proaching the value N just before n becomes greater than $2N$.

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Properties of Germanium Doped with Iron. II. Photoconductivity

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Photoconductivity in n- and p-type Fe-doped Ge was measured at 77°K. The impurity photoconduction in both types has approximately the same spectral dependence, indicating ionization energies of about 0.3 ev. The intrinsic photoconductive response measured at 0.83 ev was found to be a function of sample composition, the photosensitivity increasing as the samples became more n-type. Intrinsic photosensitivity and the time of response seem linearly related. For n-type samples of highest sensitivity the minimum detectable radiation level at 0.83 ev was estimated to be 2×10^{-13} watt. In such samples quenching effects were found in the spectral region from 0.3 ev to 0.7 ev. Experimental results are discussed in terms of a model in which the impurity center is capable of accepting two excess electrons.

INTRODUCTION

IN the preceding paper[1] it was shown that iron introduces energy levels near the middle of the forbidden region of germanium. The temperature-resistivity measurements located levels 0.27 ev from the conduction band and 0.34 ev from the valence band. It was also shown that the presence of iron in n-type germanium produces effects which can be described in terms of a trapping of photoinjected carriers.

This paper will describe the results of some measurements on the spectral dependence of impurity photoconduction in iron-doped germanium which yield values of the impurity ionization energies. It will also describe some measurements of the intrinsic photoconduction and of quenching phenomena which it is believed bear on the aforementioned trapping effects.[2]

EXPERIMENTAL

Samples were obtained in the form of small bars whose dimensions averaged about $3\times5\times10$ mm. These were cut from the original ingots in such a way as to maximize sample homogeneity. Fused Sn contacts were used for n-type samples. Fused Sn or In contacts were used for p-type samples. The data quoted here were obtained from samples for which temperature-resistivity data were also available. Seven n-type samples (from four ingots) and five p-type samples (from four ingots) were studied. Samples were mounted in a cryostat which was located at the exit port of a Perkin-Elmer spectrometer equipped with a CaF_2 prism. Unless otherwise stated all data were obtained at 77°K.

For the samples which possessed a high intrinsic sensitivity, the problem of distinguishing the true from the stray light response was severe. For example, at photon energies less than ~0.35 ev, even when a Ge filter was used and when the stray light was supposedly monitored by use of a thick glass block, false signals often obtained. Where this occurred the residual response occurring at a monochromator setting of ~0.15 ev was subtracted from the response observed at the higher energies. The correction was only important in the lowest decade of response.

Unless otherwise specified, the data quoted refer to measurements using unmodulated light. A sample was maintained at constant voltage (in most cases 6 volts) in a series circuit consisting of the sample, a battery, and a load. For photocurrents in the range 10^{-12}–10^{-6} amp, the load was a resistor. The current was detected using a "vibrating-reed electrometer" as a voltmeter across the load resistance. For larger photocurrents, the load was simply a sensitive ammeter. At low voltages (<20 volts), the photocurrent was usually linear in voltage. Nonlinearity appeared to be a function of the contacts and with care it could be minimized.

IMPURITY PHOTOCONDUCTION

Figures 1 and 2 show the spectral response of the photoconductivity of n- and p-type Fe-doped germanium at 77°K. The curves shown are typical of those found for all samples studied. The resolution of these curves into two spectral regions is obvious. Above

[1] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954).
[2] R. Newman and W. W. Tyler, Phys. Rev. **94**, 1419 (1954). Describes a preliminary report of this work.

~0.7 ev intrinsic photoconduction dominates. Between 0.8 ev and 0.7 ev the photoresponse decreases about 4 decades. Below 0.7 ev the impurity photoconduction is dominant.

The assignment of a point of relative response to define the optical ionization energy for the impurity photoconduction is at best arbitrary. For the present data, the gradual way in which the response changes from a slowly to a rapidly varying function of photon energy makes any definition even more ambiguous. Perhaps the most that should be said is that the ionization energies found from the resistivity data lie in the spectral region where one would define the photoconductive edge. That is, the optical threshold is in the vicinity of 0.3 ev for both *n*- and *p*-types.

It is perhaps surprising that the spectral response curves of *n*- and *p*-type samples are so closely similar. From the resistivity data, a difference in the optical data might have been expected. The anticipated difference of ~0.07 ev for corresponding points on the response curves should have easily been detected.

INTRINSIC PHOTOCONDUCTION

As pointed out in the previous paper, at low-temperatures, Fe in *n*-type germanium produces traps which cause long times of response in the photoconductivity and, by the related time integration effect, high photosensitivity. The effects are similar to those observed in CdS at room temperature, for example.[3]

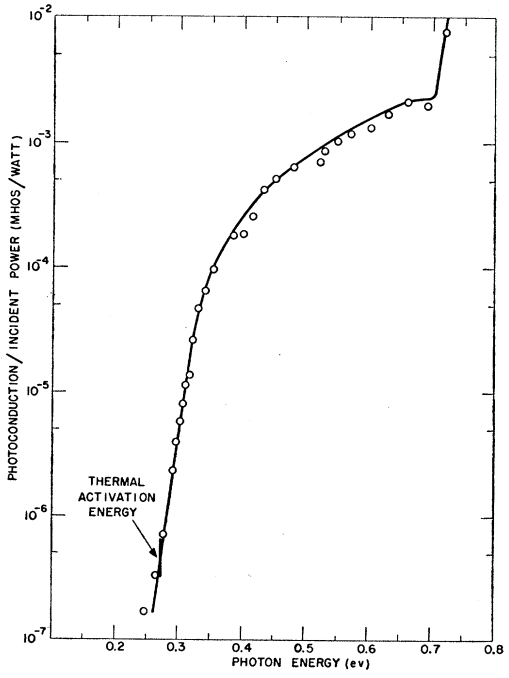

FIG. 1. Photoconductive spectrum of *n*-type Fe-doped Ge (sample 112*L*).

[3] A. Rose, RCA Rev. 12, 362 (1951).

The previous paper describes a method of growing a single Fe-doped crystal which contains *p*- and *n*-type regions which show high resistance at low temperature. It was of interest to take a series of samples from such a crystal and compare their intrinsic photoresponse. It was observed that their sensitivity increased as they became more *n*-type. Figure 3 shows the photocurrent *vs* incident light intensity at 0.83 ev at a fixed applied voltage for four samples cut from the same crystal. One sample was *p*, the others *n*-type. Curves of resistivity *vs* reciprocal temperature for these samples are shown in Fig. 13 of the previous paper.[1] The samples show a linear photocurrent-intensity curve over a large range of response. It is noteworthy that a region of nonlinearity could be reached with the most light sensitive sample. The break in the curve for this sample occurs for a carrier concentration of the order of 10^{10}–10^{11}/cm^3. If the break corresponds to a transition to a range in which trapping effects saturate and additional photocurrent is limited by a simpler and faster recombination process, then the number quoted is perhaps an estimate of the density of traps which are present in the sample.

It was of interest also to test the so-called reciprocity law which predicts that the speed of response and the sensitivity of the photoconductor are inversely related. Figure 4 shows the photocurrent/unit intensity *vs* time constant for the same series of samples shown in Fig. 3 and one additional sample of high sensitivity from another ingot. The ordinate is the dc photocurrent obtained at an incident light intensity of 10^{-8} watt

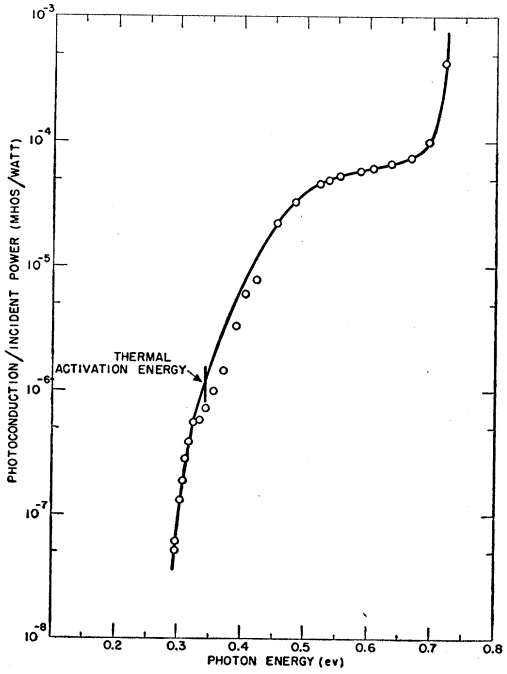

FIG. 2. Photoconductive spectrum of *p*-type Fe-doped Ge (sample 112*H*).

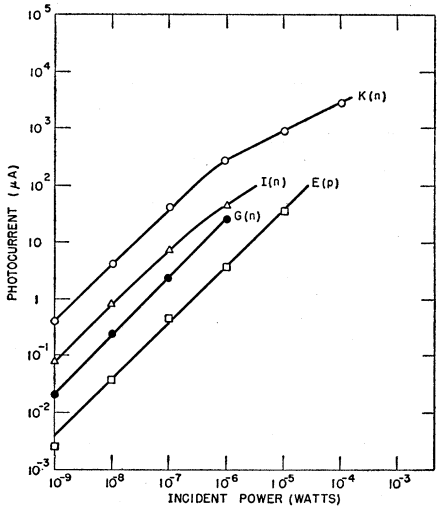

FIG. 3. Intrinsic photocurrent *vs* incident power (photon energy = 0.83 ev) for a series of samples from ingot No. 110. Sample *E* is *p*-type; samples *G*, *I*, and *K* are increasingly *n*-type in that order. The applied voltage was 6 volts.

divided by 10^{-8} watt. The abscissa is arbitrarily defined as the time required for the sample to recover in the dark from a "light on" resistance of about 10^4 ohms to a resistance of 10^7 ohms.[4] Using this definition, however, one does find a reasonably linear relationship between photosensitivity and a time constant describing the major part of the photoeffect. It should be pointed out that the recovery of resistance after exposure to light never approximates a simple exponential relationship and that no such linear relationship holds for recovery times characteristic of the long tails of the response (see preceding paper).

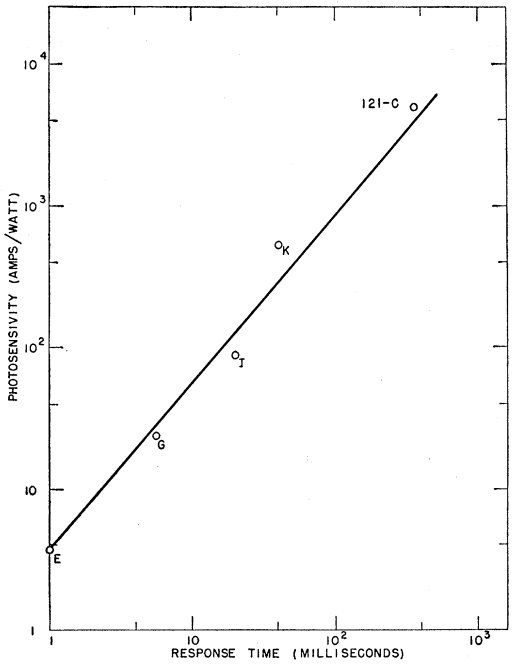

FIG. 4. Photosensitivity at a photon energy of 0.83 ev *vs* response time (see text) for a series of samples from ingot No. 110 (*E*, *G*, *I*, *K*) and a sample from ingot No. 121.

[4] These recovery times were obtained by H. H. Woodbury from photographs of oscilloscope tracings. The definition was one governed by experimental convenience.

The high photosensitivity of *n*-type Fe-doped germanium at low temperatures suggested its use as a detector of thermal radiation. We have made preliminary tests of its characteristics in this connection. With several of the more sensitive samples at 77°K, using the Perkin-Elmer 13 cps phase-sensitive system with an over-all effective band width of approximately 1 cycle, it was possible to detect 10^{-11} watt of 1.5-μ radiation with a signal-to-noise ratio of $\sim$50. This puts the minimum detectable radiation level at about 2×10^{-13} watt. In some rather crude tests, we found that our most sensitive samples were comparable to a commercial PbS cell cooled to 77°K in their ability to detect the thermal radiation from a low-power thermal source. The slow response and the limited spectral region of high sensitivity probably circumscribe the use of *n*-type Fe-doped germanium as a thermal detector.

QUENCHING

In samples of highest intrinsic photosensitivity and of slowest response, the phenomenon of quenching was encountered. Quenching in germanium had previously been found in certain *n*-type Au-doped crystals.[5] The phenomenon can be described as follows: A crystal is made to photoconduct by illuminating it with radiation occurring in the fundamental region. When the crystal is subsequently irradiated by monochromatic radiation in a certain spectral region of photon energies less than the fundamental limit, the photocurrent through the sample is reduced, i.e., quenched. Figure 5 illustrates the effect. It shows the steady state effect on different dc background photocurrents (the dashed lines) of monochromatic radiation simultaneously falling on the sample. The different background levels were obtained by varying the intensity of a fluorescent light. The intensity of monochromatic light at any particular photon energy was the same for the four curves shown. These curves were not corrected for the change in monochromatic light intensity with wavelength. However, this correction does not significantly alter the quench spectrum.

The lowest photocurrent curve of Fig. 5 is, of course, the normal photoconductive curve of the type illustrated in Fig. 1. The remaining curves are characteristic of the quenching process. Assume that the total photoresponse to the monochromatic light is a simple sum of a normal component (the lowest curve) and a quench component. Then because of the low relative magnitude of the normal component its contribution to the upper three curves is negligible. Thus the curves

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

shown probably give a good representation of the spectral efficiency of the quench process. If this is so, then, in contrast to the case of gold where the quenching appeared as sharp bands, the quench spectrum here has more the appearance of a continuum with a low energy threshold in the vicinity of 0.3 ev. This is more clearly brought out if one plots the difference between the quenched photocurrent and the background photocurrent against photon energy.

The transient effects in the quenching will be mentioned only briefly. In the quenching condition, when quench light is turned on the photocurrent rises rapidly to a maximum (peak transient) and then decays slowly to a lower value which is usually less than the photo-

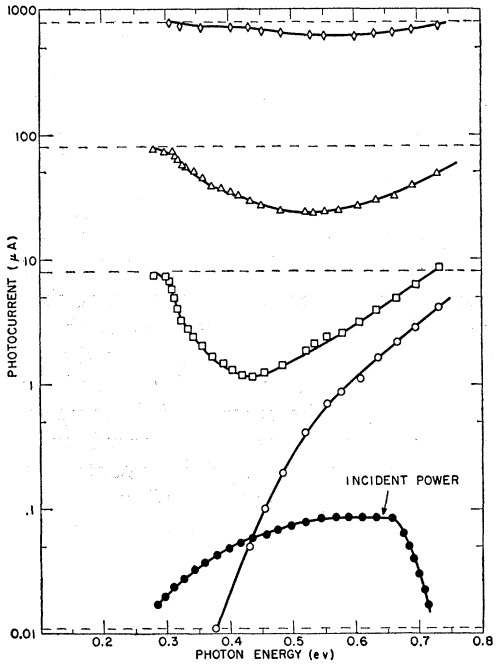

FIG. 5. Quench spectrum of an *n*-type Fe-doped Ge sample (82*C*) at different levels of background photocurrent (dashed lines). Ge filter on monochromator. Six volts applied. The bottom curve (solid circles) shows the power spectrum of the monochromatic beam.

current set by the background light. When the quench light is turned off, the photocurrent rapidly drops and then recovers slowly to the value set by the background. In the Au-doped germanium, it was found that the "quench-light-on" decay time depended upon the intensities of the different light sources. Whereas the time constant for recovery with the quench light off was independent of them and also substantially independent of temperature in the 77°K to 20°K interval. A similar situation occurs here. The "quench-light-off" time constant for recovery was about 1 sec at both 77°K and 20°K. In passing, it should also be mentioned that the magnitude of the quenching increased at lower temperatures. For example, under conditions where a

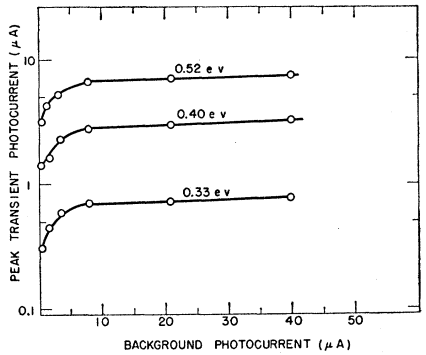

FIG. 6. Peak transient photocurrent at several photon energies *vs* background photocurrent for a sample showing quenching (82*C*). Six volts applied.

background photocurrent was 40 percent quenched at 77°K, a photocurrent of the same amount was 90 percent quenched at 20°K.

There appears to be an interaction between the impurity photoconduction and intrinsic photoconduction. That such an interaction should exist is not surprising. Altering the number of carriers in the conduction and valence bands must alter the population of carriers located at centers in the forbidden region, from which the impurity photoconduction is thought to arise. Figures 6 and 7 illustrate the effects observed. Figure 6 shows the effect for a sample which exhibits quenching. Here the peak transient photocurrent (defined in the foregoing) observed oscilloscopically when monochromatic light in the impurity range is turned on is plotted against the background photocurrent produced by a fluorescent light. The peak transient can probably be identified with the normal component of photoconductive response in situations where quenching is present. It is of interest to note that the impurity photoconduction, as so measured, increases asymptotically with increasing background photocurrent. The increase is about a factor of two from its value in the absence of any background light. This is suggestive of the sort of process that *could* occur if the Fermi level (in the dark) was located at the impurity center responsible for the impurity photoconduction.

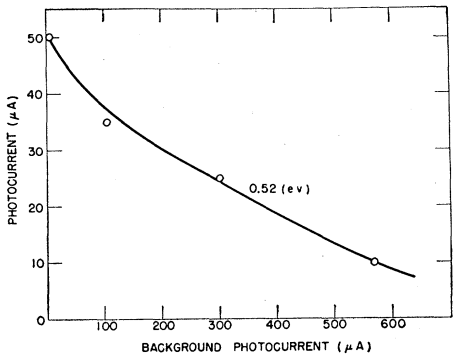

FIG. 7. Steady state photoresponse at 0.52 ev *vs* background photocurrent for an *n*-type sample (110*K*). Six volts applied.

In contrast, Fig. 7 shows the interaction effect in an n-type sample not showing any quench effect, but showing a relatively high intrinsic photosensitivity. Here the steady state increment in photocurrent produced by radiation in the impurity range decreases as the background level increases. By way of check on the method, the incremental response produced by monochromatic light in the intrinsic range was found to be essentially independent of the background level in both cases as would be expected for the range of currents involved.

DISCUSSION

As pointed out above, the spectral dependence of the impurity response for both n- and p-type samples was substantially the same. However, the photoconductive yield measured at some representative point, say 0.5 ev, differed markedly for the two types. The photoconductance/incident power expressed in arbitrary units was in the range 1–10 units for p-type samples and in the range 10^2–10^4 for n-type samples. The time constants for n-type samples were from 10 to 100 times that of p-type samples. It is thus possible to account for about a factor of 10^2 in the yield by the time constant effect. The remaining factor of 10^2 may reflect differences in the population numbers of the active centers and in their appropriate transition probabilities.

The arguments concerning the connection between trapping effects and quenching effects in germanium are discussed elsewhere.[5] In brief, they postulate that the background light produces hole electron pairs. The holes become trapped and by so doing inhibit normal recombination. The function of the quenching light is to empty the hole traps and allow the holes to recombine via recombination centers, thus reducing the electron population in the conduction band and consequently the over-all photoconductivity.

The impurity conditions of a sample in which quenching is found are unknown. There is some indication that it occurs only in ingots with a relatively light doping of iron. In any event, the samples which show the effect are the ones which show the highest photosensitivity and the longest times of response. This is offered as some evidence for the trapping hypothesis.

In the preceding paper a mechanism for trapping was suggested. It involved the trapping of a hole by a doubly negative charged iron center. By this mechanism, if the concentration of iron is relatively constant in an ingot, the number of traps will increase with the number of excess electrons. This idea can be used to account for the increased photosensitivity and longer recovery times of a series of samples from a single ingot as they become increasingly n-type. It also has implications as to the interaction that should be observed between intrinsic and impurity photoconduction. Namely, suppose the impurity photoconduction in, say, n-type material, involves excitation of an electron from the upper iron state to the conduction band. By the model, hole trapping involves depopulating this upper iron state. Thus, the creation of holes by the intrinsic photoconductive process should decrease the impurity photoconduction. Evidence for this is perhaps illustrated in Fig. 7. On the other hand, in samples where the trapping effect seems most marked and where quenching effects are present, intrinsic photoconduction appears to *increase* the impurity effects (see Fig. 6). At the moment the resolution of the contradiction is not apparent.