In conclusion, the evidence available from measurements on aluminum, vanadium, tin, and thallium (possibly also indium) strongly supports the contention that the electronic specific heat in the superconducting phase is an exponential function of temperature. However, the variation in the values of the constants A and α does not yet permit the existence of a law of corresponding states to be concluded without reservation.

5. ACKNOWLEDGMENTS

We wish to acknowledge the considerable assistance in the experimental work provided by Mr. Edgar E. Magee, Jr., and the technical assistance of Mr. George Smith. We wish also to record our appreciation of the assistance to the low temperature program at Amherst College provided by Research Corporation, who made available a research assistantship for Mr. Magee, and by the National Science Foundation.

PHYSICAL REVIEW

VOLUME 105, NUMBER 4

FEBRUARY 15, 1957

Ionization Rates for Holes and Electrons in Silicon

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The ionization rates for holes and electrons in silicon at high electric fields have been evaluated from data on the multiplication of reverse-biased junctions. In Si, electrons have a higher ionization rate than holes. The variation of ionization rate with field strength is in good agreement with theory.

INTRODUCTION

T has been demonstrated that in both germanium and silicon, reverse biased junctions break down as a result of a solid state analog of the Townsend β -avalanche theory.¹⁻³ In germanium it was possible to detect the difference between the roles of holes and electrons in the breakdown process.³ Differences in the functional form of multiplication vs reverse voltage, depending on whether the initial current entering the junction consisted of holes or electrons, were analyzed to give the ionization rates for holes and electrons as a function of field strength. In the case of the silicon experiments,² the initial currents entering the junction were composed of both holes and electrons; and the detection of a difference between their ionization rates was rendered either difficult or impossible.

In the work reported here for silicon, initial current consisted of predominantly one carrier type; and differences between the ionization rates for holes and electrons were detected.

It is interesting that in silicon the ionization rate is higher for electrons than for holes, while the opposite holds in germanium.

As in Ge, the ionization rates, as a function of field, could be brought into agreement with Wolff's⁴ theoretical treatment of the problem by a suitable choice of parameters.

THEORY

The Townsend β -discharge theory for solids, pictures multiplication and breakdown of pn junctions as occurring when electrons and/or holes are accelerated to energies sufficient to create hole-electron pairs by collisions with valence electrons. This can occur in the high fields in the depletion region of a reverse biased junction. Electrons or holes, entering the depletion region from the p or *n* side of the junction, respectively, create electron-hole pairs. These collision products are then accelerated until they have sufficient energy for pair production and so on. This gives a multiplication of the original current appropriate to every field distribution and therefore every voltage for a given junction. This multiplication, for an original current composed of only one type of carrier, is given by³

$$1 - \frac{1}{M} = \int_0^w \alpha_i(E) \exp\left[-\int_0^x \left[\alpha_i(E) - \beta_i(E)\right] dx'\right] dx, (1)$$

where M is the multiplication, w is the width of the depletion region, and $\alpha_i(E)$ and $\beta_i(E)$ are, respectively, the ionization rates for the initial and secondary particles.

For a complementary set of step junctions consisting of a pn^+ and np^+ with the same net density of impurity centers on the high resistivity side, it is possible to solve for the ionization rates for holes and electrons separately if the multiplication of initial current coming from the high-resistivity side vs voltage conforms to the empirical law

$$M = \frac{1}{1 - (V/V_B)^n}.$$
 (2)

Then the expression for the ionization rate of the initial

¹ K. G. McKay and K. B. McAfee, Phys. Rev. 91, 1079 (1953).
² K. G. McKay, Phys. Rev. 94, 877 (1954).
³ S. L. Miller, Phys. Rev. 99, 1234 (1955).
⁴ P. A. Wolff, Phys. Rev. 95, 1415 (1954).

particle at the maximum field in the junction is of the form³

$$\alpha(E_M) = \frac{2n_{\alpha}}{W_B} \left(\frac{E_M}{E_{MB}}\right)^{2n_{\alpha}-1} \times \exp\left[\frac{1}{2}W_1^2 \int_0^{E_M} (\alpha_i - \beta_i) dE\right], \quad (3)$$

where W_B is the width of the junction and E_{MB} the maximum field in the junction at breakdown. W_1 is the width of the junction at 1 volt total reverse bias in magnitude (dimensionally cm/voltsⁱ) and n_{α} is the appropriate parameter in Eq. (2) for the junction in which the initial particle is α . The exponential term in (3) is given by

$$\exp\left(-\frac{1}{2}W_1^2\int_0^{E_M}(\alpha_i-\beta_i)dE\right)=-\frac{H'(y)}{H(y)},$$

where $y = (E_M / E_{MB})^{2n\beta}$ and H is the solution to the Bessel-type equation

$$H^{\prime\prime}-(n_{\alpha}/n_{\beta})y^{(n_{\alpha}/n_{\beta})-1}H=0.$$

Here n_{β} is the value of the parameter in Eq. (2) for the complementary junction. W_B and E_{MB} are determined from breakdown voltage experiments. Therefore a complete solution for $\alpha_i(E_M)$ and $\beta_i(E_M)$ for any value of $E_M \leq E_{MB}$ is obtainable from measurement of n_{α} and n_{β} appropriate to the set of complementary junctions.

EXPERIMENT

In a previous paper³ it has been shown that accurate multiplication data is most easily gathered from experiments on transistors. One of the principal reasons for this is that the injected current coming from the emitter and entering the reverse biased collector is then uniformly either electrons or holes depending on whether npn or pnp transistors are used. However, because suitable transistors were not available, the multiplication measurements in silicon were conducted with diodes. The carriers were injected on the high-resistivity side of the step junctions by means of light irradiation.



FIG. 1. Plot of 1-1/M vs V/V_B for an np^+ Si step junction with V_B approximately 35 volts (slope=1/3.7) and for a pn^+ Si step junction with V_B approximately 39 v. (Slope= $\frac{1}{2}$.)

TABLE I. The parameter n as a function of breakdown voltage and conductivity type.

п	VB	High- ρ side of step junction
4 3.7 3.7 3.4 2.0 1.9 1.4	47.5 35 17 6.5 39 34 13	n type $n type$ $n type$ $n type$ $p type$ $p type$ $p type$ $p type$

Since the junctions, for which multiplication data are given below, were made by an alloy process, a metallic layer covered the low-resistivity side and prevented injection of carriers on that side of the junction. Furthermore, the lifetime on the low-resistivity side is considerably lower than on the high side and therefore many more of the optically generated minority carriers would reach the junction from the high- rather than from the low-resistivity side if there were injection on both sides.

The validity of this kind of measurement was checked for the case of a Si graded junction between moderate resistivity p and heavily doped n material. The variation of multiplication with voltage was the same for carriers injected by light irradiation as it was for electrons injected by a nearby junction on the p side.

Junction current was measured as a function of junction reverse bias. The increase of current with bias was considered to be the result of avalanche multiplication. These curves were taken at several different initial current levels (or injection levels). This confirmed the supposition that the increase in current was multiplicative rather than due to some kind of leakage. The values of the parameter n in Eq. (2) were obtained for a range of np^+ and pn^+ Si junctions, in which the empirical formula (2) was found to hold, by plotting $\ln(V/V_B) vs \ln(1-1/M)$. Figure 1 shows typical plots of such data for both an np^+ and a pn^+ junction. Table I gives the values of n determined in this manner.

In silicon, there is a significant departure from the empirical multiplication expression, $M = [1 - (V/V_B)^n]^{-1}$, for junctions with higher breakdown voltages. This makes the method of analysis described above inapplicable at field strengths below about 350 kv/cm. In general, at these lower field strengths and higher breakdown voltages the multiplication falls off more rapidly in both np^+ and pn^+ junctions because the ionization rates are steeper functions of field in this region.

The other information necessary for calculation of the ionization rates is the width of the junction and the maximum field in the junction at breakdown. These data are obtained from measurement of the breakdown voltage, V_B , as a function of N_I , the net density of impurity centers on the high resistivity side of the step



FIG. 2. The breakdown voltage of Si step junctions as a function of the net number of impurity centers per cc on the high-resistivity side of the junction.

junction Then

where

$$W_1 = [1.317 \times 10^7 / N_I]^{\frac{1}{2}}$$
 for Si,
 $E_{MB} = 2V_B / W_B$.

 $W_B = W_1 (V_B)^{\frac{1}{2}},$

Figure 2 gives the results of measurements of V_B vs N_I for np^+ and pn^+ Si step junctions. The net number of impurity centers for each junction was determined from measurements of capacitance per unit area. This data is in good agreement in the region of overlap with data given by $McKay^2$ for np^+ junctions when resistivity is converted to N_I by use of Prince's⁴ mobility values. When the data of Herlet and Patalong⁵ on V_B vs ρ for ρn^+ junctions are similarly converted to V_B vs N_I , there is distinct disagreement. The data of Herlet and Patalong can be brought into agreement with Fig. 2 if their resistivity values are halved. Perhaps this resistivity discrepancy is caused by thermal resistivity changes wrought by the diode fabrication process. The identity in V_B for the same N_I for np^+ and pn^+ junctions, shown in Fig. 2, is in agreement with the situation in Ge and the theory.³ Incidentally, from Fig. 2 it appears that V_B can be represented by $V_B = K N_I^{-0.66}$ from 10 v to 300 v for Si. The deviation from this law at high values of N_I is a reflection of the tendency toward saturation of ionization rates at very high field strengths.⁴ The fact that at no point is there any tendency toward a slope of -1 on this logarithmic plot also shows that there is no breakdown attributable to ordinary Zener breakdown³ (constant critical field) even well above maximum field strengths of 10^6 v/cm. Multiplication of injected current increasing to breakdown was clearly observed in junctions down to a breakdown voltage of 6.5 v.

From the above data, namely the n values and the V_B vs N_I curve for Si, two sets of complementary junctions were chosen for calculation of electron and hole ionization rates. These were

Set I: $V_B=13$, $n_{\alpha}=1.4$, $n_{\beta}=3.7$, $E_{MB}=660$ kv/cm, Set II: $V_B=35$, $n_{\alpha}=1.9$, $n_{\beta}=3.7$, $E_{MB}=520$ kv/cm.

Here, n_{α} refers to multiplication with electrons as original particles, n_{β} refers to holes as original particles. The values of $\alpha_i(E_M)$ and $\beta_i(E_M)$ were determined for (E_M/E_{MB}) equal to 0.95, 0.85, and 0.75 and are plotted in Fig. 3 along with the previously determined values for Ge³ for comparative purposes. Again, as in Ge, points obtained from the two sets of junctions are in excellent agreement with each other as they should be if ionization rates are only a function of field strength. The ionization rate for electrons is greater than that for holes in Si whereas the opposite holds true for Ge. This situation is reflected in the inversion of the relative values of n_{α} and n_{β} for the two semiconductors

There is a check possible on the ionization rates determined as above. It can be shown that the quantity $(-4/W_{1^{3}})(dW_{1}/dE_{MB})$, which was used by McKay to determine the ionization rate at E_{MB} when the difference between holes and electrons is neglected, should lie between the ionization rates for holes and electrons at E_{MB} . This quantity when evaluated from the V_B vs N_I data given in Fig. 2 falls almost exactly halfway between the curves for holes and electrons shown in Fig. 3. What this means is that the breakdown data are consistent with the multiplication data.

⁴ M. B. Prince, Phys. Rev. 93, 1204 (1954).

⁵ A. Herlet and H. Patalong, Z. Naturforsch. 10a, 584 (1955).

Wolff's theory⁴ allows a theoretical calculation of ionization rate vs electric field strength involving the proper choice of two parameters, the energy threshold for electron-hole pair production, E_0 , and the mean free path for electron (or hole) phonon collisions, λ . Theoretical curves for electrons and holes, calculated with $E_0 = 1.5$ ev and $\lambda = 70$ A and $E_0 = 3.5$ and $\lambda = 100$ A, respectively, are also shown in Fig. 3. They are in fair agreement with the experimental data It is surprising that the energy threshold required for a fit should be so different for electrons and holes However, the numbers obtained do agree with data given by McKay and McAfee¹ on the efficiency of ionization for α particles bombarding silicon They report 3.6 ± 0.3 electron volts per electron-hole pair produced. If it is assumed that the electrons and holes, which are the end products of the shower resulting from the α particle, are each uniformly distributed in energy between the respective band edge and energy threshold, then on the average the energy necessary to create an electron-hole pair would be the sum of the energy gap, one-half the E_0 for electrons, and one-half the E_0 for holes. This gives 1.1 ev+(1.5/2) ev+(3.5/2) ev=3.6 ev.

It is possible that the unexpectedly very different threshold values obtained for electrons and holes in fitting the theory and the experimental data are a reflection of the inadequacy of the theory. For example, the mean free path for phonon collisions may not be constant. On the other hand, the vastly different band structure for electrons and holes in silicon could be responsible for large differences in the threshold for pair production for the two particles. If the exact shape of the bands were known, it would be possible to compute the thresholds. For example, in the case of spherical energy surfaces, the threshold would be 1.5 times the energy gap for electron and hole masses taken equal.⁴

CONCLUSIONS

Ionization rates for electrons and holes in high fields have been obtained from multiplication and breakdown data for Si junctions. Whereas in Ge the ionization rate was higher for holes, in Si the ionization rate is higher



FIG. 3. The ionization rates for holes and electrons in Si and Ge. $\circ \bigtriangleup \bigtriangledown \Box$ denote experimental data. Dashed lines indicate theoretical curves.

for electrons than for holes. The best fitting of Wolff's theory for the variation of ionization rate with electric field to the experimental data for the two particles yields the following parameters:

- Energy threshold for pair production by electrons, 1.5 ev; by holes, 3.5 ev.
- Mean free path for phonon collisions by electrons, 70 A; by holes, 100 A.

ACKNOWLEDGMENTS

The author wishes to acknowledge the considerable assistance in the preparation of junctions and data gathering of W. C. Meyer and J. R. DeCostanzo and the many discussions on this subject with K. G. McKay and P. A. Wolff.