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# CHAPTER 1

## THE ELEMENTARY PROPERTIES OF SEMICONDUCTORS

### 1.1 Early work on semiconductors

The history of research on the substances now generally known as semiconductors is a long one, extending over more than a century. Much of the early work was carried out under very great difficulties, which are only appreciated now with the fuller understanding which we have of the subject. The purity of the materials available to the early workers fell far below the very high standards which we now know to be necessary if unambiguous results are to be obtained. It is, nevertheless, a high tribute to the skill and care of many experimenters that, in spite of this, semiconductors had been recognized as a distinct class of substances and their main properties appreciated long before a comprehensive theory was available to account for them. That mistakes were made is not surprising. A few substances included once in the class have now been shown to be metals, and a number of substances thought to show metallic behaviour have now been shown, when pure, to be semiconductors.

The first feature used to distinguish this class of electrical conductors from metals and other poor conductors was their negative temperature coefficient of resistance—i.e. their resistance generally falls as the temperature is raised, while that of a metal rises. Michael Faraday would appear to have been the first to notice this effect, when carrying out experiments on silver sulphide.† This criterion is now known to be inadequate, and over a certain range of temperature the resistance of a semiconductor may increase as the temperature is raised, particularly if it contains a fair amount of impurity. At high temperatures, however, a point is reached where a rapid decrease in resistance sets in as the temperature is further increased. Again, certain metallic films show a negative temperature coefficient of resistance as may also polycrystalline ingots of some metals. These effects are now known to be due to oxide films or actual gaps separating the individual crystals but led to the metals titanium and zirconium once being listed as semiconductors.

† *Experimental Researches in Electricity*, series IV (1833), §§433–9; also *Beibl. Ann. Phys.* (1834), 31, 25.

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With these exceptions in mind, however, it is generally true to say that pure semiconductors have a negative temperature coefficient of resistance. They are generally associated with a number of other properties which have been used to distinguish them, and which we shall now discuss. It must be admitted, however, that no infallible criterion was available till the quantum theory of solids gave an understanding of the reasons for the various properties observed.

Except at temperatures not much below their melting point, semiconductors have resistivities considerably higher than good metallic conductors, and also much less than good insulators have. The range of resistivities in solids is indeed enormous. A good metallic conductor has a resistivity of the order of  $10^{-6} \Omega \text{ cm.}$  at room temperature, whereas semiconductors have generally room temperature resistivities in the range  $10^{-3}$  to  $10^6 \Omega \text{ cm.}$  There are, moreover, a great many substances with resistivities in this range which are not semiconductors as we now define them. Good insulators, on the other hand, have resistivities of the order of  $10^{12} \Omega \text{ cm.}$

The progress made in the next forty years after Faraday's observations was not very great, though it was noted by various workers that substances belonging to the class of 'poor conductors' had exceptionally high values of their thermo-electric power, e.g. tellurium. Two important advances were made in 1873 and 1874. The phenomenon of rectification was observed by F. Braun† using substances like lead sulphide and iron pyrites, and photo-conductivity was observed in selenium by W. Smith.‡ Other substances were soon found to show some of these effects but not necessarily all of them. These were mainly metallic sulphides and oxides and the element silicon.

After this, a great deal of work was carried out and a class of substances, called semiconductors (*halbleiter*), with these properties began to emerge. An excellent review of this early work has been given by K. Lark-Horowitz,§ together with a very extensive bibliography containing over 350 references. Earlier reviews by B. Gudden|| also deal extensively with this phase and discuss in some detail the problems of identifying semiconductors.

The main properties of these substances which emerged were:

- (a) negative temperature coefficient of resistance;
- (b) resistivity in range roughly  $10^6$  to  $10^{-3} \Omega \text{ cm.}$ ;

† *Ann. Phys. Chem.* (1874), **153**, 556.

‡ *J. Soc. Telegraph Engrs* (1873), **2**, 31.

§ 'The New Electronics', in *The Present State of Physics* (American Assn. for the Advancement of Science, Washington, 1954).

|| *Ergebn. exakt. Naturw.* (1924), **3**, 143; (1934), **13**, 223.

- (c) generally high thermo-electric power, both positive and negative relative to a given metal;
- (d) rectifying effects or at least non-ohmic behaviour;
- (e) sensitivity to light—either producing a photo-voltage or change of resistance.

It was not long before the important part played by impurities came to be appreciated. It was noted that some of the properties, in particular the negative temperature coefficient of resistance at high temperatures, were always the same for a given substance. Others varied considerably from sample to sample. The former were called 'intrinsic' properties. This variation hampered the study of the 'intrinsic' properties as one could never be quite sure that an observed effect was not due to impurities. This doubt has only very recently been removed, now that impurities in many semiconductors can be accurately controlled.

A most important event, as it turned out later, took place in 1879 with the discovery of the Hall effect,† the transverse voltage developed across a conductor carrying a current in a magnetic field. Although at this time the electron had not been discovered, so that the idea of number of current carriers had not arisen, this effect turned out to be the key to understanding electrical conduction in semiconductors, and in distinguishing them from other poorly conducting substances. The reason for this is, as one shall see, that a measurement of the Hall voltage enables us to determine directly the number of current carriers per unit volume, and also whether they are positively or negatively charged. It also enables us readily to distinguish ionic conduction from electronic conduction, a distinction which is very necessary, as the conductivity due to the former increases rapidly with temperature, and may lead to a false conclusion.

The various methods of distinguishing between ionic and electronic conduction have been discussed by K. Lark-Horowitz (*loc. cit.*) in some detail and also the difficulties of interpretation caused by failure to make the distinction. Before the use of the Hall effect the distinction was usually made by noting whether electrolytic transport took place or not. The Hall effect due to an ionic current is, as we shall see, negligible compared with that due to the electronic current and this allows the latter to be identified.

The electronic conductivity of a substance depends on two factors, the number of current carriers per unit volume and the ease with which the carriers move through the substance under an applied electric field. The latter, which is generally known as the carrier mobility, and which

† E. H. Hall, *Amer. J. Math.* (1879), 2, 287.

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we shall define more precisely later (see § 5.1, equation (14)) generally tends to decrease as the temperature is raised, especially at the higher temperatures, and this accounts for the decrease in conductivity of metals with increasing temperature. For these, the number of current carriers remains constant as shown by Hall effect measurements on metal foils. For a semiconductor, however, the number of current carriers increases rapidly with temperature, especially at higher temperatures and this accounts for the rapid decrease in resistance. Here then we have the essential distinction between a metal and a *pure* semiconductor. We emphasize the word *pure*, since too much impurity may mask the distinction. A metal is a conductor with essentially a constant number of current carriers—a pure semiconductor is one in which the number increases as the temperature is raised.

The first systematic use of the Hall effect to study semiconductors appears to be due to K. Bacdeker† using CuI. Detailed studies of a large number of substances were made by J. Königsberger,‡ using the Hall effect and other properties listed above. It was found that the number of current carriers in semiconductors was very much less than in metals but that their mobility, in general, was somewhat higher. One very important result of this work was that the elements silicon, selenium and tellurium were classed as semiconductors. It was much later that germanium was added.§ Königsberger fully appreciated the distinction outlined above.

A very interesting observation was made regarding the sign of the current carriers. This was sometimes found to be negative as expected for electrons but was also found in many instances to be positive, and even to change sign from positive to negative as the temperature was raised. Positive Hall coefficients had also been found for certain metals and this gave rise to a theoretical puzzle which was not solved till the advent of the quantum theory.

##### 1.1.1 'Excess' and 'defect' semiconductors

A considerable amount of work on a large variety of substances thought to be semiconductors was carried out between 1910 and 1930 but not a great deal of fundamental progress was made. Increased interest in these substances was aroused about 1930 largely due to the stimulus of technological applications. Hall effect, conductivity and thermo-electric power measurements were mainly used for their study and it was shown

† *Phys. Z.* (1909), **29**, 506.

‡ *Jb. Radioakt.* (1907), **4**, 158; *ibid.* (1914), **11**, 84.

§ E. Merriott, *Proc. Nat. Acad. Sci., Wash.* (1925), **11**, 743.

that the sign of the Hall effect, at low temperatures, and of the thermo-electric power are generally the same. A study of the chemistry of a number of semiconducting compounds led C. Wagner† to identify two distinct types of semiconductor—'defect' and 'excess' semiconductors. The substances concerned were mainly metallic oxides and sulphides and the 'defect' semiconductors were those with a metallic content less than that corresponding to stoichiometric composition, i.e. oxydized compounds. They generally showed a positive Hall coefficient at low temperatures and a positive thermo-electric power. The 'excess' semiconductors were 'reduced' compounds and had an excess of metal. They had generally a negative Hall coefficient at all temperatures. For the 'defect' semiconductors the Hall coefficient sometimes became negative at high temperatures. These are what we now call respectively *p*-type (*p* for positive) and *n*-type (*n* for negative) semiconductors. The importance of this work was in showing the vital part played by deviations from stoichiometric composition in determining the properties of compound semiconductors.

### 1.1.2 The alkali halides

Although they are not strictly semiconductors but insulators, mention must be made of the large amount of research carried out by R. W. Pohl‡ and his collaborators on the alkali halides, since this helped greatly to clarify many of the properties of semiconductors. One of the main reasons for choosing this group of substances was that they may be readily obtained in the form of large single crystals of high purity. Much of the work on the metallic oxides and sulphides was carried out with compressed powders and evaporated or chemically deposited thin films. These are now known frequently to give very misleading results. It should be noted that the conductivity in the alkali halides is mainly ionic in character but electronic conductivity may be produced by illumination with ultra-violet light. Study of this photo-conductivity paved the way for understanding the similar effect produced by visible light and infra-red radiation in semiconductors.

### 1.1.3 Surface and bulk effects

Much of the uncertainty of the early work on semiconductors arose through a failure to differentiate between effects which arise in the bulk

† *Z. Chem. Phys. B* (1930), **II**, 163; *ibid.* (1933), **22**, 195.

‡ This work was started about 1920. A good account of some of it is given by Pohl in *Proc. Phys. Soc.* (1937), **43**, 3. See also, N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, 1940).

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of the material and those which are characteristic of the surface or of the interface between two different materials. Extensive use of compressed powder samples accentuated the surface effects. It was later thought that a negative temperature coefficient of resistance is always a bulk effect but it is now known that this is by no means so. Rectification was rightly classed as a surface or interface effect but a great deal of confusion arose over photo-voltaic and photo-conductive effects. This has not been entirely clarified at the moment for the highly photo-conductive thin layers used in infra-red detectors (see § 12.7).

For a few semiconductors, natural crystals were available for study, for example, lead sulphide (galena), but these were usually of doubtful purity. A new phase in the study of these substances has begun in the past decade with the growth of synthetic crystals of a number of semiconductors. It is mainly with this phase of the work that we shall be concerned in this book. The use of single crystals has enabled not only the separation of the bulk and surface properties but has also enabled the surface and the interface between two types of semiconductor, or between a semiconductor and a metal, to be studied in much greater detail. Such studies have shown in no uncertain way how very misleading results may be obtained when such surfaces are not taken into account, as for example, in polycrystalline materials.

### 1.2 Applications of semiconductors

The first important application of semiconductors was to provide rectifiers for low-frequency alternating currents. Such rectifiers, using selenium, were made as early as 1886 by C. E. Fritts† although they were not used to any extent in power engineering or in electronic equipment till much later. The copper oxide rectifier was introduced by L. O. Grondahl and P. H. Geiger‡ in 1927 and came to be used extensively as a low-power rectifier in battery chargers, wireless sets, etc. The development of selenium rectifiers on a commercial scale also began to take place at about the same time and these have now largely replaced the copper oxide type in electronic equipment. The development of these rectifiers has led to a great deal of work on both copper oxide and selenium. In spite of this the amount of detailed fundamental knowledge of their properties as semiconductors is still rather scanty compared with what we now know of element semiconductors such as germanium and silicon. In the case of selenium this is largely due to its complex crystal structure and to the

† *Amer. J. Sci.* (1883), **26**, 465.

‡ *Trans. Amer. Inst. Elect. Engrs* (1927), **46**, 357.

existence of different forms, together with the difficulty of obtaining the substance in a pure state. The photo-conductive properties of selenium, and of copper oxide, have been used to provide exposure meters for photography and photo-cells which are widely used in the film industry for transforming the markings on the sound track into electric currents for amplification and reproduction by loud-speakers. Such cells are also used in a number of automatic devices such as burglar alarms, train counters, etc.

Although radio waves had been demonstrated by Hertz in 1888, it was not until about 1904† that it was appreciated that the rectifying properties of semiconductors could be used to provide a detector of the high-frequency currents set up in an electric circuit by these waves. In the following few years a great variety of substances were tried. The discovery that a fine wire, or 'cat's whisker', in contact with a crystal of semiconducting material made an excellent rectifier for high-frequency currents led to a great increase in the sensitivity of radio receivers, and this type of device was widely used in the early days of broadcasting. The two substances generally preferred were silicon and lead sulphide, the latter being in the form of natural crystals of galena. An interesting controversy arose as to whether the rectification effects were electrical or thermal in origin. This was settled by the extensive work of G. W. Pierce‡ who showed that there could be no doubt that they are electrical.

The crystal detector was soon replaced by the thermionic valve and had largely become obsolete by 1939. With the development of very short wavelengths (of the order of 10 cm. and less) for radar it came into its own once again, since no other device was found to act as an efficient rectifier or frequency changer at these extremely high frequencies. Silicon proved to be the best substance for this application. The British work in this field has been described by B. Bleaney, J. W. Ryde and T. H. Kinsman§ and a full account of this and the American work has been given by H. C. Torrey and C. A. Whitmer.|| The stimulus of this application led to a great deal of fundamental work on silicon, particularly at the Bell Telephone Laboratories and at Purdue University in the U.S.A. Germanium, being the next element to silicon in the same column of the periodic table, was also extensively studied in both of the above laboratories. Since it has a much lower melting point and is easier to purify, it was a more suitable substance than silicon for fundamental

† J. C. Bose, U.S. Patent, 755840 (1904).

‡ *Phys. Rev.* (1907), **25**, 31; *ibid.* (1909), **28**, 153; (1909), **29**, 478.

§ *J. Inst. Elect. Engrs*, IIIA (1946), **93**, 847.

|| *Crystal Rectifiers* (Radiation Laboratory Series) (McGraw Hill, 1948).



## 8 ELEMENTARY PROPERTIES OF SEMICONDUCTORS

studies and soon became the semiconductor about which far more was known than about any other. Although it was not effective when first tried as a radar detector it found a very important use in the development of small compact rectifiers for use at low frequencies—the so-called germanium high back-voltage diodes. As it turned out, its study as a semiconductor was most fortunate since it led to the discovery of transistor action (see § 12.3) by J. Bardeen and W. H. Brattain† and to the invention of the transistor or crystal triode‡ in the Bell Telephone Laboratories.

The detailed study of transistor action and of the controlled injection of current carriers into semiconductors by W. Shockley, G. L. Pearson and J. R. Haynes,§ led to an enormous increase in research on the properties of germanium, and later of silicon, as it was realized that the transistor was capable of playing a large part in the future development of electronics, and might well replace a substantial fraction of the vast number of vacuum tubes used by the electronics industry. The large research effort employed in transistor development has led to a far better understanding of the fundamental properties of germanium and silicon. The transistor effect has itself proved to be a most powerful tool for investigating the fundamental properties of semiconductors so that the interaction between pure and applied research has been most fruitful. We defer discussion of transistor action till Chapter 12.

Another group of semiconductors which has found important applications is that known as the infra-red photo-conductors, particularly the sulphide, selenide and telluride of lead. These have been used to make the most sensitive infra-red detectors so far available for the important region of the infra-red spectrum between  $1.5$  and  $7\mu$ . This in turn led to a great deal of work on these substances, started in Germany during the years 1940–45 and greatly extended in recent years in a number of laboratories, and particularly at the Royal Radar Establishment, Malvern. Recent work on these substances and the development of infra-red detectors has been reviewed by R. A. Smith.¶ The properties of these detectors and their use in infra-red spectroscopy have been fully described by R. A. Smith, F. E. Jones and R. P. Chasmar.¶

† *Phys. Rev.* (1949), **75**, 1208.

‡ Accounts of the research work which led to the discovery of transistor action are given by W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, 1950), ch. 2, and by G. L. Pearson and W. H. Brattain, *Proc. I.R.E.* (1955), **43**, 1794.

§ *Bell Syst. Tech. J.* (1949), **28**, 344.

¶ *Advanc. Phys.* (1953), **2**, 321; *Sci. Mon.* (1956), **82**, 3.

¶ *The Detection and Measurement of Infra-red Radiation* (Oxford University Press, 1957).