discussion of the effect of a competitive nonphotoconductive process on the magnitude of the photoconductive response is given in Appendix 4.

The spectral response curves are of particular interest since both intrinsic and impurity photoconductivity are present, but well separated so that there is no ambiguity in identifying them. Since the measurements did not extend beyond 25 microns, it was not possible to determine the long-wavelength limit of impurity photoconductivity for the specimens under consideration. In the case of the pure silicon (Si I 101), the spectral response curve has dips at the wavelengths of the absorption bands associated with lattice vibrations. Where this lattice vibration absorption is considerably smaller than neutral impurity absorption, as for specimens Si I 119 and Si I 123, such dips are not evident.

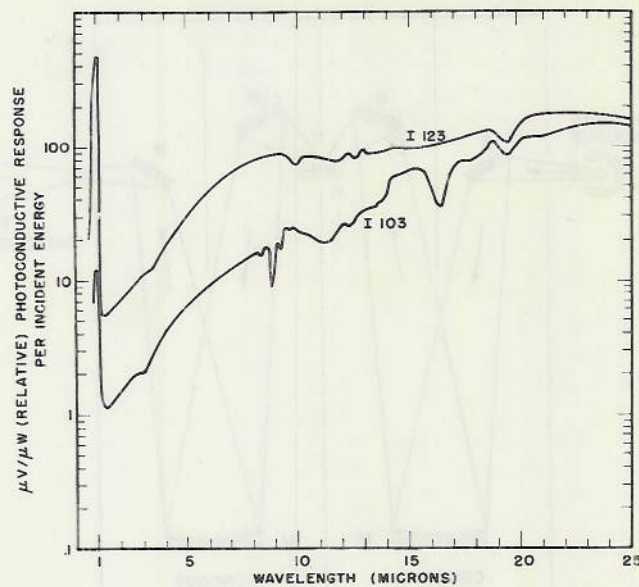


Figure 20 - Photoconductive response of silicon I 103 and I 123 over the range of wavelengths from 0.9 to 25 microns

In the initial experiments, it was noted that the dark resistance at liquid helium temperature was many orders of magnitude smaller than the value predicted from the concentration of impurities and the thermal ionization energies. This was at first attributed to the effect of room-temperature background radiation, which is unavoidably present in such experiments, particularly since the specimens are quite photoconductive over the range of wavelengths where room temperature black-body radiation is peaked. A shutter was therefore incorporated in the dewar which, when closed, completely cut off external radiation, and the effect of background radiation on the resistance at liquid helium temperature was determined. It was found that for the pure silicon, Si I 101, the true dark resistance at 4.2°K with the shutter closed was greater than 10^{12} ohms, the measurements being limited by surface leakage in the apparatus. When the shutter was open, the resistance dropped to about 10^8 ohms, the actual value depending on the size of the aperture used. However, the fractional changes in resistance of relatively impure silicon, Si I 123 and Si I 119, were less than 1%. Thus, background radiation did not account for the rather low resistance of the two impure silicon specimens.

An estimate was also made of the magnitude of the time constant of the photoconductive response. For this purpose the infrared radiation was modulated by square-wave chopping, and the a-c output from the photoconductor circuit was applied to a wide-band amplifier and an oscilloscope. No apparent change was found in the shape of the square-wave signal for chopping rates up to 2 kc. We may therefore conclude that the time constant for the photoconductive response is less than 5×10^{-5} sec.

A spectral response curve was also obtained at liquid helium temperature for a Bell Telephone Laboratory specimen of high-back-voltage germanium. The intrinsic response exhibits a tail at the absorption edge which appears to extend out to 6 microns, but there is no evidence for impurity photoconductivity at longer wavelengths.

Discussion

These measurements demonstrate for the first time the existence of photoconductivity beyond 6 microns. This photoconductivity extends at least as far as 25 microns, which is the long-wavelength limit of the KBr prism. The results are also of interest because intrinsic and impurity photoconductivities are clearly separated in silicon. In addition, since the semiconductor properties of silicon are fairly well established, and interpretation of the experimental results appears possible with a minimum of assumptions.

The specimens for which photoconductivity data were obtained have thermal-ionization energies of the order of 0.04 to 0.05 ev, corresponding to long-wavelength limits of 25 to 30 microns which are beyond the range of the KBr prism. The absorption and photoconductivity data nevertheless do give an indication of the agreement between the optical- and thermal-ionization energies of the impurities. For example, the thermal-ionization energy of the donor atoms in the pure specimen Si I 101 is in the range of 0.05 to 0.06 ev, as determined from the dependence of the thermal-ionization energy on donor concentration. The optical-ionization energy, determined from the fact that the long-wavelength limit occurs beyond 25 microns, is somewhat less than 0.05 ev. It is intended to extend the measurements to longer wavelengths by using a KRS-5 prism in order to determine these long-wavelength limits more precisely. In the case of the silicon containing 0.001% B (Si I 119), for which a fairly accurate value of thermal-ionization energy is available, it will be especially of value to compare the optical- and thermal-ionization energies.

It should be pointed out in this connection that although the hydrogen-like model predicts a well-defined long-wavelength limit of absorption and photoconductivity associated with a well-defined ionization limit of the neutral impurities, the experimental long-wavelength limit will probably be somewhat smeared. This is expected because the impurity energy levels probably have a range of ionization energies due to the inhomogeneous distribution of impurities and to the interaction of the impurity levels with the thermal and zero-point vibrations of the lattice. It should be possible to demonstrate photoconductivity considerably beyond 25 microns by using silicon with higher impurity concentrations since the impurity ionization energy decreases with increasing impurity content, or in germanium where the ionization energies are lower than in silicon. At liquid-helium temperature, the residual conductivity, (which increases with increasing impurity content) and the decrease in radiation intensity with wavelength will probably be the deciding factors which determine the longest wavelength limit of photoconductivity which can be attained with silicon.

Since both intrinsic and impurity photoconductivity measurements are obtained under identical conditions in the same specimen, it is possible to make a comparison of their relative magnitudes and to estimate the relative magnitudes of the various parameters which determine the response. This comparison is hindered by the absence of data on the relative time constants of impurity and intrinsic photoconductive response, and by the fact that the intrinsic absorption coefficients are orders of magnitude greater than the impurity absorption coefficients. At the present time, therefore, it is possible to make only a qualitative comparison. For this purpose it is necessary to have an expression for the intrinsic photoconductive response in semiconductors containing an appreciable density of charge carriers due to donor or acceptor impurities. Although the equilibrium densities of electrons and holes are no longer equal, the analysis is only slightly more complicated than that for the intrinsic photoconductive response in the absence of impurities.

For purposes of discussion, let us consider the case of an n-type semiconductor ($n_e \gg n_h$) and assume that $\gamma_D \ll 1$ so that throughout the photoconductor $n_e \gg \Delta n_e$. At sufficiently low temperatures where $N_D \gg n_e$, the change in the equilibrium density of free electrons at any temperature due to steady-state radiation in a layer dx is given

by the approximate relation,

$$\Delta n_e = \frac{Q_L I_0 (1 - \exp(-\alpha_L l))}{2 B_L n_e l} \quad (38)$$

The corresponding increase in the equilibrium density of holes is given by

$$\Delta n_h = \frac{Q_L I_0 (1 - \exp(-\alpha_L l))}{B_L n_e l} \quad (39)$$

If we assume that the mobilities of electrons and holes are approximately equal, the intrinsic photoconductive response is given by

$$\frac{\Delta \sigma}{\sigma} = \frac{3}{2} \frac{Q_L I_0}{B_L n_e^2 l} (1 - \exp(-\alpha_L l)) = \frac{3}{2} \frac{\gamma_L}{\alpha_L l} (1 - \exp(-\alpha_L l)) \quad (40)$$

Thus, the equation for intrinsic photoconductive response of an n-type semiconductor is, except for a small factor, the same as that for an intrinsic semiconductor (Equation 22).

The intrinsic response (Equation 40) may be expected to differ in magnitude from the impurity response (Equation 25) as a result of differences in the recombination constants and absorption coefficients. A rough idea of the relative magnitudes of the recombination constants B_L and B_D for the two cases can be obtained from the fact that intrinsic photoconductivity can be observed at room and at liquid-hydrogen temperatures where impurity photoconductivity is not observable. We can conclude from this that B_L is considerably smaller than B_D . It should be pointed out that the intrinsic recombination constant B_L is determined by both surface and volume recombination processes,¹⁵ whereas the impurity recombination constant is determined only by volume recombination processes. This arises from the fact that in intrinsic photoconductivity the electron and hole pairs which are produced can diffuse through the crystal without producing space charges, whereas in impurity photoconductivity the single free charge-carrier which is produced does not diffuse away from the immobile ionized impurity because of space-charge effects. Furthermore, available data on the life-time of holes injected into n-type silicon indicate that surface recombination is the primary process which limits the lifetime.¹⁶ In addition, it is possible to alter greatly the lifetime of the injected charge carriers by treating the surface in various ways.

Theoretical values of the recombination constant for impurities having thermal-ionization energies of 0.07 eV were calculated by means of the hydrogen model for processes in which the recombination takes place with the emission of radiation (Appendix 2). The values of the recombination constant which are given in Table 5 for liquid-nitrogen and liquid-helium temperatures are much too small to account for the observed time constants of the photoconductive response. If, then, we take $10^{14}/\text{cm}^3$ as an upper limit for the number of free charge-carriers at liquid-helium temperature in Si I 119, the calculated time constant is 0.25 sec, which is very much longer than the upper limit for the experimental value of 5×10^{-5} sec. It is more probable, therefore, that the recombination of an electron with an ionized impurity takes place by nonradiative processes involving the emission of phonons. A similar

¹⁵ Haynes, J. R., and Shockley, W., Phys. Rev. **81**, 835-843 (1951)

¹⁶ Shockley, W., Electrons and Holes in Semiconductors. D. Van Nostrand Co., Inc., (1950) Chapter 3, p. 66 ff

result has been obtained for recombination of electrons and holes where the optical recombination process was also shown to be less probable than the "radiationless" recombination process (16). More quantitative data will be obtained shortly on the photoconductive time constants for both intrinsic and impurity photoconductivity in the same specimen, which, when combined with data for n_e , should yield empirical values of the intrinsic and impurity time constants (Equation 31).

TABLE 5
Optical Recombination Constant ($E_0 = 0.04$ ev)

Temperature °K	Thermal Velocity v (cm/sec)	Recombination Cross-section C (cm ²)	Recombination Constant B (cm ³ /sec)
177	5.48×10^6	2.0×10^{-21}	1.1×10^{-14}
4.2	1.24×10^6	3.2×10^{-19}	4.0×10^{-13}

The role played by excitons in the intrinsic photoconductive response is, as yet, somewhat uncertain. As pointed out earlier, even if they are stable at liquid-helium temperature, they would very likely ionize one or more neutral impurities. The net result of the absorption process would then be to generate ionized impurities and the corresponding free charge-carriers, whose rate of recombination would then determine the intrinsic photoconductive response. Unfortunately, in the absence of data on intrinsic absorption at liquid-helium temperatures, it is not possible at present to make a quantitative comparison of the intrinsic and impurity response at comparable absorption coefficients. It is, of course, likely that excitons are involved, if at all, only near the absorption edge and that photoconductivity at shorter wavelengths is primarily due to direct photoionization processes.

The relatively large residual conductivity of samples Si I 119 and Si I 123 observed at liquid-helium temperature may possibly arise from the existence of some impurity centers having a very low or zero activation energy. In view of the limited solubility of the impurities in silicon, it would seem to be plausible that a small number of impurity atoms either have one or more impurity atoms as neighbors, or else are located at lattice defects or at the surface of the crystal and therefore have lower ionization energies.

The photoconductivity which was observed with germanium in the region 2-6 microns is probably due to lattice photoionization in the vicinity of defects. The inability to observe impurity photoconductivity in germanium may be explained in several ways. For one thing, the absorption cross-section of neutral impurities in germanium with ionization energies of .01 ev are considerably smaller, on the basis of a hydrogen model, than the corresponding values in silicon. In addition, the residual conductivity of the specimen at liquid-helium temperature was fairly high. Both of these factors would lead to low photoconductive response. Furthermore, in the absence of information concerning the relative magnitudes of the recombination constants, it is not possible to predict the relative magnitude of the photoconductive response in silicon or in germanium. It is also possible, on the other

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hand, that the use of the hydrogen model in germanium is not valid. For example, it has been suggested recently that the impurities in germanium form a partially filled band.¹⁷ If this is actually the case, the optical and photoconductive properties of the impurities in germanium may be completely different from those in silicon.

SILICON

The interest in infrared detectors which are sensitive in the region of wavelengths of 8 to 12 microns stems from the fact that the atmosphere is transparent at these wavelengths, and from the fact that thermal radiation for temperatures near 300°K has its peak in this range of wavelengths (Figure 21). Silicon is the first known infrared photoconductor to meet the spectral requirements. It also has the short time-constant required for rapid scanning applications. It remains now only to discuss whether silicon has a sufficiently low minimum detectable signal to be suitable in the various military applications.

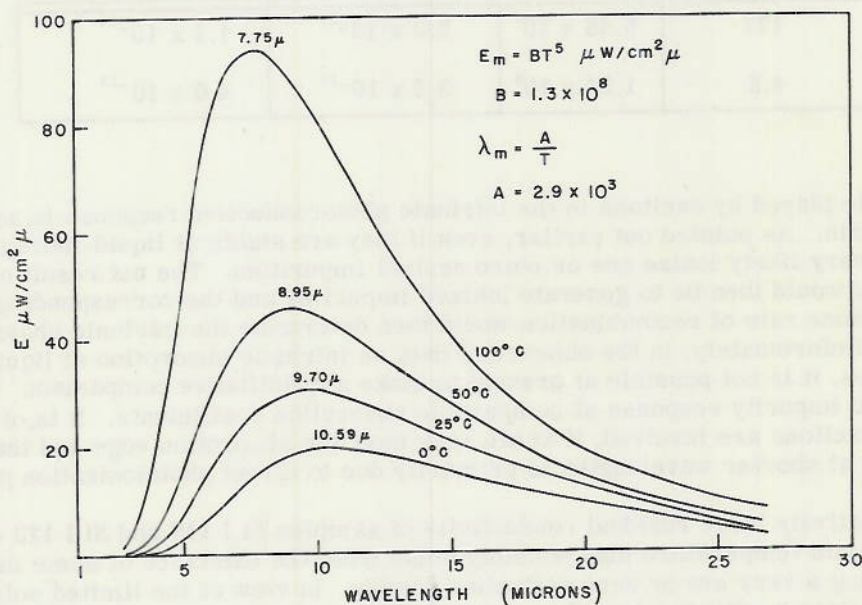


Figure 21 $\frac{1}{2}$ Spectral distribution of black body radiation in $\mu\text{w}/\text{cm}^2 \mu$ for black bodies at different temperature

Semiconductor Noise

The smallest radiation intensity which can be detected by a photoconductor is dependent on both the magnitude of the photoconductive response and magnitude of the electrical noise generated in the photoconductor, which includes thermal noise and current noise as well as noise generated in the associated electronic circuits.¹⁸ When background radiation is

¹⁷ Hung, C. S., and Gliessman, J. R., Phys. Rev. 79, 726-727 (1950); Hung, C. S., Phys. Rev. 79, 727-728 (1950)

¹⁸ Nyquist, H., Phys. Rev. 32, 110-113 (1928); Miller, P. H., Jr., Proc. Inst. Radio Eng. 35, 252-256 (1947); McDonald, D. K. C., Research 1, 194 (1948)

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superimposed on the incident radiation signal, there is an additional noise due to the fluctuations in background radiation¹⁹ which is generally negligible. All a-c signal and noise voltages will be rms values. The total noise voltage, which appears at the input of the amplifier when a current is passing through the semiconductor, consists of thermal noise and current noise,

$$V(T + I) = (\overline{V_T}^2 + \overline{V_I}^2)^{\frac{1}{2}} \quad (41)$$

where $\overline{V_T}^2$ is the mean-square thermal noise voltage and $\overline{V_I}^2$ is the mean-square current noise voltage. When a photoconductive signal is also present, the total voltage (signal plus noise) at the input of the amplifier, neglecting the noise due to the fluctuation in background radiation, is

$$V(T + I + P) = (\overline{V_T}^2 + \overline{V_I}^2 + \overline{V_P}^2)^{\frac{1}{2}} \quad (42)$$

where $\overline{V_P}^2$ is the mean-square photoconductive signal.

Thermal noise arises from spontaneous fluctuations in the motion of the charge carriers and is present whether a field is applied or not. Owing to these fluctuations, the net current through a cross-section of the semiconductor is not zero, but will show random fluctuations even in the absence of an applied voltage. The thermal noise power per bandwidth Δf is given by the Nyquist relation

$$P_T(f) \Delta f = \frac{(\overline{v(f)} - \overline{V})^2}{R} \Delta f = 4kT\Delta f \quad (43)$$

where v is the instantaneous voltage, $\overline{V}$ is the mean voltage and R is the effective resistance at the input to the amplifier. According to this relation, which has been verified experimentally, thermal noise power in a given bandwidth is determined solely by the temperature, and the noise power per cycle is independent of frequency.

Current noise, on the other hand, may be considered to result from fluctuations in the density of the free charge-carriers and therefore from fluctuations in the resistance of the semiconductor. Unlike thermal noise, however, it is present only when current passes through the semiconductor and its magnitude depends on the dimensions of the specimen. Current noise may be generated at the contact between a metal and a semiconductor as well as in the bulk of the semiconductor.

When the series load resistance is matched to the semiconductor, the current noise power per bandwidth Δf can be written in terms of the fluctuations in the resistance of the semiconductor as

$$P_T(f) \Delta f = \frac{(\overline{v(f)} - \overline{V})^2}{R} \Delta f = i^2 R \left(\frac{\overline{r(f)} - R}{R} \right)^2 \Delta f. \quad (44)$$

Since resistance fluctuations in adjacent regions of the semiconductor (whose size depends on the frequency and the nature of the semiconductor) are not correlated, the mean-square fractional fluctuation of the resistance of the semiconductor depends on the dimensions of the specimen.

¹⁹ Fellgett, P. B., J. O. S. A. 39, 970 (1949)

This dependence in a rectangular semiconductor is given by (Appendix 3)

$$\left(\frac{\overline{r(f) - R}}{R} \right)^2 = \frac{s^3}{l_x l_y l_z} \left(\frac{\overline{\Delta r_s(f)}}{r_s(f)} \right)^2 \quad (45)$$

where s^3 is the volume of the largest element of volume which is uncorrelated with neighboring elements $\Delta r_s(f)$ is the instantaneous fluctuation in resistance of the volume element, r_s is the average resistance of the volume element, and l_x, l_y, l_z are the linear dimensions of the semiconductor. The current noise power per cycle is accordingly

$$P_I(f) \Delta f = \frac{i^2 R s^3}{l_x l_y l_z} \left(\frac{\overline{\Delta r_s(f)}}{r_s(f)} \right)^2 \Delta f. \quad (46)$$

Thus, current noise power per cycle is proportional to the size of the largest volume element which is uncorrelated with neighboring elements and inversely proportional to the volume of the square.

Recent investigations of current noise in silicon and germanium²⁰ indicate that current noise in two adjacent sections of the semiconductor are highly correlated when the lifetime of the charge carriers is greater than the transit time between the two sections. There is very little information available on the dependence of current noise on temperature or on the resistance of the semiconductor.

Experimentally it has been shown that the noise power per cycle varies inversely with frequency. The current noise power per bandwidth can therefore be written

$$P_I(f) \Delta f = \frac{c i^2 R \Delta f}{f} \quad (47)$$

where c is a constant which depends on the dimensions and the nature of the semiconductor.

Minimum Detectable Signal

As a measure of the minimum detectable signal²¹ one generally employs the intensity of radiation in watts/cm² for which the ratio of signal power to noise power per cycle is unity. This value of the radiation intensity is called the "equivalent noise input" (ENI) of the radiation detector. In the case of photoconductors, it varies with the current through the specimen since both the photoconductive response and the current noise increase with current while the thermal noise remains independent of current as long as there is no change of temperature due to electrical heating of the specimen. For sufficiently low currents, the thermal noise will be greater than current noise. As the current through the specimen increases, current noise increases and becomes larger than the thermal noise, and simultaneously the photoconductive response increases. This is shown schematically in Figure 22,

²⁰ Montgomery, H. C., and Shockley, W., Phys. Rev. 78, 646 (1950)

²¹ Jones, R., J. O. S. A. 39, 327 and 344 (1949)

where the rms values of the photoconductive signal, current noise, thermal noise, and signal-plus-noise voltages are plotted as a function of the supply voltage. At high current densities the temperature of the specimen may increase because of electrical heating. This causes an increase in density of the free charge-carriers which decreases the photoconductive response and, therefore, leads to lower ENI values. In practice, the optimum ENI for a given photoconductor is determined experimentally by increasing the applied voltage, if feasible, until a maximum signal-to-noise level is achieved. It is generally desirable in this connection, to use, wherever possible, a load resistance which matches the dark resistance of the photoconductor, since under these conditions the signal-to-noise ratio for a given current through the specimen is a maximum.

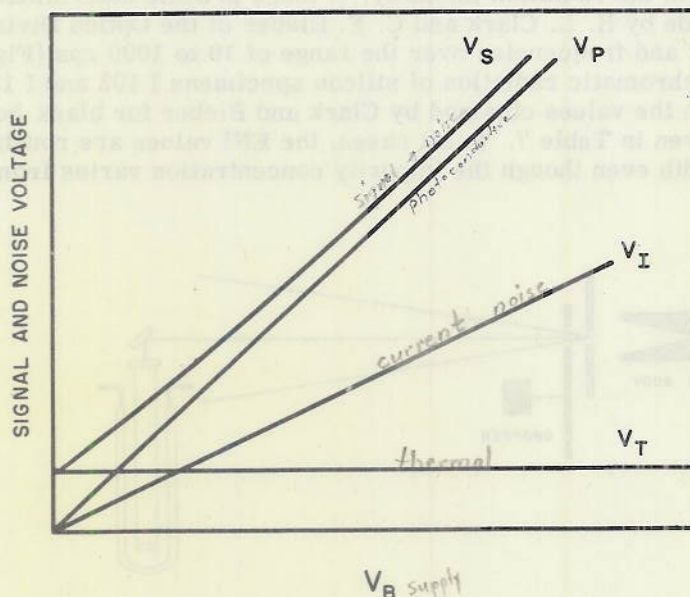


Figure 22 - Schematic curves of photoconductive response V_P , current noise V_I , thermal noise V_T , and the resultant root mean square signal-plus-noise voltage V_S versus supply voltage

In obtaining ENI values for radiation detectors, there is an essential difference between photoconductors and thermal detectors, arising from differences in their spectral response, which should be taken into consideration. Thermal elements are coated with optical blacks which absorb radiation uniformly over all wavelengths, whereas photoconductors generally exhibit a strong wavelength dependence as a result of the variation of their absorption coefficient with wavelength, and the variation with wavelength in the number of photons per unit-intensity of radiation. In the case of thermal detectors, therefore, it is sufficient to know the total intensity of incident radiation in order to obtain their ENI values. In photoconductors, the ENI depends on the particular distribution of wavelengths of the incident radiation and it is therefore desirable to use monochromatic radiation and to obtain data, in the region of interest, on the ENI as a function of wavelength.

Experimental Results

Circuits similar to those used to obtain the photoconductive response were used to measure noise and ENI. In determining the ENI, the supply voltage was increased until the signal-to-noise ratio was a maximum. The supply voltage was then fixed at this point

and the noise voltage was determined with only background radiation incident on the photoconductor. Monochromatic radiation of the desired wavelength was then allowed to fall on the photoconductor, and its intensity was adjusted with the monochromator slits until the signal + noise voltage was two times the noise voltage. The beam was then reflected by the Perkin-Elmer exit mirror and thermocouple mirror onto the thermocouple, and the amount of radiation at the thermocouple was determined from the thermocouple reading by using its known sensitivity. This value of the total beam radiation at the thermocouple was then multiplied by a factor correcting for reflection losses at two windows and for the fraction of the radiation beam incident on the photoconductor to obtain the radiation intensity incident on the photoconductor. This determination of ENI thus involved the use of a calibrated thermocouple to obtain the radiation intensity. A more precise determination of the ENI of Si I 103 was also made by H. L. Clark and C. F. Bieber of the Optics Division using a black body source at 200°C and frequencies over the range of 10 to 1000 cps (Figure 23). The data on the ENI for monochromatic radiation of silicon specimens I 103 and I 123 are given in Table 6 together with the values obtained by Clark and Bieber for black body radiation for sample I 103 are given in Table 7. In all cases, the ENI values are roughly 10^{-8} watts/cm² for a 1 cycle bandwidth even though the impurity concentration varies from specimen to specimen.

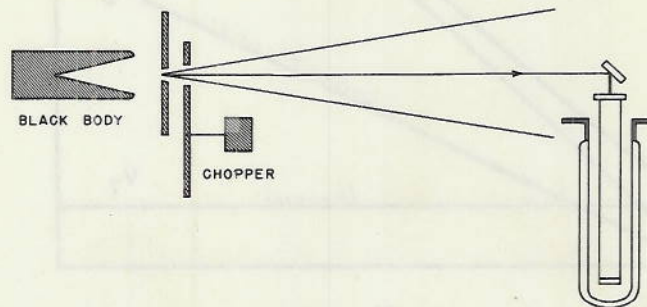


Figure 23 - Schematic diagram of optical setup for measuring ENI using radiation from a black body

TABLE 6
ENI Data (Monochromatic Radiation - 10 Microns)

Silicon Specimen	Sensitivity* $\mu\text{v}/\mu\text{w}$ $V_b = 1 \text{ volt}$	Chopping Frequency (cyc/sec)	ENI** (w/cm ²)
I 103	120	10	3×10^{-8}
I 123	11	1080	1×10^{-8}

* For matched load resistance

** For 1 cps bandwidth

TABLE 7
ENI Data for I 123 (Black Body Radiation)

Frequency cps	Sensitivity* $\mu\text{v}/\mu\text{w}/\text{cm}^2$	ENI** w/cm^2
10	31.4×10^2	15.6×10^{-8}
100	24.6	13.4
1000	25.3	1.74

* Open circuit rms $\mu\text{v}/\mu\text{w}/\text{cm}^2$, $V_B = 180$ volts

** For 1 cps bandwidth

Cell Area 0.5 cm^2 (from Clark's records)

Typical curves of photoconductive response signal, current noise, and signal-to-noise, plotted as a function of the applied voltage, are given in Figure 24 for silicon I 103. In making measurements of the photoconductive signal and noise, no attempt was made in these preliminary experiments to obtain absolute values; the values given in the figure are relative. As expected, the current noise voltage was found to be proportional to the applied voltage. The photoconductive response curve, on the other hand, showed a decrease in slope at the higher voltages which is probably associated with the decrease in resistance brought about by heating. The signal-to-noise ratio of silicon I 101 appears still to be increasing with applied voltage at 495 volts.

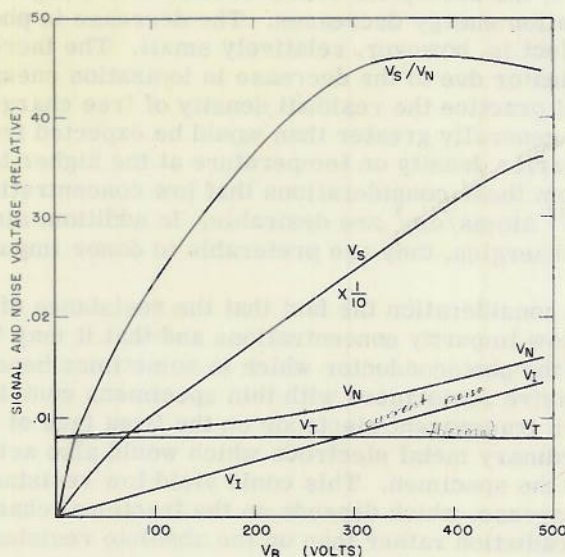


Figure 24 - Curves of signal and noise voltage and signal-to-noise vs. supply voltage for silicon I 103

Discussion

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In view of the short time constant, ENI values of 10^{-8} watts/cm² are rather promising, particularly since they were obtained without any special effort to select the materials or otherwise to obtain optimum conditions. It is reasonable to expect that improved ENI values would be obtained by properly selecting the materials and conditions under which they are used. Let us consider, for example, some of the factors which determine the photoconductive response and noise:

Photoconductive Response - Since we are interested in detecting small signals and since the impurity absorption coefficients are relatively small, we can assume that $\gamma \ll 1$. In terms of the absorption cross-section and thermal-ionization energy of the impurities, the photoconductive signal at low temperature may therefore be written as

$$\frac{\Delta\sigma}{\sigma} = \frac{Q_D I_0 (1 - \exp(-\epsilon_D N_D l))}{2B_D l N_D \exp(-E_D/kT)} \quad (48)$$

Optimum values of the photoconductive response may be obtained by decreasing the thickness of the specimen to a point where $\alpha l \ll 1$ at the wavelengths under consideration. Under these conditions the photoconductive response takes the form

$$\frac{\Delta\sigma}{\sigma} = \frac{Q_D I_0 \epsilon_D}{2B_D N \exp(-E_D/kT)} \quad (49)$$

Although the photoconductive signal does not depend explicitly on the impurity concentration according to this equation, the impurity concentration does influence the photoconductive signal indirectly. This is due to the decrease in optical and thermal ionization energies of the impurities with increase in impurity density which then affects not only the free-charge-carrier density, but also to a lesser extent the absorption cross-section. As seen from Figure 14, the absorption cross-section in the region of 8 to 12 microns decreases as the ionization energy decreases. The decrease in photoconductive response associated with this effect is, however, relatively small. The increase in the exponential term in the denominator due to the decrease in ionization energy produces a much larger effect. In actual practice the residual density of free charge-carriers at liquid-helium temperature is generally greater than would be expected from the known dependence of free-charge-carrier density on temperature at the higher temperatures. It appears, therefore, from these considerations that low concentrations of impurities of the order of 10^{16} to 10^{17} atoms/cm³ are desirable. In addition, since acceptor impurities have higher ionization energies, they are preferable to donor impurities.

We must take into consideration the fact that the resistance of the specimen may become very large at low impurity concentrations and that it may be difficult to match the dark resistance of the photoconductor which is sometimes beneficial. It may be possible to avoid excessive resistances with thin specimens containing low concentrations of impurities by using a transparent electrode on the front face of the specimen and, on the opposite face an ordinary metal electrode which would also act as a mirror to reflect the radiation back into the specimen. This could yield low resistances without affecting the photoconductive response, which depends on the fractional change in resistance produced by the infrared radiation rather than on the absolute resistance.

Going to lower temperatures than 4.2° K would probably not improve the photoconductive signal since the residual charge density probably does not depend appreciably on

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temperature. This is particularly true for specimens with low concentrations of impurities, such as the pure silicon I 101, where the residual charge-carrier density is determined by background radiation. For such cases, it is of course important to keep the angular aperture for the background radiation as small as possible without interfering with that for the infrared signal.

Noise - Although there is as yet no satisfactory theory for current noise in semiconductors, some information is available about the factors which determine its magnitude. There seems to be good evidence that current noise associated with metal-semiconductor contacts and with grain boundaries is generally larger than the corresponding noise associated with the bulk of the semiconductor.²² The inhomogeneity of the specimen thus plays an important role in determining the magnitude of current noise. By using single crystals in which the impurities are distributed homogeneously, it should be possible to decrease current noise to a point where it is determined by the electrode-semiconductor contact alone.

As pointed out above, current noise voltage is inversely proportional to the square root of the volume of the semiconductor. For a given thickness, therefore, the current noise voltage is inversely proportional to the square root of the area of the semiconductor on which the radiation is incident. The photoconductive response is independent of the area; accordingly, when thermal noise can be neglected, the ENI of a photoconductor in watts/cm² is inversely proportional to the square root of the area.

The effect of thickness on the ENI is somewhat different. The current noise voltage is inversely proportional to the square root of the thickness. The photoconductive response, on the other hand, may be independent of thickness, when $\alpha l < 1$, or it may be inversely proportional to the thickness when $\alpha l > 1$. Accordingly, the ENI will decrease as the thickness increases when $\alpha l < 1$, and will increase for values of l such that $\alpha l > 1$. There will therefore be an optimum value of thickness which gives the best ENI at intermediate values of l where $\alpha l \approx 1$.

ACKNOWLEDGMENT

This project has benefited considerably by the cooperation of many individuals and institutions. Among those who deserve special mention are Dr. W. Shockley and several other members of the staff of Bell Telephone Laboratories, Dr. J. Bardeen, Dr. H. B. Briggs and Dr. H. Montgomery for helpful discussions and for supplying many of the specimens used in this investigation; Dr. H. E. Stauss of the Electric and Magnetic Alloys Branch of the Metallurgy Division of NRL for making available specimens of pure silicon; and Mrs. Bertha W. Hervis of the Crystal Branch of the Metallurgy Division for carrying through many of the measurements and calculations.

* * *

²² Shockley, W., *Electrons and Holes in Semiconductors*; D. Van Nostrand Co., Inc. (1950) Chapter 12, p. 342ff

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APPENDIX I

Intrinsic Photoconductivity in Impurity Semiconductors

The equilibria between ionization and recombination processes in a layer dx at depth x of an n-type semiconductor in the impurity range of temperature, for the dark and the light cases, (neglecting diffusion of the free charge-carriers under a gradient) take the form

(a) for electrons:

$$\text{Dark: } A_L n_L + A_D n_D = B_L n_e n_h + B_D n_e n_d \quad (50)$$

$$\text{Light: } Q_L I_0 \alpha_L \exp(-\alpha_L x) dx - A_L n'_L - A_D n'_D = B_L n'_e n'_h + B_D n'_e n'_d \quad (51)$$

(b) for holes:

$$\text{Dark: } A_L n_L = B_L n_e n_h \quad (52)$$

$$\text{Light: } Q_L I_0 \alpha_L \exp(-\alpha_L x) dx + A_L n'_L = B_L n'_e n'_h \quad (53)$$

(c) for donor atoms:

$$\text{Dark: } A_D n_D = B_D n_e n_d \quad (54)$$

$$\text{Light: } A_D n'_D = B_D n'_e n'_d \quad (55)$$

In addition to these equations, we have the electrical neutrality equations:

$$\text{Dark: } n_e = n_d + n_h \quad (56)$$

$$\text{Light: } n'_e = n'_d + n'_h \quad (57)$$

In the impurity range of temperature, we can assume that $n_h = 0$ and therefore that $n'_h = \Delta n_h$ and $n_e \approx n_d$. We will also assume that $n_e \gg \Delta n_e$ which is equivalent to assuming that $\gamma \ll 1$, and that $n'_L \approx n_L$.

From Equation (52) and Equation (53) we obtain

$$\begin{aligned} \Delta n_h &= \frac{Q_L I_0 \alpha_L \exp(-\alpha_L x) dx + A_L n_L}{n_e B_L} \\ &\approx \frac{Q_L I_0 \alpha_L \exp(-\alpha_L x) dx}{n_e B_L} \end{aligned} \quad (58)$$

Similarly from Equations (54) and (55) we obtain the relation

$$-A_D \Delta n_d = B_D (n'_e n'_d - n_e n_d) \quad (59)$$

Using the electrical neutrality relations we obtain an equation for Δn_e in terms of Δn_h

$$\Delta n_e = \left(\frac{A_D + B_D n_e}{A_D + 2 B_D n_e} \right) \Delta n_h \quad . \quad (60)$$

Most of the impurities will be present in un-ionized form at very low temperatures so that $n_D \gg n_d$. Under these conditions we can neglect A_D relative to $B_D n_e$ and write

$$\Delta n_e \approx \frac{\Delta n_h}{2} \approx \frac{Q_L I_0 \alpha_L \exp(-\alpha_L x) dx}{2 B_L n_e} \quad . \quad (61)$$

By combining Δn_e with Δn_h we obtain Δn_d

$$\Delta n_d = \Delta n_e - \Delta n_h = - \frac{Q_L I_0 \alpha_L \exp(-\alpha_L x) dx}{2 B_L n_e} \quad . \quad (62)$$

Finally, on integrating over the thickness of the photoconductor and assuming the mobility of electrons and holes to be equal, we obtain for $\Delta \sigma / \sigma$ the approximate relation

$$\frac{\Delta \sigma}{\sigma} = \frac{3 Q_L I_0}{2 B_L n_e^2 l} \left[1 - \exp(-\alpha_L l) \right] \quad . \quad (63)$$

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APPENDIX II

Optical Recombination Constant

The impurity recombination constant B is related to the capture cross-section of the ionized impurity for the free charge-carrier as follows:

$$B = Cv, \quad (64)$$

where C is the capture cross-section of an impurity, and v is the thermal velocity of the electron which is given by

$$v = 4 \sqrt{\frac{kT}{2\pi m}} \quad (65)$$

An optical capture cross-section can be calculated by means of the hydrogen model for processes in which the electron, having a thermal kinetic energy of W, recombines with the ionized impurity with the emission of radiation $h\nu = W - E_0$. The optical capture cross-section C_0 , which depends on W and E_0 , is given by

$$C_0 = \frac{2^7\pi}{3} \frac{e^2}{mc^2} \frac{h}{mc} \frac{\nu_0^3}{\nu^2(\nu - \nu_0)} f(n') \quad (66)$$

where the various symbols have the same significance as in the equation for optical cross-section of neutral impurities. For values of W small relative to E_0 , the optical capture cross-section is given by

$$C_0 = 1.67 \times 10^{-22} \left(\frac{E_0}{W} \right) \left(1 + \frac{E_0}{W} \right)^{\frac{2}{3}} \quad (67)$$

where $W = \frac{3KT}{2}$.

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APPENDIX III

Dependence of Current Noise on the Dimensions of the Semiconductor

Consider the rectangular semiconductor shown in Figure 15b which is divided into small cubical volume elements. These are the largest volume elements whose mean-square fluctuations in resistance $(\Delta r_s)^2$ depend on the frequency and are not correlated with their neighbors and, whose dimensions, s^3 , depend on frequency. We wish to calculate the current-noise power of the semiconductor in terms of $(\Delta r_s)^2$. This is done by joining the ijk -th volume element with others into the ij -th strip parallel to the current flow, then into the i -th layer, and finally into the whole volume.

The mean-square fluctuation in resistance of the ij -th strip of the semiconductor parallel to the direction of current flow and having a cross-section s^2 and length $l_1 = n_1 s$ is given by

$$\overline{(\Delta R_{ij})^2} = \sum_{k=1}^{k=n_1} \overline{(\Delta r_{ijk})^2} = n_1 (\overline{\Delta r_s})^2 \quad (68)$$

The resistance of the strip is

$$R_{ij} = \sum_{k=1}^{k=n_1} r_{ijk} = n_1 r_s \quad (69)$$

where r_s is the resistance of a volume element. The corresponding expressions for the conductivity σ of the strip and its mean-square fluctuation are

$$\sigma_{ij} = \frac{1}{R_{ij}} = \frac{1}{n_1 r_s} \quad (70)$$

$$\overline{(\Delta \sigma_{ij})^2} = \left(\frac{\sigma_{ij}}{R_{ij}} \right)^2 \overline{(\Delta R_{ij})^2} = \frac{(\overline{\Delta r_s})^2}{n_1^3 r_s^4} \quad (71)$$

The mean square fluctuation in conductivity of the i -th layer having a thickness s , length $l_1 = n_1 s$ and width $l_2 = n_2 s$ is the sum of the fluctuations of its strips

$$\overline{\Delta \sigma_i}^2 = \sum_{j=1}^{j=n_2} \overline{(\Delta \sigma_{ij})^2} = \frac{n_2}{n_1} \frac{(\overline{\Delta r_s})^2}{r_s^4} \quad (72)$$

The conductivity of the layer is

$$\sigma_i = \sum_{j=1}^{j=n_2} \sigma_{ij} = n_2 \sigma_{ij} = \frac{n_2}{n_1 r_s} \quad (73)$$

Similarly, the mean square fluctuation in conductivity of the entire semiconductor having a thickness $l_3 = n_3 s$ is obtained by adding those of its layers

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$$\overline{(\Delta\sigma)^2} = \sum_{i=1}^{i=n_3} \overline{(\Delta\sigma_i)^2} = n_3 \overline{(\Delta\sigma_i)^2} = \frac{n_3 n_2}{n_1} \frac{(\overline{\Delta r_S})^2}{r_S^4} \quad (74)$$

The conductivity of the entire semiconductor is

$$\sigma = \sum_{i=1}^{i=n_3} \sigma_i = \frac{n_2 n_3}{n_1 r_S} \quad (75)$$

When a current I is flowing through the semiconductor, and its matched load resistance, the current noise power per bandwidth Δf is given by

$$P_I(f) \Delta f = I^2 R \frac{(\overline{\Delta R})^2}{R^2} \Delta f = I^2 R \frac{(\overline{\Delta\sigma})^2}{\sigma^2} \Delta f \quad (76)$$

In terms of the resistance and mean square fluctuation in resistance of the volume element s^3 , this relation takes the form

$$\left. \begin{aligned} P_I(f) \Delta f &= I^2 R \frac{1}{n_1 n_2 n_3} \left(\frac{\overline{\Delta r_S(f)^2}}{r_S} \right) \Delta f \\ &= \frac{I^2 R s^3}{l_1 l_2 l_3} \left(\frac{\overline{\Delta r_S(f)^2}}{r_S} \right) \Delta f \end{aligned} \right\} \quad (77)$$

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APPENDIX IV

Effect of Competitive Optical Processes on the Photoconductive Response

The total radiation dI absorbed in a layer dx at a distance x from the surface at which the radiation is incident is given by

$$dI = dI_1 + dI_2 = I_0(\alpha_1 + \alpha_2) \exp\left\{-(\alpha_1 + \alpha_2)x\right\} dx \quad (78)$$

where α_1 is the absorption coefficient for the photoconductive absorption band, α_2 is the absorption for the nonphotoconductive absorption band, dI_1 is that part of the adsorbed radiation which is effective in freeing electrons from the un-ionized donor impurity atoms, and dI_2 is that part of the absorbed radiation which is not effective in producing photoconductivity. Under these conditions the equilibrium equation for the density of free electrons in the light is given by

$$\frac{dn'_e}{dt} = A_D(N_D - n'_e) + Q_D I_0 \alpha_1 \exp\left\{-(\alpha_1 + \alpha_2)x\right\} - B_D n'_e n'_d = 0 \quad (79)$$

and the change in the density of free electrons produced by the absorbed radiation in a layer dx is given by

$$\Delta n_e = n_e \left[1 + \frac{Q_D I_0 \alpha_1 \exp\left\{-(\alpha_1 + \alpha_2)x\right\}}{B_D n_e^2} \right]^{\frac{1}{2}} dx. \quad (80)$$

On integrating over the thickness of the photoconductor and assuming that $\gamma_D \ll 1$, we obtain for the photoconductive response in the presence of competing optical absorption

$$\left(\frac{\Delta\sigma}{\sigma}\right)_{1+2} = \frac{Q I_0}{2 B n_e^2 l} \left(\frac{\alpha_1}{\alpha_1 + \alpha_2}\right) \left(1 - \exp\left\{-(\alpha_1 + \alpha_2)l\right\}\right) \quad (81)$$

whereas in the absence of competing optical absorption the photoconductive response would be given by

$$\left(\frac{\Delta\sigma}{\sigma}\right)_1 = \frac{Q I_0}{2 B n_e^2 l} \left(1 - \exp(-\alpha_1 l)\right). \quad (82)$$

The relation between the two values of the photoconductive response is accordingly given by

$$\begin{aligned} \left(\frac{\Delta\sigma}{\sigma}\right)_{1+2} &= \left(\frac{\alpha_1}{\alpha_1 + \alpha_2}\right) \left(\frac{1 - \exp\left\{-(\alpha_1 + \alpha_2)l\right\}}{1 - \exp\left\{-\alpha_1 l\right\}}\right) \left(\frac{\Delta\sigma}{\sigma}\right)_1 \\ &= C \left(\frac{\Delta\sigma}{\sigma}\right)_1. \end{aligned} \quad (83)$$

The effect of competing optical absorption on the photoconductive response may be considered for three limiting cases.

(1) $\alpha_1 l \ll 1$ and $\alpha_2 l \ll 1$. Under these conditions, the reduction factor is unity. The presence of competing absorption does not affect the photoconductive response. This condition corresponds to the case where the radiation absorbed by both processes is only a very small fraction of the incident radiation.

(2) $\alpha_1 l \ll 1$ and $\alpha_2 l \gg 1$. Under these conditions, the photoconductive response is reduced by a factor $1/\alpha_2 l$. The photoconductive response varies inversely as the product of the thickness l and the absorption coefficient of the nonphotoconductive absorption band.

(3) $\alpha_1 l \gg 1$ and $\alpha_2 l \gg 1$. Under these conditions, the photoconductive response is reduced by a factor $\alpha_1/(\alpha_1 + \alpha_2)$. The magnitude of the photoconductive response depends on the relative magnitudes of α_1 and α_2 . There is no reduction on photoconductive response when $\alpha_1 \gg \alpha_2$. On the other hand when $\alpha_2 \gg \alpha_1$, the photoconductive response is reduced by a factor α_1/α_2 .

It is of interest to apply Equation (83) to the photoconductive response in silicon I 103 at 9 microns where there is an appreciable absorption band due to lattice vibrations. The absorption data indicate that $\alpha_2 \approx 3 \text{ cm}^{-1}$. The absorption coefficient for un-ionized impurity atoms is very much less than 1 cm^{-1} . For $l = 0.5$, this means that $\alpha_1 l \ll 1$ and $\alpha_2 l \approx 1.5$. The reduction factor, C , is accordingly

$$C = \frac{1}{\alpha_2 l} [1 - \exp(-\alpha_2 l)] \approx 0.6 \quad (84)$$

which is in agreement with the value $C \approx 0.6$ obtained from the dip in the photoconductive response curve.

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APPENDIX V
Symbols

- a Radius of the orbit of bound charge in silicon.
- a_0 Radius of Bohr orbit for hydrogen.
- A Thermal ionization probability.
- A_A Thermal ionization probability per second for unit density of acceptor atoms to form holes and ionized acceptors.
- A_D Thermal ionization probability per second for unit density of donor atoms to form electrons and ionized donors.
- A_L Thermal ionization probability per second for unit density of lattice atoms to form electron-hole pairs.
- B Recombination probability.
- B_A Probability of recombination per second for unit density of holes to combine with ionized acceptors.
- B_D Probability of recombination per second for unit density of electrons to combine with ionized donors.
- B_L Probability of recombination per second for unit density of electrons to combine with holes.
- c Geometrical constant.
- e Electronic charge.
- ϵ Optical absorption cross-section.
- E Energy gap or ionization energy.
- E_A Thermal energy gap between the acceptor impurity level and the full band.
- E_D Thermal energy gap between the donor impurity level and the conduction band.
- E_E Energy of the lowest exciton level.
- E_H Ionization energy for atomic hydrogen.
- E_I Thermal energy gap between the valence and the conduction band.
- E_0 Ionization energy for K-shell electron.
- f Frequency (audio).

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h	Planck's constant.
i	Current.
I_0	Intensity of incident monochromatic radiation.
k	Boltzmann constant.
K	Equilibrium constant.
l	Thickness.
$\left. \begin{matrix} l_1 \\ l_2 \\ l_3 \end{matrix} \right\}$	Dimensions of semi-conductor.
m	Mass of electron in free space.
m_e	Mass of electron in conduction band.
m_h	Mass of hole in full band.
m^*	Effective mass of electron or hole.
n_a	Density of ionized acceptors (number per cc).
n_A	Density of neutral acceptors,
n_d	Density of ionized donors.
n_D	Density of neutral donors.
n_e	Density of free electrons.
n_h	Density of free holes.
n_L	Density of un-ionized lattice atoms.
N	Effective density of states in the conduction band.
N_A	Total density of ionized and un-ionized acceptor atoms.
N_D	Total density of ionized and un-ionized donor atoms.
N_L	Total density of ionized and un-ionized lattice atoms.
n_a' to N_L'	Primed symbols refer to corresponding densities in the light.
P_I	Current noise power.
Q_A	Number of ionized acceptor-and-hole pairs formed by unit intensity of absorbed radiation.

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- Q_D Number of ionized donor-and-electron pairs formed by unit intensity of absorbed radiation.
- Q_L Number of electron-hole pairs formed by unit intensity of absorbed radiation.
- r Length.
- r_s Average resistance of element of volume s^3 .
- R Resistance.
- R' Resistance in the light.
- R_s Series load resistance.
- R_y Rydberg constant.
- s^3 Volume of largest element of volume which is uncorrelated with neighboring elements.
- t Time.
- T Absolute temperature.
- v Instantaneous voltage, or velocity.
- V Voltage or interaction potential.
- $\bar{V}$ Mean voltage.
- V_B Battery voltage.
- V_I Current noise voltage.
- V_P Photoconductive signal voltage.
- V_T Thermal noise voltage.
- x Unit of length.
- Z Effective charge of ion core.
- α_A Optical absorption coefficient for acceptor impurity absorption.
- α_D Optical absorption coefficient for donor impurity absorption.
- α_L Optical absorption coefficient for intrinsic lattice absorption.
- γ_A Ratio of optical to thermal generation of charge carriers at $x = 0$ for photoconductivity of acceptor impurities.

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$\gamma_{\bar{D}}$	Ratio of optical to thermal generation of charge carriers at $x = 0$ for photoconductivity of donor impurities.
γ_L	Ratio of optical to thermal generation of charge carriers at $x = 0$ for intrinsic photoconductivity.
ϵ	Optical absorption cross-section.
κ	Static dielectric constant.
κ_0	Optical dielectric constant.
λ	Wavelength.
μ_e	Mobility of electrons.
μ_h	Mobility of holes.
ν	Frequency (optical).
ν_0	Ionization frequency.
ρ	Resistivity.
σ	Electrical conductivity.
σ_e	Electrical conductivity by electrons.
σ_I	Intrinsic conductivity.
σ_h	Electrical conductivity by holes.
τ	Average lifetime of free-charge carriers.

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