IMPURITY BAND PHOTOCONDUCTIVITY IN BORON-DOPED SILICON

by

M. WALTER SCOTT


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of
PHYSICS

We accept this thesis as conforming to the
required standard

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April, 1966
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ABSTRACT

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Photoconductivity of holes in the valence band was also measured in order to obtain lifetimes and capture cross sections. Assuming the mobility in this region to be determined by neutral impurity scattering, the hole lifetime was estimated to be $\sim 10^{-9}$ sec and the capture cross section of ionized boron $\sim 3 \times 10^{-10}$ cm$^2$. Assuming similar lifetimes for the holes in impurity bands, the peak mobility in band 3 and 4 was found to be $\sim 150$ cm$^2$/volt-sec.

The d.c. characteristics of the various samples, while at low temperature and exposed to room temperature radiation, were measured during the course of this investigation. All samples were observed to have a non-linear dependence between the current and applied field, terminated by a non-destructive low field breakdown.
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CHAPTER I

INTRODUCTION

If a group III impurity, such as boron, is introduced into a perfect silicon lattice an infinite series of stationary states localized at the impurity will be formed (Kohn 1957). As the impurity concentration is increased, the average spacing between impurities will decrease and overlap will occur between wavefunctions associated with particular impurities. This overlap between impurity wavefunctions will broaden the levels, as has been experimentally observed (Newman 1956, Colbow 1963). At sufficiently high concentrations the excited state wavefunctions of neighbouring impurities will overlap to such an extent that the levels begin banding. By this we mean that the excited state wavefunctions can no longer be considered as being localized at a particular impurity, but extend throughout the crystal. These bands of non-localized states are called the impurity bands. As the concentration increases, these bands will begin overlapping with each other and the valence band, effectively reducing the ionization energy of the impurity.

In order to explain the anomalous behavior of the resistivity and Hall constant in semiconductors at low temperatures (see list of references in Ray and Fan 1960) Erginsoy (1950) suggested that conduction could occur through these excited state impurity bands. The anomalies observed can be summarized as follows. As the temperature is decreased the resistivity and Hall constant increase exponentially, as expected. At a certain temperature (which depends on impurity concentration) the resistivity begins increasing at a different rate with temperature, corresponding to a different activation energy of the holes. This change
in activation energy is believed to correspond to the excitation of holes into the excited state impurity bands.

Baltensperger (1953) used a simple model in which the impurities form a regular sub-lattice to investigate the formation of impurity bands. The effect of varying the impurity concentration on both the broadening of the levels and the mobility in these bands was discussed using hydrogenic wavefunctions to describe the impurity states.

The effects of disorder on the formation of impurity bands was investigated by James and Ginzburg (1953) for a one dimensional array of impurities. In this randomly distributed array the impurity band no longer has definite edges as calculated by Baltensperger, and, in fact, the only remaining indication of the original impurity level is a maximum in the density of states at the original energy. In addition, the density of states tails off on both the low and high energy sides of the impurity level.

The previous experimental investigations of impurity band conduction have always used thermal generation as the means of exciting carriers into the impurity bands. The difficulty with this method is that the holes assume an energy distribution which will extend over the valence band as well as the impurity bands. The effects of the impurity bands will be masked by conduction in the valence band.

A more direct method of exciting the carriers will be used in this experiment. By photo-exciting the holes with monochromatic light only into the impurity excited states and measuring the resultant conductivity changes the existence of the impurity bands could be revealed without being masked by conduction in the valence band.

The photoconductive process in semiconductors can be described quite
simply in its most general sense. Incident photons excite current carriers (holes) from one state into an excited state in which the mobility is different from the original state. The carrier will live for an average length of time $\tau$ in this excited state before returning to its original state, either directly or through some intermediate states. When in the excited state, the change in mobility of the carrier will change the conductivity of the material. This change in conductivity can be detected as a change in current through the sample.

The energy levels of the boron impurity in relation to the valence band structure of silicon is shown in fig. I. The hole is shown in the impurity ground state, where it will normally be unless excited either thermally or optically. Incident photons of energy less than $E_I$ (wavelength longer than $25 \mu$) will excite the holes into the impurity excited states whereas photons with energy greater than $E_I$ will excite the holes into either the $P_{3/2}$ or $P_{1/2}$ valence bands.

The excitations into impurity excited states is of particular interest since no conductivity change will result from these excitations until such time as the excited states have formed non-localized impurity bands with a non-zero mobility.

In addition to depending on the change in mobility of the hole between the initial and final state, the observed change in conductivity
will depend critically on the lifetimes of the excited hole. This lifetime is determined either by the rate of recombination of carriers directly with impurity ground states, or by the rate with which they become trapped by localized excited states of the impurities. These trapping centers will be boron impurities which have been ionized either by compensating centers or by incident radiation. The mechanism of capture of free holes by these centers has been discussed by Lax (1960) in his theory of giant traps. In this mechanism the capture probability decreases rapidly as the energy of the recombining holes is increased, so that the lifetime could be increased by exciting the holes to a high energy or by increasing their average energy with an applied field.

In this experiment the photoconductivity was measured over a range in wavelengths covering excitations into the excited states (impurity bands) to excitations into the \(P_{1/2}\) valence band. These measurements were carried out at a fixed biasing current through each sample to obtain the relative spectral response curves for the different impurity concentrations. To investigate the effects of the applied field on the lifetime of the excited holes, the photoconductivity was measured as a function of the bias current through the sample for fixed wavelengths of light.

The interpretation of the data from these measurements was complicated by a non-ohmic behavior of the sample resistance. This "non-ohmicity" of the samples increases with the applied field and is associated with a heating of the holes by the applied field. At sufficiently strong fields the average energy of the holes is increased to such an extent that impact-ionization of neutral impurities produces a non-destructive breakdown of the sample.
CHAPTER II

EXPERIMENTAL PROCEDURE AND APPARATUS

The experimental problems involved in observing photoconductivity and the effect of band formation on the photoresponse are as follows:

(a) Fabrication of electrical contacts on the silicon which would not generate electrical noise at low temperatures.

(b) Irradiation of the sample with long wavelength infra-red radiation while the sample is kept at liquid helium temperature.

(c) Detection of the resistance change produced by this radiation.

A. SAMPLE PREPARATION

Wafers of the desired material were cut from single-crystal ingots of silicon using a diamond abrasive wheel. These wafers were ground flat with #600 SiC on a glass plate. The impurity concentration was then determined from a four-point probe measurement of the room-temperature resistivity. The resistivities used were 1.2 $\Omega$-cm\(^1\), 0.47 $\Omega$-cm\(^1\), 0.11 $\Omega$-cm\(^1\), and 0.047 $\Omega$-cm\(^2\) corresponding to impurity concentrations of 1.2 $\times 10^{16}$/cm\(^3\), 4.5 $\times 10^{16}$/cm\(^3\), 4.5 $\times 10^{17}$/cm\(^3\), 1.5 $\times 10^{18}$/cm\(^3\) respectively. In order to measure the field, the sample was cut with an ultra-sonic impact grinder as shown in fig. 1. The specimen was epoxied to a 3/4" diameter synthetic sapphire window

1 Supplied by Dow-Corning
2 Supplied by Semi-Elements Inc.
0.040" thick to provide support for the weak side arms and also to provide electrical isolation and thermal contact for the samples.

The epoxy used was a specially prepared low viscosity epoxy suitable for forming thin layers which did not crack when cooled (Glass 1964). The samples were ground down to the desired thickness, where possible, as mentioned above and then etched in hot NaOH. The thicknesses used were 2.26 mm ($1.2 \times 10^{16}$), 0.74 mm ($4.5 \times 10^{16}$), 0.23 mm ($4.5 \times 10^{17}$) and 0.23 mm ($1.5 \times 10^{18}$), with a possible deviation of $\pm 0.02$ mm on all samples. The samples were then ready for the contacts to be put on.

**CONTACTS**

Various methods of producing acceptable electrical contacts to the silicon were tried. These contacts were then judged according to the following requirements:

(a) Low noise

(b) Ability to cycle from room temperatures to helium temperatures without change in their characteristics

(c) Sufficient physical strength in order to minimize the necessity of special handling techniques

(d) Ease of fabrication.

The following methods were tried in order to produce the contacts, but unfortunately did not prove too successful. It is worthwhile to indicate the difficulties encountered with these methods and why they
were not as successful as the method used.

Pure indium was applied to the etched silicon surface with an ultrasonic soldering iron. This procedure greatly increased the breakage rate of the samples and the time of fabrication, but did not improve the noise characteristics of the contacts.

Pure gallium was applied to the freshly etched surface. This contact was easy to produce and had lower noise than the indium but suffered from a serious drawback. The contact cracked after cycling between 4.2 °K and room temperature, invariably breaking off part of the sample.

Gold was plated on the surface and alloyed with the silicon. This contact was poor in that it had a high contact resistance and produced a high level of electrical noise. These contacts also had the practical disadvantage of being quite difficult to apply.

The simplest method found to produce the most consistent low-noise contacts was to apply 100% indium solder to the silicon. The indium was melted on the tip of a small soldering iron and then rubbed against the contact area. By rubbing the silicon with the molten indium, the outer oxide layer on the indium bead could be broken and the silicon "wet" with fresh indium. Gold leads were then attached to the indium.

Care had to be taken with the thin samples since an uneven heating caused them to crack. This prevented the use of an optimum thickness for the two heavier doped samples.

The contacts were tested by measuring the sample resistance with a Wheatstone bridge for the two directions of current flow through the sample. If the resistances in the two directions were not within one percent of each other the contact could generally be improved by sparking through the contact with a Tesla coil. This broke down rectifying
barriers which were sometimes present (Ray and Fan 1961).

If the resistances could not be matched within the specified tolerance by sparking, the indium was removed and the surface of the silicon lightly ground and re-etched. A new contact was then made and tested. This procedure was repeated until the contacts were satisfactory.

B. **THE SPECTROMETER**

The spectrometer consisted of a Model 12B Perkin-Elmer infrared monochromator with exit optics modified to accommodate a liquid helium cryostat. Over the range 25 to 35 microns (35 to 50 meV.\(^3\)) a plane diffraction grating, with 30 lines per mm., blazed at 30 microns was used as the dispersing element. Two NaF residual ray plates were also used in this range to reduce unwanted shorter wavelength radiation (shorter than \(\sim 15\mu\)). This was kept to less than one percent of the desired radiation. The grating provided fairly high resolution (0.25 meV. at a maximum slit width of 2.0 mm.) but could not cover all the desired wavelengths.

To cover the shorter wavelengths the grating was replaced with a KBr prism. This covered the range 15 to 25 microns (50 to 100 meV.) but had a lower resolution than the grating (0.5 meV. at 25 microns to 1.3 meV. at 15 microns). Two LiF residual ray plates limited the stray radiation to less than one percent of the desired radiation in this region.

A Perkin-Elmer thermocouple with a CsI window was used to detect the light which was supplied by a globar source operating at about 1300 °C. The responsivity of the thermocouple was taken to be 4 microvolts per

\(^3\) The notation meV. will be used to denote \(10^{-3}\) electron volts.
microwatt, according to manufacturers specifications, and the signal produced from it was used to calculate the photon flux on the samples. The light beam was chopped at the source at 870 cps with a sectored wheel driven by a synchronous motor. The chopper assembly had to be mounted on gromets to prevent vibrations from the wheel reaching the cryostat.

The spectrometer was calibrated with water vapour absorption lines present at these wavelengths (Blair et al. 1962). In order to make photo-conductive measurements, however, these water vapour absorption lines had to be eliminated as much as possible. This was done by flushing the spectrometer continuously with dry nitrogen obtained by boiling liquid nitrogen. All but the strongest of these water vapour absorption lines could thus be eliminated.

C. THE DEWAR AND SAMPLE MOUNTING

A metal dewar was used to cool the sample. It consisted of an outer liquid nitrogen jacket and an inner helium container to which the sample was attached. Light reached the sample through a CsI window which was removable to allow sample mounting.

Sapphire spacers were used to electrically insulate the sample from the dewar, yet provided sufficient heat conduction to keep the sample approximately at helium temperatures. The sample was held in place with a copper retaining plate screwed snug against the sapphire backing. This would also provide additional cooling for the sample. The method of mounting is illustrated in fig. 2. Effects of strain due to differential contraction from both from the sapphire backing and from the dewar is negligible since the expansion coefficient for sapphire is only slightly different than for silicon. Any effect on the boron spectrum would be negligible since, at the high concentrations used here, the lines are
FIG. 2: Method of sample mounting.
exceedingly broad to begin with. In addition, the strain would be localized to the back face of the specimen whereas the bulk of the absorption occurs in the front portion.

The sample was mounted on the side opposite the window in order to restrict its view of room temperature radiation from the inside of the spectrometer. The determining aperture was the opening in the nitrogen shield surrounding the sample holder. From geometric considerations, the photoconductor was estimated to subtend a solid angle of approximately 0.14 steradians. Assuming the spectrometer box radiates as a black body at 300 °K, the total number of background photons incident on the sample was estimated to be $1.5 \times 10^{17}$ photons per second (Smith, Jones and Chasmar 1958).

**D. DETECTION SYSTEM**

In order for detectible signal to be obtained from the photoconductor, it had to be biased from a fairly stable source. A satisfactory method is to use a regulated voltage supply in series with an R-C filter. The filter eliminated any ripple and short term instabilities which would affect the measurements. The biasing network is shown in fig. 3.

The signal from the photoconductor was applied to the input of a high impedance preamplifier ($\sim 50\,\text{M}\Omega$ at 870 cps), kept as close to dewar as possible in order to minimize electrical pick-up and cable capacitance. Nevertheless, with the fairly high impedance samples and load resistors used, considerable 60 cps signal

![Biasing Network](image)
was present at the input.

A CK 5886 electrometer tube was used as the amplifying element in the preamplifier. It was operated in a standard plate-follower circuit with a gain of approximately 1.5 over a wide frequency band. Electrometer tubes are designed to operate at low voltages and with very small grid currents (2 x 10^-13 amp.) in order to provide high input impedances. To provide a leakage path from the grid, a $10^{11}$ Ω resistor was used. Fig. 4 shows a schematic diagram of the preamplifier circuit used.

Further amplification was obtained with a Tektronix Model 122 low noise preamplifier with a bandpass of 80 cps to 1 Kc. The remainder of the 60 cps signal (and harmonics) were filtered out with a wide band filter. This filter was necessary to prevent the input stages of the following tuned amplifier (40 cps bandwidth at 870 cps), from being overdriven. The tuned amplifier also determined the noise bandwidth of the system. The signal was then rectified and displayed on a Brown strip-chart recorder.
The d.c. characteristics of the samples were measured using a standard four-point probe measuring technique. The current was measured with a Model 425-A Hewlett-Packard D.C. micro-volt ammeter and the field with a Fluke, Model 801, differential voltmeter connected across two of the side arms. The total voltage drop across the sample was measured to determine the contact resistance.

Noise spectra for the samples were measured with a General Radio Model 736-A waveanalyser.

A block diagram of the complete detection system is shown schematically in fig. 5.
FIG. 5: Block diagram of complete detection system.
CHAPTER III: RESULTS AND ANALYSIS

A. SIGNAL FROM A NON-OHMIC PHOTOCONDUCTOR

The problem is to calculate the photocurrent produced by radiation incident on the sample with an additional complication of a non-linear dependence of detector current on applied field (Pultey 1964).

The photoconductor is connected in a circuit as shown in the accompanying figure. The voltage $V_B$ applied to the load resistor $R_L$ and the bulk resistance of the photoconductor $R$ will establish the operating point

$$I = \frac{V_B}{R_L + R}, \quad V = \frac{V_B R}{R_L + R} \quad (1)$$

The sample resistance, $R = R(Q,V)$, appearing in equation (1) depends on both the voltage $V$ and the incident radiation $Q$.

For the purposes of this discussion we will assume that the amplifier connected across the sample has an infinite input impedance so no current is drawn from the photodetector. The effects of a finite input impedance will be discussed in the following section.

When infrared radiation illuminates the sample, the sample resistance will change and, as a result, the voltage appearing across the sample will change. The quantity of interest, therefore, is the change in voltage, $dV$, produced by the incremental change in the photon flux, $dQ$.

From equation (1),
\[
\frac{dV}{dQ} = \frac{V_B}{R_L + R} \quad \frac{dR}{dQ} - \frac{V_B R}{(R_L + R)^2} \quad \frac{dR}{dQ},
\]

or

\[
\frac{dV}{dQ} = \frac{IR_L}{R_L + R} \quad \frac{dR}{dQ}
\]

(2)

Since \( R = R(Q,V) \),

\[
\frac{dR}{dQ} = \left( \frac{\partial R}{\partial Q} \right)_V + \left( \frac{\partial R}{\partial V} \right)_Q \frac{dV}{dQ}
\]

(3)

Equation (2) can now be written as

\[
\frac{dV}{dQ} = \frac{IR_L}{R_L + R} \left\{ \left( \frac{\partial R}{\partial Q} \right)_V + \left( \frac{\partial R}{\partial V} \right)_Q \frac{dV}{dQ} \right\}
\]

(4)

The quantity \( \left( \frac{\partial R}{\partial V} \right)_Q \) can easily be evaluated from the current-voltage characteristics of the sample. At any point on this curve the resistance is defined as \( R(Q,V) = V/I \). At a particular value of the flux \( Q \), the resistance along the characteristic will vary as

\[
\left( \frac{\partial R}{\partial V} \right)_Q = \frac{1}{I} - \frac{V}{I^2} \left( \frac{\partial I}{\partial V} \right)_Q
\]

(5)

Defining the dynamic (or a.c.) resistance as

\[
R_{ac} = \left( \frac{\partial V}{\partial I} \right)_Q
\]

gives

\[
\left( \frac{\partial R}{\partial V} \right)_Q = \frac{1}{I} \left[ 1 - \frac{R}{R_{ac}} \right]
\]

Equation (4) will then be
which can be solved for the change in voltage \( \frac{dV}{dQ} \).

\[
\frac{dV}{dQ} = \frac{IR_L}{R_L + R} \left( \frac{\partial R}{\partial Q} \right)_V + \frac{R_L}{R_L + R} \left( 1 - \frac{R}{R_{ac}} \right) \frac{dV}{dQ},
\]

In most practical applications the circuit is designed so that \( R_L \gg R_{ac} \). For this case the change in voltage appearing across the photoconductor is

\[
\frac{dV}{dQ} = \frac{IR_{ac}}{R} \left( \frac{\partial R}{\partial Q} \right)_V (1 + \frac{R_{ac}}{R_L}).
\]

Denoting the quantity \( \left( \frac{\partial R}{\partial Q} \right)_V dQ \) by \( \Delta R \), the signal voltage is

\[
dV = IR_{ac} \frac{\Delta R}{R}.
\]

This can be put in terms of the generated photocurrent and sample conductance as

\[
i_s = I \left| \frac{\Delta G}{G} \right|.
\]

B. THE PHOTOCONDUCTOR AS A CIRCUIT ELEMENT

If we consider the photoconductor as a voltage source, it is clear that the best operating procedure is to make the input impedance of the detector circuitry large in comparison with the resistance of the photoconductor. This condition could not be fulfilled, however, since the
lead-in wires to the helium container loaded the preamplifier input with 113 pf. capacitance, reducing the input impedance to 1.6 MΩ. Corrections had to be made to the measured signal in order to determine the signal appearing across the photoconductor.

In all samples the metal-semiconductor contact resistance was comparable to the sample resistance. This further reduced the measured signal. The sample behaved as a voltage source with an internal resistance made up of the bulk resistance of the material in series with the contact resistance. The a.c. equivalent of the detector is as follows:

![A.C. equivalent of the photoconductor.](image)

FIG. 6: A.C. equivalent of the photoconductor.

- **R\text{ca}** is the a.c. resistance at the contacts determined from the total voltage drop across the sample
- **R\text{sa}** is the a.c. resistance of the bulk sample
- **e\text{s}** is the voltage generated by the sample
- **R\text{L}** is the load resistor in parallel with the input resistance of the preamplifier
- **C** is the stray capacitance across the sample
- **e\text{o}** is the voltage appearing at the input of the amplifier.

From elementary circuit theory the load impedance \( Z_o \) is given by

\[
Z_o = \frac{jX_c R_L}{R_L + jX_c}, \quad \text{where} \quad X_c = \frac{1}{\omega C}
\]
For all cases $X \ll R_L$, so

$$Z_0 \ll jX_c.$$ 

The signal applied to the amplifier is

$$e_o = \left| \frac{Z_0}{Z_0 + R_{ca} + R_{sa}} \right| e_s.$$

In terms of measurable quantities, the measured signal is

$$e_o = \frac{e_s}{\left[ 1 + \left( \frac{R_{ca} + R_{sa}}{X_c} \right)^2 \right]^{1/2}} \quad (9)$$

Because of the capacitive loading of the sample, the measured voltage is only a fraction of the generated voltage. This did not affect the measurements in general since the limiting noise was also generated in the sample. As a result, the noise was decreased by the same factor, keeping the signal to noise ratio constant.

The use of a lower modulation frequency would reduce the effect of the stray capacitance and increase the measured signal. However, the signal to noise ratio decreased at lower frequencies because of increasing noise generated by the sample. This, therefore, made it advantageous to use the high modulation frequency.

C. D.C. CHARACTERISTICS

The current-voltage characteristics for the various impurity concentrations are shown in figs. 7 and 8. In all cases the samples were exposed to the same amount of background radiation and were approximately at the same temperature, except for the sample with $1.5 \times 10^{18}$ impurities/cm$^3$ which was maintained at 2.4 K. All samples
FIG. 7: Current - voltage characteristics of two samples at helium temperatures. Both samples are exposed to the same room temperature radiation.
FIG. 8: Current-voltage characteristics of two samples at helium temperatures. Both samples are exposed to the same room temperature radiation.
exhibited a non-linear dependence of current on applied field even at the lowest fields measurable. This non-linearity increased with field until breakdown occurred. The breakdown is a non-destructive "run-away" of the current associated with carrier multiplication as neutral impurities are impact-ionized by energetic holes (Sclar and Burstein 1957, Koenig and Gunther-Mohr). No apparent damage is done to the material since the results can be reproduced many times during a run. The breakdown field was found to vary approximately as $N_A^{-3/4}$ over the impurity range $10^{16}$ impurities/cm$^3$ to $5 \times 10^{17}$ impurities/cm$^3$. The observed values are given in table I.

The log $I$ vs log $E$ curves were linear at low field strengths with a slope which decreased as the impurity concentration increased. The value for the slopes are given in table I.

TABLE I
D. C. Characteristics

<table>
<thead>
<tr>
<th>Impurity Concentration atoms/cm$^3$</th>
<th>Breakdown Field volts/cm</th>
<th>Initial Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.2 \times 10^{16}$</td>
<td>$45 \pm 3$</td>
<td>$1.35 \pm 0.05$</td>
</tr>
<tr>
<td>$4.5 \times 10^{16}$</td>
<td>$130 \pm 10$</td>
<td>$1.27 \pm 0.10$</td>
</tr>
<tr>
<td>$4.5 \times 10^{17}$</td>
<td>$700 \pm 30$</td>
<td>$1.10 \pm 0.05$</td>
</tr>
<tr>
<td>$1.5 \times 10^{18}$</td>
<td>$2.2 \pm 0.1$</td>
<td>$1.03 \pm 0.02$</td>
</tr>
</tbody>
</table>

The value of slope quoted corresponds to an average obtained from a number of separate runs along with the spread in the measured values. The differences in slope measured for each sample were attributed to slight temperature variations during the consecutive runs. This was a result of the mounting method and could not be eliminated.

The characteristics were checked at a lower temperature
(approximately 2.4 °K) for the three lower concentration samples and it was found that the breakdown field did not change with temperature but the initial slope decreased with temperature. The resistance of the samples also increased, indicating that the recombination rate (or lifetime) of the free holes generated by background radiation is slightly temperature dependent. This effect of temperature on the recombination rate will be discussed later.

Using the characteristic curves and assuming a mobility given by neutral impurity scattering (Erginsoy 1950, Sclar 1956), the equilibrium number of free holes was calculated to be about $10^7$ for the concentrations $1.2 \times 10^{16}$, $4.5 \times 10^{16}$ and $4.5 \times 10^{17}/\text{cm}^3$ at low applied fields. For the most heavily doped sample there were about $10^{12}$ free holes at 2.4 °K.

The sample with $1.5 \times 10^{18}$ Boron/cm$^3$ had a d.c. characteristic which did not conform with that of the other samples. It had a much lower resistance and lower breakdown field than expected (2.2 volts/cm). At this impurity concentration the material is nearly degenerate, so thermal generation of holes will be important even at these temperatures. This is evident in the estimate of the number of holes present in the sample. In addition, the energy needed to ionize neutral impurities is much less than the normal ionization energy of the boron, resulting in a low breakdown field. In order to observe photoconductivity in this sample the temperature had to be reduced to 2.4 °K.

D. SPECTRAL RESPONSE

The spectral response, or generated photocurrent per incident photon, was measured for the four impurity concentrations and the
results are shown in figs. 9 and 10. The curves shown are the generated photosignal normalized to a constant photon flux of $5 \times 10^{12}$ photons/sec incident on the samples. All samples were exposed to the same flux of background radiation and all operating at 0.5 microamp. bias, except for the $1.5 \times 10^{18}$ sample which was operated at 40 microamperes.

Fig. 9 shows the region extending over wavelengths shorter than the wavelength required for ionization. The large dips at 64 meV. and 82 meV. are due to lattice absorption (Collins and Fan 1954). Each sample appears to have a maximum response at photon energies between 90 to 100 meV., with the peak response decreasing with increasing impurity concentration. The increase in response in this region is believed to be partly due to the effect of the $P1/2$ valence band. Holes excited into this band have a smaller effective mass than those in the other bands (Zwerdling et al. 1959) so we would observe a larger photocurrent.

Previous measurements of impurity photoconductivity at lower impurity concentrations (Burstein et al. 1954) show a definite threshold energy, corresponding to the impurity ionization energy, below which there was no response. A fairly definite threshold was observed at the concentration $1.2 \times 10^{16}$/cm$^3$ but had almost completely disappeared at $1.5 \times 10^{18}$ atoms/cm$^3$. Considerable flattening off of the response had occurred for this sample for photon energies up to 20 meV. below the top of the valence band.

A more detailed picture of the response in the region of the excited states is given in fig. 10. Here it is evident that the excited states are definitely affecting the photo response at low photon energies. The first kink is present even at the lowest concentration ($1.2 \times 10^{15}$ atoms/cm$^3$) and is at the same energy as the group of
FIG. 9a: Photo-current vs. photon energy normalized to a constant photon flux of $5 \times 10^{12}$ photons/sec at all energies. Current through samples is 0.5 $\mu$A.
FIG. 9(b): Photo-current vs. photon energy normalized to a constant photon flux of $5 \times 10^{12}$ photons/gsec.

- $A = 4.5 \times 10^{17} \text{photons/cm}^2$ (units of $10^{-10}$ amp.)
- $B = 1.5 \times 10^{18} \text{photons/cm}^2$ (units of $10^{-10}$ amp.)

Photo-current in units of $10^{-12}$ amp.
FIGURE 10

Photo-current in the region of the impurity excited states. The photo-current is normalized to a uniform flux of $5 \times 10^{12}$ photons/sec at all energies. The arrows marked 2 to 9 indicate the position of impurity excited states. Vertical scales used for the various concentrations are as follows:

- $+ - 1.2 \times 10^{15}/\text{cm}^3$ - arbitrary scale is used, curve gives relative response only.
- $x - 1.2 \times 10^{16}/\text{cm}^3$ - as indicated (L. H. Scale)
- $o - 4.5 \times 10^{16}/\text{cm}^3$ - multiply left hand scale by 1/2.
- $\Delta - 4.5 \times 10^{17}/\text{cm}^3$ - multiply left hand scale by 1/5.
- $\Box - 1.5 \times 10^{18}/\text{cm}^3$ - use right hand scale.
excited states 5 to 9, indicated by the arrows (Colbow 1963, Burstein et al. 1956). The response moves out to the states 3 and 4 at a concentration of $1.2 \times 10^{16}$/cm$^3$ and for state 2 some signal was measured at a concentration of $4.5 \times 10^{16}$/cm$^3$. It appears that the response does not increase significantly in the region of state 2 with another 10 fold increase in concentration (to $4.5 \times 10^{17}$ impurities/cm$^3$). At this concentration it does not appear that much response will be obtained from state 1 although this could not be checked. Increasing the concentration by another factor of 3 (to $1.5 \times 10^{18}$/cm$^3$) produced a large change in the response, probably extending it to energies well below the first excited state.

For the two lowest concentration samples the response had a definite cut-off as indicated in fig. 10, with no response observed below the respective cut-offs. For the 10 fold increase in concentration from $1.2 \times 10^{15}$ to $1.2 \times 10^{16}$ atoms/cm$^3$ this cut-off shifted 4 meV. to lower energies. For all higher concentrations used no definite cut-off was observed, only a gradual decrease in response out to the lowest attainable energies.

The response curves for all the samples have an inflection point around 46 meV., the quoted low concentration ionization energy of boron (Burstein et al. 1956). This "shoulder" is most evident for the lowest concentration sample and could possibly be due to other excited states of the boron lying between 44 and 46 meV. The rapid rise at higher energies is due to transitions directly into the valence band.

The very sharp shoulder at 46.5 meV. observed for the $1.2 \times 10^{16}$/cm$^3$ sample is likely due to an uncertainty in the determination of the number of incident photons. A strong water vapour absorption peak occurs at this energy and complete cancellation of the effects of these peaks proved
troublesome. Fairly strong water vapour absorption peaks also occurred at 40.5 and 43 meV., with the result that the kinks at these points may not be quite as well defined as is shown. However, the maximum error at these two points will not exceed ± 20% so that changes in response are definitely occurring in these regions.

The curve for the concentrations $1.2 \times 10^{15}/\text{cm}^3$ has been included for a quantitative comparison only. The response shown is only a relative response with the value at 48 meV. arbitrarily taken at $100 \times 10^{-12}$ amp. The reason quantitative measurements could not be made on this sample was partly because a sample thick enough to absorb all the incident radiation could not be mounted in the cryostat. In addition, the d.c. characteristics for this sample could not be reproduced from run to run even after several attempts had been made at improving contacts to the material. During each run the relative photo response was measured and was reproducible to within 5% from run to run. Because of this reproducibility it is believed the results are due to the boron and not extraneous contact effects.

E. PHOTOCONDUCTIVITY MEASUREMENTS

The quantities which are of practical importance in photoconductive measurements are the signal and noise at the input of the amplifier, and how these quantities vary with bias current. These quantities are shown in figs. 11 for different impurity concentrations. Since the signals have not been corrected for the detector impedance, all samples appear to have a different behavior with bias current. The effect of the decreasing detector resistance with increasing current is very noticeable in the signal measured from the $4.5 \times 10^{17}/\text{cm}^3$ sample. At large currents the measured signal begins increasing rapidly because of the decreasing sample resistance.
FIG. 11(a): Measured signal and noise as a function of biasing current through the $1.2 \times 10^{16} / \text{cm}^3$ sample.

$8.2 \times 10^{12} \text{ photons/sec} @ 75 \text{ meV}$. 
FIG. 11(b): Measured signal and noise as a function of biasing current through the $4.5 \times 10^{16}/\text{cm}^3$ sample.
FIG. 11(c): Measured signal and noise as a function of biasing current through the $4.5 \times 10^{17}/\text{cm}^3$ sample.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
8.2 \times 10^{12} \text{ photons/sec @ 75 meV.}

FIG. 11(d) : Measured signal and noise as a function of biasing current through the $1.5 \times 10^{18}$/cm$^2$ sample.
The signal from the $1.5 \times 10^{18}/\text{cm}^3$ sample has a completely different current dependence at high currents because of the initial low resistance of the sample. The low resistance of this sample meant that all the signal generated at the sample was applied to the input of the amplifier without loss.

If the effect of the sample resistance is taken into account, the photosignal has a field dependence as shown in figs. 12. For all samples the generated photosignal increases with field up to the region where the characteristics becomes quite non-linear. For further increases in the field the photosignal saturates or else decreases.

This behavior is understandable if one considers equation (7) derived earlier,

$$e_S = I R_{ac} \left| \frac{\Delta G}{G} \right|,$$

where $e_S$ is the generated photosignal. The signal which is generated depends on the field dependent dynamic resistance, $R_{ac}$, which decreases rapidly with applied field near breakdown, thereby decreasing the photosignal. A comparison with the characteristics (figs. 7 and 8) shows that the saturation effect does occur in the region of increasing non-linearity.

The measured noise voltage, also shown in figs. 11, generally increases with increasing current through the samples. All the samples had peaks in the noise curves which were quite reproducible although could be changed by tampering with the contacts. Because of these large variations in noise output after a modification in the contacts the noise is assumed to be associated with current flow through potential barriers at the contact. In addition to the noise, however, the contacts introduce an effective resistance in series with the photoconductor which
FIG. 12(a) : Photo-signal appearing across the $1.2 \times 10^{16}/\text{cm}^3$ sample as a function of applied electric field.

Photon flux is $8.2 \times 10^{12}/\text{sec}$ @ 75 meV.
FIG. 12(b): Photo-signal appearing across the $4.5 \times 10^{16}$/cm$^3$ sample as a function of applied electric field.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
FIG. 12(c) : Photo-signal appearing across the $4.5 \times 10^{17}/\text{cm}^3$ sample as a function of applied electric field.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
FIG. 12(d) : Photo-signal appearing across the $1.5 \times 10^{18}/\text{cm}^3$ sample as a function of applied electric field.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
contributes to the loss in signal (see section B). The measured contact resistance is shown in fig. 13 for different currents through the samples. The current dependence observed here is similar to that found in boron-doped germanium photoconductors with similar contacts (Wallis and Shenker 1964).

The noise characteristics of the samples were generally quite different for the two different directions of current flow through the samples. For each sample the direction of minimum noise was determined in order to obtain the largest signal to noise ratio when making photoconductive measurements. The curve of rms noise voltage vs frequency is shown in fig. 14 for the two directions of current flow through the 1.2 x 10^{16}/cm^3 sample. This sample had the greatest difference in noise characteristics for the two current directions in addition to the lowest signal to noise ratio of all the samples. For both current directions, however, there was a definite similarity in the behavior of the noise with frequency. The observed decrease in the noise at higher frequencies prompted the use of 870 cps as the modulating frequency rather than a lower frequency.

The signal to noise ratio goes through a maximum before decreasing near breakdown for each of the samples. The maximum observed S/N ratio decreased with decreasing impurity concentrations. It is not known if the higher concentration samples are inherently less noisy or if it is just a property of these particular contacts.
FIG. 13: Resistance due to contacts vs. bias current through samples.
FIG. 14: Noise spectra for the $1.2 \times 10^{16}/\text{cm}^3$ sample for two directions of current flow. Bias current = 1.0 $\mu\text{a}$. 
CHAPTER IV: THEORY AND DISCUSSION

A. IMPURITY PHOTOCONDUCTIVITY

The problem of impurity photoconductivity can be treated in a simple yet instructive manner since diffusion and space charge effects can be neglected (Burstein 1954, Bube 1950, Putley 1964, Rittner 1954). In addition, we will assume that the effect of traps present in the material can be neglected, so that the carrier is free to participate in conduction during the time between generation and recombination.

Consider a p-type semiconductor at low temperatures containing $N_A$ acceptors/cm$^3$ and $N_D$ donors/cm$^3$ with $N_D \ll N_A$. For shallow impurities (group III) in silicon liquid helium temperatures are required to keep the number of thermally ionized acceptors, and hence the number of free holes, small. The "dark" conductivity of the sample will then be determined by the flux of background photons incident on it. Because of an exponential decay of the photon flux through the sample thickness, the densities of generated carriers will vary throughout the sample volume.

Consider a layer of the material of thickness $dx$, lying a distance $x$ below the surface. Let $n_f(x)$, $n_u$ and $n_i$ be the densities of free holes, unionized acceptors and ionized acceptors in this layer. We will assume that the following conditions hold:

$$n_f(x) \ll n_u,$$

$$n_f(x) \ll n_i, \quad n_i \ll N_D,$$

$$n_u = N_A - N_D - n_f(x) \ll N_A - N_D$$

Because $N_D$ and $N_A$ are uniform throughout the sample, $n_i$ and $n_u$ will not depend on the depth below the surface.
The equilibrium number of holes will be determined by the balance between the total rate of generation and the total rate of recombination (Koenig 1962).

$$\frac{dn_f(x)}{dt} = A_T(N_A - N_D) + A_B(x)(N_A - N_D) - B_T N_D n_f(x) + A_I(N_A - N_D)n_f(x)$$

$$- B_I n_f^2(x)N_D$$

$$= 0 \quad (10)$$

The terms $A_T(N_A - N_D)$ and $A_B(x)(N_A - N_D)$ are the rates of generation of holes by thermal excitation and by background radiation. At liquid helium temperature the thermal generation term $A_T(N_A - N_D)$ will be negligible in comparison to $A_B(x)(N_A - N_D)$. The term $A_I n_f(x)(N_A - N_D)$ is the rate of ionization of the neutral impurities caused by the collision of energetic free holes with the impurities. The terms containing $B_T$ and $B_I$ will be the corresponding recombination rates of the free holes.

$B_T N_D$ is the rate of recombination of the free holes via a direct recombination with the ionized impurities with the excess energy of the holes being carried off by phonons. The giant trap mechanism (Lax 1960) is assumed to be the method of capture of the holes by the ionized impurities. In this process the hole is first captured into one of the highly excited states of the impurity, with the excess energy and momentum being carried away by acoustic phonons. The hole then decays in steps to the ground state with the emission of phonons or photons at each step. These final steps will undoubtedly limit the rate of decay into the ground state, but the capture rate will be determined by the initial capture into an excited state.

In order for a state to be effective as a trap, its binding energy
will have to be greater than $kT$ to prevent the hole from being thermally re-excited into the band. Lowering the temperature permits contributions from states of increasing radius resulting in increased capture cross sections. This explains the increase in sample resistance on lowering the temperature from 4.2 °K to 2.4 °K as was mentioned in chapter III.

$B_f n_f^2(x)N_D$, on the other hand, represents recombination via the Auger process in which the excess energy and momentum of the recombining hole is carried off by another free hole. This term will be negligible for the low field measurements when $n_f$ is small, but may become important near breakdown. Since we are interested in the lower field regions, we will neglect this term.

The equilibrium concentrations of holes, within the limits of these approximations, is

$$n_f(x) = \frac{A_B(x)(N_A - N_D)}{B_fN_D - A_I(N_A - N_D)} \quad (11)$$

The rate of generation of free holes by the background at $x$ can be written as

$$A_B(x)(N_A - N_D) = \int_0^{\lambda_c} (1 - R) N_o(\lambda) \propto(\lambda)e^{-\propto(\lambda)x} d\lambda \quad (12)$$

where: $\propto(\lambda)$ is the absorption constant and $R$ the reflection coefficient at wavelength $\lambda$,

$\lambda_c$ is the long wavelength cut-off of photons capable of ionizing the impurities,

$N_o(\lambda)$ is the number of photons/sec with wavelengths between $\lambda$ and $\lambda + d\lambda$ incident on the surface.
This number is calculated assuming that the background radiation is emitted by a 300 °K black-body. The total rate of generation in the sample is obtained from equation (12) by an integration over the sample thickness, \(d\), with the result

\[ A_B (N_A - N_D) = \int_0^\infty (1 - R) N_0(\lambda) \left(1 - e^{-\alpha(\lambda)d}\right) \, d\lambda. \]

Since all the samples were made thick enough to absorb all the radiation, we have

\[ 1 - e^{-\alpha(\lambda)d} \ll 1. \]

The above equation can then be written as

\[ A_B (N_A - N_D) = Q_B, \quad (13) \]

where \(Q_B = (1 - R)Q'_B\) is the number of photons/sec absorbed by the sample and

\[ Q'_B = \int_0^\infty (1 - R) N_0(\lambda) \, d\lambda \]

is the total number of photons/sec incident on the sample. We will use \(R = 0.31\) as the reflection coefficient of silicon (Bichard and Giles 1962).

Using equation (13), the total number of free holes in the sample is

\[ N_f = \frac{Q_B}{B_T N_D - A_I (N_A - N_D)}, \quad (14) \]

It is convenient to introduce a lifetime, \(\tau\), defined as

\[ \tau = \frac{1}{B_T N_D - A_I (N_A - N_D)}, \quad (15) \]

which represents the time during which holes are free to contribute to conduction. When impact ionization is unimportant this time is the usual
recombination time, $1/B_T N_D$, of the free holes with ionized acceptors.

Using this definition, equation (14) can be written

$$N_f = Q_B C.$$  

When photoionization radiation is incident on the sample the number of free holes rises above this equilibrium value and the sample conductance increases. If there are $Q_i' (\lambda)$ photons per second of wavelength $\lambda$ to $\lambda + d \lambda$ incident on a sample of reflectivity $R$, the rate of generation at a distance $x$ below the surface will be

$$f(x) = Q_i' (\lambda) \alpha (\lambda) e^{-\alpha(\lambda) x}$$

where $Q_i (\lambda) = Q_i' (1 - R)$ is the number of photons/sec being absorbed by the sample.

The new equilibrium concentration of free holes will be determined by

$$\frac{d n_f'(x)}{dt} = A_B(x) n_u' - B_T N_i n_f'(x) + A_I n_u' n_f'(x) + f(x)$$

$$= 0$$

where $n_f'(x)$, $n_u'$ and $n_i'$ are the new concentration of free holes, unionized acceptors and ionized acceptors. For the case of small signals

$$n_i' \approx N_D \quad \text{and} \quad n_u' \approx N_A - N_D.$$

Thus equation (16) becomes

$$\frac{d n_f'(x)}{dt} = A_B(x) (N_A - N_D) - B_T N_D n_f'(x) + A_I (N_A - N_D) n_f'(x) + f(x)$$

$$= 0$$

The change in free hole concentration in this layer is easily shown to be
\[ n_f'(x) - n_f(x) = \Delta n_f(x) = \frac{f(x)}{B_T N_D - A_I (N_A - N_D)} , \quad (19) \]

or

\[ n_f(x) = f(x) \tau . \]

Because of the variation in free carrier density with depth in the sample, the significant parameter will be the total number of generated carriers, \( \Delta N_f \), obtained from equation (19) by an integration over the thickness \( d \);

\[ \Delta N_f = Q_i \tau . \quad (20) \]

These equations are particularly useful in explaining the non-ohmic behavior of the samples at low fields and also the phenomena of breakdown (Koenig 1958, Sclar and Burstein 1957, Koenig and Gunther-Mohr 1957). To do so, however, we have to consider the fact that the coefficients \( B_T \) and \( A_I \) will be functions of the lattice temperature and the hole distribution function \( f(\epsilon) \). The distribution will itself be dependent on the applied field \( \mathcal{E} \) and the lattice temperature. At low field strengths impact ionization is negligible so the number of holes is determined by the recombination rate, which decreases as the energy of the hole increases (Lax 1960). This has a direct consequence on the d.c. characteristics, with the non-linearity at low fields being due to the changing distribution function and the resultant modification in recombination rate (Picus 1962). The change in the distribution will occur in order to establish a new equilibrium between the rate of absorption of energy from the field and rate of dissipation of energy to the lattice. The increase in the average energy corresponds to an increase in temperature of the system of holes. At sufficiently high fields the average energy will become of the order of the impurity ionization energy and impact ionization will occur.
The net effect of an increasing field is a decrease in the recombination rate and an increase in the impact-generation rate with the result that the lifetime begins increasing rapidly. The d.c. characteristics of each sample display this behavior: a rapidly increasing conductance for fields preceding breakdown followed by a much more rapid increase at breakdown.

Using equations (16) and (20), we can relate the measured photocurrent (equation (8)) to more fundamental parameters characterizing the holes. A material with \( N_f \) free holes (given by equation (16)), with mobility \( \bar{\mu} \) will have a conductance

\[
G = \frac{N_f e \bar{\mu}}{12} = \frac{Q_B \bar{\tau} e \bar{\mu}}{12},
\]

where \( \bar{\tau} \) is written as the lifetime of these holes, and \( l \) the distance between contacts. The change in conductance produced by the photoionization radiation of wavelength \( \lambda \) is clearly

\[
\Delta G(\lambda) = \frac{Q_i(\lambda) e \mu(\lambda) \tau(\lambda)}{12}
\]

where \( \mu(\lambda) \) is the mobility and \( \tau(\lambda) \) is the lifetime of the holes excited by radiation of this wavelength. Because both parameters \( (\mu(\lambda) \) and \( \tau(\lambda) \)) may depend on the final energy of the excited hole, we will have to distinguish between the lifetimes and mobilities appearing in equations (21) and (22). The dependence of these two parameters on the energy of the excited holes will be discussed in the following sections.

For constant illumination the photocurrent produced (equation (8)) will depend directly on the product \( \mu(\lambda) \tau(\lambda) \) for the excited holes. First introduced by Gudden and Pohl (1921), the \( \mu(\lambda) \tau(\lambda) \) product (or schubweg) gives the distance a free hole will travel in the direction
of the applied electric field in a time $\tau(\lambda)$ per unit applied field. The longer this distance can be made, the greater the change in conductance for a fixed illumination. An obvious method for increasing the distance is through the lifetime. For low field strengths $\tau(\lambda)$ is inversely proportional to the concentration of compensating centers, estimated to be $1 \times 10^{13}$ atoms/cm$^3$, so it would appear that it could be made as long as desired by a further reduction in $N_D$. In practice, however, much lower compensation is virtually impossible with the present methods of crystal preparation. In addition, the effect of other crystal defects and recombination mechanisms would place an upper limit on $\tau(\lambda)$.

The conductance change produced by irradiating the samples with 75 meV. photons is shown in fig. 15 for different values of applied electric field. The factor $Q_i(\lambda)e/1^2$ appearing in equation (22) is a constant at this wavelength (i.e. field independent) so the field dependence of $\Delta G(\lambda)$ will be due to changes in $\mu(\lambda) \tau(\lambda)$ with field.

For each sample there is a region at low field strengths for which $\mu(\lambda) \tau(\lambda)$ increases with field before reaching a plateau. The drift distance per unit field of the holes then remains relatively constant as the field is further increased. Near breakdown fields, however, each sample shows a rapidly increasing $\mu(\lambda) \tau(\lambda)$ due to a rapid increase in lifetime. This variation with electric field was measured at three other photon energies and the results are shown in fig. 16 for the $4.5 \times 10^{16}$/cm$^3$ sample. Two of the photon energies used were slightly lower than the low concentration ionization energy (46 meV.) and one was slightly higher.
FIG. 15(a): Conductance change $\Delta G(\lambda)$ in the $1.2 \times 10^{16} / \text{cm}^2$ sample produced by 75 meV. photons vs. applied electric field.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
FIG. 15(b): Conductance change $\Delta G(\lambda)$ in the $4.5 \times 10^{16}/\text{cm}^3$ sample produced by 75 meV photons vs. applied electric field.
$8.2 \times 10^{12}$ photons/sec @ 75 meV.

**FIG. 15(c):** Conductance change $\Delta G(\lambda)$ in the $4.5 \times 10^{17}$/cm$^3$ sample produced by 75 meV. photons vs. applied electric field.
FIG. 15(d): Conductance change $\Delta G(\lambda)$ in the $1.5 \times 10^{18}/\text{cm}^3$ sample produced by 75 meV. photons vs. applied electric field.

$8.2 \times 10^{12}$ photons/sec @ 75 meV.
FIG. 16: Conductance change $\Delta G(\lambda)$ at different photon energies vs. applied electric field for the $4.5 \times 10^{16}/\text{cm}^3$ sample.
The conductance changes at these different wavelengths have essentially the same field dependence as the changes measured for this sample at 75 meV. (shown in fig. 15). This similarity at the different wavelengths was also observed for the $1.2 \times 10^{16}/\text{cm}^3$ and $4.5 \times 10^{17}/\text{cm}^3$ samples. Since the $\mu(\lambda)\tau(\lambda)$ product has the same field dependence at all the wavelengths measured, the relative shape of the spectral response curves for a particular sample (figs. 9 and 10) will not depend on the value of field used when making the measurement.

The exact reasons for the particular field dependence of $\Delta G(\lambda)$ shown in fig. 15 is difficult to determine because neither $\mu(\lambda)$ nor $\tau(\lambda)$ could be measured separately in this experiment. A quantitative estimate of either one of these parameters will involve estimates about the other, so will rely on a certain number of assumptions being made. The method used to separate the two factors is discussed in the following sections.

B. HOLE MOBILITY AND LIFETIME

1. MOBILITY

As we have seen in the previous section, the observed conductance changes depend on both the mobility and lifetime of the photoexcited holes. In this section we shall show how the mobility may be estimated in order to obtain the lifetime of the holes. The mobilities obtained in this section will apply to holes in the valence band and are not assumed to apply to holes in impurity bands. The mobility of holes in these bands will be discussed in a later section.

Since the energies of excitation are never very large, the holes will remain in the vicinity of the valence band maximum. The regular
Valence bands of silicon will, therefore, be replaced by a single parabolic band with a constant effective mass. Because of this we can write the mobility as

$$\mu = e \frac{\langle T \rangle}{m^*}$$

where $\langle T \rangle$ is an integral involving the momentum relaxation time, $T$ (capital tau), of the holes.\(^4\) In general $T$ will depend on the energy of the holes, so changing the distribution either by applying an electric field or by photo-excitation of the holes with photons of different energy will change the mobility. However, for impurity concentration greater than $\sim 10^{16}/\text{cm}^3$ the dominant scattering mechanism is assumed to be elastic scattering from the neutral impurities (Sclar and Burstein 1957, Sclar 1956, Erginsoy 1950, Yamashita 1960). In this case $T$ is independent of the hole energy so we could write

$$\mu = e \frac{T}{m^*}$$

(23)

for the entire band. The mobility was calculated by Erginsoy (1950) to be

$$\mu = \frac{1.43 \times 10^{22} \eta}{K N_N} \text{ cm}^2/\text{volt-sec}$$

where $K$ is the dielectric constant, $\eta = m^*/m_e$, and $N_N$ is the density of neutral impurities. Using a density of states effective mass, $m^* = 0.6 m_e$, the mobility of holes in the valence band will be taken as

$$\mu = \frac{7.15 \times 10^{20}}{N_N} \text{ cm}^2/\text{volt-sec}$$

Since $N_n \ll N_A - N_D$ and $N_D \ll N_A$, this can be written as

$$\mu = \frac{7.15 \times 10^{20}}{N_A} \text{ cm}^2/\text{volt-sec} \quad (24)$$

Table II gives the valence band mobilities of the four different samples used in subsequent lifetime calculations.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>atoms/cm$^3$</td>
<td>cm$^2$/volt-sec</td>
</tr>
<tr>
<td>$1.2 \times 10^{16}$</td>
<td>$6.0 \times 10^4$</td>
</tr>
<tr>
<td>$4.5 \times 10^{16}$</td>
<td>$1.6 \times 10^4$</td>
</tr>
<tr>
<td>$4.5 \times 10^{17}$</td>
<td>$1.6 \times 10^3$</td>
</tr>
<tr>
<td>$1.5 \times 10^{18}$</td>
<td>$4.8 \times 10^2$</td>
</tr>
</tbody>
</table>

The assumption of elastic scattering is questionable at high electric fields where the average energy of the holes is of the order of the ionization energy (Yamashita 1961). The possible interactions with impurities in this case would include either (a) impact ionization of the impurity, (b) excitation of the bound hole to an excited state, or (c) inelastic scattering from the impurity accompanied by emission or absorption of a phonon. The effect of these additional loss mechanisms on the mobility of holes is not known at this time.

Because of the $1/N_A^2$ dependence of mobility inferred by neutral impurity scattering, the measured change in conductance $\Delta G(\lambda)$, given by equation (22), will also vary as $1/N_A$. The effect of concentration on $\Delta G(\lambda)$ is shown in fig. 17 for holes excited by photons of four different energies. These energies range from excitation well into the
FIG. 17: Dependence of conductance change $\Delta G(\lambda)$ on impurity concentration for various photon energies.

Photon energies used:
- $\times$ - 75 meV.
- $\square$ - 50 meV.
- $\circ$ - 42 meV.
- $\Delta$ - 39 meV.
valence band (75 meV.) to excitation into the excited state bands (39 meV.). At all wavelengths considered $\Delta G(\lambda)$ has essentially the same concentration dependence, with $\Delta G(\lambda)$ varying approximately as $N_A^{-3/2}$ with impurity concentration.

As we have mentioned previously, the values of $\Delta G(\lambda)$ measured here depend on both the mobility and lifetime of the holes. This deviation of $\Delta G(\lambda)$ from a $1/N_A$ dependence is therefore attributed to a variation in lifetime for the different samples, due probably to slightly greater levels of compensation as the impurity concentration is increased.

The important point regarding fig. 17 is the fact that there is a similar concentration dependence at photon energies corresponding to excitation into the excited state impurity bands as well as into the valence band. This would imply that the impurities act as hole scatterers even in these excited state bands. The implication of this will be discussed in the section dealing with impurity band conduction.

2. LIFETIME

Using the values of mobility obtained in the previous section we can now determine the lifetime of holes excited into the valence band. The lifetime of carriers (holes) is of interest both for practical and theoretical reasons. The lifetime determines the signal obtained from the photoconductor, restricting its "detecting ability" and frequency response. Through the lifetime, information can be obtained regarding capture mechanisms of free carriers and capture cross sections of the capturing centers.

In actual photoconductivity measurements, the measured lifetime is an average over holes distributed in energy with a distribution function $f(\varepsilon)$. This lifetime is determined by a total recombination probability, $B_T$, which
can be related to the capture of individual holes by the ionized impurities in the following manner.

If $B(\varepsilon)$ is the capture probability for a free hole of energy $\varepsilon$ by an ionized impurity (Lax 1960), then the capture cross section of the impurity, $\sigma(\varepsilon)$, is defined as

$$B(\varepsilon) = \sigma(\varepsilon) v(\varepsilon)$$

where $v(\varepsilon)$ is the speed a hole of energy $\varepsilon$ would have. This defines the recombination time (or lifetime) for holes of this energy,

$$\tau(\varepsilon) = \frac{1}{N_D B(\varepsilon)},$$

where $N_D$ is the density of capture centers (ionized impurities). For the distribution $f(\varepsilon)$, the average capture probability, $B_T$, is defined as

$$B_T = \sigma_T \langle v \rangle$$

where

$$\sigma_T = \frac{1}{\langle v \rangle} \int_0^{\varepsilon_m} \sigma(\varepsilon) v(\varepsilon) f(\varepsilon) \, d\varepsilon$$

is the total capture cross section and

$$\langle v \rangle = \int_0^{\varepsilon_m} v(\varepsilon) f(\varepsilon) \, d\varepsilon$$

is the average velocity. $\varepsilon_m$ is the maximum energy the holes can have. The measured lifetime is

$$\tau = \frac{1}{B_T N_D}.$$

If we assume there is no interaction between the free holes, the distribution can be separated into two parts according to the origin of the holes. The background radiation, by the nature of its spectral distri-
bution, will excite carriers over a large energy spread. The averages over this distribution, denoted as $\bar{E}_T$, $B_T$ and $\bar{\sigma}_T$, are instrumental in determining the d.c. characteristics of the samples. On the other hand, holes photoexcited by the infrared radiation will have a spread in energy, $d\varepsilon$, determined by the spectrometer spectral slit width. The average over this distribution determines the measured photoconductive lifetime $\tau(\lambda)$, which in turn determines the measured conductance change $\Delta G(\lambda)$ (figs. 15).

Using equations (21) and (22), the fractional change in conductance produced by radiation of wavelength $\lambda$ will be

$$\frac{\Delta G(\lambda)}{G} = \frac{Q_i(\lambda)\tau(\lambda)\mu(\lambda)}{Q_B \bar{\tau}}.$$

If we restrict the following discussion to excitation into the valence band, then we can use the assumption of a constant mobility over the whole band. In this case $\mu(\lambda) = \bar{\mu}$, so the fractional change in conductance reduces to

$$\frac{\Delta G(\lambda)}{G} = \frac{Q_i(\lambda)\tau(\lambda)}{Q_B \bar{\tau}}.$$

The fractional change in conductance produced by 75 meV. radiation is shown in fig. 18 for the four samples used. For each sample $\Delta G(\lambda)/G$ is slightly field dependent, indicating that the lifetime of holes excited by 75 meV. photons $(\tau(\lambda))$ has a field dependence different from the lifetime of holes excited by background radiation $(\bar{\tau})$.

Using the assumption that the mobility is constant throughout the valence band and determined by equation (24), we can calculate $\bar{\tau}$ and $\tau(\lambda)$ from equations (21) and (22). The d.c. characteristics (figs. 7 and 8) determine the conductance $G$, from which we can obtain $\bar{\tau}$, whereas the measured conductance changes, $\Delta G(\lambda)$, at 75 meV. (figs. 15) were used to
FIG. 18: Fractional change in conductance $\Delta G(\lambda)/G$ produced by 75 meV. photons vs. applied electric field.
FIG. 19(a) : Photoconductive lifetime $\tau(\lambda)$ at 75 meV. and d.c. lifetime $\tilde{\tau}$ vs. applied electric field for the $1.2 \times 10^{16}/\text{cm}^3$ sample.
FIG. 19(b): Photocductive lifetime $\tau(\lambda)$ at 75 meV, and d.c. lifetime vs. applied electric field for the 4.5 x 10$^{16}$/cm$^3$ sample.

Lifetime in sec.
FIG. 19(c): Photoconductive lifetime $\tau(\lambda)$ at 75 meV, and d.c. lifetime vs. applied electric field for the $4.5 \times 10^{11}/\text{cm}^3$ sample.
FIG. 19(d): Photoconductive lifetime $\tau(\lambda)$ at 75 meV vs. applied electric field for the $1.5 \times 10^{18}/\text{cm}^3$ sample.
obtain \( \tau(\lambda) \). These lifetimes are shown in fig. 19 for different applied fields on the samples. In fig. 19 (d) only \( \tau(\lambda) \) has been plotted for the \( 1.5 \times 10^{18}/\text{cm}^3 \) sample since \( \tau \) could not be determined. In this sample the "dark" conductance \( (G) \) was determined by thermal generation of free holes and not photo-generation by the background as in the other samples. Since this thermal generation rate is unknown, no estimate of \( \tau \) could be obtained.

For all samples \( \tau \) has a field dependence similar to that obtained from lifetime measurements made on germanium (Koenig et al. 1962, Shenker et al. 1964). The photoconductive lifetime, however, appears to be considerably different. At low fields \( \tau(\lambda) \) increases more rapidly with field than \( \tau \), but then reaches a plateau prior to breakdown. The reason for this plateau is not known, but may be the result of assuming a field independent mobility in the calculations.

The fact that \( \tau \) lies below \( \tau(\lambda) \) for three samples should not be taken as being significant because of the uncertainties involved in determining the incident photon fluxes. \( Q_B \) is obtained from the total photon flux emitted by a black body while \( Q_\lambda(\lambda) \) relies on an estimate of the thermocouple responsivity obtained from manufacturer's specifications. Both estimates have an uncertainty of at least a factor of two, so the exact position of \( \tau \) relative to \( \tau(\lambda) \) is uncertain.

The dependence of \( \tau(\lambda) \) on the incident photon energy is assumed to be the cause of the energy dependence in the measured photocurrent (fig. 19). At the higher photon energies considerable time is spent by the energetic holes in thermalizing with the lattice before recombination occurs (Hoenig 1960, Levitt and Hoenig 1961, Koenig 1958). This increased lifetime produces the increase in the measured signal at higher photon energies. This increase in photosignal cannot be entirely attributed to lifetime effects,
however, since there is the possibility of conduction in the P1/2 band at these energies, as has been previously mentioned.

An estimate of the total recombination probability for the holes, $\overline{B_T}$, and the capture cross section of the ionized impurities, $\overline{\sigma_T}$, can be obtained from $\overline{\epsilon}$. The rms average velocity of holes with a density of states effective mass, $m^* = 0.6m_e$, described by a Maxwell-Boltzmann distribution at the temperature of the lattice is $1.6 \times 10^6 \text{cm/sec}$. Using this velocity and the low field lifetime of $2 \times 10^{-10} \text{sec}$ obtained from figs. 19, the recombination probability $\overline{B_T}$ is

$$\overline{B_T} = \frac{1}{\overline{\epsilon} N_D} \approx 5 \times 10^{-4} \text{cm}^3/\text{sec},$$

and the capture cross section is

$$\overline{\sigma_T} = 3 \times 10^{-10} \text{cm}^2.$$

Using Lax's theory (1960), the capture cross section for a Boltzmann distribution was calculated to be $\sim 5 \times 10^{-9} \text{cm}^2$, which is larger than the observed cross section. The difference between the two results may be due to the relatively large impurity concentrations used here. The theory includes contributions from the very highly excited states of the impurity. However, these states have become non-localized because of overlap, so a hole is no longer trapped at any particular impurity when in these states. This decrease in the number of available trapping states would make the capture cross section smaller, as observed.

This could also explain the unusually large lifetime measured for the $1.5 \times 10^{18}/\text{cm}^3$ sample (fig. 19 (d)). Since this sample is nearly degenerate, all the excited states are ineffective in the capture process. The only means of decay, therefore, is by a transition directly from the
excited state bands to the ground state band. From fig. 19 (d), the lifetime of holes in this sample is

\[ \tau(\lambda) \approx 3 \times 10^{-5} \text{ sec} \]

so the corresponding recombination probability constant and cross section for this sample are

\[ B_T \approx 3 \times 10^{-9} \text{ cm}^3/\text{sec} \quad \text{and} \]

\[ \Sigma \approx 2 \times 10^{-15} \text{ cm}^2 \]

This value of \( B_T \) is the same order of magnitude as the phonon-recombination probability constant for a direct recombination via phonon emission derived by Gummel and Lax (1955).

C. IMPURITY CONDUCTION

1. CONDUCTION MECHANISMS

Because of the variety of effects which are loosely classed as impurity conduction or impurity band conduction, it is necessary to clarify the separate conduction mechanisms. The effects of impurities can generally be classified according to their concentration in the material in the following manner.

a) At low impurity concentrations the average spatial separation of impurities is large and hence the energy spectrum of each impurity is unaffected by the presence of other impurities. At low temperature all the ground states of the impurities will be occupied except for a small fraction which remain ionized because of compensation. Conduction is possible in this system through a process of phonon-assisted transitions between the neutral and ionized centers. This conduction via a "hopping" procedure is normally referred to as impurity conduction (Miller and
Abrahams 1960, Kasuya 1958, Pollack 1965, Mott and Twose 1960). Conduction via this process depends critically on the impurity concentration and the degree of compensation. Since conduction occurs by a process of discontinuous jumps, the usual description in terms of mobility and mean free paths of the carrier is no longer appropriate.

b) At very large impurity concentrations considerable overlap between ground state impurity wave functions broadens these levels to such an extent that the levels merge with the valence band. At these concentrations the impurities should no longer be treated as a perturbation on the normal energy spectrum of the lattice. Instead, the problem becomes one of finding the effects of fluctuations in the periodic potential caused by the impurities on the band structure of the material. The effects of random distributions of impurities on the band structure have been discussed by Kane (1963), Bonch-Breuvich (1962) and Matsubara and Toyozawa (1961). In this case the material is described as being degenerate with conduction being essentially a metallic form of conduction. Once the impurity states have merged with the band, the impurities will act as scattering centers for the carriers. A further increase in impurity concentration results in a reduced mobility due to increased scatterings.

c) Between the extremes of low concentration, and high concentration, a variety of effects occur which are classed as "impurity band" conduction. At fairly high concentrations, but lower than for (b), interactions between impurity ground states will produce a band extending throughout the crystal which is separated from the valence band. This band is generally referred to as "the impurity band". The width of this band increased with impurity concentration until it overlaps the valence band.

The main factors determining the mobility in this impurity band are
the correlations between holes associated with different impurity centers and the extent of overlap between impurity wavefunctions. When correlations are dominant (at lower concentrations), then it is a good approximation to assume that the holes will be localized at the impurity sites. Compensating centers are again necessary for conduction. When overlap energy is dominant, however, conduction is possible without compensation because the hole is no longer localized at a particular impurity. The translational energy of a hole in the band will depend on the amount of overlap, so that an increase in overlap would increase its effective mobility.

A similar type of band formation was postulated to occur for the excited states of the impurities (Erginsoy 1950). Because of the larger spatial extent of these excited states, this banding will occur at concentrations considerably smaller than those required for ground state banding. Conduction in these excited state impurity bands was suggested as a possible explanation of the anomalous behavior of the resistivity and Hall constant for p-type germanium at intermediate concentrations (Fritzsche 1955).

2. CONDUCTION IN IMPURITY BANDS

The possibility of conduction in the energy bands of an impurity was examined by Baltensperger (1953) for the case of a periodic lattice of impurities. The semiconductor is characterized by an effective mass \( m^* \) of the hole in the valence band, and by a dielectric constant \( \varepsilon \).

A cellular method was used in order to compute the energies of the excited state impurity band edges as shown in fig. 20. The Wigner-Seitz polyhedra surrounding each impurity are approximated by spheres of radius

\[
r_s = \left( \frac{3}{4\pi} \right) \frac{1}{N_A^{1/3}}
\]

(25)
FIG. 20: Formation of the 1s and 2p impurity bands from hydrogenic wavefunctions (after Baltensperger). Broadening of the levels vs. distance between impurities in terms of the effective Bohr radius $a^*$. 
where \( N_A \) is the density of impurities. Within each cell the hole was assumed to satisfy an effective mass Schrödinger equation

\[
\frac{\hbar^2}{2m^*} \nabla^2 \psi + \left( \frac{e^2}{Kr} + \varepsilon \right) \psi = 0 \quad (26)
\]

where \( \frac{e^2}{Kr} \) is the potential acting on the hole, and \( \varepsilon \) is the energy of the hole in the state \( \psi \).

The general solutions of (26) are the regular hydrogenic wavefunctions

\[
\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi).
\]

The energy of the hole is given by

\[
\varepsilon_n = -\frac{e^2}{2Ka^*n^2} \quad (27)
\]

where

\[
a^* = \frac{\pi^2 K}{m^*e^2} \quad (28)
\]

and where \( n \) is to be determined by appropriate boundary conditions obtained from the requirement that the wavefunctions have the form of Bloch functions. The excited states in this way are given "band" properties, allowing the holes to move throughout the material when excited into one of these "bands".

An effective mass \( m^+ \) can be introduced to characterize the dynamic property of a hole whose energy lies in an impurity band. This effective mass is defined in terms of the bandwidth, \( \Delta \varepsilon \), of the impurity band by

\[
\Delta \varepsilon = \frac{\hbar^2 k^2}{2m^+} \quad (29)
\]

where \( k \) is defined by
Combining the previous equations, \( m^+ \) can be written in terms of the effective mass \( m^* \);

\[
\frac{m^*}{m^+} = 0.171 \left( \frac{r_s}{a^*} \right)^2 \frac{\Delta \epsilon}{e^2/2a^*} \quad (31)
\]

Writing the mobility in the valence band as

\[
\mu = \frac{e \tau}{m^*} \quad (32)
\]

and the mobility in the impurity band as

\[
\mu^+ = \frac{e \langle \tau \rangle^+}{m^+} \quad (33)
\]

then

\[
\frac{\mu^+}{\mu} = \frac{m^*}{m^+} \frac{\langle \tau \rangle^+}{\tau} \quad (34)
\]

It should be noted here that we are able to write the mobility in the impurity bands as

\[
\mu^+ = \frac{e \langle \tau \rangle^+}{m^+} \quad (33)
\]

because we have already assumed that \( m^+ \) is a constant over the entire impurity band. This assumption is contained implicitly in equation (29) where we have written the width of the impurity band as

\[
\Delta \epsilon = \frac{\hbar^2 k^2}{2m^+} \quad (29)
\]

This assumption implies that there is a parabolic dependence of energy on the wavenumber vector for the entire Brillouin zone. Even though this
assumption is not entirely realistic, it will allow us to make some comparison between theory and experiment.

In equation (33), $\langle T \rangle$ is the average scattering time or momentum relaxation time of holes in the impurity band and $\tau$ is the scattering time for holes in the valence band. From the variation of $\Delta G(\lambda)$ with concentration (shown in fig. 17), we have concluded that once there is sufficient overlap of the wavefunctions so conduction in an impurity band is possible, the neutral impurities hinder conduction by scattering the holes. In the case of the perfect impurity lattice, however, we have taken the effect of the impurities into account by assigning an effective mass $m^+$ to the holes. The holes would then be able to move freely throughout the crystal without scattering from these impurities. This scattering of holes by the impurities could be accounted for if we make a modification in the model of a perfect impurity lattice.

In an actual semiconductor the impurities do not form a periodic array but are randomly distributed throughout the material. The resulting impurity bands cannot be expected to have well defined edges as have been calculated, nor can they have such well defined band properties. For example, the requirement that the non-localized wavefunctions have the form of Bloch functions could not be satisfied since there is no longer translational periodicity associated with the impurity lattice. The concept of band formation will have to be interpreted as the transition from localized to extended wavefunctions with a decrease in the importance of correlation between holes. By introducing this randomness we are able to have the holes interact with the impurities again. Now, however, the holes do not scatter from the impurities in the usual way, but scatter from the "randomness" in the distribution. The variation of the hole mobility with concen-
tration in these bands will then be determined by the variations of $m^+$ and the scattering time, $\langle T \rangle^+$. Fig. 21(a) shows the change in $m^*/m^+$ with the concentration of impurities for the 2p band as calculated by Baltensperger (1953). Since $m^*$ is a property of the host lattice and can be considered a constant, fig. 21(a) in effect shows the variation of $m^+$ with concentration. There is an initial rapid decrease in $m^+$ as the band begins forming, followed by a much less rapid decrease as the concentration further increases. The scattering time, on the other hand, would be expected to decrease as the total number of impurities which deviate from the regular array increases at higher impurity concentrations. In fact, if we assume the scattering time $\langle T \rangle^+$ to be inversely proportional to the impurity concentration, then we could write the impurity band mobility as

$$\mu^+ = \beta \frac{m^*}{m^+} \mu,$$

(32)

where the proportionality constant $\beta = \langle T \rangle^+/T$ is independent of the impurity concentration.

This assumption regarding $\langle T \rangle^+$ is equivalent to stating that the number of scattering centers, which is the number of impurities out of place in a periodic array, is directly proportional to the number of impurities present. It does not assume that the scattering times $\langle T \rangle^+$ and $T$ are the same, only that they have the same dependence on concentration. For this reason we can only find a relative dependence between $\mu^+$ and $\mu$ in terms of the factor $\beta$. Using the theoretical values of $m^*/m^+$ shown in fig. 21(a) and valence band mobilities given in table II, we can find the mobility of holes in the 2p band at different concentrations. The mobility in the band is shown in fig. 21(b).
FIG. 21(a) : Ratio of effective mass in the valence band $m^*$ to effective mass in the 2p impurity band vs. impurity concentration (Baltensperger 1953).

FIG. 21(b) : Theoretical mobility in the 2p impurity band $\mu^+$ in terms of the dimensionless parameter $\beta$ vs. impurity concentration.
in terms of the dimensionless constant $\beta$. Here we can see the effects of two competing processes on $\mu^+$, namely the rapid increase as the band begins to form, followed by the decrease when scatterings become dominant.

Comparing the values of $\mu^+/\beta$ given in fig. 21(b) with the mobilities listed in table II, we see that $\mu^+/\beta$ is considerably larger than the valence band mobility for all concentrations greater than $\sim 4 \times 10^{16}/\text{cm}^3$. Since the impurity band mobility is not expected to exceed the mobility in the valence band, we would require that $\beta < 1$. The consequence of assuming particular values of $\beta$ will be discussed later.

The formation of the impurity bands and the subsequent changes in mobility in these bands with concentration have been experimentally observed for two separate impurity bands. Fig. 22 shows the changes in conductance observed in the different samples when holes are excited into the impurity bands. The top curve is for excitation into the band composed of states 3 and 4, while excitation into the band at state 2 produces the conductance changes shown in the bottom curve (states labelled as in Colbow 1963). For both of these bands we see the initial, fairly rapid, rise in mobility as the bands begin forming followed by the decrease when scatterings dominate. This transition to non-localized wavefunctions occurs at a lower concentration for states 3 and 4 than for state 2. This is to be expected since the higher excited states (3 and 4) have a larger spatial extent, so overlap becomes important at lower impurity concentrations.

The exact behaviour of $\Delta G(\lambda)$ during the initial increase is difficult to determine, but it is felt that the curves shown are reasonably justifiable. For both bands we have concentrations for which the
FIG. 22: Measured conductance change $\Delta G(\lambda)$ produced by excitation of holes into two different impurity bands vs. impurity concentration.
measured $\Delta G(\lambda)$ is zero or at least $\Delta G(\lambda) < 0.001 \times 10^{-12}$/ohm, so that we know conduction does not occur in these impurity bands for all concentrations. In the case of states 3 and 4, the photocurrent is zero for the $1.2 \times 10^{15}$/cm$^3$ sample at this energy, but is non-zero for the $1.2 \times 10^{16}$/cm$^3$ sample. All that can be said about this band, therefore, is that the transition to non-localized wavefunctions occurs at a range of concentrations intermediate to $1.2 \times 10^{15}$ and $1.2 \times 10^{16}$ impurities/cm$^3$. Similarly, the increase in $\Delta G(\lambda)$ for state 2 indicates that these states become non-localized between $1.2 \times 10^{16}$ and $4.5 \times 10^{16}$ impurities/cm$^3$.

In order to compare the measured variations in $\Delta G(\lambda)$ with the results of Baltensperger's theory, we have had to make use of an additional fact which should be clarified. Since $\Delta G(\lambda)$ depends on both the lifetime of the holes as well as their mobility, what is actually shown in fig. 22 is the variation in $\mu(\lambda)\tau(\lambda)$ with concentration in the two bands. This is the same difficulty that was encountered in fig. 17 where we have $\mu(\lambda)\tau(\lambda)$ for higher energy photons. The deviations in these curves from a $1/N_A$ dependence was attributed to an increase in lifetime at the higher concentrations. The decrease in lifetime required to produce this deviation from a $1/N_A$ concentration dependence is only a factor of about 4 over the concentration range $10^{16}$/cm$^3$ to $5 \times 10^{17}$/cm$^3$. The decrease in $\Delta G(\lambda)$ in the impurity bands over the same range in concentration (fig. 22) is much greater than this, being, in fact, almost a factor of 100. Therefore, we can conclude that the concentration dependence observed in $\Delta G(\lambda)$ (fig. 22) is due almost entirely to variations in mobility in these bands.
The exact concentration dependence of the mobility in these bands could not be determined since the decrease in lifetime with increased concentration is known only approximately. The qualitative picture we have obtained of the mobility in these bands is as follows. The mobility initially increases rapidly as the states become non-localized, reaches a peak, and then is reduced by further increases in impurity concentration. Within the limits of the assumptions used, Baltensperger's simple theory appears to give a reasonably good qualitative explanation of the experimental results. As has been the problem throughout the experiment, quantitative estimates of either the mobility or lifetime in these impurity bands will involve further assumptions.

From the theory we have the mobility in the 2p band in terms of the dimensionless parameter $\beta$. If we assume that the lifetimes in each of these bands is the same as in the valence band, then we will be able to estimate $\mu^+$ and $\beta$ from the measured conductance changes (fig. 22). If we take $\tau(\lambda)$ to be $\sim 10^{-9}$ sec (see fig. 19), then the peak mobility for the band at states 3 and 4 is

$$\mu^+ \sim 150 \text{ cm}^2/\text{volt-sec}.$$  

For state 2, using the same lifetime the peak mobility is

$$\mu^+ \sim 75 \text{ cm}^2/\text{volt-sec}.$$  

This means that the dimensionless quantity $\beta$ will have to be $\sim 3 \times 10^{-3}$ for states 3 and 4 and slightly less for state 2. The low values of peak mobilities for these bands was not unexpected since conduction is occurring through a fairly narrow band, which usually implies a lower mobility for the carriers.
On the other hand, suppose that the decrease in signal at these low energies is due to lifetime effects and that the mobility in these states is approximately the same as in the valence band. In this case \( \beta \approx 0.1 \) and the lifetimes are:

\[
\begin{align*}
\tau_3(\lambda) &\sim 10^{-11} \text{ sec for holes in states 3 and 4,} \\
\tau_2(\lambda) &\sim 4 \times 10^{-12} \text{ sec for holes in state 2.}
\end{align*}
\]

Even though the lifetimes obtained with the second assumptions are not unreasonable, it is felt that the first case is more representative of what is occurring. This is that the lifetimes in these states is \( \sim 10^{-9} \) sec, but that the mobilities in these impurity bands are much lower than in the valence bands.

Further modifications in the results of the simple model introduced by the randomness are as follows. The effects of a random distribution on the impurity levels has been investigated for a one dimensional lattice by James and Ginzbarg (1953) and for an actual semiconductor by Matsubara and Toyozawa (1961). For both of these cases the density of states has a maximum at the original energy but tails off on both the high and low energy sides, with the high energy tail merging with the valence band. It has been shown (Bonch-Breuvich 1962) that the impurities will also produce a diffuse edge on the valence band. This "band tail" will extend well into the forbidden region, but with a density of states which decreases rapidly away from the band edge.

This smearing out of both the impurity bands and the valence band would account for the lack of more definite peaks in the photoresponse (fig. 10) and for the lack of a definite cut-off at low energies. In
addition to increasing the broadening, it has been shown (Aigrain 1954) that the interaction between the impurities would increase for a random array. This would mean that band formation should occur at concentrations lower than those indicated by Baltensperger. The degree to which this will affect the estimates is not known however, but could shift the peak in $\mu^+$ (fig. 21 (b)) toward lower concentrations.

The concept of impurity band formation in the excited states has been questioned by Fritzsche(1955). A difficulty arises in the model of Erginsoy and Baltensperger because of the use of ordinary impurity wavefunctions in the formation of the impurity bands. An excited state associated with a particular impurity can be occupied only if all the other excited states and the ground state of this impurity are unoccupied. This would limit the number of available excited states which are able to participate in the conduction to the number of ionized impurities present. At low temperatures the only ionized impurities present will result from compensating centers. The number of available states, therefore, would be limited to such an extent that conduction through these states would be exceedingly small.

However, once there is sufficient interaction between the excited states to form the band we cannot consider holes in these states to be associated with any one particular impurity, but to the entire system of impurity atoms. In this way conduction through these excited states would proceed as in a regular band.
CHAPTER 5

CONCLUSIONS

From the results of this experiment we may conclude that the excited states of the impurities form bands of non-localized states extending throughout the crystal. It appears as if there is a fairly sharp transition region over which the impurity states go from being localized at the impurities to being band-like states. Over this region of impurity concentrations the mobility of holes in these states increases rapidly as was predicted by Baltensperger. Once these states become non-localized however, it appears as if further increases in impurity concentration act to reduce the mobility in these bands. This can be accounted for by considering a more realistic semiconductor in which the impurities are distributed randomly throughout the material. For this case we can consider the holes as being scattered by the random fluctuations in potential at different positions throughout the crystal caused by this random arrangement. These scatterings quickly become dominant over further increases in mobility due to increased overlap, so the mobility decreases with the addition of more impurities.

From the nature of photoconductivity measurements, the results are obtained in terms of the product $\mu(\lambda)\tau(\lambda)$ for the excited holes. This prevented the mobilities in the individual impurity bands from being determined directly. This variation of the lifetime-mobility product with photon energies was displayed in the photo-response measurements shown in figs. 9. Here again, the variations in photo-response could not be unambiguously attributed to either variations in the hole mobility or lifetime at these higher energies. To remove
An attempt was made to separate the two factors by assuming the mobility in the valence band to be governed by elastic scattering from neutral impurities. Using the mobilities obtained with this assumption, the lifetime of holes excited into the valence band (by 75 meV photons) is found to be approximately $10^{-9}$ sec. This indicates that the ionized boron impurities have capture cross sections of about $3 \times 10^{-10}$ cm$^2$, which is in reasonable agreement with the results of Lax's theory of giant traps (1960). A more exact determination of the capture cross section is difficult because of the uncertainty in the density of compensating centers.

In excited state bands it is most likely that the lifetime of holes is approximately the same as in the valence band. This leads to impurity band mobilities less than $\sim 150$ cm$^2$/volt-sec, which is a reasonable mobility for conduction through a narrow band.

The effect of impurity banding was also observed on the capture cross section of the ionized impurities. At high impurity concentrations the excited states are no longer capable of trapping the holes so the cross section is greatly reduced. Because of this, exceedingly long lifetimes ($\sim 3 \times 10^{-5}$ sec) were obtained for the nearly degenerate sample of concentration $1.5 \times 10^{18}$/cm$^3$.

A decrease in the recombination probability with increased hole energy, as indicated by Lax (1960), provides a qualitative explanation of the non-ohmic nature of the d.c. characteristics at low fields. All samples exhibited this non-ohmic behaviour, and also all samples were characterized by a critical breakdown field. This breakdown is caused by the heating of the holes at high fields to energies of the order of the impurity ionization energy. These energetic holes are then capable of impact-ionizing
the impurities producing the run-away in hole multiplication.

The non-ohmic behavior of the sample has direct repercussions on the photosignal produced by the incident radiation. For a fixed illumination on the sample the photo-voltage appearing across the sample reaches a saturation value as the applied field is increased. Further increases in field decrease the observed photo-voltage as the sample resistance decreases.

A more direct determination of the mobility or lifetime of holes in the impurity bands would necessitate further measurements. The mobility could be obtained from a photo-Hall experiment while time dependent photoconductivity experiments would yield lifetimes. However, the high resistance of the samples at low temperatures combined with the low levels of illumination available in the far infrared would make the photo-Hall experiments difficult. Likewise, the short time scales involved in lifetime determinations would hamper time dependent photoconductive measurements.
APPENDIX A:

PERFORMANCE OF BORON-DOPED SILICON AS A FAR INFRARED DETECTOR

The performance of these particular samples as radiation detectors will be rated in terms of the usual criteria used to measure detecting ability (see for example Jones 1959, Jamieson et al 1963). First, however, the various ratings used in measuring the detecting ability will be presented.

RESPONSIVITY (R): The responsivity of a detector is defined as the output voltage divided by the power output in watts. The responsivity is useful in determining signal strengths to be expected from the detector but does not indicate the minimum detectible power.

NOISE EQUIVALENT POWER (N.E.P.): This gives the incident power required to produce an output equal to the noise voltage. The N.E.P. is obtained by dividing the rms noise voltage by the responsivity and is therefore given in units of watts. This rating of a detector will determine the minimum power which can usefully be detected.

DETECTIVITY (D): The reciprocal of the N.E.P. is called the detectivity. This gives the signal to noise ratio of the detector per unit incident power.

D*: The D-star or specific detectivity is, in effect, the detectivity measured with a bandwidth of one cycle per second and reduced to a responsive area of one cm², and usually given in units of cm cps¹/²/watt. It is related to the detectivity by

$$D^* = (A \Delta f)^{1/2} D,$$

where A is the area of detector and \( \Delta f \) is the bandwidth of the system. Because the detectivity often varies with different operating conditions, the quoted \( D^* \) is usually given with the parameters associated with the
Table III
Comparison of Detecting Ability of Various Types of Infrared Detectors

<table>
<thead>
<tr>
<th>Type</th>
<th>R (Volts/Watt)</th>
<th>N.E.P. (Watt)</th>
<th>D* cm cps²/watt</th>
<th>Cut-Off Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermocouple</td>
<td>2-20</td>
<td>10⁻¹⁰</td>
<td></td>
<td>≈ 25 cps</td>
</tr>
<tr>
<td>Go lay Cell</td>
<td>6 x 10⁻¹¹</td>
<td>2 x 10⁹</td>
<td></td>
<td>≈ 25 cps</td>
</tr>
<tr>
<td>Lead Sulfide Cell</td>
<td>10⁻¹¹</td>
<td>10¹¹</td>
<td></td>
<td>≈ 1 KC</td>
</tr>
<tr>
<td>Ge (B)</td>
<td>10⁻¹¹</td>
<td>2 x 10¹¹</td>
<td></td>
<td>≈ 10⁸ cps</td>
</tr>
<tr>
<td>Si (B)</td>
<td>2 x 10³</td>
<td>5 x 10⁸</td>
<td></td>
<td>≈ 10⁸ cps</td>
</tr>
<tr>
<td>1.2 x 10¹⁶/cm³</td>
<td>10⁻⁸</td>
<td>4 x 10⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5 x 10¹⁶/cm³</td>
<td>1.2 x 10⁻⁹</td>
<td>5.5 x 10⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5 x 10¹⁷/cm³</td>
<td>8 x 10⁻¹⁰</td>
<td>4.5 x 10⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5 x 10¹⁸/cm³</td>
<td>10⁻⁹</td>
<td>4.5 x 10⁹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 Data for Perkin-Elmer Thermocouple and Golay Cell obtained from Jamieson et al. 1963.
6 Kodak Ekton Detectors.
7 Shenker et al. 1964.
measurement. For example, the measurements made here will provide

\[ D^*(E, f, \Delta f) \]

with \( E = \) the photon energy (75 meV.), \( f = 870 \) cps and
\( \Delta f = 40 \) cps.

A comparison of these different ratings is given in Table III for various types of infrared detectors and the samples used in this experiment.

As can be seen from Table III, the silicon samples make rather poor detectors in spite of their large responsivity. In addition to their small detecting ability, other difficulties would be encountered which are not included in the table. In order for these samples to detect radiation they must be maintained at liquid helium temperatures and be well shielded from background radiation. This immediately limits the practical usefulness of these materials. In addition, there is not a uniform responsivity over the range of wavelengths used. This would be particularly troublesome in the thicker samples in the region of the lattice absorption peaks.

For an ideal detector the limiting noise sources which are generally inescapable will be the following (Petritz 1959, Moore and Shenker 1965, Smith et al. 1958).

(a) Nyquist noise in the load resistor and detector.

(b) Amplifier noise.

(c) Generation - recombination noise.

This last noise source is the result of fluctuations in the flux of incident photons which cause fluctuations in the rate of generation of carriers combined with fluctuations in the recombination rates of the carriers. This process sets the ultimate limit to the detecting ability of the material and detectors operated under this limitation are said to be background limited (van Vliet 1958).

The noise from these sources is considerably less than the noise encountered, so the detectors are not operating even near their ultimate
limit. The excess noise is attributed to the contacts used here. Although the methods we have used to produce contacts are fairly successful for germanium detectors (Shenker et al. 1964), they do not allow the ultimate detecting ability to be achieved for silicon photodetectors.
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