RADIATIVE RECOMBINATION IN SEMICONDUCTORS

V. S. VAVILOV

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1. INTRODUCTION

THE recombination of electrons and holes in semiconductors is one of the most important physical processes determining the properties and possibilities of application of semiconductors in electronics and in other fields. The direct recombination of an electron with a hole with the emission of a photon, as well as the radiative transitions of electrons into local defect or impurity levels, is in many cases a "higher-order process." That is, the overall rate of recombination is determined by radiationless transitions. Nevertheless, in the period since 1952, the study of the spectra of the infrared "recombination radiation" has given important information on the band structure, the defect and impurity energy levels, and the lattice vibrations of germanium, silicon, and a series of other semiconductors. It has been ascertained that in semiconductors with narrow forbidden bands, for instance InSb and PbS, the probability of radiative recombination is near to unity.

Recombination radiation is one of the types of luminescence. It is possible that the study of radiative recombination upon "electric" excitation by injection of carriers across p-n junctions will be useful with regard to the theory of electroluminescence. We should note that the luminescence of silicon carbide crystals upon passage of an electric current, which was discovered by O. V. Losev[37] in 1923, may be considered both as one of the types of electroluminescence and as the recombination radiation of SiC, which is a semiconductor with a wide forbidden band.

Since radiative recombination in semiconductors will be discussed below in applications in which the term "recombination radiation" has been rather widely used, this term will be used further, although there is no difference in principle between recombination radiation and luminescence.

One must consider that, to the extent that sensitive detectors of infrared radiation have been perfected, the study of recombination-radiation spectra will become a generally accepted method of study of impurities and of the structure of semiconductor crystals, just as measurements of optical absorption and photoconductivity have so become.

In this review we present the fundamental theoretical conceptions about radiative recombination in semiconductors and the experimental results obtained up to 1958.

2. THE THEORY OF THE DIRECT RECOMBINATION OF ELECTRONS AND HOLES WITH EMISSION OF PHOTONS

The process of emission of a photon in the direct recombination of an electron and a hole may be considered as the reverse of the absorption of a photon in the "fundamental band." That is, it is the reverse of the case in which a photon is absorbed and an electron-hole pair appears. On the basis of the light-absorption data for germanium in the wavelength region between 1 and 2 μ, and of the fact that the quantum yield in this region is equal to unity,[2] van Roosbroeck and Shockley[3] have estimated the probability of radiative recombination in germanium. Under conditions of thermodynamic equilibrium, the number of radiative recombinations in the frequency interval $d\nu$ is equal to the number of electron-hole pairs generated by thermal radiation. The generation of pairs per unit time per unit volume, is equal to $P(\nu)\,\rho(\nu)$, where $\rho(\nu)\,d\nu$ is the density of photons in the interval $d\nu$ in the crystal and $P(\nu)$ is the probability per unit time of the absorption of a photon of frequency ν. Integration over all frequencies gives the total number of recombinations per unit volume per second, i.e., the rate of recombination R:

$$R = \int P(\nu)\,\rho(\nu)\,d\nu. \qquad (1)$$

It will be shown below that the principal part of this integral for any semiconductor is associated with a relatively narrow band of frequencies near the edge of the spectral region of "intrinsic" absorption.

In a steady-state deviation from thermal equilibrium, the rate of radiative recombination R_c may be written as

$$R_c = \frac{np}{n_i^2} R, \qquad (2)$$

since the number of direct recombinations must be proportional to the product of the concentrations of electrons n and holes p, and must coincide with R when $np = n_i^2$, as occurs under equilibrium condi-

tions. From the expression for R_c, the characteristic "relaxation time" (or "lifetime") may be calculated for small deviations from equilibrium, under the assumption that recombination takes place by radiation alone. If Δn and Δp are small increments to the equilibrium concentrations, and $\Delta n = \Delta p$, then it follows from Eq. (2) that[4]

$$\Delta R_c = \left(\frac{\Delta n}{n} + \frac{\Delta p}{p}\right) R_c$$

and

$$\tau = \frac{np}{n+p} R_c. \qquad (3)$$

In a strongly doped semiconductor of n- or p-type with equilibirum carrier concentrations $n = n_0$ and $p = p_0$, the equilibrium concentrations of the minority carriers are small, and the lifetimes for radiative recombination are

$$\left.\begin{aligned} \tau_p &= \frac{p_0}{P} = 2\frac{p_0}{n_i}\tau_i = 2\frac{n_i}{n_0}\tau_i, \\ \tau_n &= \frac{n_0}{R} = 2\frac{n_0}{n_i}\tau_i = 2\frac{n_i}{p_0}\tau_i, \end{aligned}\right\} \qquad (4)$$

where $\tau_i = n_i/2R$ is the lifetime in the semiconductor showing intrinsic conductivity. The value of the cross-section σ for recombination interaction of an electron and a hole is

$$\sigma = \frac{R}{n_0 p_0 v} = \frac{R}{n_i^2 v}, \qquad (5)$$

where v is the average thermal velocity of the carriers.

In order to calculate the spectral density of photons $\rho(\nu)$ in the frequency interval $d\nu$, use is made of the expression

$$2 \cdot 4\pi k^2\, dk = \frac{8\pi}{c^3}\left[n^3\left(1 + \frac{d\ln n}{d\ln \nu}\right)\right]\nu^2\, d\nu, \qquad (6)$$

where n is the index of refraction, c is the velocity of light, and $k = n\nu/c$ is the wave number.

Hence,

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\,\frac{n^3\frac{d\ln n\nu}{d\ln\nu}}{\exp(h\nu/kT) - 1}. \qquad (7)$$

The probability $P(\nu)$ of absorption of a photon can be written as

$$P(\nu) = \alpha v_g,$$

where $\alpha = 4\pi n\kappa\nu/c$. Here κ is the absorption index determined experimentally from the spectral dependence of the transmission of the material,* and the quantity v_g is the group velocity of the wave packet:

$$v_g = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)} = \frac{c}{n}\frac{d\ln\nu}{d\ln n\nu}.$$

Thus

$$P(\nu)\,\rho(\nu) = \alpha(\nu)\, v_g(\nu)\,\rho(\nu) = \frac{32\pi^2\varkappa n^3}{c^3}\,\frac{\nu^3}{\exp(h\nu/kT) - 1}. \qquad (8)$$

The total rate of radiative recombination R per unit volume may be expressed as

$$R = 32\pi^2 c\left(\frac{kT}{hc}\right)^4 \int_0^\infty \frac{n^3 \varkappa u^3\, du}{e^u - 1}. \qquad (9)$$

or in a form which is convenient for calculation,

$$R = 1.785 \cdot 10^{22}\left(\frac{T}{300}\right)^4 \int_0^\infty \frac{n^3 \varkappa u^3\, du}{e^u - 1}\ \mathrm{cm^{-3}\ sec^{-1}}, \qquad (10)$$

where $u = h\nu/kT$. The lower limit of the integral is in practice not equal to zero but to u_0, which corresponds to the "optical" width of the forbidden band, i. e., the minimum energy of photo-ionization, $u_0 = E_{g_0}/kT$.[5] At long wavelengths, other mechanisms of light absorption occur; in particular, in semiconductors with narrow forbidden bands, intense absorption by carriers not associated with generation of pairs may occur at sufficiently high temperatures.

For a quantitative estimate of the rate of radiative recombination in germanium, van Roosbroeck and Shockley made use of the experimental data on the spectral dependence of n and $n\kappa$ published in reference 6. The numerical integration of expression (10) gave at 300°K the value $R = 1.6 \times 10^{13}$ $\mathrm{cm^{-3}\ sec^{-1}}$. In Fig. 1 are shown the dependences on $h\nu/kT$ of the quantity $P(\nu)\,\rho(\nu)$, and of the factors of the integrand in (10). These factors are the quantity $U = 1.785 \times 10^{22}\ u^3/(e^u - 1)$, which depends on the spectral density of photons, and $n^3\kappa$, which is determined by the properties of the semiconductor, in the given case, germanium. At 300°K, only an infinitesimally small fraction of the photons have enough energy to generate pairs; the crossing of the

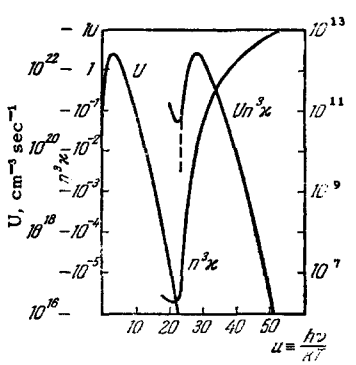


FIG. 1. Relation of the probability of radiative recombination in germanium to the energy of the photon and the temperature, according to the data of van Roosbroeck and Shockley.[3]

*It is assumed all of the light absorption is involved in the generation of pairs, as is true for very pure single crystals of germanium and silicon. For many other semiconductors, such reliable data on the absorption in the fundamental band have not yet been obtained; for crystals which are not highly perfect, additional ineffective absorption or light-scattering may take place.

TABLE I. Lifetime with respect to radiative recombination

E_g^0 (ev)	Substance	n_i (cm^{-3})	R ($cm^{-3}\,sec^{-1}$)	$\tau_R = \frac{n_i}{2R}$ (sec)	τ_{obs} (sec) (maximum)
1.1	Si	$1.4 \cdot 10^{10}$	$2 \cdot 10^{9}$	3.5	10^{-3}
0.7	Ge	$2.4 \cdot 10^{13}$	$3.7 \cdot 10^{13}$	0.3	10^{-3}
0.37	PbS	$3 \cdot 10^{15}$	$1.4 \cdot 10^{20}$	10^{-5}	$9 \cdot 10^{-6}$
0.22	PbSe	$2 \cdot 10^{17}$	$3.3 \cdot 10^{22}$	$3 \cdot 10^{-6}$	—
0.27	PbTe	$6 \cdot 10^{16}$	$1.8 \cdot 10^{22}$	$1.7 \cdot 10^{-6}$	—
0.18	InSb	$2.2 \cdot 10^{16}$	$2.6 \cdot 10^{22}$	$0.4 \cdot 10^{-6}$	$0.1 \cdot 10^{-6}$

curves for U and $n^3\kappa$ forms a sharp maximum in the region approximately between u = 25 and u = 32. The rise in the curve for $n^3\kappa$ in the region u < 22 is associated with the absorption of light by free carriers; in calculating the probability of radiative recombination and the form of the emission spectrum, this part of the curve was discarded, while the curve $P(\nu)\rho(\nu)$ was extrapolated downward by the dotted line. Using the value $n_i^2 = 3.1 \times 10^3\, T^3 \exp(-9100/T)$, the authors obtained the value $\tau_i = 0.75$ sec. Analogous calculations based on more precise data on the edge of the absorption band in germanium[7] gave a value $\tau_i = 0.3$ sec.[8]

It is known that, even in the purest single crystals of germanium with intrinsic conductivity, the lifetime of the nonequilibrium carriers does not exceed several milliseconds. It has been shown that dislocations and structural defects play the role of "recombination centers."[9,10] Thus, even in crystals not containing the typical "recombination" impurities such as Cu, the lifetime is not determined by radiative recombination.* The same is even more true for silicon, as the technique of purification of the latter is still significantly lacking in perfection.

A theory based on the principle of detailed equilibrium permits us to conclude that in semiconductors with narrow forbidden bands, radiative recombination must be a considerably more probable process than it is in germanium and silicon.

Burstein and Egli[8] have used the existing data on light absorption in a number of semiconductors with varying widths of the forbidden band in order to estimate the rate of radiative recombination. The results of their calculations are given in Table I.

In the right-hand column are given the maximum experimentally observed lifetimes of electron-hole pairs. One can see from the table that radiative recombination must be a probable process for semiconductors with narrow forbidden bands; it is possible that in some cases this will be the factor determining the lifetime of nonequilibrium carriers.

A theory of recombination has been discussed above, involving transitions of electrons from the conduction band into the valence band. We may discuss "extrinsic" radiative transitions, starting with the same basic assumptions. There have been as yet no studies on the calculation of spectra of "extrinsic" recombination radiation and its probability in such semiconductors as Ge and Si, although the question of the relation of radiative and nonradiative transitions has been discussed rather widely in the literature on luminescence[12] and semiconductors.[13] Qualitative considerations make us assume the existence of narrow maxima of extrinsic recombination radiation. As will be seen below, this radiation has been detected in a number of cases.

3. EXPERIMENTAL METHODS OF EXCITATION AND STUDY OF RECOMBINATION RADIATION SPECTRA

In studies of the spectra of recombination radiation, either of two methods of generating the necessary excess concentration of carriers has been used. These are excitation by short-wavelength light[14] and injection of carriers by passing a current through an n-p junction in the p-n direction.[1,15,16] The first method was especially convenient in the study of the characteristic radiation of germanium and silicon. A diagram of the apparatus for study of the recombination-radiation spectra of germanium is shown in Fig. 2. Light from the incandescent tungsten lamp passes through the water filter of 10-cm thickness, and is focused on the thin germanium plate. The radiation emitted from the back of the plate is analyzed by the spectrometer. According to the measurements of Haynes, the water filter transmits less than 10^{-10} of the light flux having wave-

*The most recent work of Dash et al.,[11] who obtained single crystals of Ge and Si without dislocations, would permit one to expect long lifetimes; however, the recombination of carriers in these crystals has not yet been studied.

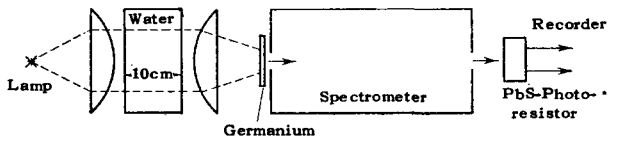


FIG. 2. Diagram of the apparatus for study of the radiative recombination spectra of germanium. Radiation from the lamp with wavelengths up to 1.4 μ. is used for excitation.

lengths over 1.4 μ, while the germanium plate being studied transmits less than 10^{-10} of the light flux of wavelengths shorter than 1.4 μ. That is, the light from the source (the lamp) cannot reach the spectrometer, and the measured radiation can be only recombination or heat radiation. For silicon, a similar method requires the use of a KG-1 Zeiss filter or other filter in addition to the water, since water transmits wavelengths less than 1.4 μ, whereas silicon is transparent in this region.

When electric excitation is used, i. e., injection across a p-n junction, an important problem is that of bringing about the emergence of the radiation from the specimen. In fact, for the simplest experimental geometry (Fig. 3a), a considerable part of the light flux is subject to total internal reflection, and does not reach the entrance slit of the spectrometer. A considerable increase in the intensity of the radiation emerging from the crystal may be attained by using a specimen in the form of a Weierstrass sphere or a "lens".[16] In this case (Fig. 3b, c), the radiating volume is approximately a hemisphere with a radius of the order of magnitude of the diffusion distance of the minority carriers, and with the point

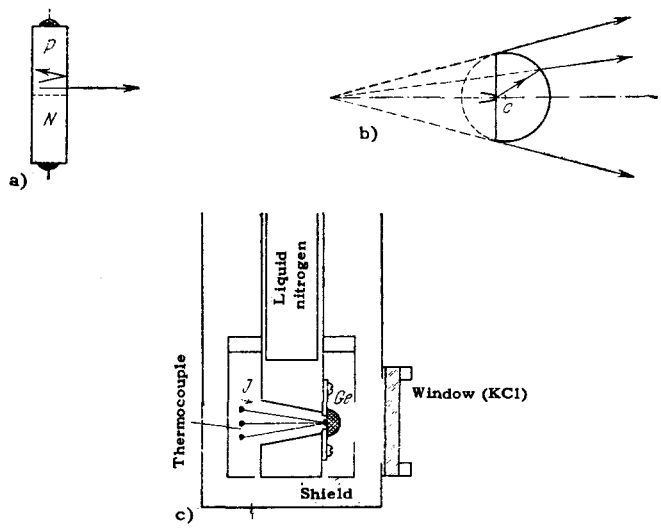


FIG. 3. a – decrease in intensity of recombination radiation due to total internal reflection; b – single crystal of germanium or silicon made into the form of a Weierstrass sphere. The radiation is excited by injection of carriers through the contact K. c – diagram of an apparatus for experiments with chilled crystals.

of injection at its center. In case of injection across a p-n junction of small area or a point contact, a considerable fraction of the carriers recombine at the surface; by making use of the sharp focusing of the optical system, which includes the Weierstrass sphere, one may study separately the "surface" and "volume" recombination radiation. Such a specimen geometry is convenient for the study of extrinsic radiation; the spectrum of the intrinsic radiation, corresponding to the transition between bands, is strongly distorted because of absorption. With a complicated geometry, this distortion is difficult to take into account.

Bolometers and thermocouples, which are used as nonselective detectors in infrared spectrometers, e. g., instruments of the IKS-11, IKS-12, or Perkin-Elmer types, are not sensitive enough to record the spectra of recombination radiation. Hence, specially selected PbS photoresistors are used for the purpose.[17]

The noise level in the best of these photoresistors is very low, and one may attain a full utilization of their sensitivity simply by using a chilled radiation screen to protect the photoresistor from the background thermal radiation corresponding to 300°K. Modulation of the exciting light or injection current permits one to apply synchronous detection of the signal; thus one may obtain a better signal-noise ratio by virtue of the increase in the recording time of the spectrum. According to a private communication from P. Aigrain, it has been possible to detect reliably the recombination radiation of germanium appearing with an injection current of one ampere, when concentrated into a narrow beam by the Weierstrass sphere and a reflector, at a distance of one km.

To study the recombination of semiconductors with a width of the forbidden band greater than 1.1 ev (i.e., for silicon), photographic plates can be used.

4. SPECTRA OF THE INTRINSIC AND EXTRINSIC RECOMBINATION RADIATION OF GERMANIUM

a) "Intrinsic" Radiation

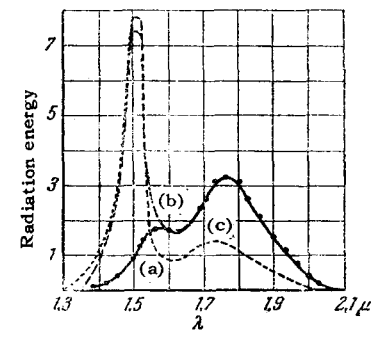
By analogy with the established concept of the "intrinsic" conductivity of semiconductors which is associated with transitions of electrons from the valence band into the conduction band, we shall designate the radiation which arises in the reverse transition as "intrinsic." The most detailed and important experimental data on intrinsic recombination radiation have been obtained for germanium. Without referring to the early papers in which this radiation was discovered, we shall discuss the results of

Haynes,[14] who used the method of photoexcitation with thin plates of germanium. The wavelength dependence of the radiation intensity in the range from 1.3 to 2.1 μ must be corrected for absorption so that it may be compared with theory, even for very thin plates (in the described experiments, from 1.2×10^{-2} to 1.3×10^{-3} cm thick). If the diffusion distance is considerably greater than the thickness, and the rate of surface recombination is small enough, as may be attained by special etching, we may consider the bulk lifetime and the concentration of carriers to be the same throughout the thickness of the specimen. The initial flux of recombination radiation $J_{0\lambda}$, the wavelength λ and the flux measured outside the plate J_λ are connected by the relation

$$J_{0\lambda} = \frac{J_\lambda \alpha_\lambda d}{1 - e^{-\alpha_\lambda d}},$$

where α_λ is the absorption coefficient as a function of λ, d is the thickness of the specimen; $\alpha d > 1$. The formula is approximate, since it does not take into account reflection at the germanium—air interface. However, the change in the reflection coefficient over the range 1.4—2.1μ is small in comparison with the changes in α.

After correction of the experimental data, a clearly marked maximum appeared at $\lambda = 1.52\,\mu$ (0.81 ev), along with the previously observed maximum at 1.75 μ (0.70 ev), the latter agreeing well with the width of the forbidden band of germanium at 300°K (Fig. 4). At first, the interpretation of the maximum was difficult; the published experimental data of Dash and Newman[7] and of Fan,[5] who discovered a clearly marked structure in the absorption edge of germanium, showed that the application of the early results of Briggs,[6] obtained with thin sputtered films, to single crystals of germanium could not be justified. By carrying out a numerical integration of formula (10) in the theory of van Roosbroeck and Shockley, Haynes obtained good agreement with his own data. The experimental relation between the emitted energy and the wavelength for a very thin plate ($d = 1.3 \times 10^{-3}$ cm) is shown by the solid curve (a) with dots.



——— Experimental curve

——— Experimental curve corrected for self-absorption

-------- Curve constructed from the absorption data of Dash et al.[7] and the theory of van Roosbroeck and Shockley.[3]

FIG. 4. The spectrum of the intrinsic recombination radiation of a thin germanium plate.

Curve (b), constructed by taking absorption into account, leaves no doubt of the existence of a second maximum, which is barely noticeable on curve (a). If we take into account the fact that the relative intensity of the emergent radiation increases at long wavelengths, because of multiple internal reflection, the coincidence of the experimental curve with theory must be considered good. The radiation having a maximum at 1.52 μ is apparently caused by vertical transitions with k = 0, as had already been assumed for absorption processes,[18] while the radiation with a maximum at 1.75 μ (0.70 ev) is caused by "indirect" transitions with the participation of phonons. Thus, the minimum (000) in germanium occurs only 0.1 ev higher than the minimum (111).

When the temperature is lowered, the emission bands of germanium become narrower and are shifted to shorter wavelengths. The direction and magnitude of the shift of the maxima agree with the widening of the forbidden band which has been observed by Fan[5] and other authors. Quite recently,[19] fine structure has been discovered in the spectra of intrinsic recombination radiation of germanium and silicon. It was shown that the "principal" long-wavelength maximum of the radiation is accompanied by subsidiary maxima. In the opinion of the authors of the paper, the different maxima correspond to the energies of phonons of different types, i. e., the energies of interaction of the electron with the lattice in the radiative transition. This structure is observed at temperatures lower than about 30°K, and is very distinctly shown at the temperature of liquid helium.

MacFarlane and Roberts,[20] who discovered an analogous structure in a study of the absorption edge of germanium at low temperature, associate it with the formation of excitons. The question of the nature of the fine structure of the absorption edge and of the recombination radiation cannot be considered as finally settled. However, according to calculations of Haynes, the concentration of excitons, if they exist, must be so small that the recombination radiation due to decay of excitons could not be detected in his experiments.

b) "Extrinsic" Radiation

Extrinsic recombination radiation correspond-

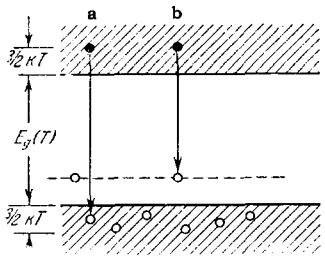


FIG. 5. Diagram of the electronic transitions in a semiconductor, accompanied by emission of photons.

ing, for example, to electronic transitions of type b (Fig. 5), may be the result of recombination processes by way of levels lying in the forbidden band. The detection of this radiation is made easier by the high transparency of the semiconductor outside its fundamental absorption band. On the other hand, great difficulties arise in the selection of sufficiently sensitive detectors for radiation of wavelengths greater than 6 or 8 μ. The radiation corresponding to transitions of electrons from unionized Group V donors must have a maximum at about 0.01 ev from the "interband" maximum for germanium; up to now this radiation has not been resolved from the fundamental intrinsic band. However, even in the first papers of the French physicists, on using a Weierstrass sphere with a specimen temperature of 77°K, a distinct maximum was found at 2.45 μ.[21] The authors associated this maximum with recombination centers in germanium with an energy level of capture at a distance of 0.22 ev from one of the bands.[22] As is known, the determination of the positions of the levels of the recombination centers, as based on data on the temperature dependence of the lifetime of carriers, involves great difficulties. The spectra of extrinsic recombination radiation may give here independent and extremely valuable information. By studying the recombination radiation from germanium which had been subjected to plastic deformation, Newman[23] showed that the maximum occurring near 2.4 μ corresponds to the energy levels of dislocations. The initial aim of his study was the discovery of radiative transitions associated with the deep levels of a series of elements (Au, Mn, Ni, Fe, Cu, etc.) in germanium. For this purpose, crystals were prepared with p-n junctions, in which the cited elements were incorporated. As is known, the solubility of these elements in Ge is very small (reference 13, Sec. 1). Independent of the nature of the impurity introduced, a maximum at 2.4 μ was observed at 80°K in all crystals in which the p-n junction had been created by fusing indium onto the specimen. On the other hand, this maximum was absent in crystals in which the p-n junctions had been generated during the growth of the single crystals. On concluding that the maximum is associated with defects and dislocations which appear in the zone of recrystallization formed when the indium is fused onto the germanium, rather than with the impurities, Newman went on to study the radiation from crystals which had been subjected to plastic shear deformation. The deformation was brought about by twisting at a temperature of 550°C under conditions which, in the opinion of the author, excluded the possibility of contamination by impurities. Annealing of the crystals at 800°C for 15 hours, which is sufficient for elimination of thermal acceptors according to reference 24, led to a small shift in the maximum (from 0.50 to 0.53 ev), and to a change in the relative intensities of the fundamental and impurity maxima of the radiation (Fig. 6). The introduction of copper atoms in a concentration of about 10^{15} cm^{-3} led to the appearance of a new maximum corresponding to 0.59 ev. As Newman himself has pointed out, this does not agree with the positions of any of the three known acceptor levels of Cu in Ge determined by other methods (0.26 ev below the conduction band, and 0.04 ev and 0.33 ev above the valence band). However, the new maximum is of complex origin, and is possibly associated with the combination of the spectra of the radiation due to copper with the radiation associated with transitions to the dislocation levels.

In conclusion, we present data on the relation between the intensity of the radiation and the method of excitation. From the theory [Eq. (2)] it follows that the rate of direct radiative recombination for small deviations from equilibrium must be proportional to the product np. In most experimental studies, the excess concentration of carriers has not been determined directly; ordinarily, the direct current through the p-n junction has been used as

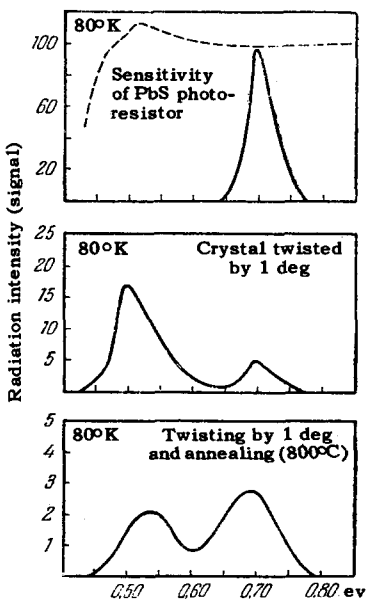


FIG. 6. Spectra of the recombination radiation of germanium subjected to plastic deformation.[23]

the measure of the deviation from thermal equilibrium. This should be considered as merely a rough approximation, since the lifetime of the carriers depends on the current, especially at high current densities of the direct current; thus the proportionality $\Delta n \sim J$ is disturbed. Nevertheless, in Newman's study,[23] the intensity of the "intrinsic" radiation varied approximately as the square of the current (Fig. 7). The same relation has been observed by other researchers.[21] The results of Newman with regard to extrinsic ("dislocation") radiation are considerably harder to understand.

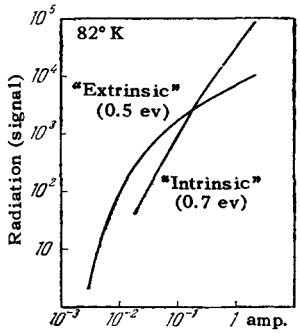


FIG. 7. Dependence of the intensities of the intrinsic and extrinsic recombination radiation of germanium on the excitation current.

The curve for the extrinsic radiation was obtained in part by use of a monochromator, and in part with a thick germanium filter which completely absorbed the "intrinsic" radiation. This curve shows that for very small injection currents, the intensity increases proportionally to the fifth power of the current. The author of the paper associates this anomaly with the presence in the vicinity of the p-n junction of a thin layer of the semiconductor with a very short lifetime.

5. RADIATIVE RECOMBINATION IN SILICON

It was shown[1] in 1952 that in the recombination of electrons and holes in Si, radiation occurs with a maximum intensity near 1.1μ. It was later possible to distinguish the intrinsic and extrinsic radiations.[26] To excite the radiation, use was made of p-n junctions obtained by introduction of impurities during the growth of the single crystals. The radiation was analyzed by means of a Perkin-Elmer spectrometer; a PbS photoresistor was used as the detector. Corrections for the sensitivity of the photoresistor and the response of the spectrometer, which varies with the wavelength, were introduced by comparison with the spectrum of a tungsten lamp having a known temperature. The radiation spectrum of silicon containing boron and arsenic as impurities is shown in Fig. 8, where the relative number of emitted photons per unit energy interval is given on the ordinate axis as a function of the energy of the photons in electron volts. At room temperature, the maximum in the

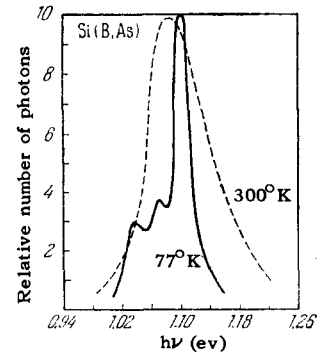


FIG. 8. Spectrum of the recombination radiation of silicon with boron and arsenic impurities at room temperature and liquid-nitrogen temperature.

radiation spectrum corrected for self-absorption corresponds to 1.088 ev. The solid line indicates the radiation spectrum at a specimen temperature of 77°K. One may see on it an extremely narrow band with a maximum at 1.100 ev and two bands of lower intensity with maxima at 1.072 and 1.038 ev. The radiation observed at room temperature and the band with the maximum at 1.1 ev at 77°K are "intrinsic" properties of silicon: it was found that they do not depend on the nature of the impurity, and agree with calculations based on optical constants and on the principle of detailed balancing. The fact is of interest that the position of the emission band corresponds to the first steep rise in the absorption band of Si,[7] that is, to "indirect" transitions of electrons from the minimum (1, 0, 0) to the upper part of the valence band with the participation of phonons. This radiation may be designated as "indirect intrinsic." The radiation associated with direct transitions has not been detected in silicon, which in this regard is essentially distinguished from germanium (see above).

The supplementary maxima at 1.072 and 1.038 ev are unequivocally associated with the type of impurities introduced into the silicon. In Fig. 5 is shown a diagram of the intrinsic and extrinsic radiative transitions; holes, which are indicated by circles, occur on the average at 3/2 kT below the top of the valence band. Acceptor levels, indicated by dashes, are partly ionized. In this case, injected electrons (solid circles in the conduction band) may recombine either with the holes in the valence band or with the holes in the acceptor levels. In the first case (intrinsic radiation), the photon will have the energy $h\nu_1 = E_g(T) + 3kT_{(\mp)}\ \hbar\omega$, where $\hbar\omega$ is the energy of the phonon through whose participation the law of conservation of momentum is satisfied. In the overwhelming majority of cases, the transitions must be accompanied by the emission of phonons, since the number of phonons which might be absorbed in such a process is very small.

For extrinsic radiation, the participation of phonons is also necessary, at least for impurity

centers with small ionization energies. The emitted photon must have an energy $h\nu_2 = E_g(T) - E_i + 3/2\ kT - \hbar\omega$, where E_i is the ionization energy of the impurity center. On the basis of data on the energy of photons corresponding to the maxima of the intrinsic radiation at 77° and 295°K, and the assumption that $E_g(T) = E_g(0) - \beta T$ (β is the temperature coefficient), the values were obtained: $\beta = 3.3 \times 10^{-4}$ ev/°K, and $E_g(0) = 1.105 + \hbar\omega$. By making use of the conclusion of Kohn[27] that the minimum (1, 0, 0) lies approximately at 3/4 the distance from the center to the limit of the Brillouin zone, and assuming that $\hbar\omega = 0.06$ ev, the authors obtained the values $E_g(0) \cong 1.165$ ev, and $E_g(295°K) = 1.07$ ev. These data are in good agreement with reference[28] and differ slightly with reference 8, where the values are $E_g(0) = 1.21$ ev, and $\beta = 4.2 \times 10^{-4}$ ev/deg K.

The influence of the nature and concentration of the impurities introduced into the silicon on the recombination radiation is shown in Fig. 9. The solid

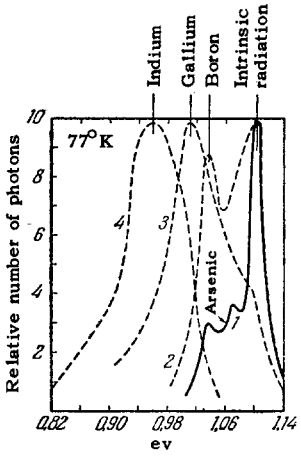


FIG. 9. The influence of the nature and concentration of impurities introduced into silicon on the recombination radiation spectra.

curve 1 coincides with the curve for 77°K given in Fig. 8. Curve 2 corresponds to a 50-fold increase in the concentration of boron, the arsenic concentration being unchanged. The large increase in the maximum at 1.039 ev indicates that this radiation is associated with the recombination of electrons and holes at un-ionized boron atoms. The nature of the maximum at 1.072 ev is not so clear; the author assumes that it is associated with the recombination of holes and electrons at un-ionized As atoms. Replacement of the boron impurity by gallium leads to a shift of the maximum to 1.015 ev (curve 3). The largest shift in the maximum — to 0.960 ev — is attained when the fundamental impurity is indium (curve 4). According to the interpretation of the phenomenon which was given, $E_i = h\nu_1 - h\nu_2 = -3/2\ kT$. In Table II are given the ionization energies, as obtained on the basis of the spectra of the recombination radiation, as determined in reference 29 from the temperature dependence of the conductivity and the Hall effect, and as determined from the spectral distribution of the photoconductivity and absorption.[30]

TABLE II.

Element	E_i (from radiative recombination data) (ev)	E_i (from thermal data)(ev)	E_i (from optical data) (ev)
B	0.051	0.045	0.046
Ga	0.075	0.065	0.071
In	0.13	0.16	0.16
As	0.018	0.049	0.056

For the maximum which was assumed to be associated with donor levels of arsenic, a large discrepancy was found, and could not be explained.

6. RADIATIVE RECOMBINATION IN SEMICONDUCTOR COMPOUNDS (InSb, GaSb, InP, PbS)

An experimental estimation of the total number of photons in the recombination radiation was carried out by Moss and Hawkins[31] for InSb. As in the cases of germanium and silicon, the position of the recombination-radiation band of this semiconductor coincides with the width of the forbidden band ($E_g \cong 0.18$ ev).

Thin plates (about 12 μ) of a single-crystal indium antimonide, purified by zone melting, were used as the sources of radiation in these experiments. Excitation by light was used; the glass lenses by which the light from the tungsten lamp was concentrated on the InSb plate completely eliminated the entire long-wavelength part of the spectrum; the radiation from the InSb was focused on the monochromator slit by an f/0.8 reflector. A sensitive thermopile was used as the radiation detector. The recombination-radiation spectrum of InSb is shown in Fig. 10. On taking into account the absorption and reflection losses, the authors came to the conclusion that the radiative recombinations amount to as much as 80% of the total number of recombinations, and estimated the possible error of their experiments as ±50%. This result agrees with the theoretical predictions (Table I). The number of photons emitted into the surrounding space per second by an InSb plate in Moss' experiments amounted to about 10^{14}; as in the experiments mentioned above with plates of Ge and Si, the greatest losses occurred due to total internal reflection and absorption of the radiation.

Braunstein[32] studied the spectra of the recombination radiation of the intermetallic compounds GaAs, GaSb, and InP, and obtained for all these semiconductors an approximate agreement between

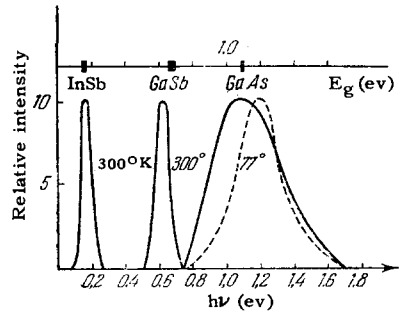


FIG. 10. Spectra of the recombination radiation of intermetallic compounds.

the positions of the emission bands and the absorption edges (Fig. 10). In order to excite the radiation, use was made of injection of the minority carriers from point-rectifying contacts or from large-area contacts made by coating the etched surface of the crystal with silver paste. In comparing the positions of the maxima of the emission bands with the values of E_g of the intermetallic compounds, one must keep in mind the fact that, on account of the insufficient degree of purity and perfection of the crystals, the determination of the "optical" width of the forbidden band Eg_0 is complicated by the presence of other types of absorption not associated with the generation of electron-hole pairs. In these cases, from our point of view, additional data are necessary in order to determine whether the observed emission bands are of intrinsic or extrinsic character. Thus, for instance, the emission maximum of GaSb at 300°K corresponds to 0.625 ev, while the width of the forbidden band is 0.67 ev[33]; this discrepancy, as the author himself points out, occurs also for GaAs. The emission maximum for GaAs corresponded to 1.10 ev at 300°K, whereas the width of the forbidden band, according to the data of Welker,[34] is equal to 1.35 ev. In all the semiconductors studied by Braunstein, the intensity of the radiation was proportional to the direct current through the rectifying junction. This may apparently be explained by the high concentration of excess carriers (about 10^{17} cm^{-3}).

The recombination radiation of lead sulfide was discovered by L. N. Galkin and N. V. Korolev,[35] who studied thin polycrystalline films of this compound. In his most recent study, Scanlon[36] has obtained data on the absorption edge in single crystals of PbS, and has calculated the lifetime of the carriers with respect to radiative recombination; this turned out to be approximately equal to 6×10^{-5} sec at 300°K. Apparently these data are somewhat more accurate than the values given in Table I (about 10^{-5} sec). On the basis of the band structure of PbS, one may not exclude the possibility that two maxima in the intrinsic radiation exist, corresponding to the direct and indirect electronic transitions.

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