

Recombination Radiation from Silicon Under Strong-Field Conditions

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In an attempt to determine the distribution in energy of hot electrons and holes in silicon placed in an intense uniform electric field, measurements have been made of the spectral distribution of recombination radiation at 77°K (field strengths up to 3700 v cm⁻¹) and at 20°K. No change in the spectrum with field was observed, other than a rise in temperature of 6° at 77°K due to Joule heating at 3700 v cm⁻¹ in the sample, from which it was concluded that recombination radiation at these temperatures arises predominantly from the decay of excitons formed from the hot carriers, and that the excitons have a thermal distribution of energy at the lattice temperature. In addition, results are given for the spectrum of the radiation from avalanche breakdown regions in reverse-biased silicon *p-n* junctions at 77° and 300°K; no differences were detected in the range of energies 1.0–1.4 eV, from which it was concluded that exciton decay does not contribute to the observed radiation at 77°K.

INTRODUCTION

MEASUREMENTS of electrical conductivity¹ on a wide variety of semiconducting materials have shown departures from Ohm's law as the electric field strength is increased. The corresponding decreases in mobilities of the charge carriers (electrons or holes) have been interpreted theoretically² as the consequence of carrier heating in strong electric fields. In order that the energy gained by the carriers from the field may continue to be transferred to the lattice as the field increases, the mean energy of the carriers increases from its equilibrium value.

More direct evidence for the existence of hot electrons is provided by observations³ of the impact ionization of neutral impurity atoms in semiconductors at low temperature, and by measurements⁴ of the amplitude of the spin resonance signal from electrons bound to donors at low temperature in silicon, which indicate an increase in the spin temperature under strong-field conditions related to the increase in temperature of hot electrons. In addition, attempts have been made to determine the temperature of hot electrons by measurements of piezoresistance,⁵ and of thermoelectric power,⁶ as a function of electric field strength; these experiments all indicate the existence of heating effects under uniform field conditions.

The experiments to be described here, in which the intensity distribution in the intrinsic recombination radiation from silicon was determined under strong-field

conditions, were undertaken in the hope of measuring directly the distribution in energy of the hot carriers. On the hypothesis that the recombination radiation arises in direct phonon-assisted transitions of electrons from the conduction band to the valence band, its spectral distribution is determined by the energy distribution of the carriers.⁷ However, the results of this investigation indicated⁸ that intrinsic recombination radiation in silicon, at least at temperatures below 77°K, arises predominantly from the decay of excitons rather than from direct recombination of electrons and holes; thus the spectrum of the radiation reflects the distribution of kinetic energies of the excitons. It was therefore not possible to determine the carrier energy distribution from these measurements. The experimental results leading to this conclusion are described in detail in the following paper.

A description is also given of experiments on the radiation emitted from regions where avalanche breakdown is taking place at a reverse-biased silicon *p-n* junction at 77°K and 300°K; in this case, of course, the electric field is extremely nonuniform.

EXPERIMENTAL PROCEDURE

To provide adequate intensity of the recombination radiation, a large excess carrier density must be generated in the semiconductor to which a strong electric field is applied to heat the carriers. This dual requirement was achieved with *p-π-n* diode structures, biased strongly in the forward direction; they were fabricated by the diffusion of boron and phosphorus into opposite sides of a thin wafer of high-resistivity *p*-type silicon (acceptor density $\sim 10^{13}$ cm⁻³), from which were cut samples approximately 1 mm by 0.5 mm. (We use π to denote high-resistivity *p*-type silicon.)

The injected carrier densities (n, p) in the π region of width $2d$ (Fig. 1) and the electric field strength E increased with diode current in the forward direction.

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¹ Reviewed by J. B. Gunn, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1957), Vol. 2, p. 211; S. H. Koenig, *J. Phys. Chem. Solids* 8, 227 (1959).

² W. Shockley, *Bell System Tech. J.* 30, 990 (1951).

³ E. J. Ryder, I. M. Ross, and D. A. Kleinman, *Phys. Rev.* 95, 1342 (1954); W. Kaiser and G. H. Wheatley, *Phys. Rev. Letters* 3, 334 (1959).

⁴ G. Feher, *Phys. Rev. Letters* 3, 135 (1959).

⁵ E. G. S. Paige, *Proc. Phys. Soc. (London)* 72, 921 (1958).

⁶ M. Stenbeck, *Izvest. Akad. Nauk S.S.S.R. Ser. Fiz.* 20, 1560 (1956) [translation: *Bull. Acad. Sciences U.S.S.R.* 20, 1430 (1956)].

⁷ J. R. Haynes, M. Lax, and W. F. Flood, *J. Phys. Chem. Solids* 8, 392 (1959).

⁸ L. W. Davies, *Phys. Rev. Letters* 4, 11 (1960).

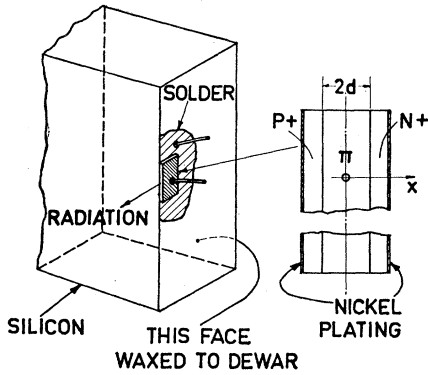


FIG. 1. Mounting of silicon $p\text{-}\pi\text{-}n$ diode, with (inset) details of diode structure.

If n, p are large compared with the equilibrium carrier density in the π region, then⁹

$$\begin{aligned} n = p &= n_0 \cosh(x/L), \\ E &= E_0 \operatorname{sech}(x/L), \end{aligned} \quad (1)$$

where n_0, E_0 are the excess carrier density and electric field, respectively, at the center of the π region, and L is the diffusion length. Thus if

$$d \lesssim L,$$

there is a substantially uniform distribution of excess density and electric field in the π region. Measurements of lifetime by an open-circuit diode voltage decay method¹⁰ gave $\tau = 0.088 \mu\text{sec}$ at 77°K on the sample of Fig. 5 for example, for injection levels $\sim 10^{16} \text{ cm}^{-3}$; combined with an estimated value $\sim 100 \text{ cm}^2 \text{ sec}^{-1}$ for the ambipolar diffusion coefficient, this gives a diffusion length $L = 3.0 \times 10^{-3} \text{ cm}$, somewhat greater than the π -region half-width $d = 2.2 \times 10^{-3} \text{ cm}$. The width of the π region was determined by capacitance measurements, with an accuracy of $\pm 10\%$; the result was in good agreement with the value calculated from the diffusion treatment given in the fabrication process.

The electric field strength in the π region was calculated from the potential drop across the diode, making allowance for the built-in potential at the two junctions, and assuming the PD across p and n regions to be negligible. For the case $d = 0.73 L$ above, we have from Eq. (1)

$$E_0 = 1.085(V'/2d), \quad (2)$$

where V' is the PD across the π region; thus the minimum value of the electric field (at the boundaries of the π region) is

$$E_{\min} = 0.85(V'/2d). \quad (3)$$

In the course of the experiment the diode was biased strongly in the forward direction by a pulse of duration

$1.5 \mu\text{sec}$; the turn-on time was less than $0.5 \mu\text{sec}$ under the experimental conditions and measurements were restricted to the final $1.0 \mu\text{sec}$. When the pulse was turned off, the carriers cooled to lattice temperature in a time $\sim 10^{-10} \text{ sec}$, while the recombination radiation decayed with a time constant $\sim 10^{-7} \text{ sec}$ only. In order to differentiate between recombination radiation emitted by hot and by cold electrons, the detector was gated so that radiation from hot electrons only was allowed to contribute to the results; this stringent requirement of the time constant of the detector led to the choice of a photomultiplier detector.

The experimental arrangement is shown schematically in Fig. 2, with the diode mounting shown in more detail in Fig. 1. The diode was mounted in high vacuum, in good thermal contact through one of its broad faces with a block of silicon $\sim 2 \text{ mm}$ thick to which it was soldered. This block was waxed directly to the copper wall of the Dewar. The face of the diode nearer the spectrometer was polished to increase the output of the recombination radiation; a fivefold enlarged image of the diode was formed at the entrance slit of the spectrometer, whose width was approximately equal to one-third the width of the π -region image.

The pulse generator consisted of a length of coaxial cable charged to the required voltage, and discharged by a mercury contact relay (*WE 276B*) operated by a multivibrator at $\sim 30 \text{ cps}$. The particular unit used was capable of holding off 3 kv , and passed current pulses of up to 60 amp in this application. The resultant current pulse passed through the diode sample and a matching series resistor; the pulse triggered the sweep of a dual beam oscilloscope (*Tektronix 551*) and was displayed on the upper beam. The recombination radiation from the sample was analyzed by a quartz prism spectrometer (Hilger, $f/4.4$) and detected by an infrared photomultiplier tube (*RCA 7102*) cooled to $\sim 90^\circ\text{K}$. The output of the photomultiplier, consisting of pulses (duration $\sim 5 \mu\text{sec}$) which corresponded to the libera-

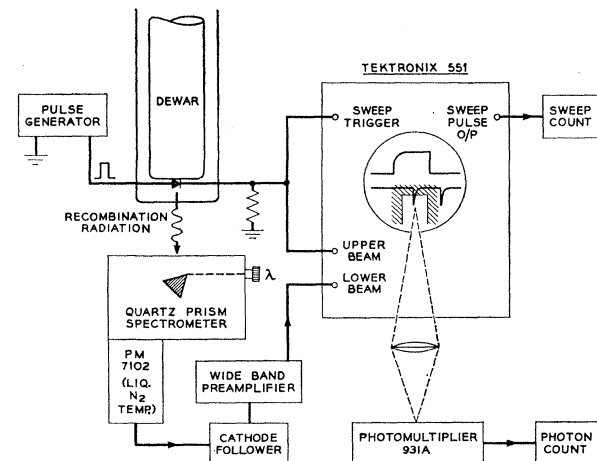


FIG. 2. Block diagram of apparatus.

⁹ A. Herlet and E. Spenke, *Z. angew. Phys.* **7**, 149 (1955).

¹⁰ S. R. Lederhandler and L. J. Giacoletto, *Proc. Inst. Radio Engrs.* **43**, 478 (1955); L. W. Davies, report in preparation.

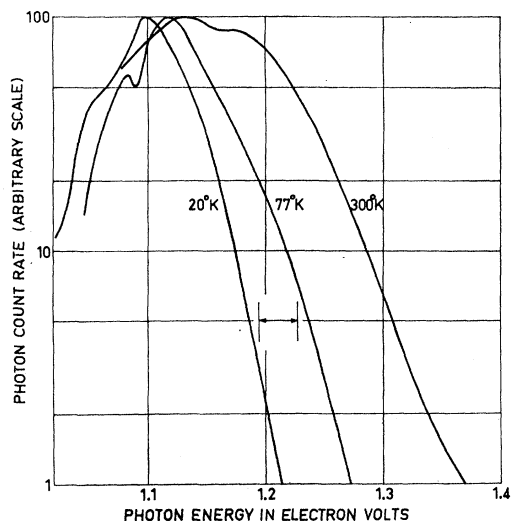


FIG. 3. Observed spectrum of recombination radiation from silicon p - n - n diode at three different temperatures.

tion of individual photoelectrons from the cathode, was amplified and displayed on the lower beam of the oscilloscope. All connecting cables were shielded to obviate spurious pickup signals. By masking the screen of the oscilloscope suitably,¹¹ only those pulse signals were visible which corresponded to the emission of recombination radiation during some chosen interval of the current pulse. An image of the unmasked portion of the screen was formed on the cathode of a 931A photomultiplier, whose output was monitored and counted; the ratio of the counts of 931A output pulses (photons) and oscilloscope sweeps was a measure of the relative intensity of recombination radiation at a given setting of the spectrometer. Relatively large intensities of the radiation could be accommodated by an increase in the sweep speed of the oscilloscope. Owing to radiative transfer in the plane of the oscilloscope screen phosphor there was a small output pulse from the 931A tube even when no photon pulses were displayed on the lower beam; it was necessary to set the triggering level of the 931A output counter to discriminate against these signals. Drift in the vertical position of the lower beam trace, or more rarely in the brightness of the trace could lead to changes in the magnitude of both these types of output signal pulse; the output of the 931A tube was therefore monitored continually, and occasional adjustments made to trace position or screen intensity as required.

Since the resolving time of the 931A output counter [Berkeley 55 10] was $1 \mu\text{sec}$, the occurrence of more than one photon pulse during a sweep was registered as a single count only. It was necessary to make corrections for this defect. In a large number of sweeps with constant probability p of the occurrence of a photon pulse, the probability of r photons occurring during a

sweep is given by the Poisson distribution $p^r \exp(-p)/r!$. If in n sweeps we have n' occasions on which there are one or more photons present, then there are $(n-n')$ occasions on which no photon is observed ($r=0$); thus

$$(n-n')/n = \exp(-p).$$

It follows that the observed ratio of counts, $p' = n'/n$, is related to the required probability p by the expression

$$1 - p' = \exp(-p). \quad (4)$$

The corrections amounted at most to 7% in the measurements at the highest intensity of Fig. 3; in general, however, they were less than this, as it was possible to maintain $p' < 0.1$ by increasing the sweep speed.

In order to determine from the measurements described above the number of photons per unit energy interval of the spectrum, it was necessary to take into account the spectral response of the spectrometer and detector. This was determined from measurements of the known black-body spectrum of the radiation from a graphite block heated to 700°K , in which a hole had been drilled to a depth four times its diameter; the bottom of the hole was imaged on the spectrometer slit. The results were checked with the spectrum of an electric lamp of known color temperature. All measurements of the radiation emitted by sources which were constant in time were carried out with the arrangement of Fig. 2, but with the pulse output of the photomultiplier itself triggering the oscilloscope for a measured time interval.

SPECTRA OF RADIATION FROM P - π - N DIODES

A series of measurements were carried out on several samples at room temperature, and with the Dewar to

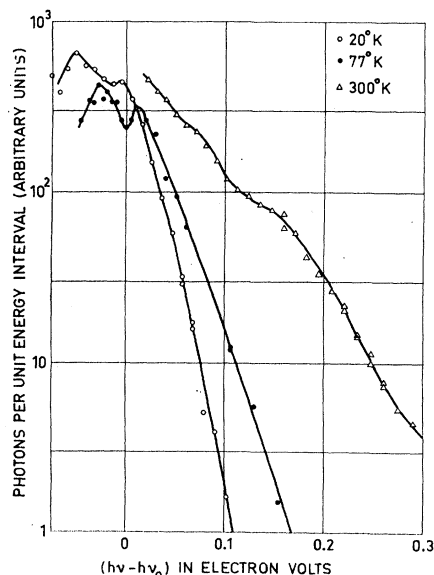


FIG. 4. Spectrum of recombination radiation, corrected for spectral response of the system and for absorption within the sample at three different temperatures.

¹¹ R. Hofstadter and J. A. McIntyre, Rev. Sci. Instr. 21, 52 (1950).

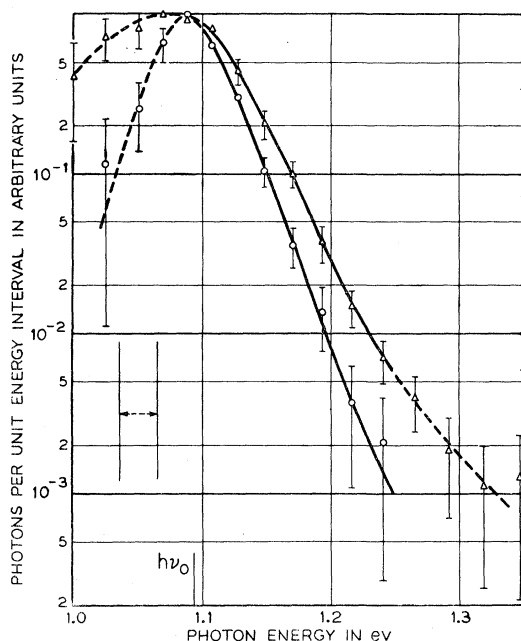


FIG. 5. Spectrum of recombination radiation from silicon p - π - n diode at 77°K, for field strengths of 300 v cm^{-1} (circles) and 3700 v cm^{-1} (triangles).

which the sample was attached filled with liquid nitrogen or hydrogen. The spectrum of the radiation emitted by one sample when passing a current pulse of 5 amp (current density 1700 amp cm^{-2}) is given for each of these temperatures in Fig. 3; normalized values of the photon counting rate are plotted as a function of photon energy. The maximum values of the photon count rates were, respectively, 3550, 11 200, and 131 000 counts sec^{-1} at temperatures of 20°, 77°, and 300°K; however, these figures give only an approximate indication of relative intensities, as the optical arrangement may have differed slightly at different temperatures. The resolving power of the spectrometer is indicated by the half-intensity width of the 1.014 μ line of the mercury spectrum.

These results were corrected for the spectral response of the system and for absorption within the sample¹² using known values¹³ of the absorption coefficient in silicon; the resulting spectra of the radiation generated within the semiconductor at each temperature are shown in Fig. 4. The relative number of photons per unit energy interval (with the same normalizing factors as used in Fig. 3) is plotted as a function of the energy difference $(h\nu - h\nu_0)$; $h\nu$ is here the photon energy, and $h\nu_0$ the energy located by extrapolation of the low-energy side of the principal recombination band observed by Haynes⁷ (emission of optical phonon) to zero number of photons: for temperatures of 20°, 77°, and 300°K,

Haynes' measurements give values of $h\nu_0$, respectively, 1.097, 1.093, and 1.052 eV.

In an attempt to determine the energy distributions of electrons and holes under hot-electron conditions, a number of measurements were made with slightly better resolution on the radiation emitted at 77°K by another sample, for which values of the field strength in the π region [E_{\min} , Eq. (3)] were calculated to range from 300 v cm^{-1} to 3700 v cm^{-1} . Measurements at the two extreme values of the field are shown⁸ in Fig. 5, together with an indication of the resolving power; the results have been corrected for spectral response of the system and for absorption in the sample. The normalizing factor amounted to 22. The range of values shown above and below each experimental point is calculated as three times the standard error of the corrected ratio of counts; it is improbable that the true value lies outside this range, from the point of view of counting statistics. The injected carrier density in the two cases was calculated on an approximate basis from a comparison of the recombination radiation intensity at 77°K with that at 300°K, where the injected density had been determined by open-circuit measurements of post-injection voltage across the diode; on taking into account the change in lifetime, with the assumption that the radiation intensity is proportional to the square of the carrier density, the values obtained were $3 \times 10^{17} \text{ cm}^{-3}$ and $1.5 \times 10^{18} \text{ cm}^{-3}$; these values are believed to be accurate only within an order of magnitude.

Measurements of this type were also carried out at liquid hydrogen temperatures; no change in the recombination radiation spectrum was detected for current densities of 1700 amp cm^{-2} and 5100 amp cm^{-2} , for which the field strengths in the π region were calculated, respectively, as 580 v cm^{-1} and 830 v cm^{-1} .

DISCUSSION

In all the spectra obtained of the recombination radiation from p - π - n diodes there were considerable contributions at photon energies $h\nu \leq h\nu_0$. This contrasts with results obtained⁷ from high-purity samples in which excess carrier densities were created by photo-ionization within the sample. The relative intensity of radiation at energies ~ 0.05 eV less than $h\nu_0$, and at energies greater than $h\nu_0$, was found to vary widely from sample to sample, and also to vary as different portions of the p - π - n structure were brought to a focus on the entrance slit of the spectrometer. In some spectra at 77°K a prominent band was observed, centered at photon energies 0.05 eV less than $h\nu_0$, and coinciding in frequency within experimental error with extrinsic recombination bands observed in boron-doped silicon by Haynes and Westphal,¹⁴ and in phosphorus-doped silicon by Silhouette.¹⁵ From these observations it was

¹² J. R. Haynes, Phys. Rev. **98**, 1866 (1955).

¹³ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **111**, 1245 (1958).

¹⁴ J. R. Haynes and W. C. Westphal, Phys. Rev. **102**, 1676 (1956).

¹⁵ D. Silhouette, Mémoire, Université de Paris, 1959 (unpublished).

concluded that a portion at least of the radiation at these energies was probably extrinsic in nature, associated with radiative recombinations of electrons and holes with unionized acceptors and donors, respectively, in the heavily doped regions at the boundaries of the π region.

The spectra in Fig. 4 show a broadening to higher energies⁷ ($h\nu > h\nu_0$) as the lattice temperature is increased; as we shall see, this corresponds to an increase in the mean thermal energies of the excitons in silicon as the temperature is raised.

The data of Fig. 5 were obtained in an attempt to determine the energy distributions of electrons and holes under hot-electron conditions, as the field strength in the π region was increased. For the case in which the calculated field strength in the π region was 3700 v cm^{-1} there was an increase in the relative intensity at higher photon energies, but this will be shown to arise from Joule heating in the sample for the duration of the current pulse.

An estimate of the temperature for the high-field case can be made on either of two hypotheses. In the first place, if we assume that the recombination radiation for $h\nu > h\nu_0$ arises from the direct phonon-assisted recombination of electrons and holes, the number of photons N_ν per unit energy interval can be calculated on the basis that the electrons and holes have an equilibrium distribution of energies at some temperature T . If we sum over the various phonon contributions, a formula due to Lax,⁷ which is in reasonable agreement with experiment, gives

$$N_\nu \propto \sum_i (1 - \nu_{0i}/\nu) \exp(-h\nu/kT), \quad (5)$$

where $h\nu_{0i}$ is the energy of the photon emitted when an electron and a hole, each of zero thermal energy, recombine directly with the cooperation of the i th phonon. On the other hand, if we assume that the observed recombination radiation arises entirely from the decay of excitons formed by the hot electrons and holes in the semiconductor, the number of photons N_ν per unit energy interval can be calculated on the basis that the excitons have a thermal distribution of kinetic energies at some temperature T . If a summation is again made over the various phonon-cooperation processes, and the probability of radiative decay of the exciton is assumed independent of its kinetic energy, we find

$$N_\nu \propto \sum_i (\nu - \nu_{0i})^{\frac{1}{2}} \exp(-h\nu/kT). \quad (6)$$

If now a comparison is made of two spectra at approximately the same lattice temperature (change in value of $h\nu_0$ insignificant), but with different carrier temperatures T_1 and T_2 , we obtain from Eq. (5), on the first hypothesis,

$$N_{\nu 1}/N_{\nu 2} = \exp\{-(h\nu/k)(T_1^{-1} - T_2^{-1})\}. \quad (7)$$

If a comparison is made on the second hypothesis [Eq. (6)], for cases in which the excitons have thermal dis-

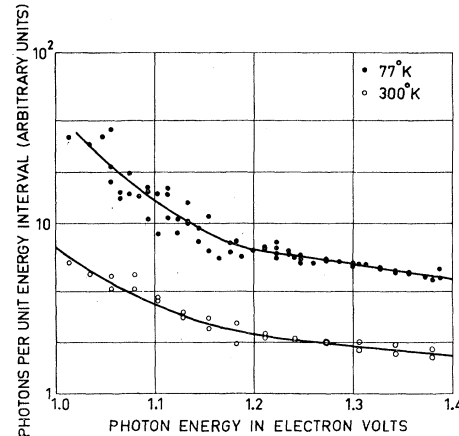


FIG. 6. Spectrum of radiation emitted from avalanche breakdown region of reverse-biased silicon p - n junction at 77°K and 300°K .

tributions of energy at temperatures T_1 and T_2 , we again obtain the ratio (7). Thus Eq. (7) may be used to analyze the data of Fig. 5, whichever hypothesis is relevant. It is worth noting that such analysis is independent of errors in the calibration of the spectral response of the system, provided the system resolving power is adequate.

At the lowest value of the field (300 v cm^{-1}) we have assumed that the charge carriers and excitons had thermal distributions of energy at the lattice temperature, i.e., $T_1 = 77^\circ\text{K}$. With the aid of Eq. (7) the value of T_2 was found which provided closest agreement with the spectrum observed at 3700 v cm^{-1} ; the two full curves in Fig. 5 are related according to Eq. (7), with a value $T_2 = 83^\circ\text{K}$. A series of measurements of spectra at values of the field strength intermediate between those of Fig. 5 showed a monotonic increase in T_2 .

A subsequent calculation of the amount of Joule heating within the π region of the sample during the current pulse yielded a temperature rise of 7°K at the mean time of observation during the pulse at 3700 v cm^{-1} ; since the thermal time constant of the diode was $\sim 10 \mu\text{sec}$, it could be assumed that it cooled to 77°K between pulses. Since this temperature rise coincided almost exactly with the temperature difference ($T_2 - T_1$) determined from Fig. 5, it was concluded that the changes observed in the recombination spectrum at increasing field strength originated entirely from Joule heating.

Although no direct observations have been made of departures from Ohm's law, or of other consequences of carrier heating, under the conditions of this experiment, it is believed that carrier heating effects were taking place at a field strength as large as 3700 v cm^{-1} . Prior¹⁶ has shown that there is only a small departure from Ohm's law in high-resistivity p -type silicon at room temperature, for fields of this magnitude. On the other

¹⁶ A. C. Prior, J. Phys. Chem. Solids **12**, 175 (1959).

hand, measurements¹⁷ of drift velocity in *n*-type silicon at 77°K show marked departures from Ohm's law at fields greater than 700 v cm⁻¹. If this result is compared with calculations¹⁸ made for germanium, a reasonable estimate is that the carrier temperature in these experiments at 3700 v cm⁻¹ was at least twice the lattice temperature. Such a temperature rise would have been easily detected in this work, if the electrons and holes had recombined directly with the cooperation of phonons. We must therefore conclude that the observed recombination radiation at 77°K arises substantially from the decay of excitons formed by the hot carriers, and furthermore that the excitons have a thermal distribution of energies at a temperature equal to that of the lattice.

These conclusions were further supported by the measurements made at 20°K, at field strengths estimated from Eq. (3) to be 580 v cm⁻¹ and 830 v cm⁻¹. In this case no measurement of the lifetime was made at the temperature of the observations, so that the distribution of excess charge and field strength within the π region according to Eq. (1) was an estimate only, based on the assumption that the lifetime did not change between 77°K and 20°K. Kaiser and Wheatley⁸ have observed avalanche breakdown, indicating electron heating effects, at fields 300 v cm⁻¹ in *n*-type silicon at 20°K, and departures from constant mobility at fields as low as 10 v cm⁻¹; therefore the observation of an unchanged spectral distribution at fields of this order, but differing by a factor 1.4, is further evidence for a radiative process involving the decay of excitons, in this case at liquid hydrogen temperatures.

The evidence available until now has not enabled one to differentiate unambiguously between the two possible mechanisms, outlined above, for the emission of recombination radiation. High-resolution absorption measurements^{13,19} on silicon at low temperature reveal effects associated with absorption by the formation of excitons, from which it would be concluded that emission at low temperature from samples containing an excess carrier density occurs by the decay of excitons. On the other hand, from observations of the emission radiation at increasing temperature, Haynes *et al.*⁷ concluded that the radiation is either all due to the recombination of electrons and holes, or all due to exciton decay, and that electron-hole recombination should dominate at room temperature. The results given here support an exciton decay process as the principal origin of the recombination radiation ($h\nu > h\nu_0$) in silicon at temperatures $\leq 77^\circ\text{K}$. Further evidence for this conclusion has since been obtained by Haynes²⁰ from an analysis of the line shape of the recombination radiation

at 83°K. On taking into account collisional broadening of the ground state of the exciton,²¹ Eqs. (5) and (6) have been used to fit the experimental results; Haynes concludes that approximately one-eighth of the radiation at this temperature originates in direct recombinations, the remainder in exciton decay processes.

The observations of Fig. 5 show the excitons in silicon under hot-electron conditions to have a thermal distribution of energies at the lattice temperature; at the same time their density is much greater than the equilibrium value at this temperature, and is presumably close to that in equilibrium with the injected carrier density, at the carrier temperature. It follows that the excitons formed from hot electrons and holes either lose substantial amounts of their energy to the lattice before decaying, or that they are formed preferentially from low-energy electrons and holes of the distribution. Interaction between electrons and holes could rapidly make up this drain on the low-energy range of the distributions.

RADIATION FROM AVALANCHE BREAKDOWN

It is known^{22,23} that the spectrum of the radiation emitted from avalanche breakdown regions in reverse-biased, diffused *p-n* junctions in silicon at 300°K extends to photon energies of at least 3.3 eV. The radiation has been attributed to two processes acting together: the direct (phonon-assisted) recombination of hot electrons and holes, responsible for photons of higher energy, and radiative intraband transitions of carriers which contribute to the radiation at the low-energy end of the spectrum, particularly that for which $h\nu \leq h\nu_0$. The photon energy at which the two processes become comparable is not known; if it is slightly greater than the energy gap, as suggested,²³ then we may hope to observe a significant change in the spectrum ($h\nu > h\nu_0$) as the sample temperature is reduced to 77°K, where the present paper shows that radiation from the direct recombination of hot electrons and holes gives way to radiation from exciton decay, with the excitons at lattice temperature.

We have measured the spectrum of the radiation emitted from avalanche breakdown regions along the edge of a diffused silicon junction²⁴ at 300°K and 77°K; the results obtained are shown in Fig. 6. The sample was again mounted in good thermal contact with a Dewar vessel in high vacuum (see Fig. 1), and a continuous current (30–60 ma) passed in the reverse direction; the equipment was less stable than for the previous experiments, which accounts for the spread of experimentally determined values in Fig. 6. No change occurred in the visual appearance of the breakdown region on cooling.

The results indicate no difference in the spectrum at

¹⁷ J. Bok, *Solid-State Physics in Electronics and Telecommunications* (Academic Press, Inc., New York, 1960), Vol. 1, p. 475.

¹⁸ R. Stratton, *J. Electronics and Control* **5**, 157 (1958).

¹⁹ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, *J. Chem. Phys. Solids* **8**, 388 (1959).

²⁰ J. R. Haynes (private communication).

²¹ This effect may give rise to part of the radiation observed here at energies $h\nu \leq h\nu_0$.

²² R. Newman, *Phys. Rev.* **100**, 700 (1955).

²³ A. G. Chynoweth and K. G. McKay, *Phys. Rev.* **102**, 369 (1956).

²⁴ Kindly lent by A. G. Chynoweth; breakdown voltage ~ 20 v.

77°K and 300°K, within experimental error, in the range of photon energies 1.0–1.4 eV. The results at 300°K are in good agreement with those of Chynoweth and McKay.²³ Taking into account that $h\nu_0=1.093$ eV at 77°K, we conclude that there is no detectable contribution to the radiation at 77°K in these experiments from an exciton decay process. If the two processes outlined above are jointly responsible for the radiation, that from the intraband transitions must therefore extend to energies $\gtrsim 1.2$ eV, so that the transition from intraband radiation to interband radiation takes place at energies considerably in excess of the band gap. In this connection, from an analysis of the spectral distribution of avalanche breakdown radiation in germanium, Wolff²⁵ has concluded that the transition in germanium occurs at an energy of 1.3 eV, i.e., approximately twice the band gap energy.

Note added in proof. A further statement on the ab-

²⁵ P. A. Wolff, J. Phys. Chem. Solids (to be published).

sence of exciton decay contributions to the avalanche breakdown radiation at 77°K has been privately communicated by A. G. Chynoweth. The critical field for dissociation of excitons is estimated to be of the order of the exciton binding energy (8×10^{-3} eV) divided by its effective radius (100 Å), i.e., 8 kv cm^{-1} . It is thus reasonable to expect the high field in the avalanche region to dissociate the exciton, if formed, so that no decay radiation is observed. The greatest field strength investigated here in $p\text{-}\pi\text{-}n$ structures was 3.7 kv cm^{-1} (see Fig. 5), less than half the estimated critical field for exciton dissociation.

ACKNOWLEDGMENTS

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Energy Bands in the Bismuth Structure. I. A Nonellipsoidal Model for Electrons in Bi

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(Received September 6, 1960)

The band structure near a minimum at a point of no special symmetry is examined for energies small compared to all band gaps except that to the next lower band. Spin-orbit coupling is included. The theory is specialized to points having the three possible symmetries of electrons in Bi and further simplifications appropriate to Bi made. The resulting nonellipsoidal energy surfaces are studied in some detail. An experiment is suggested which is capable of distinguishing between the three possibilities. Fitting the model to existing information is not carried out in this paper.

I. INTRODUCTION

THE interpretation of the very considerable body of information bearing on the structure of the conduction band in bismuth has usually been on the parabolic ellipsoidal model of Shoenberg.^{1,2} In this model, the electrons occupy six sets of ellipsoidal energy surfaces.³ One set of ellipsoids is given by

$$E(\mathbf{p}) = (\alpha_{xx}p_x^2 + \alpha_{yy}p_y^2 + \alpha_{zz}p_z^2 + 2\alpha_{yz}p_y p_z)/2m, \quad (1)$$

where x and z are chosen along a dyad axis and the triad axis, respectively, and the crystal momentum \mathbf{p}

is measured from the position of the nearest minimum in the conduction band. Two other sets are obtained by rotation of $\pm 120^\circ$ around the triad axis, the remaining three by inversion. Because one principal axis lies along a dyad axis, symmetry requires that the six energy minima lie either on the dyad axes or on the reflection planes normal to them. Typical values of the α_{ij} are those derived from a combination of de Haas-van Alphen^{1,2,4} and cyclotron resonance data^{5,6} by Aubrey and Chambers⁶:

$$\alpha_{xx}=202, \quad \alpha_{yy}=1.67, \quad \alpha_{zz}=83.3, \quad \alpha_{yz}=8.33, \quad (2)$$

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¹ D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

² D. Shoenberg, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. 2, Chap. 8.

³ G. E. Smith, Phys. Rev. **115**, 1561 (1959).

⁴ J. S. Dhillon and D. Shoenberg, Phil. Trans. Roy. Soc. (London) **A248**, 1 (1955).

⁵ J. E. Aubrey and R. G. Chambers, J. Phys. Chem. Solids **3**, 128 (1957).

⁶ J. E. Aubrey (private communication), and thesis, Cambridge University, 1959 (unpublished).