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LOW - TEMPERATURE
ELECTRICAL MEASUREMENTS
ON SEMICONDUCTORS

RADIO CORPORATION OF AMERICA
RCA LABORATORIES DIVISION
INDUSTRY SERVICE LABORATORY

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Approved

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Introduction

The presence of impurities in very small concentrations has a profound effect on the electrical characteristics of a semiconductor. These impurities may be foreign atoms or structural defects in the semiconductor crystal. This bulletin discusses only the former.

The concentration of impurities that gives rise to electrical differences is exceedingly minute. Only about one impurity atom in approximately ten million germanium atoms is needed to make the n- and p-type material used in the ordinary transistor n-p junction. In these concentrations it is virtually impossible to determine the type or quantity of impurities present by ordinary chemical or spectroscopic methods.

Electrical measurements, such as conductivity and Hall coefficient, when made over a wide temperature range including the very low temperatures (e.g., from 300°K to 4°K) can be used in an analysis which gives a great deal of information concerning the nature of the semiconductor. When carried out in detail, this analysis (not described herein) permits a quantitative evaluation of the impurity concentration, the impurity type and carrier activation energy.

The method of making these measurements and a qualitative interpretation of the results are the subject of this bulletin. This discussion will treat only germanium as an example, although the method is equally applicable to other semiconductors.

General Discussion

A. The Current Carriers in Pure Semiconductors

The atoms in a pure germanium crystal are held together by bonds formed by the four outer or valence electrons of each germanium atom. The amount of energy required to detach one of these valence electrons so that it is free to move in the crystal is 0.7 electron volt. Once the electron is freed from the atom, it can move through the crystal under the influence of an applied electric field and constitutes an electric current. In addition, the vacancy left by this electron can be filled by an electron from a neighboring atom with almost no expenditure of energy so that the vacancy or hole is also free to move through the crystal and behave electrically as a current carrier with opposite electrical sign of that of an electron. Under these circumstances, the concentration of electron carriers is equal to the concentration of hole carriers for all temperatures; such hole-electron pairs, when formed by thermal agitation of the crystal atoms, give rise to "intrinsic conductivity".

The carrier concentration in an intrinsic semiconductor depends upon the number of bonds broken by the thermal agitation which, in turn, depends upon the temperature of the crystal. The higher the temperature, the greater is the concentration of carriers. The theoretical behavior of pure germanium is shown in Fig. 1 by the line marked "intrinsic"; here, the logarithm of the concentration of either electron or hole carriers is plotted against the reciprocal absolute temperature. The slope of this line is a measure of the energy required to free an electron and a hole and corresponds to the previously mentioned 0.7 electron volt. It is seen that, at room temperature, the carrier concentration is large and thus the germanium can conduct current easily. At low temperatures, intrinsic germanium is a good insulator since there are only a few carriers available to conduct current.

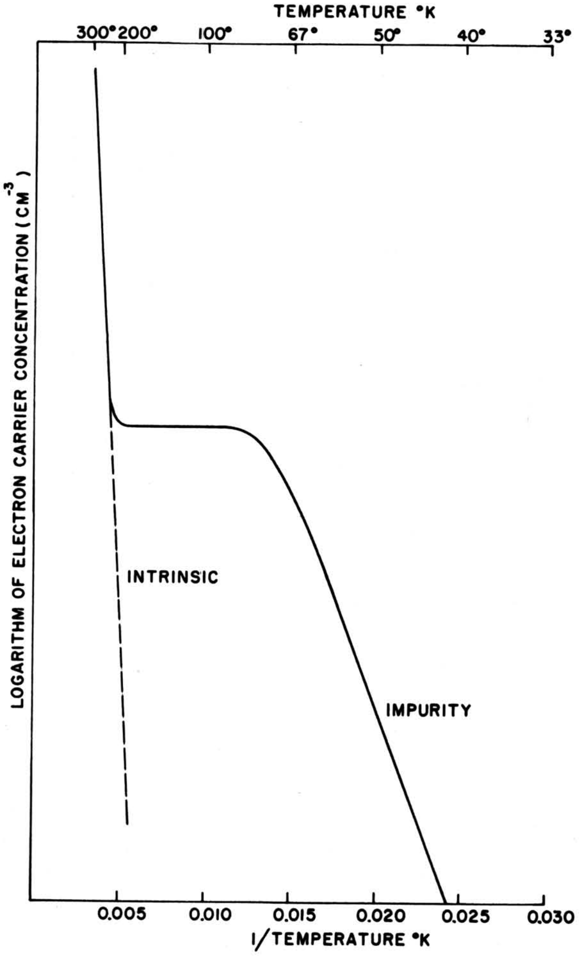

Fig. 1 - Current carrier concentration as a function of temperature.

B. *Impurities as a Source of Carriers*

When impurities are present in germanium, the impurity atoms can be located at positions in the lattice normally occupied by the germanium atoms. If these impurity atoms have more valence electrons than germanium, the extra electrons can also be released thermally from the parent atoms resulting in an excess of electrons over holes. Such a crystal is called an n-type semiconductor and the impurity atoms are called donors. Experiment and theory indicate that the binding energy of the additional electron to an impurity atom is small when the impurity atom is one valence number higher than germanium. Observed values are some ten to a hundred times smaller than the intrinsic binding energy. Examples of this type of impurity are: phosphorous, arsenic and antimony.

If the impurity atoms have fewer valence electrons than germanium, there will be incompleted bonds which can accept electrons from the neighboring germanium atoms. This creates holes similar to those described in the preceding section but bound to the vicinity of the impurity by the charge unbalance. The energy required to release such holes so that they become mobile carriers is the same order of magnitude as that needed to free electrons from a donor impurity of corresponding valence difference. The impurity atoms responsible for these holes are called acceptors and a crystal containing an excess concentration of holes over electron carriers is called a p-type semiconductor. Examples of impurities having one valence electron less than germanium are: aluminum, gallium and indium.

Because the binding energy of the excess electrons to donors, or holes to acceptors, is smaller than the binding energy of the germanium valence electrons, the behavior with temperature of the carrier concentration of an impure crystal will be different from that of an intrinsic crystal. As an illustrative example, the theoretical variation of the logarithm of the concentration of electron carriers versus inverse temperature is shown in Fig. 1 for a crystal of n-type germanium.

It is seen that, at temperatures above room temperature, the effect of the impurities in the case illustrated is masked by the intrinsic behavior of the crystal. For temperatures somewhat below room temperature, the carrier concentration is approximately constant and equals the concentration of donors. This is called the impurity saturation range. At very low temperatures, the carrier concentration decreases with decreasing temperature at a rate depending on the carrier binding energy of the donor. Thus, it is only at the very low temperatures that the character of the impurities is exposed.

C. *The Conductivity of Impurity Semiconductors*

The conductivity, that is, the reciprocal of the resistivity, of the crystal depends on the concentration of current carriers present in the crystal and on the ease with which these carriers can be moved through the crystal when an electric field is applied. For an n-type semiconductor, and one in which the contribution of holes to the current may be neglected, this relation is expressed by

$$\sigma = ne\mu$$

where σ is the electrical conductivity due to n electron carriers per cm^3 having charge e and moving with a mobility μ through the crystal.

The temperature dependence of σ is more complicated than that of n since μ, also, is temperature dependent. At a given temperature, the magnitude of the mobility is determined by the combined effects of scattering of the charge carriers by thermal vibrations of the crystal lattice and by impurity atoms. At high temperatures, scattering by the lattice is the more important. Upon cooling a crystal, the carrier mobility first increases because of the magnitude of the lattice vibrations and, therefore, the scattering of the carriers becomes smaller. At the same time, the velocity of the charge carriers decreases and scattering by impurities becomes relatively more important. At some temperature, which is determined by the impurity concentration in the semiconductor sample, the mobility will pass through a maximum. At lower temperatures, the mobility, determined primarily by impurity scattering, will decrease. This temperature dependence of the mobility may be expressed in terms of small powers of the temperature. Except in the impurity saturation range, the temperature dependence of conductivity is determined primarily by the temperature dependence of the charge carrier concentration which varies exponentially with temperature.

The theoretical conductivity of a germanium crystal containing an excess of donors is shown in Fig. 2. In the immediate vicinity of room temperature, the conductivity falls quite rapidly with decreasing temperature. This is because the intrinsic germanium electrons are giving a marked contribution to the conductivity in this temperature range. Slightly below room temperature, the carriers providing the conductivity come almost entirely from the impurities. From this temperature to a temperature about 200 degrees C lower, there is only a small change in the concentration of carriers. Over this range, however, the mobility is increasing so that the conductivity rises. With further lowering of the temperature, the concentration of carriers decreases rapidly and, in addition, the mobility also decreases somewhat. In general, the rate of decrease of carriers so predominates over the change in mobility that the slope of this portion of the curve is a fairly good measure of the carrier binding energy of the impurities.

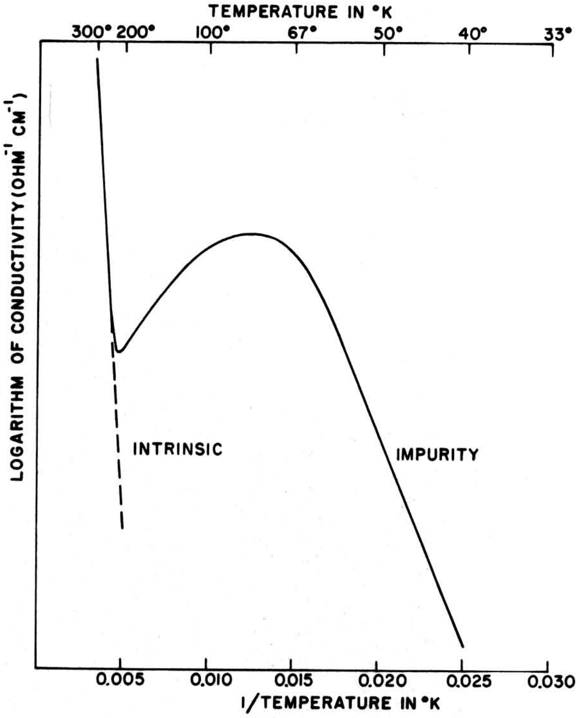

Fig. 2 – Theoretical curve of the variation of conductivity as a function of temperature for n-type germanium.

In examining a cooling curve of the type shown in Fig. 2, the extent of the intrinsic region in the vicinity of room temperature and the position of the maximum of the conductivity curve are both measures of the concentration of impurity atoms. The slope of the conductivity curve at low temperatures is a direct function of the binding energy of the impurity current carriers. Therefore, this type of measurement gives information not only as to the quantity of impurities present but also as to the binding energy of the impurities.

D. The Hall Effect in Impurity Semiconductors

To supplement the conductivity measurement, the Hall effect may be measured as a function of temperature. The Hall effect occurs when a magnetic field is applied perpendicularly to the direction of current flow in the crystal. A transverse voltage is then generated which is proportional to the product of the electric field producing the current, the magnetic field, crystal dimensions, and the current carrier mobilities.

Thus, by combining conductivity and Hall measurements on a crystal, a separation of the effect of electron carrier concentration and carrier mobility can be obtained. The electrical sign of the Hall voltage also gives, in

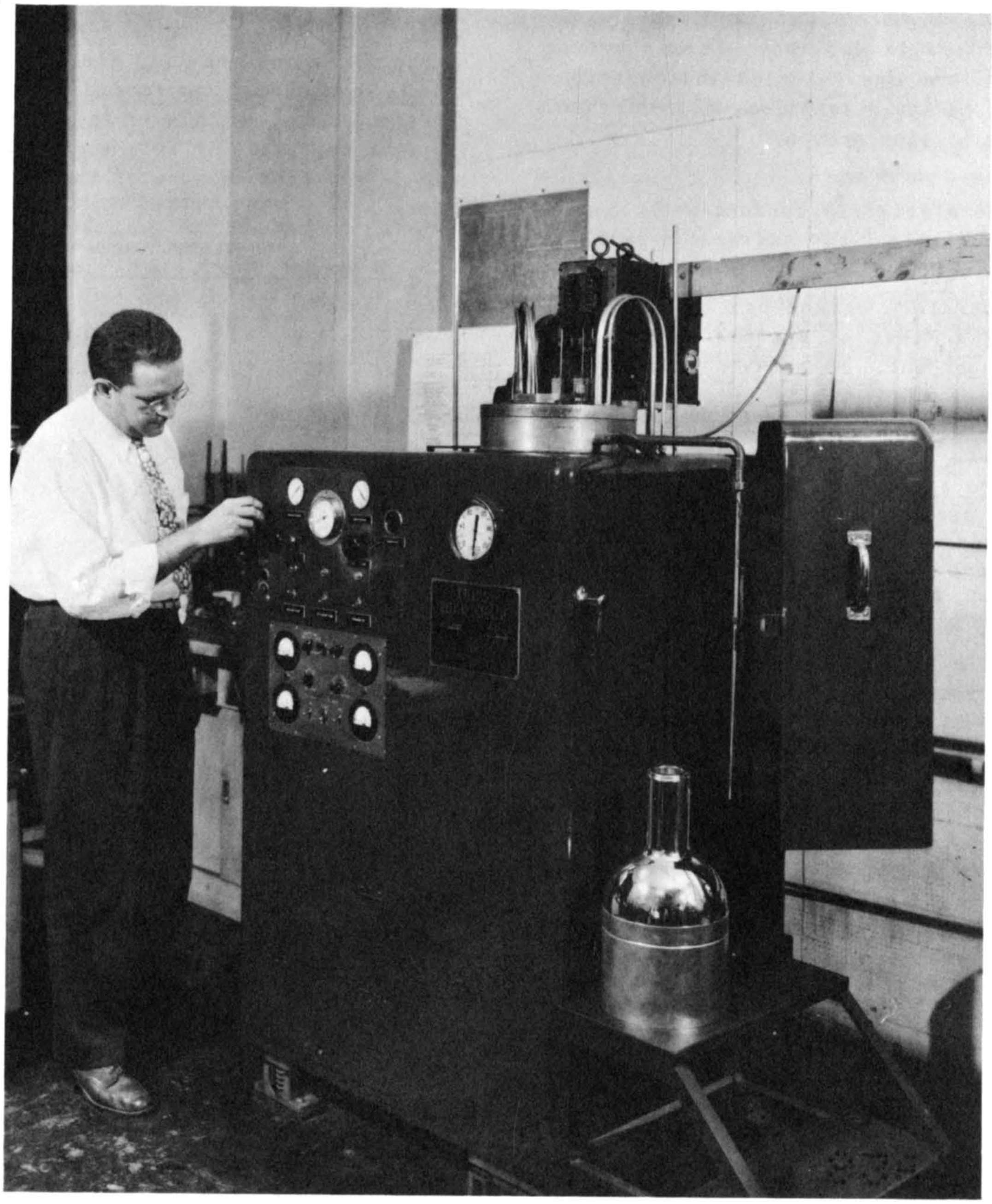

Fig. 3 - Collins liquid helium cryostat.

general, information as to whether the crystal is n-type or p-type. In general, it will suffice to make Hall measurements at only a few different temperatures. Measurements at liquid air, dry ice and room temperatures may be adequate for most purposes.

Experimental Procedure

To obtain the type of information discussed above, two kinds of measurements must be made as a function of temperature from room temperature to very low temperatures. These are conductivity measurements and measurements of the Hall effect.[1]

In order to make these measurements, facilities must be available which will permit reducing the temperature of the crystal to at least the temperature of liquid hydrogen and preferably that of liquid helium. A Collins Liquid Helium Cryostat is a commercial item that is eminently suited for the type of measurements in question. Fig. 3 is a photograph of one of these units.

To measure the conductivity as a function of temperature, a group of crystals provided with external electrical leads are placed in the Cryostat and measured during a low temperature run. Adequate means must be provided for measuring the crystal temperature. One very satisfactory method of insuring an accurate knowledge of the temperature is to mount the crystal directly on a gas thermometer whose cold chamber is suspended close to the bottom of the Cryostat. Furthermore, the crystals must be enclosed in a housing in order to prevent radiation from falling on them since their photoconductivity is sufficient to give false results unless this precaution is taken. The general procedure for a low temperature run is to start with the Cryostat at room temperature and measure the current in the various crystals as a function of voltage at intervals as the temperature falls to liquid helium temperature. With proper adjustment of the heat engine and the expansion valve in the Cryostat, the rate of cooling can be made sufficiently gradual so that the crystals are in good equilibrium with the gas thermometer. In this way, the conductivity curves on a group of six or more crystals may be taken in a period of three or four hours.

Hall measurements cannot be made directly in the Collins Cryostat. An external dewar cryostat is required having a specimen chamber small enough to fit between the poles of the magnet. The crystal with two current leads and a Hall voltage probe is mounted in the small chamber between the poles of the magnet, and Hall effect measurements are made in the usual way.

Experimental Results

The procedure outlined above for conductivity measurements has been used in the examination of a large number of germanium samples. Figs. 4 and 5 give a family of characteristic conductivity-temperature curves obtained with germanium having various degrees of purity. The highest curve is that of crystal No. 3 having a high concentration of impurities. At room temperature, the carriers from impurities completely mask the intrinsic behavior in the crystal. When the crystal is initially cooled, the conductivity rises due to the increasing mobility. Beyond about 50 degrees K, the conductivity falls, due to the decreasing number of carriers from impurities and the more gradual decrease in mobility. As the crystal is further cooled, a long, fairly straight portion of the curve (Fig. 5) is obtained which has a slope corresponding to binding energy of 0.010 electron volt.

The curve for crystal No. 2 is characteristic of a much smaller impurity concentration. As the crystal is first cooled, the decrease in intrinsic carriers causes the conductivity to fall. At slightly below room temperature, the number of intrinsic carriers becomes negligible, and the conductivity is due to impurity carriers. The concentration of impurity carriers changes only slowly in this temperature range while the mobility increases. This causes a rise in conductivity. Below a temperature of about 80 degrees K, the conductivity falls over a fairly wide temperature range, due to the

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[1] See LB-885, *Electrical Measurements on Germanium,* for a more detailed discussion of electrical measurements at room temperature on germanium.

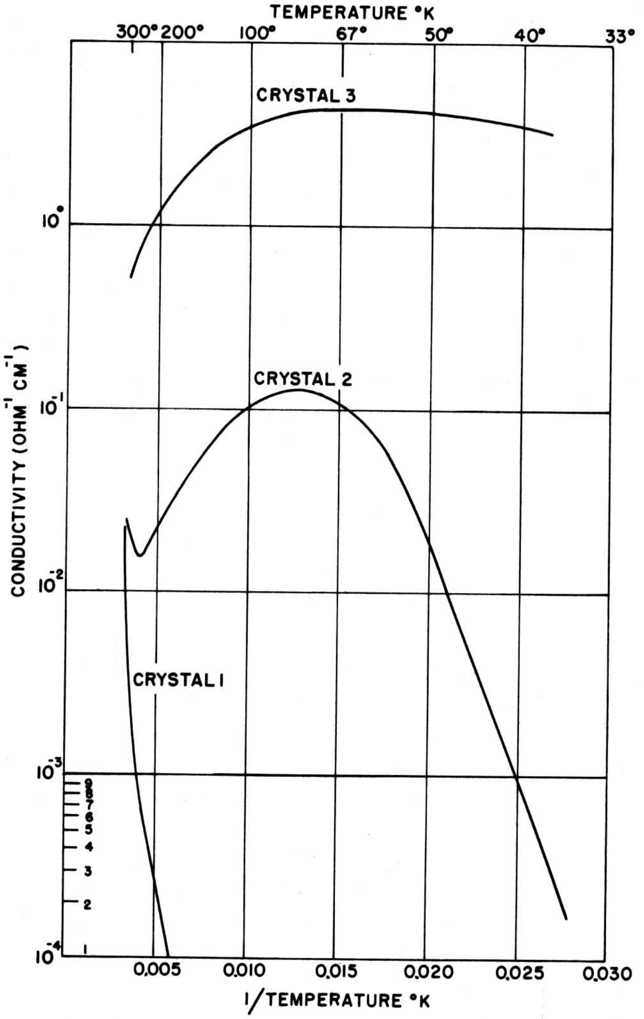

Fig. 4 – Measured conductivity as a function of temperature from 300°K to 50°K for three germanium crystals.

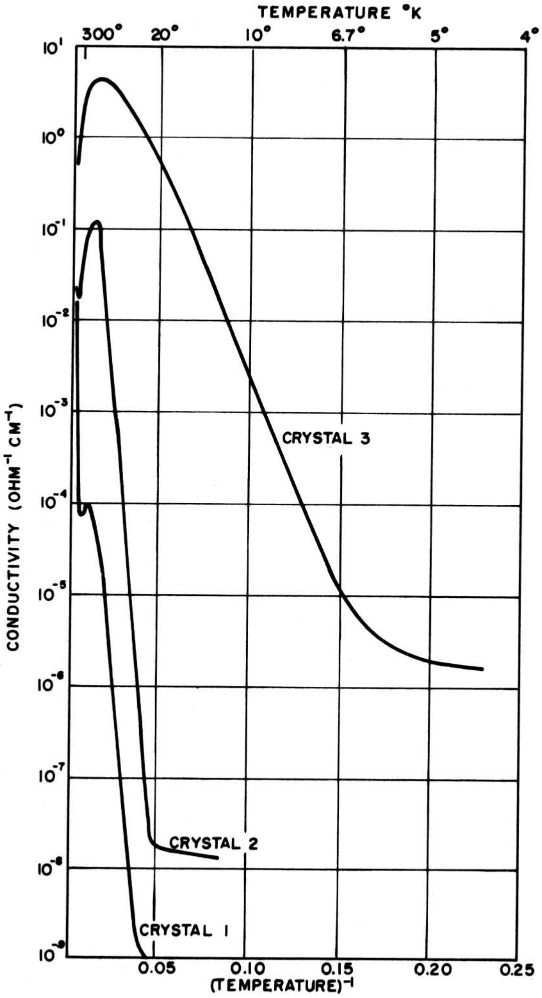

Fig. 5 – Measured conductivity as a function of temperature from 300°K to 4°K for three germanium crystals.

decrease in carrier concentration, giving an almost straight line on the plot. The slope of this line indicates a 0.047 electron volt carrier binding energy. The similarity of this curve to the theoretical curve shown in Fig. 2 is to be noted. For germanium of higher purity, in which the crystal is almost intrinsic, the lower curve for crystal No. 1 is obtained. In this curve, the impurities play only a small role, and the conductivity drops upon cooling over a long range from room temperature to some low temperature. The slope of the curve at low temperatures is again 0.047 electron volt.

The decrease in slope which occurs at very low temperatures as indicated in Fig. 5 for crystals No. 2 and No. 3 is commonly observed. The significance of this change of slope is not at present understood.

Conclusions

The properties of semiconductors which make possible the practical application of these materials in transistors, rectifiers and similar devices are due to the distinctive mechanism of current conduction existing in them. The conduction in semiconductors is due to current carriers either in the conduction band (electrons) or in the filled band ("holes") which can move under the influence of an electric field. From the standpoint of transistors, carriers originating from impurity atoms are extremely important in determining their behavior. A knowledge of the impurity concentration and carrier binding energy is important in attempting to predict the behavior of a given semiconductor.

In the research and development associated with any semiconductor device, information on the impurity concentration and carrier binding energy of its semiconductor constituents is essential. The intimate relation between these two parameters and carrier density and carrier mobility as a function of temperature, and consequently the electrical properties of the semiconductor, permits correlating the preparation of material with the performance of the completed device. Such a correlation is necessary as a guide to the direction of research.

The concentrations of impurities commonly used in semiconductors are too minute to be measured by the usual methods of chemical or spectroscopic analysis. This bulletin has described, however, another method of analysis which gives the required information. The measurement of the conductivity characteristics of a semiconductor from 300 degrees K (room temperature) to 4 degrees K may be used in an evaluation of the concentration of impurity atoms and the carrier binding energy involved.

Finally, it should be pointed out that measurements of the type outlined in this report may also form a basis for quality control of a semiconductor. In such an application, it is assumed that much would be known about the temperature dependence of the electrical properties of the semiconductor for impurity concentrations of approximately the magnitude usually used. If enough information of this type were available, measurements over the whole temperature range may not be required. For example, if it were known that only a particular impurity were present, then the conductivity vs. temperature curves would form a family with impurity concentration as a parameter. Assuming detailed knowledge of this family to be available, then the measurement of the conductivity at a few fixed temperatures would determine the impurity concentration.

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