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**RB-19**

**PHOTOCONDUCTION IN GERMANIUM AND SILICON**



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## Photoconduction in Germanium and Silicon

Germanium and silicon are probably the two best known of all of the semiconductors. Their electronic properties have been studied in great detail both theoretically and experimentally. The reason for this is that these two materials are of such great practical importance for transistors and rectifiers. Perhaps less generally appreciated is the fact that both of these materials are excellent photoconductors. Their intrinsic response extends through the entire visible spectrum into the near infrared. When doped with appropriate foreign atoms and operated at low temperatures, these materials are very effective impurity photoconductors with response extending into the far infrared portions of the spectrum.

### Introduction

An adequate understanding of the behavior of any semi-conductor which exhibits a photoconductive response when subjected to a radiation stimulus is most readily obtained by considering separately the several processes which together constitute the photoconductive process. These include (1) production, when the material is exposed to radiation, of current carriers in excess of those present in thermal equilibrium in the dark; (2) motion of carriers under the influence of an electric field; and (3) temporary or permanent removal of excess carriers by trapping and recombination.

The excitation of current carriers, either electrons or holes or both, occurs from states to which the carriers are normally bound into states in which they are free to move in an electric field. Possible excitation processes are represented in the schematic energy level diagram of Fig. 1. An ideal semi-conductor crystal may be described by an energy level diagram that includes a lower band of allowed energy states, the valence band, which is completely filled with electrons at absolute zero; a band of energies whose occupancy is forbidden; and a higher band of allowed states, the conduction band, which is empty of electrons at absolute zero. Actual semiconductor crystals always contain foreign atom impurities (either residual or deliberately added), and lattice imperfections. These introduce localized energy

levels which may lie within the forbidden band gap of the material. Such levels are donors, if they possess an ionizable electron, or acceptors, if they can accept an electron (i.e., if they possess an ionizable hole).

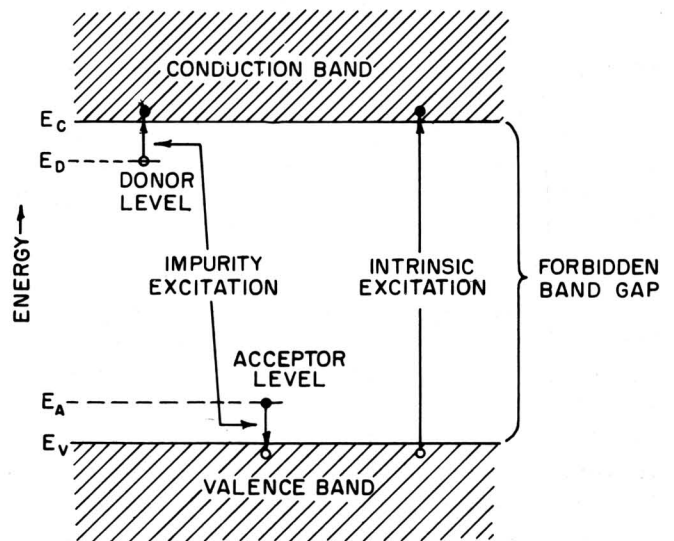


Fig. 1 - Schematic energy level diagram illustrating the excitation processes which lead to the production of free charge carriers.

Intrinsic excitation involves the transition of an electron from a state in the valence band to one in the conduction band. Each such

excitation produces one free electron and one free hole. An excitation of an electron from a donor level into the conduction band produces one free electron and one bound hole, while excitation of a hole from an acceptor level into the valence band (i.e., excitation of an electron from the valence band into the acceptor level) produces one free hole and one bound electron. These excitations may be produced either by absorption of thermal energy from the crystal lattice or by absorption of photons of radiation of appropriate energy. If the excitation is produced by absorption of photons, photoconductivity, either intrinsic or impurity, is possible.

The energy associated with a photon of wavelength  $\lambda$  is given by

$$E = \frac{hc}{\lambda} \quad (1)$$

where  $h$  is Planck's constant and  $c$  is the velocity of light. The visible spectrum includes the photon energy range from about 1.6 eV in the red to about 3.2 eV in the blue. The long wavelength threshold of photoconductivity associated with a given excitation process is given by

$$\lambda_{Th} = \frac{1.2395}{\Delta E} \text{ microns} \quad (2)$$

where  $\Delta E$  is the energy difference in electron volts between the edges of the conduction and valence bands or the energy difference between an impurity state and the edge of either the conduction or valence band, whichever is appropriate to the particular excitation process in question.

If optical excitation of carriers from impurity levels is to be possible, the semiconductor sample must be at a temperature low enough so that, in the absence of radiation, carriers are bound to the impurity levels involved. Since the impurity ionization energies  $E_D$  and  $E_A$  may be very small compared with the forbidden band gap  $E_G$ , cooling to very low temperatures may be required to satisfy this condition. Temperatures as low as those of liquid hydrogen or liquid helium may be necessary. However, photoconductive response at very low wavelengths can then be observed.

The carrier concentration in the case of thermal excitation, for a given semiconductor

and for a given set of impurity levels, is determined by the temperature of the crystal. The conductivity determined by this carrier concentration, or more precisely, the noise associated with random fluctuations in the conductivity, imposes a limitation upon the sensitivity of the material when used as a photoconductor.

The time rate of increase of the concentration of carriers excited by monochromatic radiation of wavelength  $\lambda$  in a layer of photoconductor of thickness  $dx$  at a depth  $x$  below the irradiated surface is given by

$$\left(\frac{dn}{dt}\right) = \eta(\lambda) f(\lambda) \alpha(\lambda) \exp(-\alpha(\lambda)x) \quad (3)$$

where  $n$  is the concentration of carriers of a given type,  $\eta(\lambda)$  is the quantum efficiency,  $f(\lambda)$  is the number of photons per sq. cm. per second entering the sample and  $\alpha(\lambda)$  is the absorption constant. At wavelengths for which the absorption constant is high, as in the intrinsic region, the excess carrier density is non-uniform in the  $x$  direction through the sample. If the absorption constant is sufficiently small, the above expression reduces to

$$\left(\frac{dn}{dt}\right) = \eta(\lambda) f(\lambda) \alpha(\lambda), \quad (4)$$

and a uniform density of carriers throughout the sample results. This condition usually applies for absorption in the impurity range. The absorption constant may be written as

$$\alpha(\lambda) = \sigma(\lambda) n_i$$

where  $\sigma(\lambda)$  is the absorption cross section and  $n_i$  is the concentration of unionized impurities.

The next consideration is the motion of current carriers under the influence of a field. In practice the velocity imparted to a carrier by the field is very small compared with the thermal motion of the carrier. Therefore, the photoconductive current is a small drift in the direction of the field superimposed upon a large random motion. The drift velocity can be shown to be proportional to the electric field, the constant of proportionality being known as the mobility  $\mu$ . In general, the mobility  $\mu_n$  for electrons will be different from the mobility  $\mu_p$  for holes.

The magnitude of the mobility in a given semiconductor is determined by the scattering of charge carriers by lattice vibrations, ionized

impurity centers, neutral impurity centers and lattice imperfections. These scattering processes are temperature dependent and different processes are dominant over different temperature ranges. At temperatures in the neighborhood of room temperature, the principal scattering is due to thermal vibrations of the lattice. If the band structure of the semiconductor could be represented by simple spherical surfaces in momentum space, it could be shown<sup>1</sup> that the mobility would vary with the inverse three-halves power of the absolute temperature. However, for silicon and germanium, the band structure in momentum space is more complicated so that the temperature variation for holes and electrons is somewhat greater. At low temperatures, the scattering is primarily due to impurities and imperfections in the lattice. In this temperature range, mobility decreases with decreasing temperature. Observed mobilities for germanium and silicon will be discussed in greater detail in a later section.

The excitation of carriers to the conduction and valence bands has been described above. In addition, there is a draining away of charge carriers by recombination processes. These include direct recombination, recombination at the surface of the specimen, and volume recombination at centers distributed throughout the bulk of the material. The direct recombination of holes and electrons is a relatively rare occurrence. The time constant for this process in germanium has been calculated<sup>2</sup> to be of the order of one second. Since observed lifetimes of excess carriers are rarely greater than of the order of  $10^{-3}$  second, the other recombination processes must be much more important. That direct recombination does occur in germanium and silicon, however, has been demonstrated<sup>3,4</sup> by the observation of the emission of recombination radiation in wavelength ranges corresponding to the intrinsic gap widths.

The contribution due to surface recombination depends greatly upon the physical and chemical state of the surface. Where excitation occurs throughout the volume of the crystal, surface recombination will be small compared with volume recombination. For intrinsic photoconductivity, however, where excitation occurs close to the surface, surface recombination may be important.

Volume recombination involves the capture of a charge carrier of one sign by a deep-lying

vacant level followed by the capture of a charge carrier of the opposite sign by the same level. This process is illustrated in Fig. 2. It is evident that two capture cross sections are here involved. First, the capture cross section of the level for the first type of charge carrier and second, the cross section of the occupied level for the capture of a charge carrier of the opposite sign. These cross sections may be very different in size. This recombination mechanism has been treated theoretically by Hall<sup>5</sup> and Shockley and Read<sup>6</sup>. Experimental verification of the theory has been obtained<sup>7</sup> by measurement of minority carrier lifetime as a function of the concentration of recombination centers. Copper and nickel impurities have been shown to act as recombination centers of this type in germanium. It has also been shown<sup>8</sup> that, at least, a fraction of the recombinations occur with emission of radiation of wavelengths which may correspond to the location of the recombination centers in the forbidden band gap.

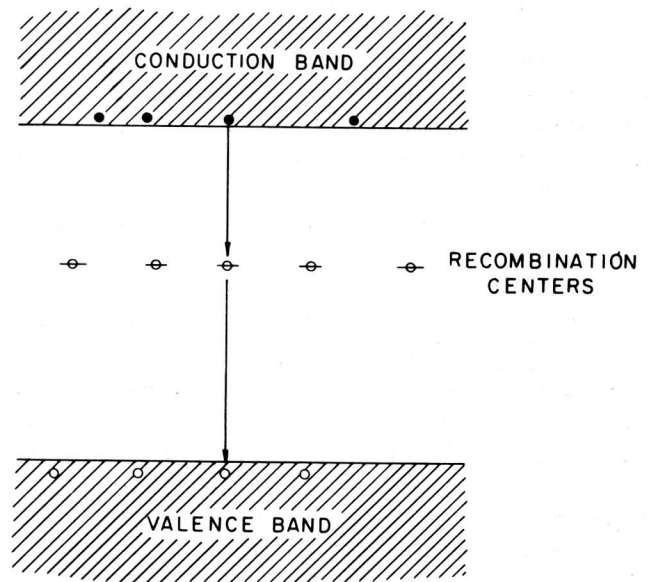


Fig. 2 - Schematic energy level diagram illustrating the process of electron-hole recombination at centers.

For steady state intrinsic photoconductivity, the rate of capture of holes and electrons must be equal to one another and to the rate of generation. Therefore,

$$n\sigma_{ec}\bar{v}_e(n_c - n'_c) = p\sigma_{pc}\bar{v}_p(n'_p) = \left(\frac{dn}{dt}\right)_e = \left(\frac{dp}{dt}\right)_e \quad (6)$$

where  $n$  and  $p$  are the concentrations of free

electrons and holes;  $\bar{v}_e$  and  $\bar{v}_p$  are the average thermal velocities of electrons and holes;  $\sigma_{ec}$  and  $\sigma_{pc}$  are the capture cross sections of the recombination centers for electrons and holes;  $n_c$  is the total concentration of recombination centers and  $n'_c$  is the concentration of centers occupied by electrons. Expressions for the response time and for the steady state photocurrent-intensity characteristics for intrinsic photoconductivity based upon equations for the rates of excitation and recombination similar to those given above have been published by many authors (e.g., see references 9 and 10).

Where impurity photoconductivity is involved, recombination occurs when the center from which a charge carrier was excited captures a replacement charge. If the only source of carriers is these centers, the condition to be satisfied for equilibrium is

$$\left(\frac{dn}{dt}\right)_e = \sigma_{ec} \bar{v}_e n^2 \tag{7}$$

or  $\left(\frac{dp}{dt}\right)_e = \sigma_{pc} \bar{v}_p p^2$

A detailed discussion of the magnitude of response of an impurity photoconductor including the effects of temperature, background radiation, compensating impurities and non-photoionizing absorption processes has been given in the literature<sup>11</sup>. However, sufficient experimental data is not yet available to provide an adequate test of the validity of this treatment.

Centers or states in the forbidden energy band may also act as trapping centers. This occurs when the activation energy of the level is small enough so that the probability of thermal re-excitation of the captured carrier is greater than the probability of recombination by the capture of a carrier of the opposite sign. A general treatment of recombination and trapping processes applicable to any photoconductor has been given by Rose<sup>10</sup>. Some experimental evidence for the existence of trapping in germanium and silicon, usually obtained by a study of the time rate of decay of photoconductivity or of the quenching of photoconductivity is now available (see references 12,13,14,15,16,17).

The photocurrent produced in a photoconductor can be expressed by the formal relationship

$$i = e \frac{\tau_0}{T} F \tag{8}$$

where F is the number of photons per second ab-

sorbed, T is the time required for a carrier to cross the specimen and  $\tau_0$  is the effective carrier lifetime. If the specimen length is L, the applied voltage V and the mobility  $\mu$ , the factor T is given by

$$T = \frac{L^2}{\mu V} \tag{8a}$$

The factor  $\tau_0$  depends upon the recombination cross section and the carrier density. In the absence of traps, this lifetime is given by

$$\tau_0 = \frac{1}{v \sigma_c n} \tag{8b}$$

where v is the thermal velocity of carriers,  $\sigma_c$  the recombination cross section and n the carrier density.

### Photoconductivity of Intrinsic Germanium and Silicon

If a determination is made of the concentration of holes or electrons as a function of temperature by measurement of the Hall coefficient and conductivity<sup>18</sup>, it is found that the activation energy of germanium in the neighborhood of room temperature is 0.68 ev. This means that as far as thermal excitation is concerned, the energy required to raise an electron from the valence band to the conduction band is 0.68 ev. This is the quantity which has been called the forbidden band gap in Fig. 1. A more detailed knowledge of the structure of both the valence and conduction bands is required, however, in order to discuss optical transitions between them. A complete description of the energy band structure would require representation in a four dimensional manifold which includes the three crystal momentum coordinates and energy. If, however, appropriate crystallographic directions are chosen, two dimensional plots of energy versus crystal momentum k for such directions contain the essential information. Fig. 3A gives such plots for germanium<sup>19</sup> for the [100] and [111] crystallographic directions and depicts the dependence of electron energy upon K for the topmost valence bands and for the bottommost conduction bands.

The thermal activation energy is the smallest distance between curves of the conduction band and the valence band indicated by the dotted lines on the figure. It will be observed

that to make this transition an electron must change its momentum. The energy required to excite an electron<sup>4, 20</sup> from the valence band to the conduction band without change of momentum at  $k = 0$  is approximately 0.8 eV. When optical excitation involves an electron and a photon only, the principle of conservation of momentum requires that the excitation be vertical. Under these circumstances, the longest wavelength which can cause a transition is approximately 1.5 microns. However, if a phonon is either generated or absorbed in the course of excitation, there can be a change of momentum and the transition need not be vertical on the diagram.

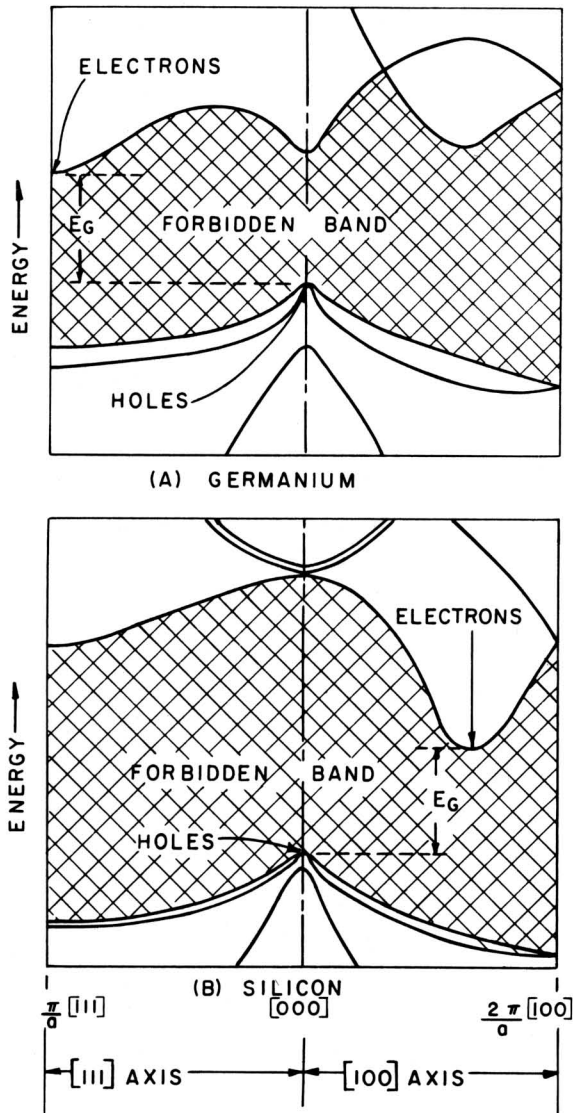


Fig. 3 - Schematic diagrams of energy band contours in germanium and silicon crystals along [111] and [100] axes in the reduced zone.

The intrinsic absorption in germanium<sup>9</sup> is illustrated in Fig. 4. The portion of the spectrum corresponding to photon energies greater than about 0.8 eV is due principally to vertical transitions and is characterized by absorption constants in the range from about  $10^3 \text{cm}^{-1}$  to about  $10^6 \text{cm}^{-1}$ . The portion of the spectrum at lower energies is due to non-vertical transitions for which the transition probabilities are smaller ( $\alpha < 10^3 \text{cm}^{-1}$ ). Recent detailed measurements<sup>20, 21</sup> of optical absorption have clearly demonstrated the existence of non-vertical transitions. Careful measurements<sup>22</sup> at the extreme tail of the absorption band permit the separate identification of transitions in which a phonon is absorbed and of those in which a phonon is emitted. A theoretical treatment of vertical and nonvertical transitions has recently been given (see references 23 and 24).

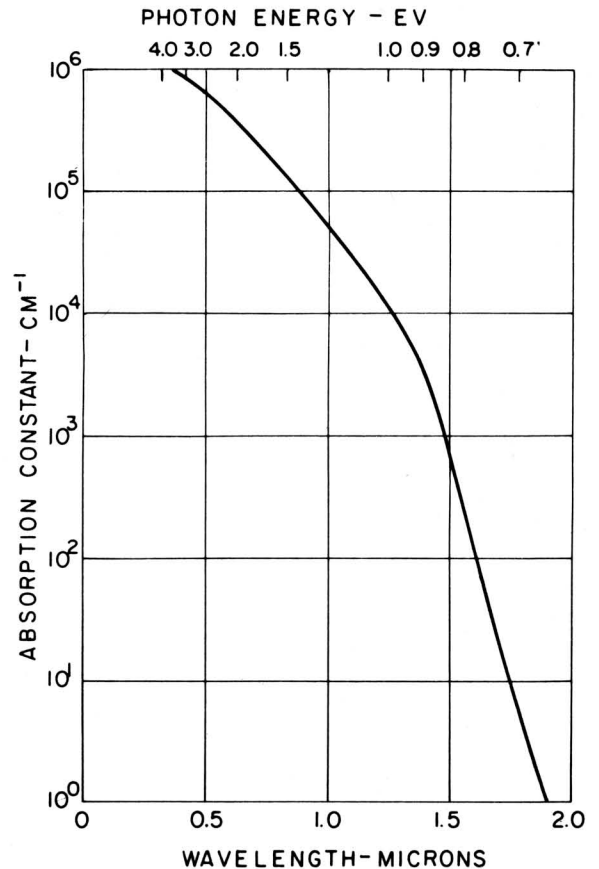


Fig. 4 - Intrinsic optical absorption in germanium.

The photoconductivity of germanium in the intrinsic range has not yet been studied in the same detail as has the optical absorption. • A



typical photoconductive response curve<sup>9</sup> for germanium at room temperature, in which the response is expressed in arbitrary units for equal numbers of incident photons at all wavelengths, is given in Fig. 5. Proceeding from short to long wavelengths, the response increases somewhat until a maximum is reached at about 1.5 microns. Beyond about 1.6 microns, the response falls rapidly to a long wavelength threshold in the neighborhood of 1.8 microns which corresponds approximately to the 0.68 eV of the minimum band separation. It may be noted that the maximum of photoconductivity occurs at approximately the wavelength at which the absorption constant begins to decrease rapidly. At short wavelengths where the absorption coefficient is very high, all of the photoconductive effect is confined to a very shallow layer on the side of the specimen upon which the radiation is incident. The high concentration of electrons and holes near the surface and the presence of additional recombination centers at the surface combine to produce rapid recombination and, consequently, a smaller photoconductive current. When the wavelength gets longer than the minimum vertical transition so that the excitation involving the production or absorption of a phonon is nonvertical, the absorption coefficient decreases and, consequently, the radiation penetrates further into the material. As a result, surface recombination becomes less and less important. Therefore, although the rate of excitation of carriers remains constant as long as all of the radiation is absorbed in the material, the lifetime of the carriers becomes longer and, consequently, the photoconductive current becomes larger. This effect may account for the rise which has been noted in the photoconductive response curve. The height of the maximum above the short wavelength portion of the curve varies considerably from sample to sample. These differences are probably due to the state of the surface and, therefore, to the magnitude of the surface recombination coefficient. The quantum efficiency, expressed as the number of electrons or holes produced per quantum absorbed, has been demonstrated to be unity over the wavelength range from 1.0 microns to the threshold within the experimental uncertainty of about 10 per cent<sup>25</sup>.

The photoconductive threshold shifts to shorter wavelengths as the temperature is lowered below room temperature. This occurs because the width of the band gap changes with temper-

ature. The temperature coefficient of  $E_G$  as determined from thermal measurements at high temperatures<sup>18</sup> is given by the equation:

$$E_G (T) = 0.785 - 3.5 \times 10^{-4} T \text{ electron volts} \quad (9)$$

Optical absorption measurements<sup>22</sup> give a quadratic dependence of  $E_G$  upon temperature at low temperatures.

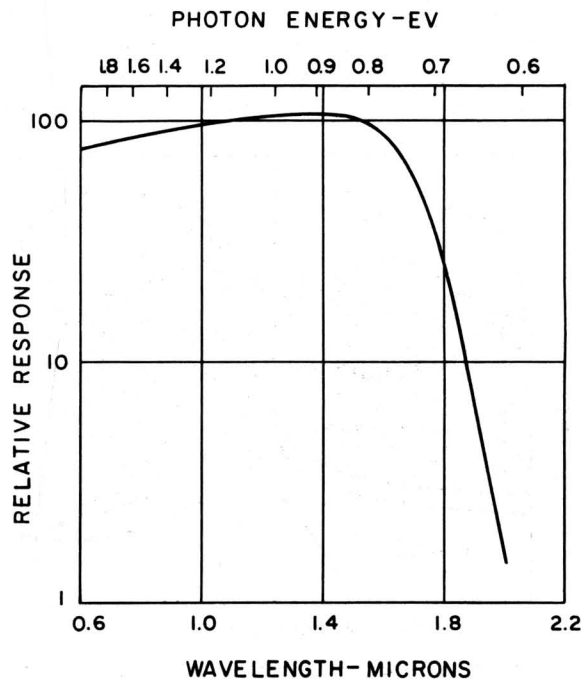


Fig. 5 - Intrinsic photoconductivity of germanium.

In the long wavelength portion of the intrinsic response where the excitation involves phonon interactions to conserve momentum, it has been pointed out that the excitation may involve either the absorption or emission of a phonon. At higher temperatures the absorption of a phonon occurs frequently and, of course, the phonon contributes energy to the excitation. This energy amounts to about 0.02 or 0.03 eV. Therefore, the long wavelength threshold at these higher temperatures occurs at photon energies smaller than that corresponding to the minimum gap width by this amount. At low temperatures, phonon absorption is less probable. Therefore, the optical transition usually occurs with the emission of a phonon. Since the phonon energy must come from the photon, the long wavelength photoconductive limit will occur at photon energies slightly greater than that corresponding to the gap width.

Like germanium, the energy band structure of silicon in momentum space (k space) is complex. Fig. 3B is a diagram of energy plotted against the momentum vector k for two crystallographic directions in silicon<sup>19</sup>. Again, the minimum activation energy involves a change of momentum. At room temperature, the minimum band gap<sup>26</sup> is 1.10 ev. The minimum gap for vertical transitions<sup>20</sup> is not less than about 1.5 ev.

silicon with as low a concentration of recombination centers as it has been for germanium. Therefore, the carrier lifetimes for silicon are smaller.

### The Impurity Photoconductivity of Germanium and Silicon

A great many different kinds of impurity atoms can be introduced into silicon and germanium to produce energy levels lying in the forbidden gap. These levels may be acceptor or donor centers depending upon the particular atoms introduced. As such, they can give rise to impurity photoconductivity. Information concerning the location of such levels within the forbidden gap may be obtained experimentally by determination of the carrier concentration as a function of temperature, which yields thermal ionization energies, or from measurements of optical absorption or photoconductivity as a function of wavelength to give optical ionization energies. For those impurities which have been investigated there is usually good agreement between the thermal and optical ionization energies.

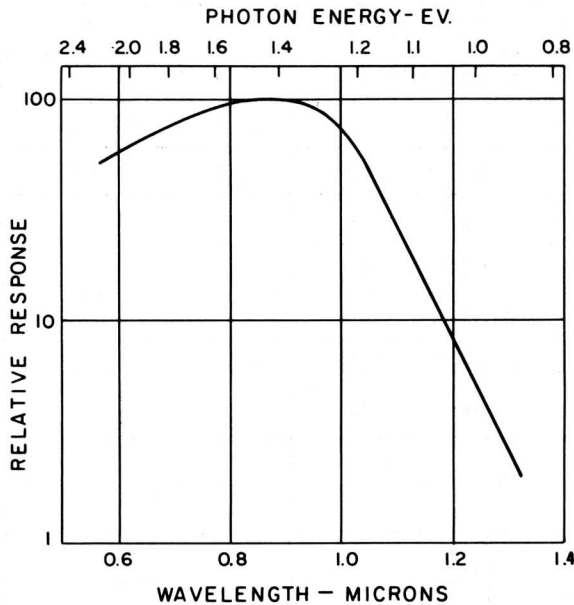


Fig. 6 - Intrinsic photoconductivity of silicon.

As in the case of germanium, a detailed study of the long wavelength tail of the intrinsic absorption yields evidence<sup>27</sup> for the existence of transitions in which phonons are absorbed or are emitted. The temperature dependence of  $E_{GX}$  as determined from thermal measurements<sup>26</sup> is given by:

$$E_G(T) = 1.21 - 3.6 \times 10^{-4}T \text{ Electron volts} \quad (10)$$

The photoconductive response of silicon resembles in its broader aspects that of germanium. Fig. 6 shows an early experimentally measured spectral response curve of polycrystalline silicon<sup>9</sup>. The thermal activation energy, absorption edge and position of intrinsic photoconductive response are consistent with one another. The photoconductivity of silicon is, in general, lower than that of germanium partly because the hole and electron mobility is lower and partly because it has not been possible to produce

The first impurity atoms to be considered are those in Column V of the Periodic Table. These atoms have one more valence electron than is required for the bonding when the atom is introduced substitutionally. The additional electron is very loosely bound to its parent atom and has a small ionization energy. It is convenient, although not strictly correct, to consider this electron as being attracted to the impurity center by a coulomb potential. This so-called hydrogenic model leads to the expectation that the ionization energy of the impurity is smaller than that of a free hydrogen atom by the factor  $\frac{1}{K^2} \cdot \frac{m^*}{m}$  where K is the dielectric constant of the crystal and  $m^*$  is an effective electron mass. It is possible to choose values of  $m^*$  such that approximate agreement is obtained with experimentally observed values of ionization energies of these impurities. The values thus obtained are 0.01 and 0.04 ev for germanium and silicon respectively. The experimental values for impurity ionization energies are given in Tables I and II. Detailed theoretical treatments<sup>28, 29, 30</sup> of impurities in germanium and silicon, which take into account the complicated band structures, have been

# Photoconduction in Germanium and Silicon

## Table I

### Impurity Ionization Energies in Germanium

Periodic Table Column	Element	Donor or Acceptor	$E_c - E_i$ ev	$E_i - E_v$ ev	Photoconductive Threshold Microns
I	Li	D	0.01 (43)		
	Cu	A		0.040 (44)	29 (31,34)
				0.31 (45)	
	Au	A; (D)		0.053 (32,33)	>15 (32)
				0.15 (32,46)	9 (16,32,34)
				0.2 (32,46)	5.5 (16,32)
II	Zn	A		0.029 (47)	>38 (31)
III	B	A		0.0104 (48)	
	Al	A		0.0102 (48)	
	Ga	A		0.0108 (48)	
	In	A		0.0112 (48)	>38 (31)
	Tl	A		0.014 (49)	
V	P	D	0.0120 (48)		
	As	D	0.0127 (48)		
	Sb	D	0.0097 (48)		
	Bi	D	0.012 (49)		
VII	Mn	A		0.16 (50)	
				0.35 (50)	
VIII	Fe	A	0.27 (51)		4.6 (17)
				0.34 (51)	4.1 (17)
	Co	A	0.31 (52)		4.6 (52)
				0.25 (52)	5.5 (52)
	Ni	A	0.30 (53)		4.6 (53)
			0.22 (7,53,54)	5.6 (53)	
	Pt	A	0.2 (47)		
				0.04 (47)	

carried to the point where reasonably good agreement with experiment has been obtained.

Impurities from Column III have one too few electrons to satisfy the bonding when present substitutionally in germanium or silicon. There-

fore, there will be one hole bound to such a center. The ionization energies of the hole for impurities of this type in germanium are given approximately by the hydrogenic model. This model, however, fails for these impurities

Table II

Impurity Ionization Energies in Silicon

Periodic Table Column	Element	Donor or Acceptor	$E_c - E_i$ ev	$E_i - E_v$ ev	Photoconductive Threshold Microns
I	Li	D	0.033 (55)		
	Au	D		$\left\{ \begin{array}{l} 0.33 \text{ (56)} \\ 0.39 \text{ (55)} \end{array} \right\}$	3.8 (57)
			0.30 (58)		
II	Zn	A		0.092 (58) 0.30 (58)	
III	B	A		0.045 (55)	
	Al	A		0.057 (55)	
	Ga	A		0.065 (55)	
	In	A		0.16 (55)	
V	P	D	0.039 (55)		
	As	D	0.049 (55)		
	Sb	D	0.039 (55)		

in silicon. There is a marked upward trend in the ionization energy from 0.045 ev for boron to 0.16 ev for indium.

The ionization energies are so small for these two classes of impurities either in germanium or in silicon that, at room temperature or even at liquid nitrogen temperature (excepting for indium in silicon), the conductivity is too high to permit impurity photoconductivity. When these materials are cooled to sufficiently low temperatures, that is, in the liquid hydrogen or liquid helium range, thermal excitation of carriers is sufficiently improbable so that the concentration of unionized centers is essentially equal to the total concentration. Under these circumstances the photoconductive response is large. The long wavelength limit for an impurity with an ionization energy of 0.01 ev should be about 120 microns.

Several elements from columns of the Periodic Table other than III and V have been investigated as impurities in germanium and silicon. Reasoning similar to that which leads to the hydrogenic model for Column III and V impurities suggests that for other impurities there

will be more than one ionization energy corresponding to successive states of ionization and that multiple ionization might be expected to involve deeper lying levels. These expectations are, in general, realized experimentally. The impurities which have been investigated are listed in Tables I and II along with ionization energies for the levels which have been observed and with photoconductive thresholds in those cases for which they have been determined. The photoconductive response curves for indium, zinc and copper doped germanium measured at liquid helium temperature shown in Fig. 7 are typical of the behavior of low ionization energy impurity photoconductors<sup>31</sup>.

For those impurities which exhibit multiple level behavior, the location of the shallowest level can be determined only if no compensating impurity is present. In order to determine the ionization energy of a second deeper lying level, an impurity of opposite conductivity type must be added in an amount sufficient to remove all of the charge carriers from the shallowest level of the multivalent impurity. A third, still deeper lying level, if it exists, can be detected by compensating both shallower levels.

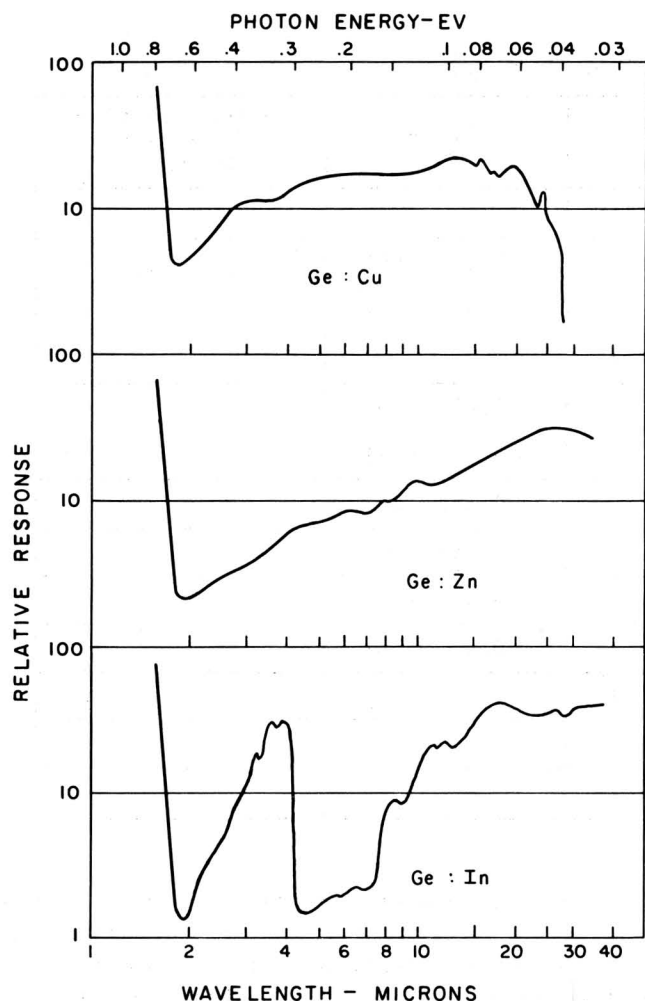


Fig. 7 - Impurity photoconductivity of copper, zinc and indium doped germanium at liquid helium temperature.

Gold as a substitutional impurity in germanium is the only example known to date of an impurity which exhibits three energy levels<sup>32, 33</sup>. The shallowest of these levels has an activation energy of about 0.05 ev and when pure gold is introduced into germanium, the material is p-type.\* If an appropriate amount of an n-type impurity is introduced into gold doped germanium, the electrons from these donor centers fill the lowest gold levels. The material thereupon exhibits an ionization energy corresponding to the second impurity level, which is located at approximately 0.15 ev above the valence band. With this large an activation energy, the mat-

\*W. C. Dunlap has recently suggested, *Bull. Am. Phys. Soc.*, Vol. 30, No. 2, p. 12 (1955), that this level is a donor level located 0.05 ev above the valence band.

erial is only slightly conducting at liquid air temperature and makes a very effective photoconductor. The spectral response<sup>16, 32, 34</sup> of this type of photoconductor is shown in Fig. 8.

The second gold level can likewise be compensated by the addition of more n-type impurity. The material is then n-type and exhibits a thermal ionization energy of about 0.2 ev. This behavior is due to the deepest lying acceptor level which is located at approximately 0.5 ev above the valence band. It is interesting to note that gold atoms can be introduced into the material in either of two ways. One is by adding the foreign atom to the molten germanium from which a crystal is to be grown. The second is to grow an intrinsic crystal and then introduce gold by diffusion. Identical results are obtained with samples prepared in either of these ways.

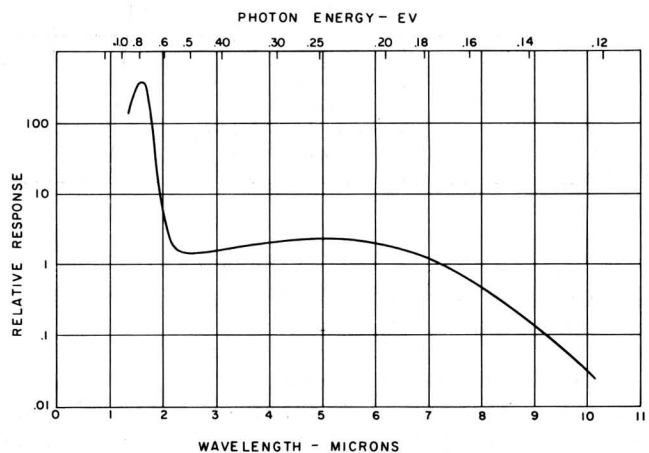


Fig. 8 - Photoconductivity of partially compensated p-type gold doped germanium at 77 degrees K.

Irrespective of whether the current carriers are due to excitation from impurity levels or excitation across the forbidden gap, their transport depends upon their mobility in the semiconductor. For high purity germanium<sup>35</sup> at room temperature, the mobility for electrons is 3900 cm/sec/volt/cm while for holes it is about 1900 cm/sec/volt/cm. The mobility for silicon is somewhat lower being in the neighborhood of 1200 cm/sec/volt/cm for electrons and 500 cm/sec/volt/cm for holes<sup>36</sup>. The mobility in both of these materials is a function of temperature. Fig. 9 is the measured mobility for a series of typical n-type germanium samples containing different amounts of impurities<sup>37</sup>. As has been

pointed out in an earlier section, the temperature dependence of mobility for germanium and silicon is somewhat different from what would be expected on the basis of the simplest semiconductor model. Experimentally it is found<sup>18</sup> that in germanium the lattice scattering mobility for electrons varies as  $T^{-1.66}$  and for holes as  $T^{-2.33}$ . In silicon<sup>36</sup> the corresponding quantities vary as  $T^{-1.5}$  and  $T^{-2.3}$ , respectively.

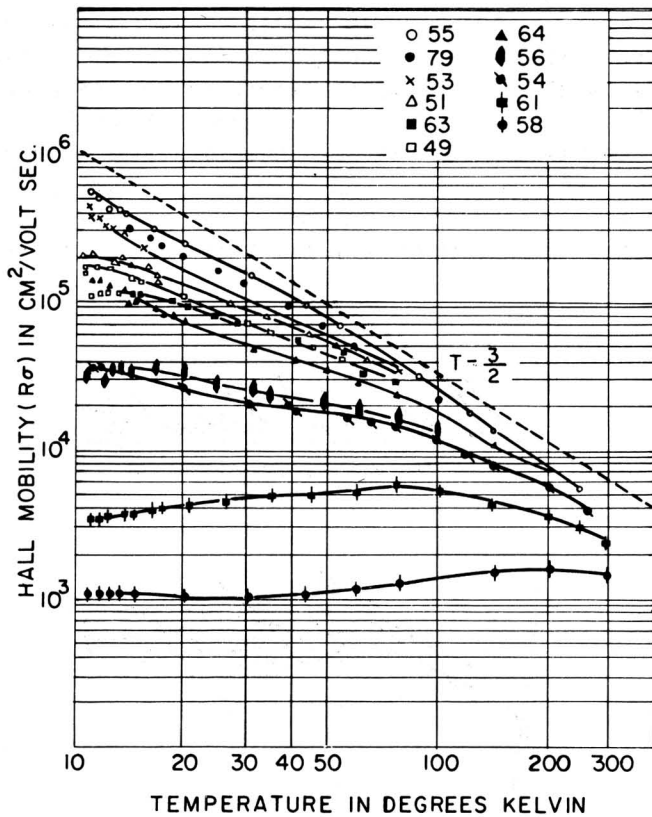


Fig. 9 - Hall mobility of a set of arsenic doped germanium samples as a function of absolute temperature.

At low temperatures the impurity scattering introduces a temperature dependence which is in the opposite direction, that is, the mobility decreases with decreasing temperature as is seen from the experimental curves. The theory of scattering by ionized impurities gives a mobility which varies approximately as  $T^{3/2}$  and inversely as the concentration of ionized impurities<sup>38,39</sup>. Scattering by neutral impurities should be temperature independent except for the dependence of the concentration of unionized impurities upon temperature<sup>40</sup>. Little is known experimentally concerning scattering by lattice imperfections. The scattering by

dislocations has been treated theoretically in the literature<sup>41,42</sup>. Such scattering is predicted to be anisotropic and to give a mobility which is proportional to  $T$ .

In order to obtain an approximate value for the photoconductive current resulting from an incident photon flux the following form of Eq. (6) may be used:

$$i = \frac{eV\mu\tau F'}{L^2} \quad (11)$$

where  $F'$  is the number of photons per second producing excitation,  $\mu = \mu_e + \mu_n$  the effective mobility which is the sum of the mobilities of the two carriers involved,  $L$  the length of the photoconductive crystal and  $\tau$  the effective lifetime of the carriers. The effective lifetime of the carriers is the time carriers are free to move through the lattice. In other words, it is the recombination time minus the length of time carriers are trapped. Lifetimes in germanium of 1000 microseconds can be achieved without too great a difficulty. For silicon, practical lifetimes are one or two orders of magnitude shorter.

### Junction Photoconductive Cells

Intrinsic germanium at room temperature has a specific resistivity of about 50 ohm-cms. The change of resistance due to amounts of light corresponding to those normally used with photoconductive cells is quite small. Expressed in other terms, the change in carrier density is often a very small percentage of the large number of carriers thermally excited in the material. Even with a coupling circuit having optimum impedance match, the sensitivity is low because of the current noise in the thermally excited current. When the material can be operated at temperatures well below room temperature, both intrinsic and suitably doped germanium are extremely practical materials for high sensitivity photoconductive cells.

Where the radiation to be detected by these cells lies in the portion of the spectrum at wavelengths smaller than 1.8 microns, it is possible to greatly increase the impedance of the cell at room temperature by introducing a p-n junction. Fig. 10 shows a schematic energy level

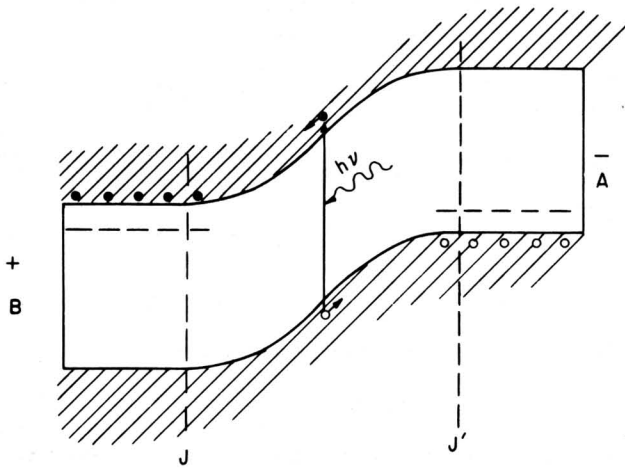


Fig. 10 - Schematic energy diagram of a p-n junction photoconductive cell.

diagram of a p-n junction photoconductive cell. In this type of photocell, almost the entire potential drop occurs across the p-n junction. On the n-side of the junction electrons are thermally excited from impurity levels into the conduction band, while on the other side of the junction the acceptor levels contribute holes to the valence band. The applied potential tends to draw holes away from the barrier toward electrode A and electrons away from the barrier toward electrode B. If a photoconductive excitation occurs, for example, in the region marked JJ' within a diffusion length of the barrier, the hole moves toward electrode A while the electron is drawn through the potential barrier and over to electrode B. This, of course, results in a photoconductive current. The junction cell is finding many practical applications.

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