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Optical Studies of Injected Carriers. III. Infrared Absorption in Germanium at Low Temperatures

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The absorption spectra of carriers injected into germanium at 302°K, 201°K, and 82°K are given. For clean material these spectra are qualitatively identical with the absorption spectra of free holes at the same temperatures. In some samples studied anomalous spectra were observed. Anomalous spectra were in general observed in samples containing Fe. The anomalies are tentatively identified with trapping effects.

THE infrared absorption produced by carriers injected into germanium at room temperature has been observed by several authors.[1-3] The important conclusion of these papers was that the absorption spectrum of the injected carriers was essentially identical with the spectrum of holes as observed in germanium made *p* type by impurity doping.[4,5] In particular the structure found in the absorption of *p*-type germanium was also found in the spectrum of injected carriers. The contribution of the injected electrons to the total absorption was presumably negligible compared to that of the injected holes.

It has been found by several authors[2,5] that very profound changes occur in the hole absorption as the temperature of the sample is changed. In particular the modifications from 300°K to say 77°K are most striking. These changes have been ascribed to changes in the distribution of hole population among overlapping branches of the valence band. Although it seemed evident from the room temperature measurements that carriers produced by injection and by impurity doping produce the same absorption effect, it was nevertheless felt worthwhile to check this conclusion by measurement of the injection spectra at low temperatures. In addition it was thought that for samples in which trapping effects are present, these effects might show up in the absorption spectra of the injected carriers.

The modulation scheme used here to detect the absorption of the injected carriers was that described in Part I (reference 1) of this series. Thirteen cps current modulation was employed and a thermocouple was used as a detector. Fused junction diodes were used. The diodes were prepared as follows: a sample was cut into a block $\sim\frac{1}{4}$ in.$\times\frac{1}{4}$ in.$\times\frac{1}{2}$ in., a junction was prepared on a large face by fusing on a large indium dot (for *n* type) or an indium-arsenic dot (for *p* type). Tinned ($\frac{1}{32}$ in.) "Fernico" was soldered onto the face opposite the junction. The operations were performed under hydrogen. Using a Wood's metal solder, the assembly was then soldered by means of the "Fernico" to a copper sample holder. The latter was inserted into a cryostat which could be used for transmission measurements.

The intermediate layer of Fernico greatly minimized the problem of the germanium cracking when cooled. No success was had when the germanium was soldered either directly to the copper or through a 10-mil thick "Fernico" strip. However, using the method described there was only one failure in the thirteen units prepared. Good heat dissipation was achieved. Operating at power levels of ~50 w resulted in less than a 10°C temperature rise for the diode at about liquid nitrogen temperature. Probably the main thermal resistance was between the sample holder and the cryostat proper.

The cryostat was placed in the sample section of a Perkin Elmer spectrometer. The radiation passed through the large faces of the diode perpendicular to the direction of current flow.

RESULTS AND DISCUSSION

In Part I of this series it was shown that at the limit where the modulation in the transmission of the sample is small then a quantity M/C is proportional to the absorption coefficient of the injected carriers. Here M is the signal obtained at a given wavelength by on-off modulation of the injection current and C is the signal obtained by complete modulation of the light beam at that wavelength, for example, by mechanical chopping of the light. In Figs. 1–3, are shown some representative plots of the quantity M/C as a function of wavelength at several temperatures. The data are quoted in arbitrary units. However, a direct measure of M/C for regions 1 mm wide adjacent to the junction on a few representative samples indicated that, for the currents used, $M/C<0.1$ at all wavelengths employed and the linear approximation is valid.

If we are correct in assuming that the spectrum of free injected carriers should be essentially identical with that of free holes, then of the spectra shown in the figures only that of Fig. 1 may be regarded as normal. Plots of the absorption spectrum of *p*-type germanium at the various temperatures can be superposed on the curves shown in this figure with excellent agreement.

The remaining figures show increasing departures from this norm. The data shown were taken in a manner

[1] R. Newman, Phys. Rev. **91**, 1311 (1953).
[2] H. B. Briggs and R. C. Fletcher, Phys. Rev. **91**, 1342 (1953).
[3] A. F. Gibson, Proc. Phys. Soc. (London) **B66**, 588 (1953).
[4] H. B. Briggs and R. C. Fletcher, Phys. Rev. **87**, 1130 (1952).
[5] Kaiser, Collins, and Fan, Phys. Rev. **91**, 1380 (1953).

identical with that used in obtaining that of Fig. 1. Caution was used to avoid sources of spurious effect. It is our belief, therefore, that the spectra shown in these curves are genuine and mainfest a new type of phenomenon.

Table I lists the different samples which have been studied, some of their room temperature properties and the characterization of their spectra at liquid nitrogen temperature as normal or anomalous. For the moment let us restrict our attention to n-type samples. Although the sampling is not exhaustive, one can probably state that equilibrium carrier density and lifetime do not, as such, determine whether a sample will show

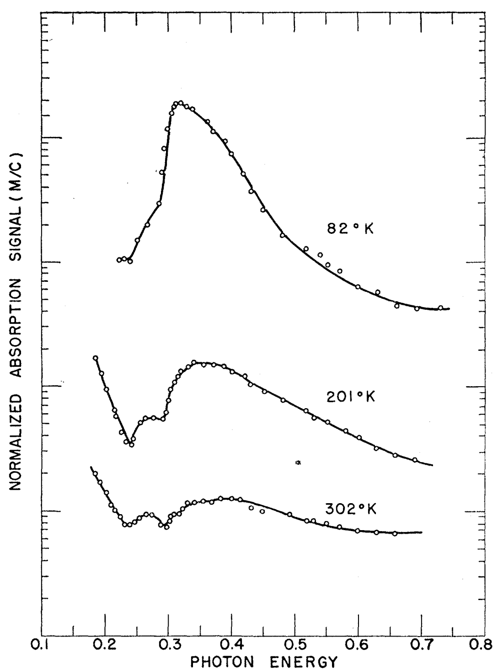

FIG. 1. Absorption spectra (arbitrary log scale) of injected carriers at several temperatures for sample M104. M is the signal obtained at a given wavelength by on-off modulation of the injection current and C is the signal obtained by complete modulation of the light beam at that wavelength, e.g., by mechanical chopping of the light (see reference 1).

anomalous behavior. For example, compare samples PC201 and DP277.

On the other hand, doping with iron seems, in general, to give samples with an anomalous spectrum. It is known that iron produces traps (probably hole traps) which are stable at low temperatures.[6] These traps are presumably responsible for the long time photoeffects and breakdown effects[7] observed in these

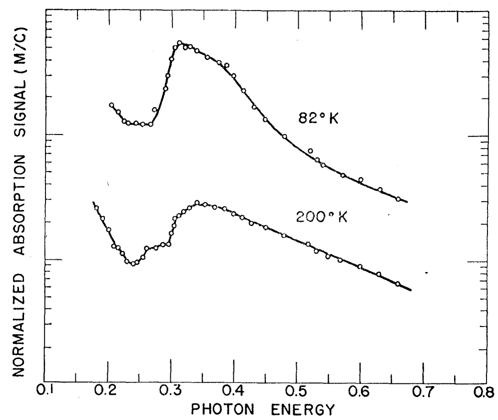

FIG. 2. Absorption spectra (arbitrary log scale) of injected carriers at several temperatures for sample P104.

samples. It is also reasonable to hypothesize that some such trapping effects are likewise producing the anomalous spectra observed here. It is worth noting that the iron-doped sample M56, the only one of this group that did not show an anomalous spectrum, likewise did not show any long time photoeffects either. N-type Au-doped samples sometimes show trapping effects too.[8] Measurements were made on two gold-doped samples. However, no anomalies were observed.

The appearance of the anomalous spectra is such as to suggest a superposition of a normal absorption curve and a more or less flat background. One is tempted to identify the latter with the effects of trapped carriers (e.g., holes in the n-type or electrons in p-type material). As a consequence of this point of view, the ratio of the intensities of the flat background to the normal (0.32 ev) peak might be expected to remain constant over a certain range of injection current, while above a certain injection level, corresponding to trap saturation, the

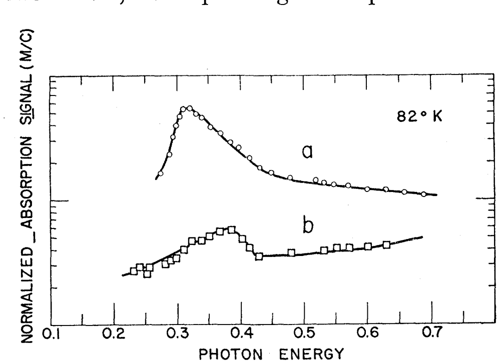

FIG. 3. Absorption spectra (arbitrary log scale) of injected carriers at 82°K for samples M108(a) and M95(b).

[6] Tyler, Woodbury, and Newman, Phys. Rev. **94**, 1419 (1954), details to be published.

[7] The breakdown effect will be described in more detail elsewhere. [W. W. Tyler, Phys. Rev. **96**, 226 (1954)]. However, briefly the phenomenon is this: An injecting electrode (e.g., In dot) is put on a piece of n-type Fe-doped germanium which goes to high resistance ($\sim10^{12}$ ohm cm) at 77°K. The diode is cooled to liquid nitrogen temperature. If a high voltage ($\sim10^2$ to 10^3 volts/cm) is applied to the diode, it breaks down and the germanium subsequently behaves as if it were n-type material with an equivalent resistivity of the order of a few ohm cm. The sample remains broken down even when the field is reduced to about 1 volt/cm. The breakdown effect can also be initiated at low voltages by illuminating the sample.

[8] R. Newman, Phys. Rev. **94**, 278 (1954).

TABLE I. Room temperature properties of various samples, and characterization of their spectra at liquid nitrogen temperature.

Sample No.	Type	ρ(ohm cm) 300°K	τ(μsec) 300°K	Impurity[a]	Spectrum (~80°K)[b]
M103	*p*	30	200		normal (1)
P104	*p*	0.5	55		abnormal (2)
M104	*n*	15	400		normal (1)
PC201	*n*	7	39		abnormal (3b)
DP277	*n*	5	55		normal (1)
E-30	*n*	25	10	Au	normal (1)
DP177	*n*	2	7	Au	normal (1)
M95[c]	*n*	45	~3	Fe	abnormal (3b)
M108[c]	*n*	40	~3	Fe	abnormal (3a)
M56	*n*	30	~3	Fe	normal (1)
M105	*n*	35	~3	Fe	abnormal (3a)
P11	*n*	30	~3	Fe	abnormal (3a)

[a] Other than conventional donors or acceptors.
[b] The numbers in brackets refer to the figure which best represents the observed spectrum at liquid nitrogen temperatures.
[c] Breakdown diodes.

peak should increase faster than the background. Unfortunately, when one goes to very high signal levels appreciable distortion in the observed spectrum will result because of the saturation of the M/C ratio. It might then be impossible to observe the effects of trap saturation even if these existed. Over the range of injection curves where our data are meaningful, we have not seen the saturation effect. Increasing the ambient light level in an attempt to saturate the traps dc-wise, likewise produced no observable effect.

CONCLUSIONS

The spectrum of injected carriers in clean germanium is shown to be qualitatively identical with the spectrum of holes in *p*-type germanium in its wavelength and temperature dependence. In some germanium samples, anomalous spectra are observed at low temperature. These anomalies may be caused by the trapping of injected carriers.

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Semiconducting Cadmium Telluride

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Both *n*-type and *p*-type conductivity can be obtained in cadmium telluride. The intrinsic band gap of cadmium telluride is 1.45 ev. Electron and hole mobilities are at least 30 cm²/volt sec. The activation energies of *p*-type impurities are much larger than those of *n*-type impurities in cadmium telluride, indicating an explanation for the failure to find *p*-type conductivity in cadmium sulfide or selenide.

INTRODUCTION

MEASUREMENTS on the conductivity of cadmium sulfide and cadmium selenide have indicated the presence of only *n*-type conductivity.[1] The purpose of this note is to report that both *n*-type and *p*-type conductivity can be obtained in cadmium telluride, the third member of this family.

EXPERIMENTAL

Crystals of CdTe were grown from a slow cooling of the reaction product of New Jersey Zinc "super-pure" Cd, American Smelting and Refining "high-purity" Te, and the proportion of impurity desired.[2] Both Cd and Te were further purified by the zone-melting process[3] before being used in this preparation. For test, crystals were shaped into approximately rectangular samples, the ends of which were plated with nickel and copper, and then leads were soldered to the plated portions.

RESULTS

Figure 1 gives the transmission data[4] from which a band gap of about 1.45 ev can be determined for CdTe. This gap should be compared with the gap of CdSe, 1.74 ev, and the gap of CdS, 2.42 ev.

It is found in general that *n*-type conductivity is obtained in CdTe if impurities are chosen from groups III or VII of the Periodic Table, and *p*-type conductivity is obtained for impurities from groups I or V. Typical point-contact rectification curves are given in Fig. 2 for *n*-type CdTe:Ga and *p*-type CdTe:Sb.

Hall effect measurements give a value of 30 cm²/volt sec as a lower limit for the mobility in both *n*-type and

[1] R. W. Smith, RCA Rev. **12**, 350 (1951).
[2] Much of the growth and treatment of these crystals was carried out by E. Blanche Lawton.
[3] W. G. Pfann, J. Metals **194**, 747 (1952).
[4] Measurements by H. B. DeVore.