Radiative Recombination in Germanium*

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(Received June 17, 1958)

The dependence of recombination radiation, U, on the excess carrier density, δp, and on the equilibrium carrier density, (n_0+p_0), was studied in 0.2 to 12 ohm-cm n- and p-type germanium by simultaneous measurements of output radiation and of photoconductivity as functions of incident light intensity. The results confirm the van Roosbroeck-Shockley theory of band-to-band recombination which predicts that $U=\mathcal{R}[(n_0+p_0)\delta p+\delta p^2]/n_i^2$, where n_i is the carrier density in intrinsic material. As predicted by the theory, a log-log plot of U *vs* δp gave a straight line with slope of 1.0 for small δp and showed a curvature asymptotically approaching a slope of 2 for δp greater than (n_0+p_0). The value of $\mathcal{R}$ was estimated from the output radiation to be 2.5×10^{13} cm^{-3} sec^{-1} which compares favorably with the previously published theoretical value of 1.57×10^{13} cm^{-3} sec^{-1}. The dependence of δp on incident light intensity shows the behavior of the effective sample lifetime, which, in most cases, increases slowly with injection level.

INTRODUCTION

ACCORDING to the theory of van Roosbroeck and Shockley,[1] band-to-band recombination in germanium is proportional to the product of the hole and electron densities. Thus if excess carriers are generated, the net rate of radiation per unit volume, U, resulting from the recombination should be given by

$$U=\mathcal{R}[(n_0+p_0)\delta p+\delta p^2]/n_i^2, \quad (1)$$

where n_0 and p_0 are the equilibrium concentrations of electrons and holes, respectively, δp is the excess concentration of holes or electrons, n_i is the intrinsic concentration of carriers, and $\mathcal{R}$ is the radiation constant of reference 1.

Newman[2] attempted to verify Eq. (1) by measuring the output radiation as a function of the current in a p-n junction. He reported a linear relationship between the output radiation and the current even for cases where δp was large compared with (n_0+p_0). However, measurements of absorption of infrared radiation on the same junctions seemed to indicate a nonlinear relationship between the current and the excess carrier concentrations.

The present work consists of a direct verification of the law in Eq. (1) by simultaneous measurements of the output radiation and optically induced excess carrier concentrations. The latter are determined from photoconductivity measurements. The absolute magnitude of the output radiation is also determined which enables an estimate of $\mathcal{R}$ to be made. This is compared with the calculated value given by van Roosbroeck and Shockley. Curves of incident light intensity *versus* δp give added information about the behavior of the effective sample lifetime as a function of δp.

Measurements of output radiation *versus* current have been obtained with p-n junctions made by alloying indium into n-type germanium. These measurements, similar to Newman's, were actually made before the optical ones and the fact that results were somewhat at variance with Newman's gave impetus for further study.

EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic diagram of the setup used for the optical injection experiments. After passing through a water filter, light from a microscope lamp was focussed on one face of a CP-4 etched[3] germanium sample. The recombination radiation was detected by a PbS cell placed close behind the sample. A special holder was designed to insure that no direct light from the lamp fell on the detector. In order to obtain the sensitivity necessary to measure the emitted radiation over a range of as much as two orders of magnitude, a very narrow band width synchronous amplifier was used in conjunction with a 750-cps light chopper. The linearity of the PbS cell—synchronous amplifier combination was checked using a point light source and the inverse square law. The absolute sensitivity of the system was determined from the spectral response of the cell and the wavelength of the emitted radiation.

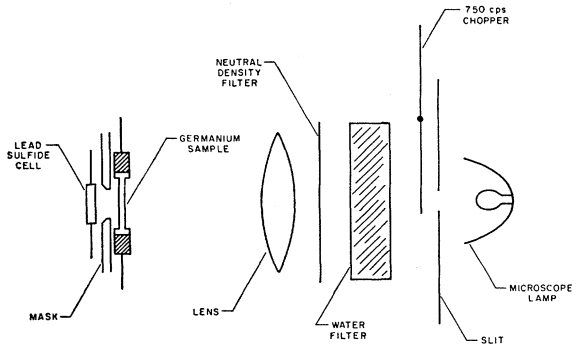

FIG. 1. Arrangement for measuring recombination radiation as a function of incident light intensity.

* The work described here was supported in part by the BuShips.

[1] W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).

[2] R. Newman, Phys. Rev. **91**, 1313 (1953).

[3] An additional quick dip in a 2 parts HNO_3, 2 parts HF, and 1 part acetic acid etch seemed to improve the radiation output and was used on some of the samples.

For the photoconductivity modulation data, the unetched ends of the rectangular germanium samples (6.4 mm×16.0 mm in size) were rhodium plated to permit spring contacts to complete an electrical circuit through the sample. The signal across a series resistance was fed into a Tektronix 541 oscilloscope with an appropriate high gain plug-in preamplifier. In most cases the dc measuring current had a small effect upon the radiation emitted and was maintained throughout a run.

Both n- and p-type germanium, ranging in resistivity from 0.2 to 12 ohm-cm, were used. The thickness of the etched portion of the samples varied from 0.2 to 0.4 mm.

Kodak neutral density filters, which were calibrated using the same light source as for the experiment, provided a range of approximately 100:1 in incident light intensity. A germanium interference filter which transmits no light of wavelength shorter than 2.1 μ served to verify that all the detectable recombination radiation lay in the intrinsic region as was expected from spectroscopic data previously taken. From these data, the peak of the output radiation curve corresponded to an energy of 0.70 ev for both electrically and optically induced radiation.

For the electrical injection experiments, large area (1.0 mm diameter) indium-alloyed diodes were prepared on disks of germanium mounted in Kovar rings. The same PbS detector was used with an external preamplifier feeding the signal into the oscilloscope. The injecting current was supplied by a mechanically chopped 3% duty-cycle pulser and could be varied in magnitude from a milliampere or less up to the order of several amperes (current density ~1000 amp/cm^2). Almost no heating effect was observed up to the last decade of current with this short-duty cycle pulser.

RESULTS

A. Recombination Radiation with Optical Injection

The excess carrier density was calculated from the photoconductivity data by assuming a uniform distribution of these carriers over an effective length, l, of the crystal. This excess carrier density gives a change in conductivity, $\Delta\sigma$, which is related to the measured change in resistance, ΔR, by the equation

$$\frac{(\mu_n+\mu_p)\delta p}{\mu_n n_0+\mu_p p_0}=\frac{\Delta\sigma}{\sigma_0}=\frac{\Delta R/R_{\text{dark}}}{1-\Delta R/R_{\text{dark}}}. \quad (2)$$

Here σ_0 is the dark conductivity of the sample, μ_n and μ_p are the mobilities of electrons and holes, respectively, and R_{dark} is the resistance in the dark corresponding to the length, l.

R_{dark} was first calculated from the resistivity and dimensions of the sample with l taken to be the length of the illuminated region. For the cases where δp was small compared with (n_0+p_0), a log-log plot of output radiation vs δp gave a slope of 1.0 as expected. For the cases where δp was comparable to (n_0+p_0) the output radiation not only increased more rapidly with δp, but increased approximately at the predicted rate. However, it was found that the exact curvature of the log-log plots depended critically on the value chosen for R_{dark}. This value is not known accurately because of possible errors in the measured resistivity of the samples, and errors in the effective length, l, arising from possible variations in the excess carrier concentrations near the electrical contacts. R_{dark} was therefore determined empirically to give the best fit between theory and experiment, and this value was compared with the value of R_{dark} calculated from the measurements. Percentage changes in δp determined from the two values of R_{dark} were of the same order as the percentage changes in R_{dark}. An equivalent error in R_{dark} in the linear cases would not affect the curvature.

A comparison of experimental and theoretical results is shown in Fig. 2 for three samples of widely different resistivity. The other seven samples tested gave similar results. In all cases tested, the agreement between theory and experiment seemed within experimental error.

Figure 3 is a log-log plot of output radiation vs the equilibrium carrier density, (n_0+p_0) for the various samples tested, for a constant value of $tA[\delta p+\delta p^2/(n_0+p_0)]$, where t is the thickness and A is the radiating area of the samples. As may be seen from Eq. (1), this plot should be a straight line with a slope of 1. Although there is considerable spread in the data, a variation

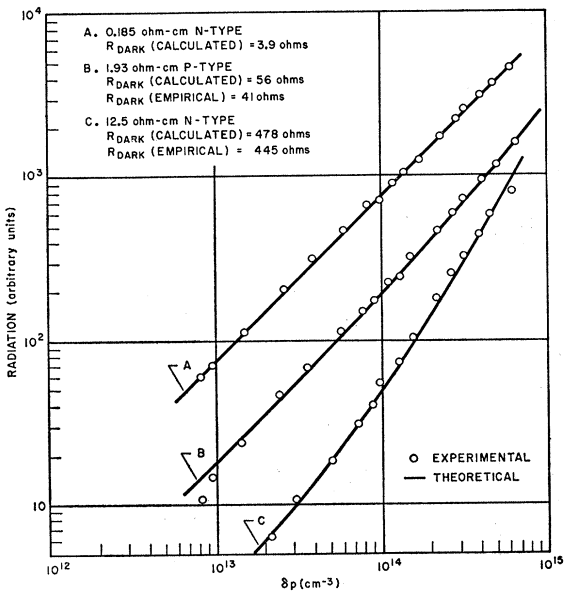

FIG. 2. Recombination radiation as a function of excess carrier density, δp, for three samples of germanium. For curves B and C, δp was calculated from photoconductivity data using values of dark resistance determined empirically to give the best fit with theory. The equilibrium carrier densities, (n_0+p_0), for the three samples are: A—8.66×10^{15} cm^{-3}, B—1.70×10^{16} cm^{-3}, C—1.30×10^{14} cm^{-3}.

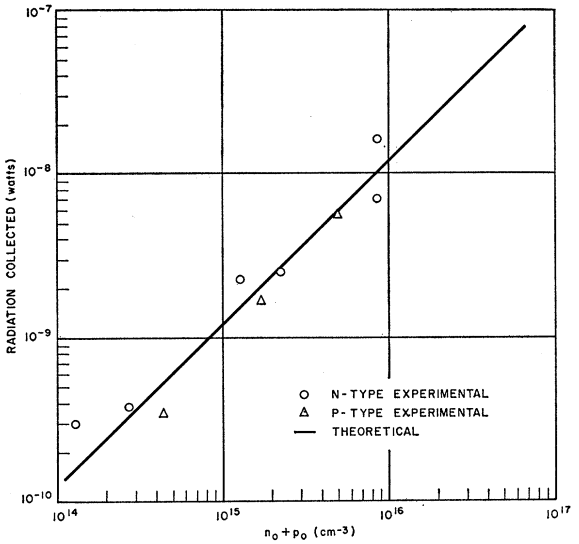

FIG. 3. Recombination radiation from various samples of germanium as a function of equilibrium carrier concentration for $t[\delta p+\delta p^2/(n_0+p_0)]=10^{12}$ cm^{-2}. Radiating area$=0.228$ cm^2.

from the curve of a factor of two or more is not unreasonable from the differences in the surface optical properties alone.

A numerical estimate of the radiation constant $\mathfrak{R}$ was made using the line drawn in Fig. 3, which effectively averages all the samples measured. The following factors were taken into account. Of the total radiation emitted approximately 1.5% falls within the critical angle of 14° from the normal to the surface. Of this, approximately $\frac{1}{3}$ gets further internally reflected. From the geometry of the system, an estimated 10% of the radiation leaving the germanium is collected. An experimental value of $\mathfrak{R}$ was thus determined as 2.5×10^{13} cm^{-3} sec^{-1} which may be compared with the theoretical value of 1.57×10^{13} cm^{-3} sec^{-1} given by van Roosbroeck and Shockley.[1] This agreement is better than might have been anticipated.

B. Effective Sample Lifetime

The effective sample lifetime, τ_{eff}, is related to δp by the equation

$$\tau_{\text{eff}}=t\delta p/I_0, \tag{3}$$

where t is the thickness of the sample and I_0 is the number of hole-electron pairs generated per sec per cm^2 of illuminated surface. From the calculations described in the preceding section, the excess carrier density, δp, is known as a function of the incident light intensity, which in turn is proportional to I_0. Hence information on the relation between τ_{eff} and δp can be derived from the data.

In most cases, the slope of a log-log plot of δp *vs* incident light was somewhat greater than 1.0 indicating a slow increase in τ_{eff} with increasing injection. An example is shown in curve A of Fig. 4. The curve asymptotically approaches a slope of 1.0 at lower light levels as might be expected from the fact that τ_{eff} should become a constant for sufficiently small δp.

In many of the samples tested, both the resistance and the output radiation drifted slowly with time after the incident light level had been altered. Most of the data were taken in a quasi-steady state before the drifting was appreciable by reducing the light intensity from an arbitrary maximum. Hence each set of quasi-steady state data is referred to a steady-state maximum value. A few tests were also made after the drift was completed. Curve B of Fig. 4 shows the final values to which δp drifted in approximately 30–60 seconds after the corresponding points on curve A had been taken. As in this case, all of the samples tested showed a greater dependence of lifetime on injection level after drift than before. For example, over the range of δp in Fig. 4, τ_{eff} increased by 60% before drift, while after drift, it increased by a factor of 5.

The time constants involved in the drifting phenomena suggest a change in charge in the outer surface states and a consequent change in surface potential. Therefore, the large variation in lifetime with δp after drift probably reflects changes in surface recombination velocity rather than changes in bulk lifetime. This is reasonable from the geometry of the samples.

It is important to note that the curves of radiation *vs* injected carrier density shown in Fig. 2 were completely independent of whether the data were taken before or after drift.

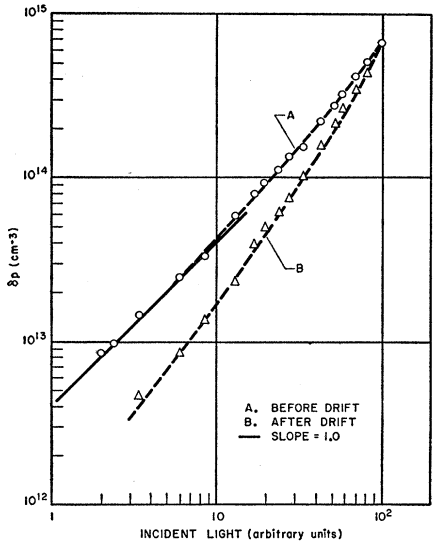

FIG. 4. Injected carrier density as a function of incident light intensity for a 1.93 ohm-cm p-type germanium sample. Curve A: Data taken in a quasi-equilibrium condition immediately after reducing the incident light intensity. Curve B: Data taken 30 to 60 seconds after curve A following completion of drift.

C. Recombination Radiation with Electrical Injection

Curves of output radiation *versus* current were taken on many diodes made by alloying indium into *n*-type germanium of various resistivities. These curves indicated that the output radiation almost always increased with the current as a power between about 1.3 and 1.7 over approximately two decades of output radiation where heating was not appreciable. An example is shown in Fig. 5.

From simple diode theory it is estimated that a current of 1 ma should correspond to an average δp of approximately 5×10^{13} cm^{-3} whereas n_0 for this resistivity germanium is 4×10^{16} cm^{-3}. The lower decades of the output radiation should thus correspond to the linear range of Eq. (1). The fact that the slope is greater than unity implies that δp increases with current more rapidly than linearly. This would be expected if the effective sample lifetime again increased with injection.

The simple power law dependence of radiation on current over much of the range tested is surprising considering the following facts. 1. Near the middle of the current range the radiation should begin to increase faster than linearly with injected carrier density according to Eq. (1). 2. In the same current range the injection efficiency, i.e., percent of total current carried by minority carriers, should start to decrease. 3. Effective sample lifetime is changing with current and is known to be increasing in the lower range.

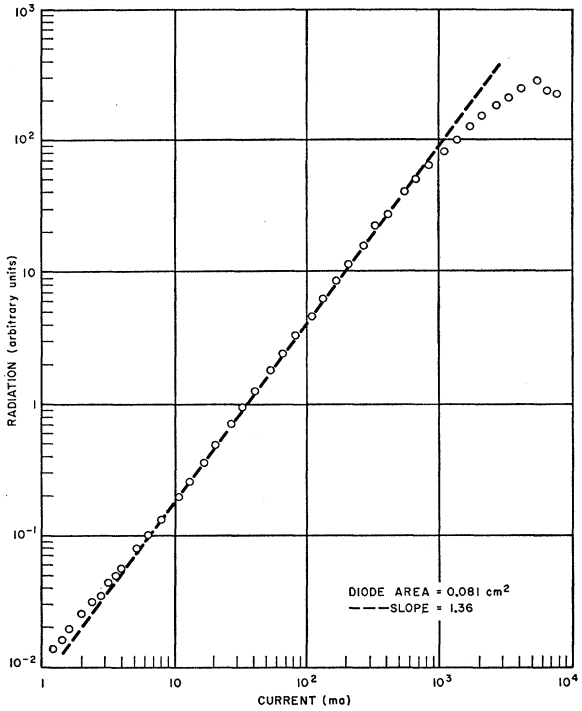

FIG. 5. Recombination radiation *vs* current for a diode made by alloying indium into 0.04 ohm-cm *n*-type germanium.

CONCLUSION

The room-temperature radiation from germanium depended on both injected carrier densities and sample resistivity as expected from band-to-band recombination theory. Furthermore the measured radiation rate yielded a radiation constant in close agreement with the theoretically predicted value.

Since the injected carrier density uniquely determines the amount of radiation produced, this relationship could be used in reverse to study the injection process itself. For example, by knowing the output radiation from a diode, it should be possible to reconstruct the variation of injected carrier density as a function of current, a dependence which is complicated by a changing injection efficiency and a changing sample lifetime.

ACKNOWLEDGMENTS

The authors wish to thank Dr. P. J. Daniel for calibration of the PbS detector, as well as for many helpful discussions and suggestions on the major portion of this work. They also wish to thank Dr. M. E. Lasser, Mr. J. Walsh, Dr. S. Zaromb, and Mr. L. W. Hershinger for their useful comments and advice, and Mr. J. Cosgrove for his preparation of the diodes used in the electrical experiments.