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A SUMMARY OF THE MEASUREMENT AND INTERPRETATION OF THE HALL COEFFICIENT AND RESISTIVITY OF SEMICONDUCTORS

by D. Michael Stretchberry

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ABSTRACT

Previously published methods of measuring and interpreting the Hall coefficient and resistivity of semiconductors are summarized. The conventional and van der Pauw methods of measurement are briefly discussed. Mobility is shown to be a function of carrier scattering in a specific semiconductor. The equations for charge carrier concentration are developed for both extrinsic and intrinsic conduction. These equations are then used as the basis for interpreting the measured experimental data. The analysis of the data near the intrinsic range and the temperature range over which the experimental measurements must be made are specified.

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SUMMARY

A knowledge of the parameters of semiconductor material is important both for basic materials research and for device development. An analysis of Hall coefficient and resistivity data measured over a temperature range will yield several of these parameters, such as the impurity doping concentrations, the impurity ionization energy, the band gap energy, and mobility. The measurement and interpretation of the Hall coefficient and resistivity are summarized from the available literature.

The conventional and van der Pauw methods of measuring Hall coefficient and resistivity are briefly discussed. The van der Pauw method was found to be advantageous for small samples.

The mobility of semiconductors is also discussed. It is related to an energy-averaged relaxation time, which is a characteristic of a particular scattering process and a specific semiconductor material. The different kinds of scattering are qualitatively discussed. The factor α, which relates the Hall coefficient to the carrier concentration, is also a function of relaxation time.

The equations for charge carrier concentration are developed for both extrinsic and intrinsic conduction. They are found to be functions of temperature and the various semiconductor parameters. These equations are then used as the basis for interpreting the measured experimental data. The method of interpretation is to estimate the equation parameters and then to calculate the carrier concentration at each temperature of interest. The parameters are varied until the calculated results match the experimental data.

The shape of the Hall coefficient and resistivity against temperature curves near intrinsic conduction is shown so that intrinsic data can be interpreted correctly.

The temperature range over which the experimental measurements must be made is discussed. There are certain characteristic parts of the plot of the logarithm of the carrier concentration against reciprocal temperature from which data must be included for extrinsic or intrinsic interpretation.

INTRODUCTION

The NASA-Lewis Research Center is currently engaged in a program which includes the determination of the basic properties of semiconductor materials, particularly for high-temperature applications. The ultimate objective is the development of devices that operate at temperatures greater than 500° C (773 K). The measurement and analysis of the Hall coefficient and resistivity as a function of temperature was picked as the method for determining the desired properties. Although there are other ways of obtaining these properties, this method is the most popular and has been used since the early days of semiconductor research. The derivations of the pertinent equations and the methods of analysis which result are well known (refs. 1 and 2). But, it was realized that the literature does not emphasize the use of the derived equations for the interpretation of experimental data and that no single source contains all of the required information. Therefore, a literature search was started, and this summary report resulted. The purpose of this report is to make available the collected information to the researcher who wants to begin using the Hall coefficient and resistivity methods. More details of the methods can be found in the references cited. This report has proved very useful to our program and should be equally useful to others.

This report summarizes the use of the Hall coefficient and resistivity data as a function of temperature to obtain several of the electrical properties of semiconductors, such as mobility, doping concentrations, the ionization energy of the major dopant, and the band gap energy. The topics discussed are applicable to all semiconductors and not limited to those suitable for high-temperature use. The introductory sections are concerned with the applicability of Hall coefficient and resistivity data (ref. 3), the measurement of these quantities (refs. 1 and 4), and the charge carrier mobility in semiconductors (refs. 5 to 8). These sections are included for a complete discussion of the problem of interpreting the data.

The applicability of the Hall coefficient and resistivity to a basic materials research program and to a device development program is illustrated by specific examples. Several of the parameters upon which device design depends are directly obtained from Hall data. The conventional and the van der Pauw methods of measurement are briefly described (refs. 1 and 4). The latter method is valuable because it is independent of the shape of the sample and, therefore, is more easily applicable to small samples. The mobility of semiconductors is discussed both as it illustrates the scattering processes taking place in the semiconductor and in its role of influencing the relation between the Hall coefficient and the charge carrier concentration (refs. 5 to 8). The bulk of the discussion is qualitative because of the complexity of mobility theory.

The equations for the charge carrier concentration were developed both for extrinsic and intrinsic conduction (ref. 2). For the extrinsic case they are a function of temperature, impurity concentrations, and the impurity ionization energy. The oversimplified uncompensated case is considered first and then generalized to the more realistic compensated case. The charge carrier concentration equation for intrinsic conduction is shown to be a function of the temperature and the band gap energy.

The bases for interpreting the measured experimental data are these equations. The carrier concentration is calculated at the required temperatures by using various sets of estimated values of the constants. By comparing the calculated results with the experimental data, those values of the constants that allow the best curve fit can be obtained. Initially, the constants of the equations are estimated from the experimental data curves. The characteristic shapes of the Hall coefficient and resistivity against temperature curves in the temperature range near intrinsic conductivity is illustrated (ref. 9). Knowledge of these characteristic shapes prevent errors being made in the interpretation of the data in this region.

Concluding the report is a brief discussion of the relevant criteria for specifying the temperature range over which the Hall coefficient and resistivity must be measured. Data must be obtained over a temperature range wide enough so that the methods of interpretation that are to be developed can be used.

APPLICABILITY OF HALL COEFFICIENT AND RESISTIVITY

A knowledge of the Hall coefficient and resistivity of a semiconductor is important both for basic materials research and device design. These measurements have proved useful since the discovery of semiconductors, and their value is illustrated by specific examples.

The band gap energy and energy levels of the impurities are basic electrical parameters of the material and are valuable in a semiconductor materials research. Also valuable is information about the transport properties of the charge carriers which an analysis of the mobility data against temperature gives.

Semiconductor device design depends on several parameters, such as the impurity concentrations (doping levels) of each material, the physical dimensions of each part of the device, the basic constants particular to the device material, the diffusion constants (or mobilities) of the charge carriers, the lifetime of the carriers, and the proposed operating temperature of the device. A knowledge of the Hall coefficient and resistivity as a function of temperature gives the designer the doping levels of the materials, the carrier mobilities (and therefore the diffusion constants), and the band gap energy. The diffusion constants can be obtained directly from the mobilities by Einstein's relation. The band gap energy affects the operating temperature of the device. The basic constants of the material (such as the breakdown electric field or the dielectric constant) can usually be measured. Normally, the physical dimensions are measured or calculated. The lifetime of the charge carriers is measured by methods not related to the Hall coefficient or resistivity. Therefore, it is evident that a substantial amount of information (but not all) is made available by an analysis of the Hall coefficient and resistivity.

The single-junction (diode) design equations are dependent, in part, on the doping levels and diffusion constants. For example, the junction capacitance of an abrupt junction is proportional to the square root of the dopant density of the more lightly doped region. The breakdown voltage is inversely proportional to this dopant density. The assumption is made that the doping atoms are completely ionized. The diffusion constant appears in equations pertaining to current flow. Two examples are the characteristic voltage-current equation of the diode and the expression for the ac impedance.

Other devices are made by combining junctions in certain configurations. There are specific considerations for each type of device, but a common requirement is good junction design. For transistors, the current gain and the four pole parameters (which specify the ac characteristics) are both functions of doping levels and diffusion constants.

It is evident that both the basic materials researcher and the device developer are interested in measuring and interpreting Hall coefficient and resistivity data. The information obtained from these relatively simple electrical measurements is of much value.

MEASUREMENT OF HALL COEFFICIENT AND RESISTIVITY

A brief description is given of both the conventional and van der Pauw methods of measuring the Hall coefficient and resistivity. References are cited to indicate where comprehensive information about both methods can be found.

Conventional Method

The conventional Hall and resistivity measurements are made on constant-thickness, single-crystal samples of semiconductor material, as shown in figure 1. The arms on each side are for ease in making contacts which will perturb the current flow through the length of the sample as little as possible. A current I (in amperes) is passed the length of the sample from A to B. If the voltage drop (in volts) from C to E is measured and the dimensions of the sample (in centimeters) are known, the resistivity can be calculated as follows:

$$\rho = \frac{V_{CE}tW}{IL} \text{ ohm-cm} \tag{1}$$

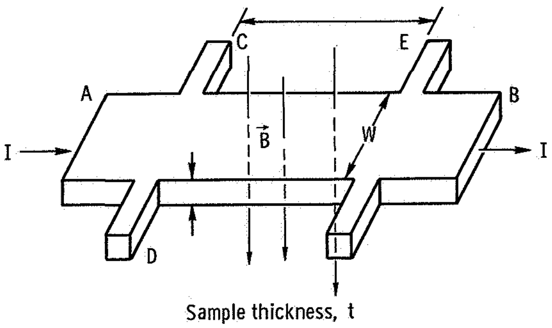


Figure 1. - Bridge-shaped sample for conventional hall and resistivity measurements. ($\vec{B}$ perpendicular to plane of crystal.)

where t, W, and L are particular dimensions of the sample as shown in figure 1. The conductivity (which is the inverse of the resistivity) can usually be written as

n-type (electrons majority carrier):

$$\sigma = \frac{1}{\rho} = n_o q \mu_n$$

(2)

p-type (holes majority carrier):

$$\sigma = \frac{1}{\rho} = p_o q \mu_p$$

where n_o and p_o are the equilibrium concentrations, μ_n and μ_p are the conductivity mobilities of electrons and holes, respectively, and q is the electronic charge. If both electrons and holes are present in equal or nearly equal concentrations, the conductivity equation is the more general equation

$$\sigma = \frac{1}{\rho} = q(n_o \mu_n + p_o \mu_p) \tag{3}$$

Analogous equations can also be written for the Hall coefficient. If in addition to the current I a known magnetic field B (in tesla) is applied perpendicular to the plane of the crystal, a voltage V_H will be observed across the width of the crystal from C to D. A measurement of V_H will allow the calculation of the Hall coefficient R_H. It is expressed in terms of measurable quantities as

$$R_H = \frac{V_H t}{BI} \times 10^4 \ \mathrm{cm^3/C} \tag{4}$$

The sign of R_H indicates the material type (i.e., for $R_H > 0$, the semiconductor is p-type; for $R_H < 0$, it is n-type).

The Hall coefficient is

n-type:

$$R_H = -\frac{\alpha}{n_o q}$$

$$(5)$$

p-type:

$$R_H = \frac{\alpha}{p_o q}$$

where α is a factor with a value usually between 1 and 2. The factor α is discussed later (in the section MOBILITY AND ITS INFLUENCE). If both types of carriers are present in equal or nearly equal concentrations, the Hall coefficient is more generally expressed as

$$R_H = \frac{\alpha}{q} \frac{p_o \mu_p^2 - n_o \mu_n^2}{(p_o \mu_p + n_o \mu_n)^2} \tag{6}$$

It can be seen from this equation that, if the Hall coefficient can be measured, the carrier concentration can be easily calculated for the case where there is only one type of carrier. When there are two types of carriers, the concentrations are not easily determined. This is discussed later in the section INTERPRETATION OF DATA. The mobility can be calculated when the Hall coefficient and resistivity are known, as is discussed in the section MOBILITY AND ITS INFLUENCE.

The material presented in this section can be typically found in elementary books on semiconductors such as Shockley's (ref. 27).

van der Pauw Method

A method of measuring the Hall coefficient and resistivity of arbitrarily shaped samples has been derived by van der Pauw (ref. 4). Only four contacts instead of the five or more normally required are necessary for both measurements. The most important advantage of this method is obvious: the sample no longer has to be machined to a particular shape. This is advantageous when only small crystals are available and machining would waste a large proportion of the sample. The only restrictions of van der Pauw's derivation are (1) the sample must be of constant thickness, (2) there must not be cavities

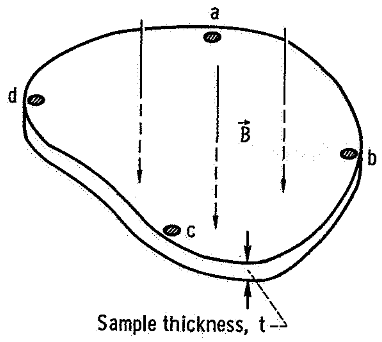


Figure 2. - Arbitrarily shaped van der Pauw sample with four electrical contacts (a, b, c, and d). ($\vec{B}$ perpendicular to plane of crystal.

in the crystal, and (3) small contacts must be made as close to the perimeter as possible. A van der Pauw sample is shown in figure 2.

The resistivity equation derived by van der Pauw is

$$\rho = \frac{\pi t}{2 \ln 2} (R_{ab, cd} + R_{bc, da}) f\left(\frac{R_{ab, cd}}{R_{bc, da}}\right) \text{ohm-cm} \tag{7}$$

The function f is given by van der Pauw in graphical form (see fig. 3). The quantity $R_{ab, cd}$ is defined, for example, to be the ratio of the voltage measured from d to c to the current flowing in a and out b. Other such ratios are defined similarly and are also expressed in ohms.

The Hall coefficient expression defined by van der Pauw is

$$R_H = \frac{t}{B} \Delta R_{ac, bd} \times 10^4 \ \text{cm}^3/\text{C} \tag{8}$$

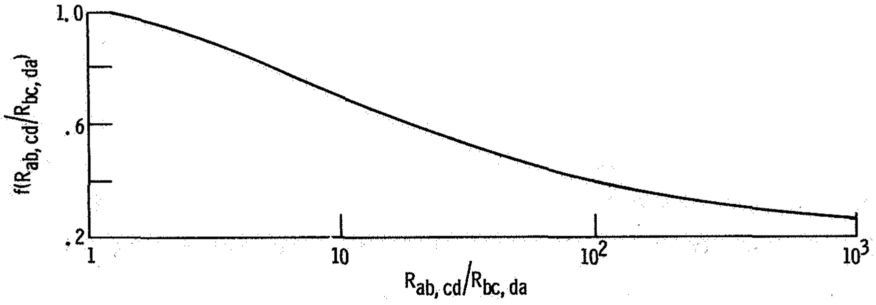


Figure 3. - Function used for determining resistivity of sample, plotted as function of $R_{ab, cd}/R_{bc, da}$.

where $\Delta R_{ac,bd}$ is the difference between $R_{ac,bd}$ without the applied magnetic field and with the field. The sign of R_H indicates the type of the semiconductor.

Influence of Thermomagnetic and Thermoelectric Effects

Thermomagnetic and thermoelectric effects can influence the Hall voltage. Some, such as the Seebeck, Nernst, and Righi-Leduc effects, can be eliminated through averaging the data obtained by reversing the current direction. Another, the magnetoresistance effect, is eliminated through averaging the data obtained by reversing the magnetic field (refs. 1 and 7). Finally, the Peltier-Nernst and Ettinghausen effects cannot be removed by data averaging but usually are small enough to neglect (ref. 7). However, their influence should be estimated to verify this assumption.

Suggested References

A popular book which describes nearly all aspects of the Hall effect is that by Putley (ref. 1). The conventional measurement of Hall coefficient and resistivity, as well as the general equipment that is required, are discussed. The thermomagnetic and thermoelectric effects and their influence on the Hall coefficient are described in detail.

The original paper by van der Pauw (ref. 4) gives the basic information on his method of measurement. In reference 7 van Daal extends the discussion of the van der Pauw method and also describes the influence of the thermomagnetic and thermoelectric effects.

MOBILITY AND ITS INFLUENCE

Several kinds of mobility are used in the semiconductor literature. They are seldom differentiated well. Mobility is defined herein since it is used often in this report. When a semiconductor is subjected to an electric field, the charge carriers are given a drift velocity. The drift velocity is proportional to the electric field. The constant of proportionality is defined as the mobility μ. The basic types of mobility depend on whether the carriers are excess minority carriers or majority carriers in equilibrium (ref. 10). The mobility for the former case is called drift mobility and for the latter case is called conductivity mobility. The distinction between the two is usually not significant. But, precisely speaking, the conductivity mobility is the appropriate mobility to use in all cases in this paper. The mobility of electrons is generally different than that of holes.

It is possible to have electron and hole conductivity mobilities, as well as electron and hole drift mobilities.

There is in general use another quantity called the Hall mobility. It is a type of conductivity mobility and is defined as

$$\mu_H = \frac{R_H}{\rho} \tag{9}$$

If equations (2) and (5) are used, it can be shown that the Hall mobility is related to the conductivity mobility by

$$\mu_H = \alpha\mu \tag{10}$$

Interest in mobility as it relates to this report is twofold. First, the analysis of mobility as a function of temperature yields information about the scattering processes which influence the movement of charge carriers in the semiconductor. Secondly, α is obtained in the study of mobility as a function of the scattering processes and of the particular semiconductor band structure.

Relating Mobility to Scattering

The relation between mobility and scattering shows that the mobility is directly dependent on the energy average of the relaxation time τ. The energy average of τ is denoted as $\langle\tau\rangle$. The relaxation time is closely related to the average time between collisions of the charge carriers. They are equal only when τ is not a function of energy. (See Smith (ref. 5) for more details.) The relaxation time is introduced as the characteristic time governing the establishment of equilibrium of the initially disturbed carrier concentration. The relaxation time as a function of energy (or, more generally, velocity) must be calculated for the specific scattering process and then energy-averaged to obtain the mobility. The factor α also depends on $\langle\tau\rangle$.

The derivation is based on the following assumptions:

(1) Spherical constant-energy surfaces in $\vec{k}$-space ($\vec{k}$-space is related to momentum space by a multiplicative constant)

(2) An n-type semiconductor with a parabolic conduction band

(3) A nondegenerate semiconductor

(4) Relaxation time τ as a function of energy only (isotropic)

The first assumption presumes that the properties of the semiconductor (such as conductivity and effective mass) are isotropic. The second assumption allows the usual density-of-states expression to be used in the derivation (see the section DEVELOPMENT OF CHARGE CARRIER CONCENTRATION EQUATIONS). The third assumption allows the use of Boltzmann statistics in place of Fermi-Dirac statistics. Also assumed is an electric field in the x-direction $\mathscr{E}_x$. This derivation appears in Smith (ref. 5), Putley (ref. 1), van Daal (ref. 7), and Blatt (ref. 6).

The result is an equation for J_x, the current density in the x-direction, as a function of $\langle\tau\rangle$, which yields the results for mobility and the factor α. This current density equation is

$$J_x = \frac{n_o q^2 \mathscr{E}_x \langle\tau\rangle}{m_n^*} \tag{11}$$

where m_n^* is the effective mass of electrons and $\langle\tau\rangle$ is defined to be

$$\langle\tau\rangle = \frac{4}{3\pi^{1/2}} \int_0^\infty \tau\epsilon^{3/2} \exp(-\epsilon)d\epsilon \tag{12}$$

where ϵ is

$$\epsilon = \frac{E - E_c}{kT} \tag{13}$$

and k is the Boltzmann constant, T is temperature, E is energy, and E_c is the energy of the bottom of the conduction band. The average drift velocity of the electrons is given by

$$\langle v_x\rangle = -\frac{J_x}{n_o q} \tag{14}$$

This relation plus the definition of mobility

$$\mu_n = \frac{|\langle v_x\rangle|}{\mathscr{E}_x} \tag{15}$$

allows the mobility to be expressed in terms of the energy-averaged relaxation time

$$\mu_n = \frac{q\langle\tau\rangle}{m_n^*} \tag{16}$$

The definition of conductivity is

$$\sigma = \frac{J_x}{\mathscr{E}_x} \tag{17}$$

Thus, it can be expressed as

$$\sigma = n_o q \mu_n \tag{18}$$

and equation (2) is verified.

The mobility has now been expressed as a function of the energy-averaged relaxation time. To calculate the dependence of mobility on any scattering process all that need be done is to determine the characteristic τ for that type of scattering and calculate its average by use of equation (12). However, this is difficult to do.

If the same type of calculation as shown in equations (11) to (18) is carried out, but including the effect of a magnetic field on the charge carriers, the result for the factor α is

$$\alpha = \frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} \tag{19}$$

Generalizing Mobility

The equations for μ and α in terms of $\langle\tau\rangle$ and $\langle\tau^2\rangle$ will be modified when the constant-energy surfaces are not spherical or when there are several equivalent energy minimums in the conduction band. Consider first the case of nonspherical constant-energy surfaces with a single energy minimum in the conduction band at $k = 0$. (The n subscript will be dropped from the mobility symbol.)

The effective mass is a function of the shape of the energy bands and therefore, in general, is a tensor quantity. It is scalar only when the constant-energy surfaces are spherical. However, when they are not spherical, a set of axes can be chosen to make the effective mass tensor diagonal. The applied electric field then can be broken up into its components along the chosen axes.

By an extension of this derivation, a set of equations similar to equation (11) results:

$$\left.\begin{aligned} J_x &= \frac{n_o q^2 \langle\tau\rangle \mathscr{E}_x}{m_1^*} \\ J_y &= \frac{n_o q^2 \langle\tau\rangle \mathscr{E}_y}{m_2^*} \\ J_z &= \frac{n_o q^2 \langle\tau\rangle \mathscr{E}_z}{m_3^*} \end{aligned}\right\} \tag{20}$$

where m_1^*, m_2^*, and m_3^* are the diagonal elements of the effective mass tensor, and therefore

$$\left.\begin{aligned} \mu_1 &= \frac{q\langle\tau\rangle}{m_1^*} \\ \mu_2 &= \frac{q\langle\tau\rangle}{m_2^*} \\ \mu_3 &= \frac{q\langle\tau\rangle}{m_3^*} \end{aligned}\right\} \tag{21}$$

The conductivity is also a diagonal tensor in terms of these axes and its components are written as

$$\left.\begin{aligned} \sigma_1 &= n_o q \mu_1 \\ \sigma_2 &= n_o q \mu_2 \\ \sigma_3 &= n_o q \mu_3 \end{aligned}\right\} \tag{22}$$

Now consider the existence of several equivalent energy minimums in the conduction band. If there are M minimums, there are n_o/M electrons per unit volume in each. Assume $M = 6$, which is the case for silicon (see fig. 4). The sum over all the electrons

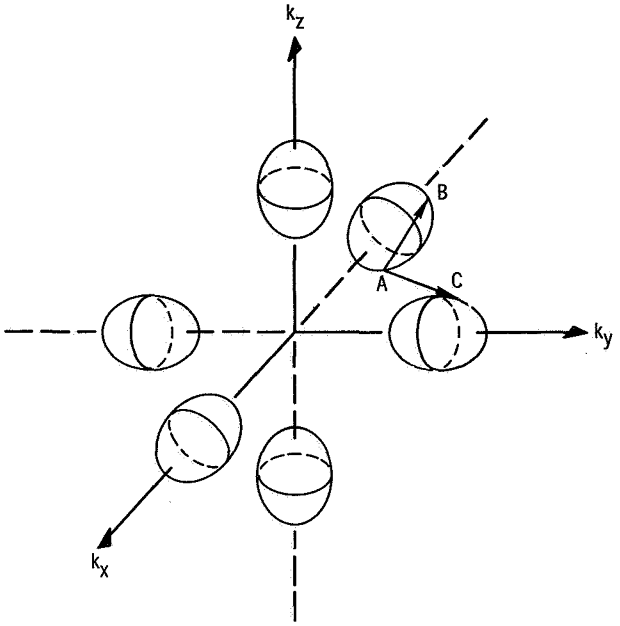


Figure 4. - Constant-energy surfaces in $\vec{k}$-space for energy just above bottom of conduction band in silicon. Minimums are at centers of ellipsoids.

(which is the sum over all six minimums) will allow the current density to be given by a symmetrical expression of the form

$$\left.\begin{aligned} J_x &= \frac{1}{6} n_o q(2\mu_1 + 2\mu_2 + 2\mu_3)\mathscr{E}_x \\ J_y &= \frac{1}{6} n_o q(2\mu_1 + 2\mu_2 + 2\mu_3)\mathscr{E}_y \\ J_z &= \frac{1}{6} n_o q(2\mu_1 + 2\mu_2 + 2\mu_3)\mathscr{E}_z \end{aligned}\right\} \tag{23}$$

Thus, all the diagonal terms of the conductivity tensor are equal, and it can be written as

$$\sigma = \frac{1}{3} n_o q(\mu_1 + \mu_2 + \mu_3) \tag{24}$$

If the conductivity and conductivity mobility are written as

$$\left.\begin{aligned} \sigma &= n_o q \mu \\ \mu &= \frac{q\langle\tau\rangle}{m_n^*} \end{aligned}\right\} \tag{25}$$

the conductivity effective mass and conductivity mobility are defined as

$$\left.\begin{aligned} \frac{1}{m_n^*} &= \frac{1}{3}\left(\frac{1}{m_1^*} + \frac{1}{m_2^*} + \frac{1}{m_3^*}\right) \\ \mu &= \frac{1}{3}(\mu_1 + \mu_2 + \mu_3) \end{aligned}\right\} \tag{26}$$

Note that the constant-energy surfaces for silicon are ellipsoids. Therefore, two of the effective masses in equations (26) will be equal ($m_1^* = m_2^* = m_T^*$) because of the symmetry of the ellipsoids, and will be different from the third ($m_3^* = m_L^*$). Equations (26) then reduce to

$$\left.\begin{aligned} \frac{1}{m_n^*} &= \frac{1}{3}\left(\frac{1}{m_L^*} + \frac{2}{m_T^*}\right) \\ \mu &= \frac{1}{3}(\mu_L + 2\mu_T) \end{aligned}\right\} \tag{27}$$

The conductivity effective mass and conductivity mobility are defined because the equations in which m_1^*, m_2^*, m_3^*, μ_1, μ_2, and μ_3 appear can be written more conveniently with m_n^* and μ. It must be remembered, however, that m_n^* and μ depend on the band structure of the semiconductor. Thus, equations (26) and (27) are not general equations for all band structures. A Hall effective mass (which is analogous to the conductivity effective mass) can be defined for use with the Hall mobility.

The factor α is also more complicated for the case when there are several equivalent energy minimums in the conduction band and nonspherical constant-energy surfaces. If the number of equivalent minimums is six, for example, α is given by (ref. 5)

$$\alpha = \frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} \frac{3(m_1^* + m_2^* + m_3^*)}{\left(\frac{1}{m_1^*} + \frac{1}{m_2^*} + \frac{1}{m_3^*}\right)^2 m_1^* m_2^* m_3^*} \tag{28}$$

If the constant-energy surfaces are ellipsoidal, $m_1^* = m_2^* = m_T^*$ and $m_3^* = m_L^*$, α becomes

$$\alpha = \frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} \frac{3C(C + 2)}{(2C + 1)^2} \tag{29}$$

where C is defined as m_L^*/m_T^*.

Scattering Processes

The derivation of a relaxation time for a particular type of scattering is not presented because of the complexity of the calculations. The different types of scattering processes are, however, qualitatively discussed. In general, the mobility will be determined at low temperatures by crystal structure defects and impurities, and at high temperatures by vibrations of the lattice. Table I lists the different possible types of scattering processes and the factor α corresponding to them. The values for α are from van Daal (ref. 7). They include only the $\langle\tau^2\rangle/\langle\tau\rangle^2$ part of α. The effective mass part is assumed to be equal to 1. References are also listed in table I.

Lattice vibrations are of two types. Acoustic vibrations are those in which an atom of a crystal and its nearby neighbors vibrate in the same direction (in phase). Optical vibrations are those in which two adjacent particles move in opposite directions (out of phase). Transverse and longitudinal vibrations can exist for both types of lattice vibration. Figure 5 illustrates acoustic and optical vibration for both the transverse and longitudinal cases.

Acoustic and optical scattering differ for polar and nonpolar crystals (see table I). Acoustic scattering for nonpolar crystals is called acoustic-mode scattering and for polar crystals is called piezoelectric scattering. Optical scattering for nonpolar crystals is called optical-mode scattering, and for polar crystals it is called polar scattering. Silicon and germanium are nonpolar crystals, and silicon carbide is polar. Whether a crystal is nonpolar or polar is determined by whether the crystal's bonds are polar or nonpolar. A polar bond will have the center of negative charge offset from the center of positive charge. Ionic bonding is polar, but covalent bonding can be either.

Early calculations of mobility considered only acoustic-mode scattering. This lead to a mobility which varies as $T^{-3/2}$. The result was obtained by Bardeen and Shockley (ref. 11). Exceptions were immediately found to the predicted $T^{-3/2}$ variation. It was determined that the band structure would have to be taken into account. Herring (ref. 12) developed the transport properties for the "many-valley" model for which the band edge occurs at a number of equivalent points in $\vec{k}$-space and for which the surfaces of constant

TABLE I. - SCATTERING PROCESSES, VALUES OF α^a, AND REFERENCES

Types of scattering	Constant relating Hall coefficient and carrier concentration, α^b	Reference
Acoustical mode (acoustical lattice vibrations of nonpolar crystals)	$3\pi/8$	11
Piezoelectric (acoustical lattice vibrations of polar crystals)	1.10	20, 7
Optical mode (optical lattice vibrations of nonpolar crystals)	-----------	21, 22
Polar (optical lattice vibrations of polar crystals)	1.10 to 1.34	23, 7
Intervalley	-----------	12
Ionized impurity	1.18 to 1.70	24, 25
Neutral impurity	1.0	13
Combination of acoustic and ionized impurity scattering	-----------	24, 26
Structure defects	1.34 to 1.40	1
Electron-hole	-----------	1
Electron-electron	-----------	1

[a] It is assumed here that the effective mass part of α equals 1.
[b] Values of α are from van Daal (ref. 7).

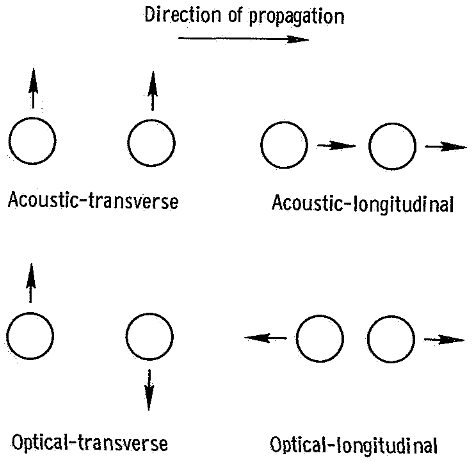


Figure 5. - Acoustic and optical vibrations for both transverse and longitudinal cases. Direction of wave motion is assumed to be to the right.

energy are multiple ellipsoids centered on each of these points. The special case of silicon is illustrated in figure 4. Since the energies of conduction electrons will be within approximately kT of each other, those electrons which are scattered without a change in energy will be represented by another point on the constant-energy surfaces of approximate thickness kT. When the scattered state is on a different ellipsoid than the original (such as A → C), this is called intervalley scattering. Intravalley scattering (A → B) occurs from one state to another state on the same ellipsoid. Intravalley acoustic-mode scattering still leads to mobility variation as $T^{-3/2}$, but intervalley scattering can cause a more rapid temperature variation. Intervalley scattering is usually considered as a separate type and not just a variation of lattice scattering.

The presence of impurities in the semiconductor also contributes to the scattering of the charge carriers. Scattering by ionized impurities yields a mobility which varies as $T^{3/2}$ (refs. 24 and 25). An expression for the mobility which results from neutral impurity scattering was obtained by Erginsoy (ref. 13). It is not temperature dependent.

Putley (ref. 1) outlines a method of separating the lattice scattering from impurity scattering. A plot of the measured mobility at a fixed temperature for a number of samples against impurity concentrations tends to an upper limit, which indicates the lattice mobility. Putley states that application of this method to materials in their early states of development has led to incorrect results because the total impurity content is reliably known.

Electron-electron, electron-hole, and structure defect scattering processes are briefly discussed by Putley and in detail by Blatt (ref. 6). Electron-electron scattering can influence other types of scattering and thus reduce the mobility.

Suggested References

An excellent reference is chapter 5 of reference 5. Smith gives a well-organized discussion of transport phenomena and scattering mechanisms. Blatt (ref. 5) discusses the theory of mobility for both metals and semiconductors. Putley (ref. 1) describes qualitatively and simply the scattering involved in nonpolar semiconductors and tabulates the mobility equations and gives references to their origins (pp. 146 and 147). Information specifically concerning silicon carbide is given by van Daal (ref. 7), and a good general discussion of mobility theory is presented by Ziman (ref. 8).

DEVELOPMENT OF CHARGE CARRIER CONCENTRATION EQUATIONS

A measurement of the Hall coefficient is a measurement of the charge carrier concentration at a specific temperature. Thus, if the carrier concentration equations can be developed as a function of temperature and other variables of interest, valuable information can be deduced from the Hall coefficient data. These equations are written for both the extrinsic and intrinsic cases. The notation and most of the material used herein are taken from chapter 3 of reference 2. Note that E_v, E_c, and E_f represent various energy levels in the usual energy band scheme. However, E_d and E_a represent the energy difference between these energy levels and the nearest band edge, that is, the conduction and valence bands, respectively, and E_g is the energy difference between the conduction and valence band edge.

Extrinsic Equations

Impurity level spin degeneracy. - Consider a semiconductor with N_d donor impurity atoms per unit volume which gives up one electron per atom. Each atom will be either ionized or neutral. Since the Fermi-Dirac distribution function f is the probability that any state of energy E will be occupied by an electron, the ratio of ionized donor atoms to neutral donor atoms is

$$\frac{N_{di}}{N_{dn}} = \frac{1 - f}{f} = \frac{1}{\exp\left(\frac{E_f + E_d - E_c}{kT}\right)} \tag{30}$$

where E_d is the donor ionization energy, E_f is the Fermi level, and f is the Fermi-Dirac distribution function:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \tag{31}$$

Equation (30) is not quite correct. The effect of impurity level spin degeneracy must be taken into account by multiplying the denominator by $1/\beta$. For the case of N_d donor impurities usually $\beta = 1/2$, because the energy level of each atom can be occupied by an electron in two ways. For acceptor impurities $\beta = 2$, most likely. Other effects can influence the statistical weights of the neutral and ionized conditions of the atoms. Therefore, β is used as a general symbol to include all the effects. A brief discussion of the effects that influence β is presented by Blakemore (ref. 2, p. 118).

Since $N_d = N_{di} + N_{dn}$, equation (30) can be rewritten to give the density of neutral donors:

$$N_{dn} = \frac{N_d}{1 + \beta \exp\left(\frac{E_c - E_d - E_f}{kT}\right)} \tag{32}$$

This equation is basic to the developments that follow.

Model for single monovalent donor impurities. Figure 6 illustrates the semiconductor model to be considered first, an n-type semiconductor with monovalent, uncompensated donors of density N_d. It is impossible to have a semiconductor which would completely satisfy this model. However, some important equations can be developed at this point and easily generalized later.

The concentration of electrons excited to the conduction band is the first quantity that must be calculated. It is equal to the integral from E_c to infinity of the product of the Fermi-Dirac distribution function and the density of electron states g(E):

$$n_o = \int_{E_c}^{\infty} f(E)g(E)dE \tag{33}$$

More precisely, g(E) is the density of states per unit energy interval in the conduction

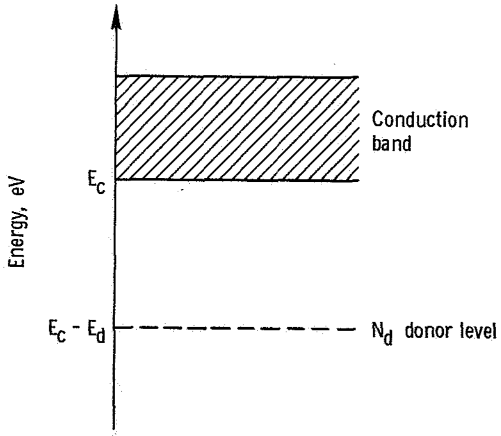


Figure 6. - Model of n-type semiconductor with monovalent impurities and no compensation.

band and is given by Blakemore as

$$g(E) = 4\pi\left(\frac{2m_n^*}{h^2}\right)^{3/2}(E - E_c)^{1/2} \tag{34}$$

where h is the Planck constant. Equation (33) is then calculated to be

$$n_o = N_c F_{1/2}(\eta) \tag{35}$$

where

$$N_c = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \tag{36}$$

and

$$\eta = \frac{E_f - E_c}{kT} \tag{37}$$

and $F_{1/2}(\eta)$ is a Fermi-Dirac integral of order 1/2. Since $N_d = N_{di} + N_{dn}$ and $n_o = N_{di}$, the expression for n_o becomes

$$n_o = \frac{N_d}{1 + \beta^{-1}\exp(\epsilon_d + \eta)} \tag{38}$$

where

$$\epsilon_d = \frac{E_d}{kT}$$

The quantity N_c is the effective density of states in the conduction band, and therefore m_n^*, which appears in N_c, is the density-of-states effective mass. It is not, in general, equal to the conductivity effective mass defined in the section MOBILITY AND ITS INFLUENCE. But like the conductivity effective mass, it is a function of m_1^*, m_2^*, and m_3^*. For materials having symmetric conduction bands, the density-of-states effective mass is $(m_1^* m_2^* m_3^*)^{1/3}$. There is a corresponding effective density of states in the valance band N_v and density-of-states effective mass for holes m_p^*.

Equation (38) simplifies if conditions are nondegenerate. If this is so, $F_{1/2}(\eta)$ and f(E) are approximated by $\exp(\eta)$. A semiconductor is nondegenerate if the doping impurity concentration is not too high, that is, if E_f is several kT less than E_c. In a degenerate system, only a small percentage of the electrons are capable of changing their energies in infinitesimal amounts. The system considered herein is nondegenerate in that every electron has a full opportunity to readjust to thermal change. Therefore, $F_{1/2}(\eta) = \exp(\eta) = n_o/N_c$, and equation (38) becomes

$$n_o = \frac{2N_d}{1 + \left[1 + \left(\frac{4N_d}{\beta N_c}\right)\exp(\epsilon_d)\right]^{1/2}} \tag{39}$$

At low temperature (where $kT << E_d$) equation (39) can be approximated by

$$n_o \approx (\beta N_c N_d)^{1/2} \exp\left(-\frac{E_d}{2kT}\right) \tag{40}$$

Plotting $\ln n_o$ as a function of 1/T results in a curve with slope $E_d/2k$. By measuring this slope, E_d can be approximated. Because of the dependence of N_c on temperature ($N_c \alpha T^{3/2}$) the actual slope is not exactly $E_d/2k$. Note that equation (40) can be applied only if

(1) Nondegenerate conditions apply.

(2) The low-temperature condition prevails, that is, $n_o << N_d$.

(3) Little or no compensation is assumed (as for this model), that is, $N_a << n_o$.

A knowledge of the temperature dependence of η, as well as of n_o, for this model is valuable. Knowing η allows the data interpreter to determine whether the nondegenerate approximation can be used to simplify the carrier concentration equation. If, at a particular temperature, η is less than -2 or -3, the semiconductor is nondegenerate at that temperature, and the simplified equation can be applied. This is the same as saying that the Fermi level E_f is 2 kT or 3 kT below the conduction band energy.

The variable η can be written for nondegenerate conditions as

$$\eta = \frac{E_f - E_c}{kT} = \ln\left(\frac{n_o}{N_c}\right) \tag{41}$$

Substituting equation (39) into equation (41) results in

$$\eta = -\ln\left\{\left(\frac{N_c}{2N_d}\right) + \left[\left(\frac{N_c}{2N_d}\right)^2 + \left(\frac{N_c}{\beta N_d}\right)\exp(\epsilon_d)\right]^{1/2}\right\} \tag{42}$$

For large T (where $kT >> E_d$), the term containing the exponential can be neglected. Thus, equation (42) reduces to

$$\eta = -\ln\left(\frac{N_c}{N_d}\right) \tag{43}$$

For small T (where $kT << E_d$), the exponential dominates, and equation (42) becomes

$$\eta = -\frac{E_d}{2kT} - \frac{1}{2}\ln\left(\frac{N_c}{\beta N_d}\right) \tag{44}$$

It is apparent that η as a function of T starts low, rises to a maximum η_m at temperature T_m, and goes down again, as shown in figure 7. Therefore, if η_m is less than -2 or -3, the semiconductor is nondegenerate at all temperatures. There will be cases when the semiconductor is degenerate throughout a certain temperature range. This temperature range is centered around the temperature T_m. Thus, it is helpful to know not only η_m, but T_m as well. Blakemore has developed a way of obtaining η_m and T_m, and his results are summarized in the following paragraphs.

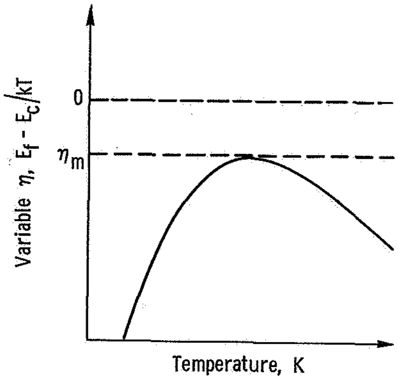


Figure 7. - Nominal temperature dependence of variable η for model of figure 6. (η_m is not necessarily less than $\eta = 0$ in all cases.)

The maximum η_m can be calculated as a function of a quantity Z, which is itself a function of N_d, β, m_n^*, and E_d but not of T. Taking the derivative of η from equation (42) with respect to T and setting the result equal to zero yield the equation

$$Z = 12\left(\frac{2\pi m_o}{h^2}\right)^{3/2} \epsilon_{dm}^{-1/2}(2\epsilon_{dm} - 3)^{-2} \exp(-\epsilon_{dm}) \tag{45}$$

where

$$\left.\begin{aligned} \epsilon_{dm} &= \frac{E_d}{kT_m} \\ Z &= N_d\beta^{-1}\left(\frac{m_o}{m_n^* E_d}\right)^{3/2} \end{aligned}\right\} \tag{46}$$

The quantity m_o is the mass of the free electron.

A universal plot can now be made of ϵ_{dm} against Z. When this plot and a knowledge of the variables of a specific semiconductor sample which make up Z are used, the temperature at which η is maximum can be determined and then η_m itself. This plot is presented in figure 8.

When equation (38) is differentiated and the condition $d\eta/dT = 0$ is imposed, a simple relation is obtained, which when combined with the root of equation (45) leads to a universal graphical relation of η_m to Z. This allows η_m to be obtained directly from the curve if N_d, β, m_n^*, and E_d of a specific semiconductor sample are known. This graph is figure 9. Figures 8 and 9 are reprinted with permission from F. S. Blakemore, Semiconductor Statistics, copyright 1962, Pergamon Press Inc.

If there is degeneracy over part of the temperature range, equation (38) cannot be solved simply (i.e., $F_{1/2}(\eta) \neq \exp(\eta)$). If $\eta < 1.3$, $F_{1/2}(\eta)$ can be approximated by $(C + \exp(-\eta))^{-1}$, where $C \approx 0.27$ and the electron concentration is calculated to be

$$n_o = \frac{2N_dN_c}{(N_c + CN_d) + \left[(N_c - CN_d)^2 + 4\beta^{-1}N_dN_c \exp(\epsilon_d)\right]^{1/2}} \tag{47}$$

For $\eta > 1.3$ numerical or graphical methods must be used to solve equation (38). Blakemore indicates the procedure to be used.

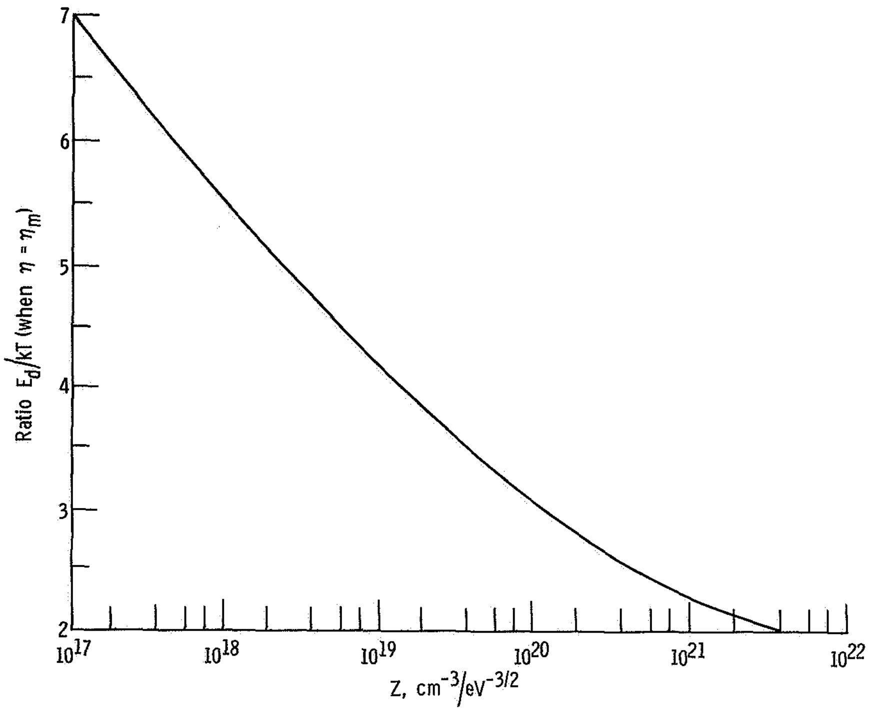


Figure 8. - Ratio of donor ionization energy to temperature E_d/kT (when $\eta = \eta_m$) as function of Z.

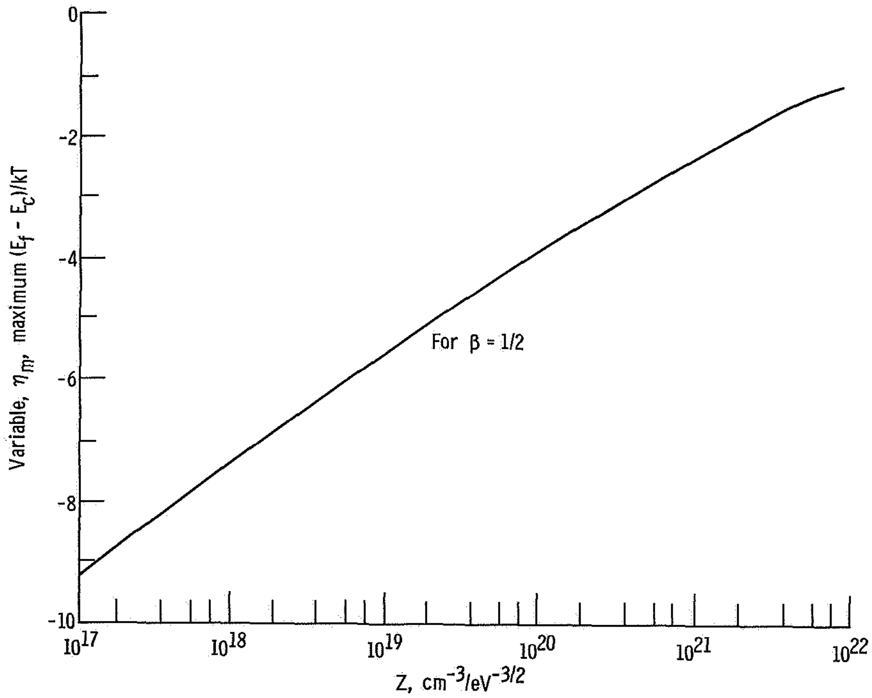


Figure 9. - Variable η_m as function of Z for impurity level spin degeneracy of 1/2. With any other value, curve should be raised by amount equal to $\ln(2\beta)$.

Model for partly compensated donor impurities. - This model assumes a donor density N_d compensated by a net density of acceptors N_a, as shown in figure 10. This model also is not completely correct; several influencing effects are discussed in the following sections.

Generally, the concentration equations are similar to those for the simple model, but they take into consideration the presence of acceptor impurities which cause the semiconductor to be compensated. It is assumed that the donor energy levels lie at an appreciable level below the bottom of the conduction band and that the net acceptor levels lie even further away than the donor levels. The Fermi level E_f is assumed to be well above the acceptor energy levels.

The acceptors, however, acquire electrons from the donor impurities. Thus, there are $N_d - N_a$ electrons to distribute between the donor levels and the conduction band. The number of ionized donors varies from N_a at low temperatures to N_d at high temperatures, but n_o can become larger than $N_d - N_a$ only if the falling Fermi level approaches another set of impurity states or its intrinsic position.

Obviously, for this particular case, the density of conduction electrons n_o plus the density of electrons lost to the acceptors N_a plus the neutral donors N_{dn} equals the total number of donors (i.e., $n_o + N_a + N_{dn} = N_d$). Therefore, when equation (32) is used,

$$n_o + N_a = \frac{N_d}{1 + \beta^{-1} \exp(\epsilon_d + \eta)} \tag{48}$$

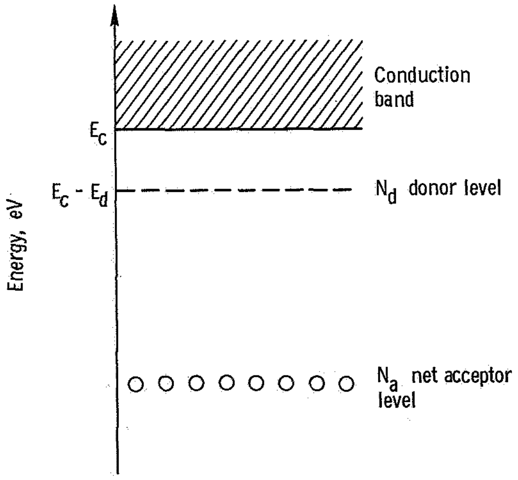


Figure 10. - Model of compensated n-type semiconductor with monovalent donor impurities.

In general, when n_o must be written as

$$n_o = N_c F_{1/2}(\eta) \tag{35}$$

and A is defined as

$$A = \frac{2\left(\frac{2\pi m_n^* E_d}{h^2}\right)^{3/2}}{N_d} \tag{49}$$

equation (48) becomes

$$\frac{1}{1 + \beta^{-1} \exp(\epsilon_d + \eta)} = \frac{A}{\epsilon_d^{3/2}} F_{1/2}(\eta) + \frac{N_a}{N_d} \tag{50}$$

When $\eta \leq 1.3$, $F_{1/2}(\eta)$ can be approximated by $(C + \exp(-\eta))^{-1}$, and equation (50) reduces to

$$n_o = \frac{2N_c(N_d - N_a)}{\left[N_c + C(N_d - N_a) + \beta^{-1}N_a \exp(\epsilon_d)\right] + \left\{\left[N_c - C(N_d - N_a) + \beta^{-1}N_a \exp(\epsilon_d)\right]^2 + 4\beta^{-1}(N_c + CN_a)(N_d - N_a)\exp(\epsilon_d)\right\}^{1/2}} \tag{51}$$

When the Fermi level is several kT below the conduction band (i.e., $\eta = -2$ or -3), $F_{1/2}(\eta) \approx \exp(\eta)$, and equation (50) reduces to

$$n_o = \frac{2(N_d - N_a)}{\left[1 + \frac{N_a}{\beta N_c} \exp(\epsilon_d)\right] + \left\{\left[1 + \frac{N_a}{\beta N_c} \exp(\epsilon_d)\right]^2 + \frac{4}{\beta N_c} (N_d - N_a)\exp(\epsilon_d)\right\}^{1/2}} \tag{52}$$

Both equations (51) and (52), when N_a goes to zero, reduce to equations (47) and (39), respectively, which were originally derived for the uncompensated model.

When compensation is small, there exists a temperature range where $N_a << n_o << N_d$. Equation (52) becomes, in this case,

$$n_o = (\beta N_c N_d)^{1/2} \exp\left(-\frac{E_d}{2kT}\right) \tag{53}$$

which is the same as equation (40). At lower temperature, however, when $n_o \leq N_a$, equation (52) becomes

$$n_o = \beta N_c \left(\frac{N_d - N_a}{N_a}\right) \exp\left(-\frac{E_d}{kT}\right) \tag{54}$$

Note the dependence of $\ln n_o$ on $1/T$. The dependence is twice as large for equation (54) as for equation (53). Since $\ln n_o$ as a function of $1/T$ is often plotted to determine E_d from the slope of the curve, care must be taken to differentiate between these equations. When compensation is large, equation (53) is never valid. For heavy compensation, equation (52) becomes, at all temperatures,

$$n_o = \frac{N_d - N_a}{1 + \frac{N_a}{\beta N_c} \exp(\epsilon_d)} \tag{55}$$

Obviously, the equations for single monovalent and partly compensated donor impurities must be applied cautiously to a real semiconductor. Forethought is needed to prevent serious errors when the experimental data are interpreted.

Model for compensated semiconductor with two monovalent donor impurity levels. - This model assumes two monovalent donor impurity levels which are compensated by a net acceptor density. The model is illustrated in figure 11. The concentrations of the two donor levels are denoted as N_{d1} and N_{d2}, respectively, and their energies are written as E_{d1} and E_{d2} with $E_{d1} > E_{d2}$.

The acceptor impurities trap N_a electrons so that the net density available is $N_{d1} + N_{d2} - N_a$. The relative magnitudes of N_{d1}, N_{d2}, and N_a must be considered, while remembering that $E_{d1} > E_{d2}$ is assumed. It is found that only two types of behavior result: $N_a > N_{d1}$ and $N_a < N_{d1}$. If $N_a > N_{d1}$, there will be no electrons at the N_{d1} level at all temperatures. This corresponds to a semiconductor which has a single type of donor impurity with an effective compensating density of $N_a - N_{d1}$. Therefore, the analysis for partly compensated donor impurities is applicable.

When $N_a < N_{d1}$, the N_{d2} levels will be full, and $N_{d1} - N_a$ electrons will be in the N_{d1} level states at 0 K. As the temperature rises, the N_{d1} donors start giving their electrons to the conduction band. When all the N_{d1} donor levels are empty, the elec-

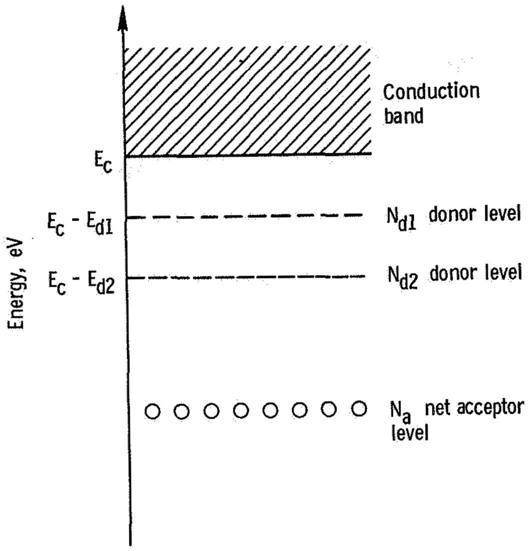


Figure 11. - Model of compensated n-type semiconductor with two independent monovalent donor impurities.

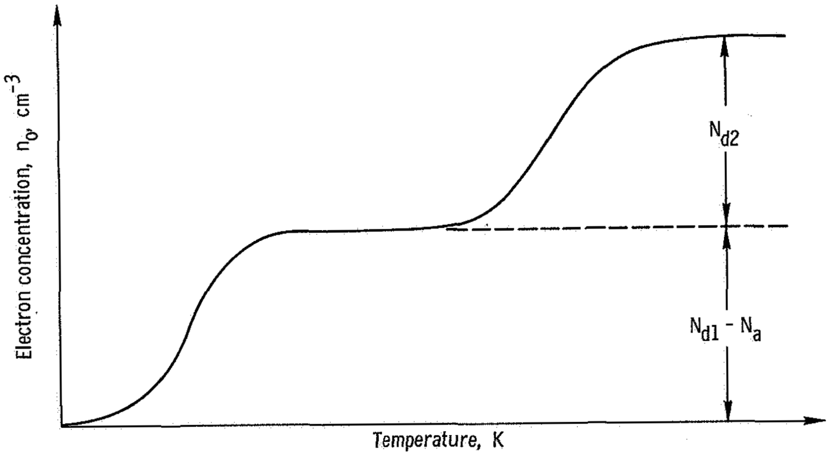


Figure 12. - Action of electron concentration as function of temperature for compensated semiconductor with two independent monovalent donor impurities.

tron concentration levels off. As the temperature increases it begins to rise until all the N_{d2} electrons are ionized, and then it levels off again. The electron concentration as a function of temperature is shown in figure 12.

To discuss the model mathematically, N_{dj} is defined at the j^{th} monovalent donor impurity (where there are a total of M different types) with ground state binding energy E_{dj}. Since the density of ionized donors is equal to the conduction band electron concentration plus the density of acceptors, the following equation holds:

$$N_a + n_o = \sum_{j=1}^{M} \frac{N_{dj}}{1 + \beta_j^{-1} \exp(\eta + \epsilon_{dj})} \tag{56}$$

And if the semiconductor is nondegenerate, $\exp(\eta)$ can be approximated by n_o/N_c. Equation (56) can then be analyzed.

There are other extrinsic doping models that are important but will not be presented. Some of these include multivalent doping atoms, amphoteric impurities (i.e., an impurity that can act either as an acceptor or a donor), and those cases influenced by lattice defects. For more information about these types of semiconductors see Blakemore (ref. 2).

Influence of excited states on carrier concentration equation. - An analogy exists between the energy level structure of atoms and the energies that a donor impurity may exhibit. Not all donor electrons have an energy at the level $E_c - E_d$. Rather this level is the donor electron ground state, and the donor electron could be in an excited state at an energy above the donor ground state. Figure 13 depicts an extended n-type compensated semiconductor problem, which is considered in the following paragraph.

Let r denote the energy state. For example, $r = 1$ is the donor ground state, and $r = 2$ is the first excited state. Then each state has a spin degeneracy β_r^{-1} and lies at energy $E_{r1} = kT\epsilon_{r1}$ above the ground state. The donor can bind an electron in a state only if it does not also have an electron bound in another state.

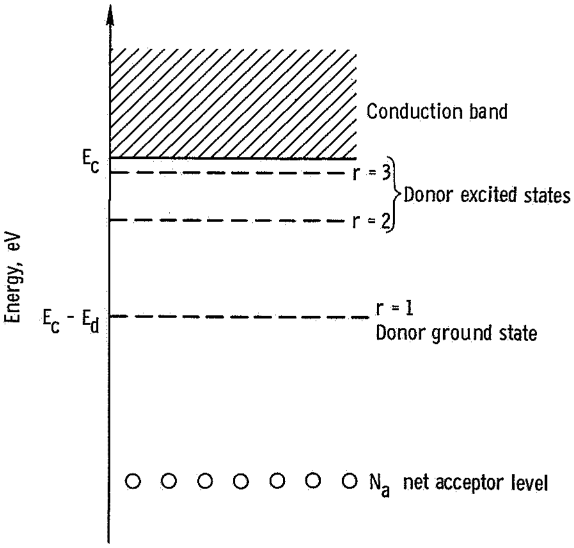


Figure 13. - Compensated n-type semiconductor of figure 10 but including donor excited states.

The resulting equation for the nondegenerate case is

$$n_o = \frac{2(N_d - N_a)}{\left[1 + \frac{N_a}{N_c\beta_1}\exp(\epsilon_d)(1 + S)\right] + \left\{\left[1 + \frac{N_a}{N_c\beta_1}\exp(\epsilon_d)(1 + S)\right]^2 + \frac{4(N_d - N_a)}{N_c\beta_1}\exp(\epsilon_d)(1 + S)\right\}^{1/2}} \qquad (57)$$

where

$$S = \sum_{r=2}^{\infty} \frac{\beta_1}{\beta_r}\exp(-\epsilon_{r1}) \qquad (58)$$

Equation (57) is quite similar to equation (52). If $S = 0$, they would be identical. Thus, the equations previously derived are influenced by the action of excited states in a simple manner. To proceed from one equation to another the term $1 + S$ must be appropriately substituted. Note that at low enough temperatures (where $kT \ll E_{r1}$), $S \ll 1$ and equations (57) and (52) coincide. At high temperatures, $n_o = N_a$. Thus, only at intermediate temperatures does S affect n_o significantly.

Other factors which influence carrier concentration equations. - It has been found that the ground-level donor energy is sometimes split into two levels which are Δ apart. This effect is a function of energy band structure. Long and Myers (ref. 14) have measured Δ for a specific case. The splitting influences the electron or hole concentration, but the details and the degree of influence are not discussed herein.

Strain (ref. 15) also affects the structure of impurity states in most materials as well as a magnetic field (ref. 16). However, except for large strains or large magnetic fields, these effects are negligible.

Intrinsic Equations

A semiconductor displays intrinsic conduction when the temperature is high enough that the carrier concentration due to thermal excitation from the valence band is larger than the concentration due to excited impurities. Analysis of data in the intrinsic region yields the band gap of the semiconductor.

Before the carrier concentration equation is written, clarification is needed concerning the total hole density p_o. The equation for total electron density n_o has already been written. The hole density can be expressed similarly as

$$p_o = N_v F_{1/2}(-\epsilon_g - \eta) \tag{59}$$

where

$$N_v = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \tag{60}$$

and ϵ_g is the band gap in units of $kT(\epsilon_g = E_g/kT)$. The hole density p_o is the integral over energy from minus infinity to the top of the valence band E_v of the product of the density of states and the Fermi distribution for holes, which is 1 minus the Fermi distribution for electrons.

In most cases (especially wide-band-gap material) the nondegenerate approximation is valid because the gap is a fairly large multiple of kT and the Fermi level is near the center. Since in an intrinsic semiconductor $n_i = n_o = p_o$ (where n_i is defined as the intrinsic concentration of holes and electrons),

$$n_i = N_c \exp(\eta) = N_v \exp(-\epsilon_g - \eta) \tag{61}$$

The intrinsic carrier concentration equation is obtained when the extreme left side of equation (61) is multiplied by n_i, the extreme right side is multiplied by $N_c \exp(\eta)$, and the square root is taken.

$$n_i = (N_v N_c)^{1/2} \exp\left(-\frac{E_g}{2kT}\right) \tag{62}$$

Another basic equation can be derived from equation (61):

$$n_o p_o = n_i^2 \tag{63}$$

INTERPRETATION OF DATA

Measured values of Hall coefficient and resistivity against temperature are usually displayed in a standard way. The carrier concentration n_o is calculated from the Hall coefficient, and then the natural logarithms of n_o and ρ are plotted as a function of inverse temperature, as in figure 14. (An n-type semiconductor is assumed throughout this section.) Each part of the curve on each plot yields a particular bit of information

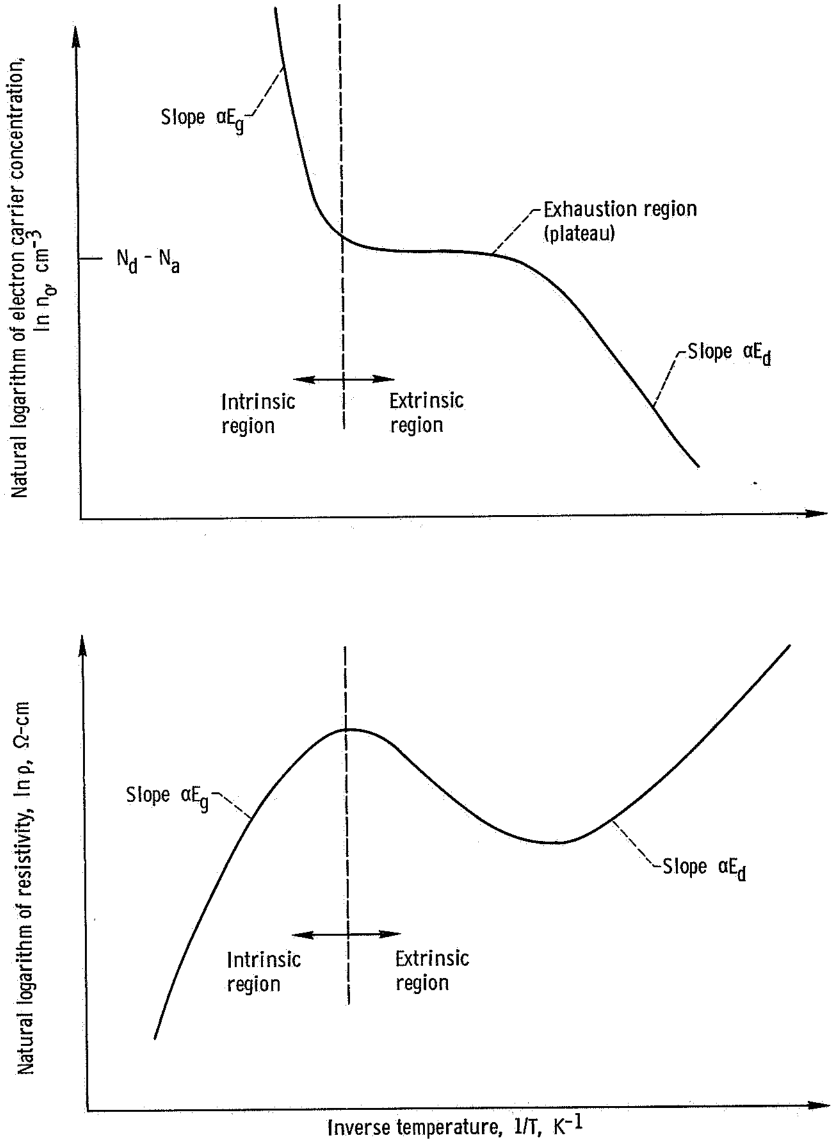


Figure 14. - Typical plots of natural logarithms of carrier concentration and of resistivity as function of inverse temperature. These plots only indicate general shape of curves.

about the semiconductor. The general shapes of the curves are shown in figure 14. Note that the slopes of the curves at both extremes of temperature are proportional to either E_d or E_g. In the extrinsic region, the carrier concentration rises as the temperature increases because more and more electrons are being excited into the conduction band. When all of the available electrons from the doping atoms are ionized, n_o will reach a constant value ($N_d - N_a$ if compensated). As the temperature rises, hole-electron pairs are generated as the thermal energy available becomes comparable to E_g. Thus, n_o increases rapidly.

Equations have been developed for each part of each curve in figure 14. The interpretation of the data involves the choosing of the correct parameters in the equations. The correct parameters, when substituted in the appropriate carrier concentration equation, will match the calculated results to the experimental data. The correct parameters are obtained by an iterative process.

Extrinsic Data

Several extrinsic equations have been developed in the previous sections for degenerate and nondegenerate semiconductors. Some estimate of the degeneracy must be made in order to pick the applicable equation. The degeneracy is determined by the position of the Fermi level. Since the Fermi level varies as a function of temperature (as well as doping), it is possible for a particular equation to be good in one temperature range and not good in another. Normally, a semiconductor must be doped to 10^{18} or 10^{19} centimeter^{-3} before it becomes degenerate. Therefore, the procedure is to estimate the maximum value of the Fermi level. And if it is several kT below the conduction band, the semiconductor is always nondegenerate. If it is at or above the conduction band, the Fermi level must be calculated more carefully as a function of temperature.

Blakemore's variable η as a function of temperature yields the degeneracy information. Even for a compensated semiconductor, η_m and T_m (where T_m is the temperature at which $\eta = \eta_m$) can be determined reasonably well by substituting $N_d - N_a$ into Z (eq. (46)) and then reading T_m and η_m from figures 8 and 9. If equation (52) is found to be unusable, equation (50) or (51) must be utilized.

Hall extrinsic data. - For this discussion it is assumed that the semiconductors in question are nondegenerate. However, much of the material is still applicable to the degenerate cases.

Blakemore (ref. 2) and Putley (ref. 1) both outline a method of interpreting experimental Hall coefficient data which Blakemore calls one of the most popular approaches. The method starts with a rearranged form of equation (52)

$$\frac{n_o(n_o + N_a)}{(N_d - N_a - n_o)} = \beta N_c \exp\left(-\frac{E_d}{kT}\right) \tag{64}$$

where the model for partly compensated donor impurities is used. The effects of excited impurity levels are neglected. Notice that the right-hand side depends on the character of the impurities and on the temperature, but not on the acceptor or donor densities. The first problem is to find values of N_a, N_d, and E_d which satisfy the equation at all temperatures. Each of these parameters can be estimated. Then, by iteration the parameters are adjusted until the calculated carrier concentration that results (using N_a, N_d, and E_d) matches as closely as required with the experimental carrier concentration data. Blakemore states that the method of least squares applied to equation (64) will give those values of N_a and N_d which give the best fit over the entire temperature range. Satisfactory results are obtained by using a repetitive method of varying the parameters until the calculated results match the experimental data (private communication from Robert P. Ulman, formerly of Lewis Research Center and now at the Addressograph-Multigraph Corp. of Cleveland, Ohio). These curve-fitting procedures are time consuming, and digital computers are helpful in doing these calculations.

There are several ways of obtaining the estimates of the parameters in question (assuming an n-type semiconductor). Either β or m_n^* (which is in the equation for N_c) must be known independently. That is, if m_n^* is known by some other type of measurement, such as cyclotron resonance, N_c can be calculated. The quantity $N_d - N_a$ can be estimated from the plateau (exhaustion region) of the curve of $\ln n_o$ against reciprocal temperature. Donor ionization energy E_d is obtained from the slope of the $\ln n_o$ against $1/T$ curve at low temperature (see eqs. (53) and (54)). Finally, N_a/β can be calculated by using equation (54) if n_o at an arbitrary low temperature is known.

Putley suggests two methods for estimating N_d and N_a. In the first method the intercepts of the low-temperature part of the plot of $\ln n_o$ against $1/T$, where equation (54) is valid, are measured. This allows $(N_d - N_a)/N_a$ to be determined. Then, from the exhaustion region of the same plot, $N_d - N_a$ is estimated and, therefore, values of N_d and N_a are obtained. In the second method, the curve at low temperature in figure 15 is extrapolated backwards using equation (54) until it intercepts the exhaustion line. At the temperature corresponding to the point of intersection, the left-hand side of equation (64) equals N_a. By estimating $N_d - N_a$ from the exhaustion region, N_d and N_a can be determined.

Often there will occur plots of $\ln n_o$ against $1/T$ in which there is more than one dip in the curve. This situation might correspond to semiconductors with two or more levels of either donor or acceptor impurities, or to impurities which can accommodate more than one electron, or to structural defects of the lattice of the semiconductor. When this is the case, the generalized equation (56) must be used in the interpretation of the data. Putley includes an excellent discussion of this problem (ref. 1, section 4.8).

Because of the temperature dependence of the quantities N_c and N_v, the plot of $\ln n_o$ against $1/T$ will not be a perfectly straight line at low temperature. This makes the calculation of the impurity ionization energy E_d inaccurate. However, if the temperature dependence of N_c is plotted on the ordinate along with n_o, the slope at low temperatures will be directly proportional to E_d. For example, assume that conditions are such that equation (54) holds at low temperatures. Notice that N_c is proportional to $T^{3/2}$. Therefore, $\ln(n_o/T^{3/2})$ can be plotted against $1/T$ to obtain a curve with a

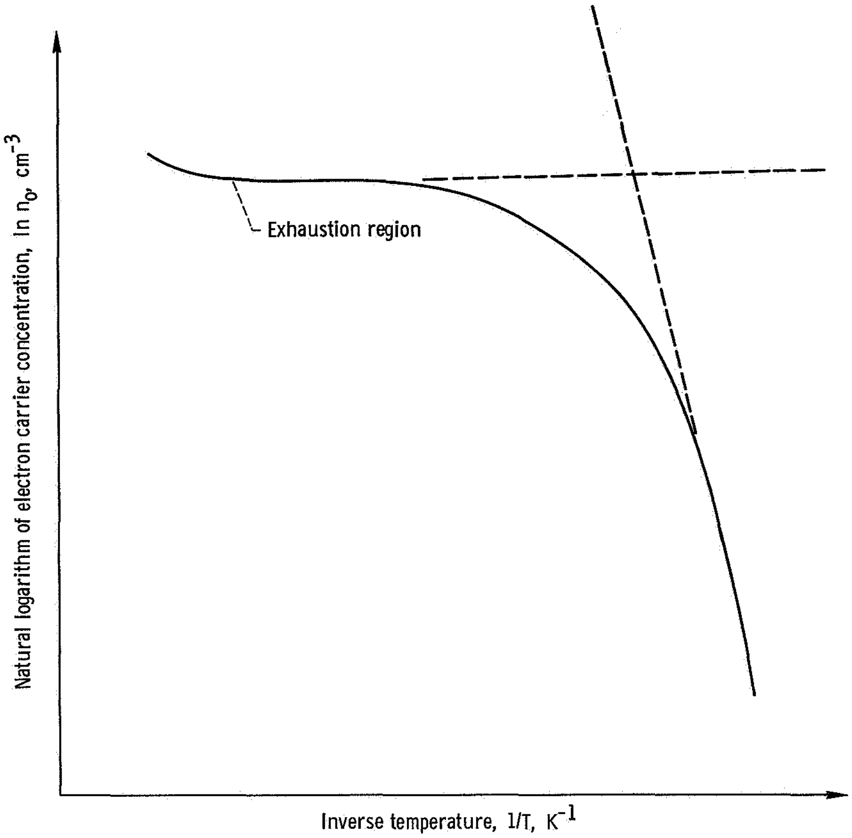


Figure 15. - Method of determining concentration of donor and acceptor impurities N_d and N_a of compensated semiconductor.

slope truly proportional to E_d.

It must be emphasized that the interpretation of the data need not follow the pattern outlined herein. There are other variations which have been used and published. For example, van Daal, Knippenberg, and Wasscher (ref. 17) have developed a method for analyzing Hall data which extrapolates the measured curves to the region of complete exhaustion. This method could be valuable in those cases where data could not be taken at sufficiently high temperatures.

The fact that impurity ionization energy becomes smaller as the impurity density is increased was shown by Pearson and Bardeen (ref. 18). At a certain density, characteristic of the host lattice and the impurity type, the impurity ionization energy actually becomes zero. The variation in E_a as a function of N_a is shown in figure 16. Care must be taken when determining the impurity ionization energy when the doping is high.

Resistivity extrinsic data. - Little has been said about the interpretation of resistiv-

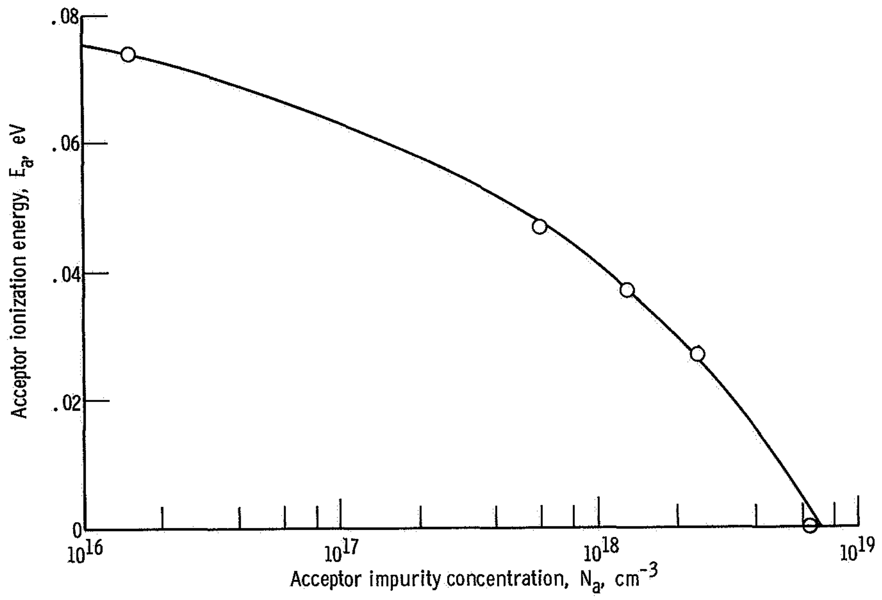


Figure 16. - Effects of boron concentration on boron acceptor ionization energy in silicon according to measurements of Pearson and Bardeen (ref. 18).

ıty against temperature data because only the impurity ionization energy can be determined from it. However, resistivity is simpler to measure than the Hall coefficient. Therefore, in the case where the Hall data ($\ln n_o$ against $1/T$ curve) does not straighten out at low temperatures and, thus, the ionization energy is still in doubt, resistivity data may be very useful. In this case, since $1/\rho = n_o q \mu_n$ (for n-type) and the mobility is not an exponential function of T at low temperatures, the exponential $\exp(-E_d/kT)$ in the carrier concentration term n_o dominates the behavior. A plot of $\ln \rho$ against $1/T$ yields the ionization level. Resistivity measurements are then emphasized at lower temperatures, and a more accurate determination of the impurity ionization energy may be possible.

Resistivity, as well as the Hall coefficient, is required to calculate the Hall mobility. A knowledge of mobility is important for device design.

Intrinsic Data

When a semiconductor is intrinsic, $n_o = p_o = n_i$, and the equations of resistivity and Hall coefficient when both types of carriers are present reduce to

$$\frac{1}{\rho} = qn_i(\mu_n + \mu_p) \tag{65}$$

and

$$R_H = \frac{\alpha}{qn_i} \frac{\mu_p - \mu_n}{\mu_p + \mu_n} \tag{66}$$

The equations are altered from the extrinsic case by the inclusion of sums and differences of the electron and hole mobilities. For example, the measured Hall coefficient cannot be directly related to the carrier concentration, as in the extrinsic case. Thus, the carrier concentration cannot be calculated unless the mobilities are known. However, the band gap energy E_g appears in the exponential term of equation (62) for the intrinsic carrier concentration. This term dominates the temperature dependence of the mobilities, and thus the slopes of the plots of $\ln R_H$ against $1/T$ or $\ln \rho$ against $1/T$ (fig. 17) give the band gap energy. Once again, as in the extrinsic case, it may be easier to measure resistivity at the temperature extreme (i.e., high temperature) of intrinsic conduction. The band gap energy E_g usually is a function of temperature (ref. 2). But if it is assumed to be a linear function of temperature,

$$E_g = E_{go} - aT \tag{67}$$

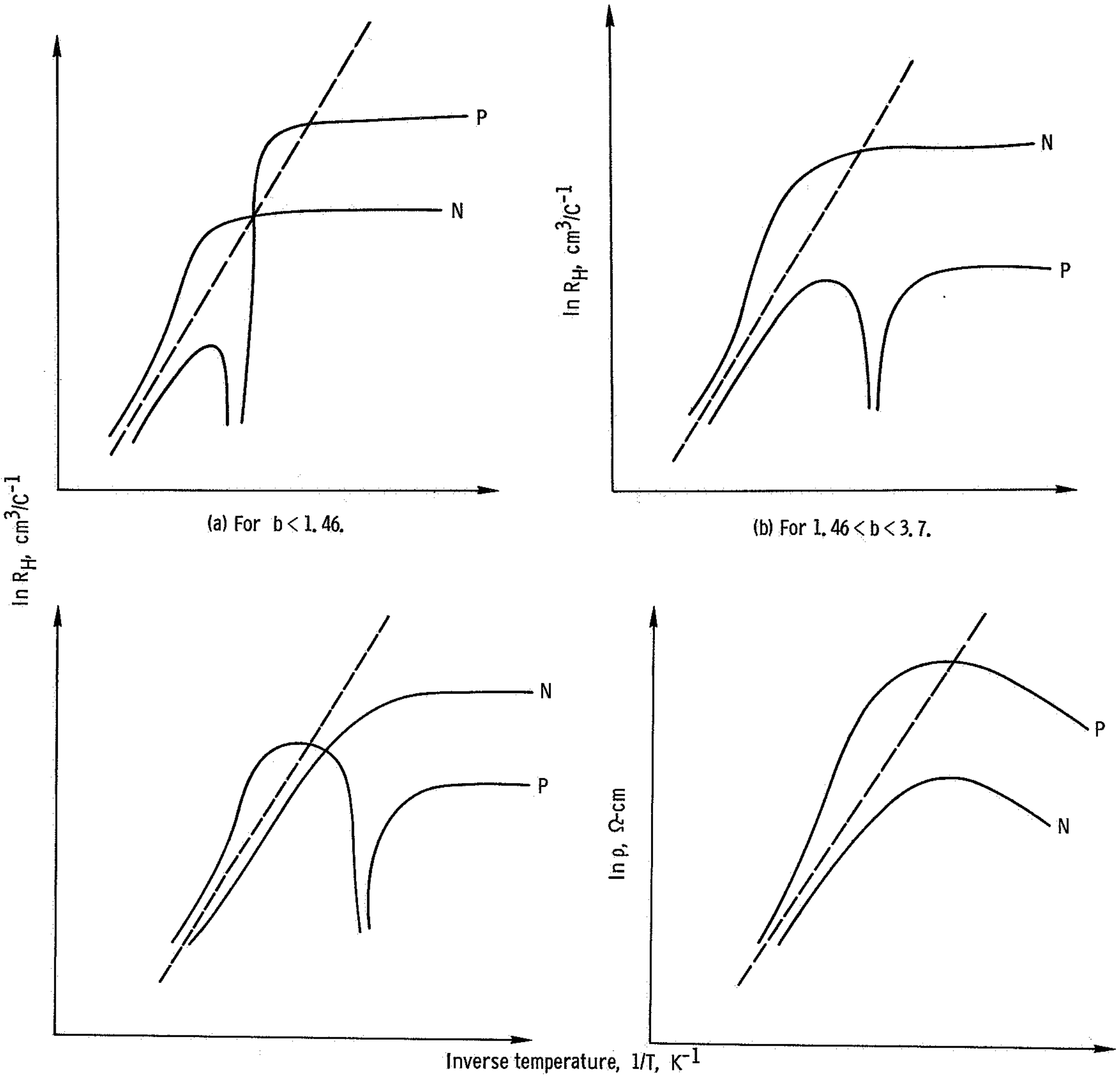
the exponential term in the carrier concentration equation becomes a constant times $\exp(-E_{go}/2kT)$. Therefore, the plots in figure 17 yield the band gap at 0 K. The band [illegible] is not necessarily a linear function of temperature, therefore the plots still appear [illegible] curved in these cases.

[illegible] the Hall coefficient is divided by the resistivity, the Hall mobility is the result. [illegible] intrinsic conduction it becomes

$$\mu_H = \alpha(\mu_p - \mu_n) \tag{68}$$

Interpretation of Data Near Intrinsic Conduction

The Hall and resistivity curves as a function of temperature take on unexpected shapes as they approach the intrinsic region. These shapes are dependent on whether the semiconductor is n- or p-type and on the semiconductor mobility ratio $b = \mu_n/\mu_p$. It is possible that the intrinsic data will be misinterpreted if these shapes are ignored. The



(a) For $b < 1.46$.

(b) For $1.46 < b < 3.7$.

(c) For $b > 3.7$.

(d) For all b.

Figure 17. - Variation of natural logarithms of Hall coefficient and resistivity with inverse temperature for three mobility ratios, $b < 1.46$, $1.46 < b < 3.7$, and $b > 3.7$. Dashed lines indicate true intrinsic slopes.

general shapes of the curves are shown in figure 17. Dunlap (ref. 19) first discussed this problem, but Hunter (ref. 9) describes it in more detail.

There are two prominent features of the curves in figure 17. The first is that the R_H for p-type semiconductors usually changes sign as the intrinsic region is approached. This feature is expressed in equation (6), since μ_n is usually greater than μ_p. The second is that R_H and ρ for some cases at some temperatures are greater than their intrinsic values (shown by the dashed line). This is known as overshoot. Thus, the resistivity for p-type semiconductors for all mobility ratios is greater than the intrinsic resistivity in a certain temperature range. As the temperature increases, the resistivity approaches its intrinsic value. It is now obvious that if measurements of R_H and ρ are not made at temperatures high enough to go beyond the overshoot region, the measured slope will be incorrect. And, therefore, the band gap energy will be incorrect.

SPECIFYING TEMPERATURE RANGE OF DATA

The Hall coefficient and resistivity must be measured throughout certain specified temperature ranges. The informative parts of the curves of n_o and ρ as a function of 1/T appear only at characteristic temperatures. Therefore, in order to ensure that enough data are collected, the required temperature range must be estimated beforehand. This is also likely to be important in terms of cost. For example, if the electrical properties of a specimen need not be measured below liquid-nitrogen temperatures (77 K), the large cost and complications of a liquid-helium cryostat can be avoided.

At low temperatures the limiting factor is the ionization energy of the impurities. The plot of $\ln n_o$ against 1/T must have a constant slope at low temperatures. As the energy levels of the impurities lie closer to the conduction band, the lowest temperature at which data must be taken decreases.

The high-temperature limit is dependent on what is to be obtained. If the band gap of the basic material is to be measured thermally, the data must extend well into the intrinsic region. To measure the doping concentrations of a particular piece of semiconductor, the measurement of the carrier concentration (i.e., Hall coefficient) must extend to the exhaustion region. There all the impurities are ionized and the carrier concentration is constant with temperature.

Obviously, the low- and high-temperature limits are peculiar to each semiconductor material. Therefore, the method of specifying the temperature range will involve searching the literature for information about the band gap and ionization energies and comparing this with known semiconductors, such as silicon and germanium. Measurements on these semiconductors must be as low as liquid-helium temperatures.

In the case of a wide-band-gap semiconductor, such as silicon carbide, the temperature range may be shifted upwards and expanded. Since the band gap is approximately 3 electronvolts for hexagonal silicon carbide, the plateau region of carrier concentration data will probably be above room temperature. Previous measurements made at the Westinghouse Research Laboratory in Pittsburgh indicate that temperatures of at least 550 to 600 K are required to obtain the necessary extrinsic data. This is nearing the intrinsic region, which occurs at temperatures above 850 K (for doping levels of about 10^{17} cm^{-3}).

The low-temperature limit for silicon carbide can be as low as liquid-helium temperatures, but, practically speaking, liquid-nitrogen temperatures are sufficient. An impurity energy level may be very close to a band edge and thus become ionized at extremely low temperatures. However, the probability of this happening in silicon carbide is probably less than in silicon (which has a band gap about one-third that of silicon carbide). Therefore, for the example of silicon carbide, the temperature range of interest would be from liquid-nitrogen temperatures to greater than 550 K. Probably the upper limit should be extended to 850 K to make certain the exhaustion region is reached. For doping levels greater than about 10^{17} centimeter^{-3}, the upper limit may need to be increased even further.

CONCLUSIONS

The measurement and interpretation of the Hall coefficient and resistivity of semiconductors were outlined, and the basic equations of carrier concentration, obtained from other sources, were summarized. Some known methods of interpreting the experimental data by use of these basic carrier concentration equations were then discussed.

In considering the applicability of the measurements to both basic materials research and device design, it was pointed out that the energy levels of the impurities, the band gap energy, and the mobility are valuable to the materials researcher. For the device designer, the mobility, the impurity ionization energies, and the doping concentrations are important. All of these quantities are obtained from an analysis of the Hall and resistivity data.

Two methods of measuring the Hall coefficient and resistivity were briefly described. The van der Pauw method is favored because in that method the semiconductor sample need not be of a particular shape. This is advantageous in the case where only small samples are available.

The mobility of semiconductors was shown to be related to an energy-averaged relaxation time which is a characteristic of a particular scattering process and a specific semiconductor material. The results of the derivation of the relation between mobility and relaxation time were given for the simplest case, where the constant-energy surfaces were spherical and there was only one energy minimum or maximum. The results were extended to the cases where the constant-energy surfaces were nonspherical and there were multiple energy minimums or maximums. Although no relaxation time calculations for specific scattering processes were given, the different kinds of scattering were qualitatively discussed. The factor α which relates the Hall coefficient to the carrier concentration resulted from the same type of derivation.

The equations for charge carrier concentration were developed for both extrinsic and intrinsic conduction. The extrinsic equations were found to be primarily functions of temperature, impurity concentrations, and the impurity ionization energy. The intrinsic equation was a function of temperature and the band gap energy. The extrinsic equations were found to be modified by different types of doping, by inclusion of excited states of the doping impurities, and by degeneracy.

This set of equations for extrinsic and intrinsic conduction was then used as the basis for developing methods of interpreting the measured experimental data. It was found that the parameters of the equations could be estimated with varying degrees of accuracy from the plot of $\ln n_0$ against $1/T$, where n_0 is the equilibrium concentration of electrons and T is temperature. By a method of iterative calculations, the estimated parameters were varied until the calculated results fit the experimental data curve. It was shown that the resistivity plot may help to obtain more accurate values of the impurity ionization energy and the band gap energy at extremely low and high temperatures, respectively.

The shape of the curves of the Hall coefficient and resistivity against reciprocal temperature near the point where intrinsic conduction begins was illustrated. It was found that knowledge of these curves was necessary for correct interpretation of intrinsic data.

The temperature range over which the Hall coefficient and resistivity must be measured in order to use the methods presented in this report was discussed. Measurements must be collected at a temperature low enough that the slope of the $\ln n_0$ against $1/T$ curve becomes constant. At high temperatures the same curve must level off at a constant n_0 (the exhaust region). If intrinsic properties of the semiconductor, such as band gap energy, are wanted, the measurement must extend well above the temperature where the semiconductor becomes intrinsic.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 27, 1968,
120-27-01-25-22.

APPENDIX - SYMBOLS

A	defined function not dependent on temperature
$\vec{B}$	magnetic field, tesla
b	conductivity mobility ratio, μ_n/μ_p
C	effective mass ratio, m_L^*/m_T^*
E	energy, eV
E_a	acceptor ionization energy, eV
E_c	energy of bottom of conduction band, eV
E_d	donor ionization energy, eV
E_{dj}	donor ionization energy of donor of j^{th} kind, eV
E_f	Fermi level, eV
E_g	band gap energy, eV
E_{go}	E_g at $T = 0$ for linear variation of E_g, eV
E_{r1}	energy difference between ground level and r^{th} level, eV
E_v	energy of top of valence band, eV
$\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z$	components of electric field, $V cm^{-1}$
$F_{1/2}(\eta)$	particular Fermi-Dirac integral
f(E)	Fermi-Dirac distribution function
$f\left(\frac{R_{ab, cd}}{R_{bc, da}}\right)$	correction factor in van der Pauw's resistivity equation
g(E)	density of states per unit energy interval in conduction band, cm^{-3} eV^{-1}
h	Planck constant, 6.63×10^{-34} J sec
I	current, A
J_x, J_y, J_z	components of current density, A cm^{-2}
k	Boltzmann constant, 1.38×10^{-23} J K^{-1}
$\vec{k}$	wave vector (components k_x, k_y, k_z make up $\vec{k}$-space), m^{-1}
L	(effective) length of bridge-shaped crystal sample, cm
$m_L^*, m_T^*, m_1^*, m_2^*, m_3^*$	components of effective mass tensor, kg
m_n^*	effective mass of electrons, kg
m_o	mass of free electrons, 9.11×10^{-31} kg
m_p^*	effective mass of holes, kg
N_a	concentration of acceptor impurities, cm^{-3}
N_c	effective density of states in conduction band, cm^{-3}
N_d	concentration of donor impurities, cm^{-3}
N_{di}	concentration of ionized donor impurities, cm^{-3}
N_{dj}	concentration of donor impurities of j^{th} kind, cm^{-3}

N_{dn}	concentration of neutral donor impurities, cm^{-3}
N_v	effective density of states in valence band, cm^{-3}
n_i	intrinsic concentration of electrons and holes, cm^{-3}
n_o	equilibrium concentration of electrons, cm^{-3}
p_o	equilibrium concentration of holes, cm^{-3}
q	electronic charge, 1.60×10^{-19} C
$R_{ab, cd}$	ratio of voltage measured across contacts d and c with current flowing into a and out b (other such ratios defined similarly), ohms
R_H	Hall coefficient, $cm^3\ C^{-1}$
S	summation of effects of energy of excited state of impurity atoms
T	temperature, K
T_m	temperature where $\eta = \eta_m$, K
t	thickness of crystal sample, cm
V_{CE}	voltage drop from C to E, V
V_H	Hall voltage, V
$\langle v_x \rangle$	x component of average drift velocity of electron, $cm\ sec^{-1}$
W	width of bridge-shaped crystal sample, cm
Z	defined function not dependent on temperature, $cm^{-3}\ eV^{-3/2}$
α	constant relating Hall coefficient and carrier concentration
β	impurity level spin degeneracy
β_j	impurity level spin degeneracy of impurity of j^{th} kind
β_r	impurity level spin degeneracy of r^{th} level
ϵ	defined variable, $(E - E_c)/kT$
ϵ_d	defined variable, E_d/kT
ϵ_{dj}	defined variable, E_{dj}/kT
ϵ_{dm}	defined variable, E_d/kT_m
ϵ_g	defined variable, E_g/kT
ϵ_{r1}	defined variable, E_{r1}/kT
η	defined variable, $(E_f - E_c)/kT$
η_m	maximum of η
μ	conductivity mobility, $cm^2\ V^{-1}\ sec^{-1}$
μ_H	Hall mobility, $cm^2\ V^{-1}\ sec^{-1}$
$\left.\begin{matrix}\mu_L, \mu_T, \\ \mu_1, \mu_2, \mu_3\end{matrix}\right\}$	components of conductivity mobility, $cm^2\ V^{-1}\ sec^{-1}$
μ_n	electron mobility, $cm^2\ V^{-1}\ sec^{-1}$
μ_p	hole mobility, $cm^2\ V^{-1}\ sec^{-1}$

ρ	resistivity, Ω/cm
σ	electrical conductivity, Ω^{-1} cm^{-1}
τ	relaxation time, sec
$\langle \tau \rangle$	relaxation time averaged over energy, sec

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