SEMI-CONDUCTOR MONOGRAPHS

PREPARATION OF SINGLE CRYSTALS

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PREFACE

THIS book attempts to bring together information on the purification of materials and on the preparation and growth of single crystals having special reference to semi-conductors. It is designed to supplement the monographs scheduled for production on other aspects of semi-conductor research. It is hoped that it may be of use to people embarking on or even actively engaged in research work in this field, and to students of physics, metallurgy and chemistry interested in these problems. The book is non-mathematical and, we hope, will be easily understood by those having no previous acquaintance with the subject. We gratefully acknowledge helpful and stimulating discussions with our colleagues in the Physics Department of R.R.E.

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INTRODUCTION

THE demand for single crystals of greater and greater purity and perfection is echoed in every branch of research concerned with the solid state. The reason is not difficult to find. The foundation stones on which so much of the recent and staggering advances in our understanding of the solid state rests are, in fact, pure, single crystals. In metallurgy, the properties of metals are being rediscovered. Iron, for instance, is a soft metal and so are titanium, tantalum and chromium. Single crystal whiskers have been grown with yield strengths 1,000 times greater than previously observed. Spectroscopists can only assign absorption bands with certainty using very pure crystals. Purity is of paramount importance also in the field of atomic energy; boron, for example, is intolerable in a reactor. Similarly, hafnium present in zirconium is intensely radioactive. Pure crystals are required by physicists to investigate radiation damage, superconductivity, nuclear and electron resonance, and by chemists for research into molecular structure. And in no field is the demand for single crystals more incessant than in semi-conductor research.

Semi-conductors are that large class of compounds having electrical conductivities intermediate between those of metals and insulators. As their name implies, they are capable of conducting electrical current in special circumstances but not so well as metals. A precise definition is difficult and depends on the property considered. The electrical conductivity of pure semi-conductor crystals usually increases with temperature—the reverse of metals. They will be thought of in this book as materials having energy gaps between 2 eV and practically zero, the energy gap being the energy separating the valence band from the conduction band.

The energy band picture of solids is a most useful concept and will be referred to frequently throughout this book. It may be thought of in the same way as the familiar energy band structure of the atom. In the atom, the electrons circle the nucleus in orbits characterized by particular energy levels. When the atoms interact to form a solid, the atomic energy levels become energy bands characteristic of that solid (*Figure 1*). These energy bands, which consist of a very large number of energy levels very close together, are still separated by forbidden regions, as in the free atom. The

electrons in the solid can be excited to high energy states in the same way as those in the atom. Excitation in the case of a semi-conductor may occur from the upper filled valence band to a higher energy conduction band. The energy required is equal to the energy gap and varies widely for different materials. The electrons
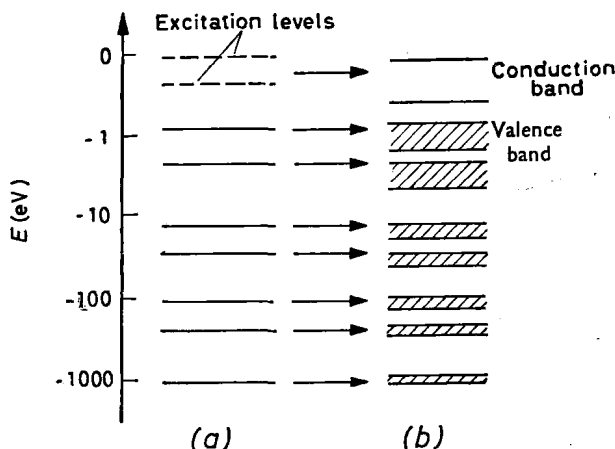

Figure 1. (a) Energy levels in a free atom; (b) Energy bands in a solid

in the conduction band are free to move through the solid and hence contribute to electronic conduction. The vacancy or 'hole' left behind in the valence band behaves as a positive charge and is also free to move about and contribute to conduction. Hence, the above definition of a semi-conductor. To complete this picture, a metal may be thought of as a material with zero energy gap and an insulator with a very large energy gap—greater than 2 eV.

As the physics of the solid state becomes better understood, so semi-conducting devices become increasingly important. The importance of the transistor is symbolized in the award of the Nobel Prize for Physics to Doctors Shockley, Brattain and Bardeen. Transistors are now replacing valves in every sphere of the electronics industry. For their manufacture, tons of germanium and silicon must be extracted, purified and grown into single crystals. They have the tremendous advantage of not requiring heated cathodes. Transistors are, however, not the only solid state devices. Diodes, rectifiers, scintillators, particle-counters, gauss meters, thermoelectric generators and coolers, magnetic switches, magneto-resistances, surge protectors, infra-red detectors and filters are

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among the rapidly growing list of applications. Semi-conductors in the form of layers are used in phosphorescent and fluorescent screens, solar energy convertors, detectors of visible and infra-red radiation (some fire alarms are of this type), resistors, capacitors, rectifiers, and the theory of the solid state is playing an increasing part in the development of newer ceramics, glasses and industrial catalysts.

Germanium and silicon are by no means the only materials which are used in semi-conduction devices. The list of materials is already extensive and includes both inorganic and organic materials. Undoubtedly, very much more is known about germanium and silicon than about any other semi-conductor, and one of the important conclusions from these extensive investigations is that the intrinsic properties of a solid cannot be ascertained until single crystals of a sufficiently high purity and perfection can be prepared. Impurities, even in concentrations less than one part per million, have pronounced effects on the semi-conducting properties of the material.

The design and scope of this book can best be illustrated by a summary of the chapters. It must be stressed that although we have made frequent reference to the work on germanium and silicon, we have done this only to illustrate general principles. Primarily, we wish to draw attention to those intermetallic compounds which we feel have considerable potential use as semi-conducting devices. The work on germanium and silicon has been discussed in detail elsewhere, whereas work on other semi-conductors has received comparatively little attention.

In Chapter 2, methods used for growing single crystals are discussed. Methods are not presented historically but in an attempt to evaluate their usefulness for any particular compound. Chapter 3 includes details of the apparatus required for crystal growing. Vacuum equipment, furnaces and methods of heating, control of temperature, and the design of apparatus for growing crystals by pulling from the melt, by the Stockbarger method, and from the vapour, are described. The purification of materials is considered in Chapters 4 and 5; techniques involving zone melting, distillation, sublimation, filtration, electro-deposition, extraction, chromotography, etc., are described. Methods of purifying the common gases used in semi-conductor preparation are very briefly outlined.

In Chapter 6 a brief summary is made of the techniques which have been useful in checking the efficiency of purification processes and in estimating the final impurity concentration in materials.

Chapter 7 deals with the preparation of intermetallic compounds. Particular attention is paid to methods of eliminating incidental contamination. Methods for cleaning and handling various crucible

materials and containers, the use of clean boxes, and the construction and use of a clean laboratory are discussed.

In the remaining chapters, crystal defects and, in particular, their relation to crystal growth are discussed: Chapter 8 outlines the types and properties of the defects found in crystals; Chapter 9 includes a discussion on how these defects are introduced during growth and how they can best be reduced to a minimum; and Chapter 10 discusses in more detail the important defect impurity atoms and how they are incorporated into the lattice. Finally, in the Appendix a table of semi-conductors with some of their properties as they have been reported is given.

So that there is no confusion in subsequent chapters we include this introduction with a short note on the electrical properties of semi-conductors.

ELECTRICAL AND OPTICAL PROPERTIES
OF SEMI-CONDUCTORS

These can be explained very simply by consideration of the energy band spacing of *Figure 1*. *Figure 2(a)* shows on a larger scale the
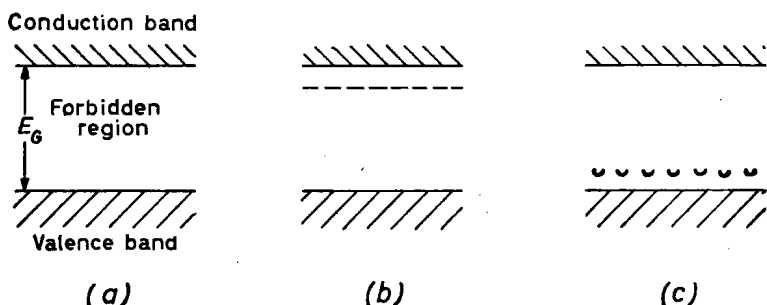

Figure 2. (a) Pure semi-conductors; (b) Semi-conductor with donor impurities (n-type); (c) Semi-conductor with acceptor impurities (p-type).

upper filled band, i.e. the valence band which contains the outer valence electrons, and the conduction band, separated by a region of width E_G normally forbidden to electrons. E_G is usually expressed in electron volts. In a semi-conductor there are just sufficient electrons to fill all the bands up to the valence band and at absolute zero the conduction band would be completely empty. At a higher temperature T collision processes give rise to a distribution of thermal energies of the electrons around kT such that an electron in the valence band has a finite chance of being excited into the conduction band even though kT is less than E_G. At temperature

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$T\,°$K the equilibrium concentration N of electrons excited thermally into the conduction band is given by

$$N = CT^{3/2} \exp\,(-E_G/2kT) \qquad (1)$$

where C is a factor characteristic of the material. Other things being equal N is thus primarily dependent on E_G.

For example, in germanium at room temperature $N = 3 \times 10^{13}$ per c.c. and in InSb at room temperature $N = 2 \times 16^{16}$ per c.c.

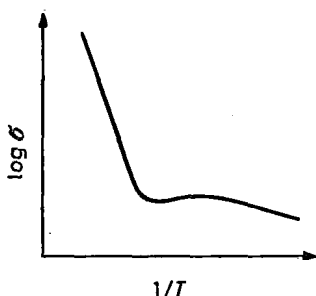N is also the concentration of positive holes in the valence band.

Figure 3. Typical log $\sigma v1/T$ curve for a semi-conductor.

Conductivity

The electrical conductivity of a pure semi-conductor depends on the value of N and is given by

$$\sigma = Ne(\mu_e + \mu_h)$$

where e is the electronic charge and μ_e and μ_h are the mobilities of electrons and holes respectively, i.e. their velocities under unit applied electric field. In some semi-conductors, but not all, the carrier mobilities are proportional to $T^{-3/2}$. Thus from eqn. 1 the conductivity varies exponentially with inverse temperature and a graph of log σ against $1/T$ should be a straight line. A typical experimental result is given in *Figure 3* where it is seen that the exponential law is followed but only at higher temperatures. The value of E_G can be calculated from the slope of the straight line region but this will be accurate only if mobilities follow the $T^{-3/2}$ law. If they follow some other law, e.g. T^{-2} the particular mobility–temperature law must be known before E_G can be calculated accurately. E_G itself varies slightly with temperature.

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The deviation of the log σ curve from the straight line at lower temperatures is due to the presence of impurities or to defects in structure or composition of the crystal. These can give rise to additional energy levels in the normally forbidden region as shown in *Figures 2(b)* and *2(c)*. *Figure 2(b)* represents the possible situation when impurity atoms have surplus electrons which can be easily detached and excited into the conduction band. These are n-type or donor impurities, e.g. phosphorous in germanium or tellurium in InSb. The conductivity at low temperatures is almost entirely due to these electrons and the material is said to be n-type. *Figure 2(c)* represents the situation when the impurity atoms have a deficiency of electrons and can easily capture electrons from the valence band, e.g. aluminium in germanium or zinc in InSb. Here the impurities are p-type or 'acceptors' and the material is p-type. When one type of carrier predominates the conductivity is given by

$$\sigma = Ne\mu$$

The particular temperature at which the log σ curve deviates from a straight line depends on the impurity concentration and the positions of the impurity levels in the forbidden region. The temperature region where impurity carriers predominate is called 'extrinsic' and the remainder 'intrinsic'. At sufficiently low temperatures the number of carriers, impurity and intrinsic can be negligibly small, unless the impurity concentration is very high, so that the semi-conductor becomes an insulator. This is the reverse of metals where, at low temperature, the resistance decreases to negligible values.

Hall effect

This is a most useful effect for determining the number and type of carriers in a conductor, and it finds its greatest application in semi-conductor measurements. It occurs when a current flows in a slice of conducting material and a magnetic field is applied at right angles to the direction of current flow as in *Figure 4*. The carriers are deflected to one side or other of the slice, depending on the relative directions of magnetic field and current and on the sign of the carriers. A transverse electric field is built up across the specimen, since more charge is carried along one side than the other, until a balance occurs, and this field can be measured with a suitable voltmeter, usually a potentiometer. The field is given by

$$E = RJH$$

where J is the current density and H the magnetic field. R is a coefficient of proportionality, the Hall coefficient, which depends

on the material. In terms of measured quantities V, H and I, where V is the Hall voltage in volts, I the total current in amps, and w and t the width and thickness of the specimen in cm, the above equation becomes

$$\frac{V}{w} = R\frac{I}{wt}H \times 10^8$$

or

$$R = \frac{Vt}{IH \times 10^8}$$

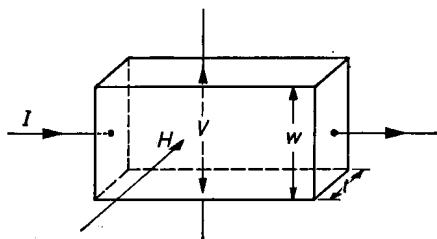The units of R are then cm³/coulomb.

Figure 4. Hall effect

The direction of V shows whether the current in the specimen is carried by electrons or positive holes, since, for the same current and magnetic field directions, carriers of opposite sign move to the same side. The magnitude of V and thus R depends on the carrier concentration and it can be shown that in a specimen where one type of carrier predominates, e.g. in an impurity region

$$R = \frac{3\pi}{8}\frac{1}{Ne}$$

thus

$$N = \frac{7\cdot35 \times 10^{18}}{R}\text{ per c.c.}$$

(In some circumstances the factor $3\pi/8$ is replaced by 1.)

Thus R can give a measure of the concentration of effective impurities, i.e. of those contributing carriers, and the nature of the contributing impurity can be inferred from the sign of V. When carriers of both types contribute to conduction, R is given by

$$R = \frac{3\pi}{8}\frac{1}{e}\frac{n\mu_e^2 - p\mu_h^2}{(n\mu_e + p\mu_h)^2}$$

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where n, p and μ_e, μ_h are the concentrations and mobilities of electrons and holes respectively. An exact analysis of Hall co-efficient curves with temperature under these circumstances is left to other books in this series.

p–n junctions

A p–n junction is formed when n- and p-type material are brought together. Such a junction will usually act as a rectifier. In practice p–n junctions are built-in during crystal growth or are formed by diffusion of suitable impurities into a crystal, or by alloying.

Optical absorption and photoconductivity

Electrons can be excited into the conduction bands by absorbing energy from incident radiation, but only if the quantum energy of the radiation is greater than E_G. If this energy is insufficient the electrons cannot jump the gap and the radiation cannot be absorbed by this process. A typical curve of absorption against wavelength for a semi-conductor is shown in *Figure 5*. The wavelength at which
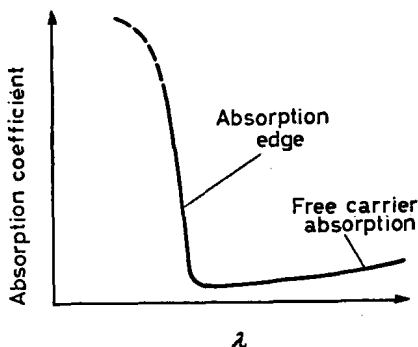

Figure 5. Spectral absorption in a semi-conductor.

the absorption falls sharply, the absorption edge, occurs when the quantum energy $h\nu$ or hc/λ becomes equal to E_G.

Thus at this wavelength $E_G = hc/\lambda = 1 \cdot 24/\lambda$ eV.

This is a recognized method of determining E_G. The use of semi-conductors as optical filters follows. Absorption beyond the edge is due to residual free carriers in the semi-conductor and can give an indication of purity.

The absorption can be used to detect radiation, since the conductivity will change when the carrier concentration is altered on absorption; this change of conductivity can be measured. This is the principle of the photoconductive detector. In practice the

radiation falling on the specimen may be chopped at a suitable frequency by a rotating sectored disc and the changes in conductivity measured by a tuned a.c. amplifier: a very stable sensitive detector results.

These are a few of the simpler properties of semi-conductors which will be referred to later in the book. A more detailed survey of these properties will be given in other books in this series.

A SURVEY OF METHODS OF GROWING SINGLE CRYSTALS

In this chapter, we have surveyed the methods used for growing single crystals, paying particular attention to those which have been applied to semi-conductors and to the degree of crystal perfection which can be obtained. Methods used may be divided into growth from the melt, from the vapour, from supersaturated solutions, by electro-deposition, by thermal diffusion and by other methods. At the present time, growth from the melt is by far the most important of these methods, but increasing attention may have to be paid to methods of growth from the vapour.
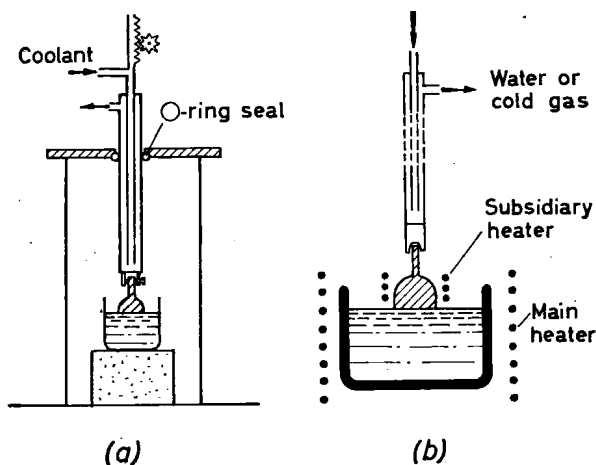

Figure 6. (a) Principle of crystal pulling; (b) Arrangement for keeping solid–melt interface planar

CRYSTAL GROWTH FROM THE MELT

Crystal pulling

Modern methods of pulling crystals from the melt have developed from the work of Nacken[1], Czockralski[2] and Kyropoulus[3]. Essentially, a small single crystal seed is dipped into the surface of the melt and slowly withdrawn (Figure 6). By arranging that the seed is slightly cooler than the melt, material solidifies on the seed as it is

withdrawn. With suitable precautions, the material withdrawn from the melt solidifies as a large single crystal. Crystals of germanium and silicon over 3 cm wide and 15 cm long are being grown in many laboratories as a matter of course. Boules of thallium and silver-activated alkali-halides, thallium bromide and iodide, caesium bromide and organic substances such as naphthalene, in sizes up to 25 × 25 × 25 cm, are also grown in industrial and research laboratories by this method. Crystals of metals such as bismuth, tin, zinc, cadmium, aluminium and intermetallic compounds such as indium antimonide, gallium antimonide, magnesium tin and bismuth telluride have been obtained.
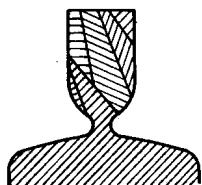

Figure 7. 'Necking' to select a single crystal seed

If a single crystal seed cannot be obtained, a seed consisting of several crystals is used. The seed is dipped into the melt and then withdrawn in the usual way. While it is being withdrawn, the temperature of the melt is increased slightly, causing the seed to taper to a narrow neck. When the neck is no wider than that required to support the final crystal, the temperature of the melt is restored to its original value and the seed increases in diameter. This process is usually effective in selecting one of the crystals in the original seed (*Figure 7*).

Another method, due originally to Czochralski[2], particularly useful for metals is illustrated in *Figure 8*. Here, melt is attracted into a capillary tube, where it usually solidifies as a single crystal and this acts as a seed crystal for subsequent pulling.

In general, a crystal is pulled from the melt in an inert atmosphere or in a vacuum. In certain cases, where the melt has a particularly high vapour-pressure, a pressure of inert gas greater than atmospheric is used. The stability of the melt is, however, the greatest limitation to this method of crystal growing. Many oxides, sulphides and selenides especially, sublime at temperatures much lower than the melting point. Further, the method offers little scope for adjusting the stoichiometry of the final crystal. (Discussed later.)

Considerable doubt exists about the conditions required for pulling the most perfect crystals from the melt. Apparatus has been

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