IMPERFECTIONS AND ACTIVE CENTRES IN SEMICONDUCTORS

by

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PREFACE

THE NUMBER of known semiconducting materials, elemental and compound, organic and inorganic, is now very large indeed. Of these the two elements, germanium and silicon, have received the greatest amount of interest and attention, so that considerably more is known about them, i.e. their purification, crystal growing properties, and their physical and semiconducting behaviour, than about any of the others. Moreover, germanium and silicon can now be grown in single crystal form with unprecedented chemical purity and physical perfection. It has long been known that semiconducting properties are highly sensitive to, if not entirely controlled by, the presence of electrically active defect centres whose role may be either chemical or physical in nature. The present volume deals primarily with the function of these centres, their accommodation in the crystal lattice and their structure. The treatment, as presented here, confines itself explicitly to germanium and silicon, but it will be evident that, except for relatively minor considerations, it is applicable to all the group IV elemental and to the III–V compound semiconductors which have the same or similar lattice structures, and indeed to the solid state as a whole. For a more detailed and specific description of the semiconducting III–V compounds, the reader is referred to the monograph in this Series by Hilsum and Rose-Innes.

It has been assumed that the reader will have some prior acquaintance with the subject of semiconductors. Electronic transport processes and solid state device behaviour have already been comprehensively discussed in the literature and are adequately covered in the other monographs of this Series. However, at the risk of repetition, brief outlines of some of the rudimentary principles of semiconduction theory in terms of the band model have been given where it has been found desirable for the sake of completeness. By way of contrast to the more common treatment of semiconductor physics some of the interesting electrical properties are then examined with reference to the chemical and physical defects in the lattice structures. In this way, it is hoped that the book will fulfil a useful teaching function and that it will also be a practical help to physicists and technologists whose interests are in semiconductors and allied fields of solid state physics.

For several years the author had the support and encouragement of many of his former colleagues at the Standard Telecommunication Laboratories, Harlow. Among those who have assisted in one way or another with the preparation of this book the author would like to express his sincere appreciation to Dr. S. G. Foord, Dr. K. O. Batsford, Mr. D. J. Dane-Thomas and Mr. H. F. Sterling. Likewise, he would like to thank the management of STL for permission to publish Figs. 531.2, 931.1, and 743.1. The suggestions and assistance of many others are also gratefully acknowledged, especially those of the drawing office and the library staff. The author is also very grateful to the secretarial staff of the Research Organization of British Insulated Callender's Cables Limited and to Miss G. Nield for typing parts of the manuscript in the shortest possible time. In addition, the author is very much indebted to Dr. H. K. Henisch, the editor of this Series of monographs, for his useful criticisms and invaluable suggestions regarding the writing and presentation of the material. To his wife in particular the author would like to express his deepest appreciation for her help and above all for her patience and encouragement during the years of preparation. Finally, the author would like to thank Dr. L. G. Brazier for permission to publish this book under the auspices of the Research Organization of British Insulated Callender's Cables.

CONTENTS

Chapter 1

FUNDAMENTAL CONCEPTS OF THE SEMICONDUCTOR CRYSTAL

1.1 INTRODUCTION

Semiconducting materials, as the name implies, fall in the intermediate class between insulators and metals from the point of view of electrical conductivity. Their conductivities (10^{-9}–10^{3} ohm^{-1} cm^{-1}) are somewhat higher than those of the insulators (10^{-22}–10^{-10} ohm^{-1} cm^{-1}) but, on the other hand, they are much lower than the metals (10^{4}–10^{6} ohm^{-1} cm^{-1}). A precise definition of semiconduction, however, is difficult and depends on the particular property being considered. One characteristic feature of most semiconductors is the observed increase in their conductivity with temperature, i.e. the converse of the behaviour in metals. However, this is not by any means a general rule which will apply rigidly over all temperature ranges, or indeed, to every semiconducting material. Important exceptions do occur and, for an account of the electrical behaviour with temperature, the reader is referred to the comprehensive treatments by Shockley (1950:**10**), Spenke (1955:**42**), Blakemore (1962:**3**), and others.

The physical properties of semiconductors which distinguish them from the metals, on the one hand, and the insulators, on the other, can be reasonably understood in terms of the energy band theory of the solid state. The specific application of the band theory to semiconductors has been exhaustively analysed in the literature and it will be assumed, therefore, that the reader is familiar at least with the basic concepts of this theory. Since a comprehensive treatment of the distinguishing features of semiconductors in terms of the band theory is beyond the scope of this book, a few introductory remarks may nevertheless be helpful.

In a metal, for example, the highest energy band containing electrons is only partly filled. As a consequence of this, the electrons have a certain freedom of movement and, under the influence of an applied electric field, they can readily transport charge through the crystal, i.e. current flows. In an insulator, on the other hand, the highest occupied band is completely filled. The electrons are unable to move when a field is applied, i.e. the conductivity of the crystal is negligibly small. As the temperature of an insulator is raised, however, its conductivity increases as a result of the thermal excitation of electrons from the highest filled band (valence band) to the lowest empty band (conduction band). In the conduction band these electrons are free to take part in conduction. The additional energy required to raise the electrons to this level is generally represented as the intrinsic or forbidden gap in the band model. This extra energy that is necessary to induce conduction in an insulator can also be provided by irradiation with high energy particles.

The conduction of a semiconductor is governed basically by the same process. The density of electrons, thermally excited into the conduction band, depends on the width of the energy gap and on the temperature. Unlike insulators, however, these materials are conducting at normal temperatures. At very low temperatures, on the other hand, their electrical conductivity becomes quite small, i.e. approaching that of the insulators.

In real crystals, in contrast to idealized perfect structures, it is the physical defects and the imperfections in the arrangement of their atoms, as well as the inevitable presence of foreign atoms (impurities) in them, which have a significant effect on their physical properties. In addition to the electrical conduction, the diffusion and precipitation of impurity atoms, the plastic deformation, optical and thermal properties, crystal growth phenomena, and numerous other physical and chemical effects all depend, for a satisfactory explanation, on the assumption of basic defect structures in the crystal lattice. In fact, it may be argued that, since all crystals are imperfect from this point of view, their properties can only be completely understood by taking into account the influences of their defects. A theory based entirely on a perfect lattice structure must inevitably be regarded as inadequate.

The aim of the present work is to describe the more significant properties and behaviour of semiconductors and to consider these, both experimentally and theoretically, in relation to the defect content of the crystal. The main emphasis will, therefore, be on these imperfections and the electrically active impurity centres, their origin, distribution, behaviour and influence on the properties of germanium and silicon crystals. The principal concern of the semiconductor technologist is the control of the crystal properties, and hence, by implication, that of the physical defects and the foreign atoms in the crystal which influence them. A knowledge of the basic concepts of the defects is not only essential for the design and fabrication of solid state devices, but it is also necessary both to the theoretical physicist in his interpretation of the semiconductor behaviour and to the experimentalist in the preparation of good single crystals.

The defects can be broadly classified into physical imperfections and chemical impurities or foreign atoms. They may be further subdivided into (a) the elementary point defects, i.e. lattice vacancies, interstitial atoms, and impurity atoms (occupying either substitutional or interstitial positions in the lattice) (b) the line defects, such as dislocations and (c) the more complex type of defects which result from the interaction of these elementary ones. Some examples of defect complexes which will be considered in detail in later chapters, in their relation to the semiconductor properties, include (1) the di-vacancy, formed by the association of two individual vacancies, (2) the vacancy–interstitial combination, commonly referred to as a Frenkel pair, (3) foreign atom-vacancy pairs, (4) vacancy clusters, constituting disks or voids and interstitial aggregates forming platelets, (5) the interaction of dislocations to form low-angle grain boundaries, (6) twin structures, (7) stacking faults, (8) the interaction of dislocations with both vacancies and impurity atoms themselves, and with the atoms of the host lattice.

As will be shown in the following pages these physical and chemical imperfections are able to behave as active centres, in the sense that they influence and, to a large extent, control the semiconductor properties. In the first five chapters of the book the point defects (vacancies and interstitials) and the line defects (dislocations) are treated in some detail from the point of view of their nature and behaviour, their role in connection with the mechanical properties of the crystal, their origin, distribution, and influence on the growth of single crystals from the melt. Although the subject matter applies specifically to the diamond lattice of germanium and silicon crystals, the principles that are established will hold quite generally for all the elemental and compound semiconductors having the same or a similar crystalline structure.

In Chapter 6, the electrically active impurities or foreign atoms are considered. These fall into two categories, i.e. (a) the desirable impurities which are deliberately added as dopes to control or modify the electrical properties of the crystal and (b) the undesirable or unwanted impurities which have a somewhat more complex electrical behaviour.

The solubility, diffusion and precipitation of both of these types of active centres are discussed in Chapter 7. In Section 8.1, the electrical characteristics of the dislocations and point defects are considered. A method for introducing point defects into crystals in numbers large enough for their properties to be experimentally determined is by the irradiation of the sample with high energy particles. A comprehensive review of the results of such experiments is presented in Sections 8.2 and 8.3. Finally, in Chapter 9, the etching properties of semiconductors, and more particularly the development of etch pits, are presented from both the experimental and the theoretical aspect. Special emphasis is placed on an interpretation of the etched features in terms of the internal defects.

1.2 SEMICONDUCTION AND THE ATOMIC LATTICE OF GERMANIUM AND SILICON

1.2.1 Some Elements of Crystallography

A knowledge of the more simple crystallographic principles governing the geometry of single crystals is desirable but not entirely necessary for understanding the subsequent discussions. For a comprehensive treatment of the subject, the reader is referred to the standard references. However, for the sake of completeness, an outline of the elementary symbolism (Miller indices), used for the identification of specific planes and directions in the crystal, will be given here.

The fundamental idea which X-ray and electron diffraction have verified is that the atoms in the crystal are arranged periodically according to definite rules of symmetry. All the semiconductor elements of group IV of the periodic table, characterized by germanium and silicon, crystallize in the cubic diamond lattice structure while the compound semiconductors, formed by various combinations of the groups III and V elements, have a similar cubic lattice structure typified by the mineral wurtzite. It is therefore only necessary to consider the rules governing cubic symmetry.

For purposes of discussion all the planes in the crystal formed by the innumerable groupings of the lattice points or positions of the atoms are identified by their Miller indices, i.e. they represent the intercepts of a plane or set of planes on the cubic axes, and are written as $(h\ k\ l)$

where *h*, *k* and *l* are whole numbers (Fig. 121.1). In a similar manner, a *direction* in the crystal is written as [*h k l*] where *h*, *k* and *l* are its geometric projections on the respective cubic axes.

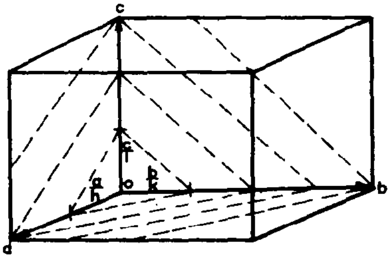

Fig. 121.1. The set of planes, indicated by broken lines, cut the *a*, *b*, and *c* axes of the unit cell into a whole number of equal parts, *a*/*h*, *b*/*k*, and *c*/*l*, respectively. The Miller indices in this example are (243).

In a given volume of crystal, those planes having the largest interplanar spacing, i.e. low Miller indices, will contain the greatest density of lattice points within them. From the point of view of the physical properties and behaviour of the crystal, these high density, low index planes are perhaps the most important and they normally constitute the natural faces or habit of the crystal, as well as the cleavage and slip planes. Likewise, in those crystal directions having low Miller indices, the population of the atoms is highest and these, too, have equal significance in the crystal properties. The more common low index planes are illustrated in the diagrams in Fig. 121.2. For example, those planes which intersect only one cubic axis are designated as (100), (010), (001), etc., those intersecting two axes are (110), (101), etc.,

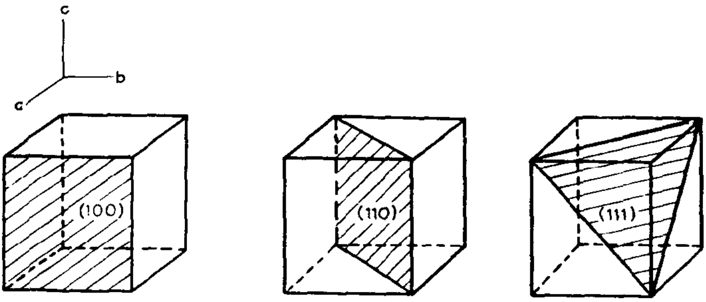

Fig. 121.2. Simple cubic lattice planes with their Miller indices.

while the octahedral planes, cutting all three axes, are (111), $(11\bar{1})$, $(1\bar{1}1)$, etc. Generally, the whole sequence of planes of a specific type, e.g. (100), $(\bar{1}00)$, (010), etc., are indicated as {100}. Similarly, the general set of directions of one type becomes, for example, ⟨100⟩, a specific direction being written as [100].

1.2.2 THE DIAMOND CUBIC LATTICE AND THE COVALENT BOND

The atomic arrangement of germanium and silicon crystals is identical with that of the carbon atoms in diamond itself. This rigid, three-dimensional network is common both to the elemental group IV semiconductors and the III–V compounds. It typifies the class of materials to be discussed in the following. A knowledge of their structure is essential for two reasons, (a) an understanding of their physical and chemical properties and the behaviour of the defects and (b) the search for new semiconducting materials with the same or similar lattice structures. A basic comprehension of the arrangement of the atoms enables the scientist not only to forecast the possible existence of structurally related materials but also to make certain predictions about their electrical behaviour.

The elementary unit cell can be regarded as two interpenetrating, face-centred, cubic lattices, mutually displaced along the body diagona by one quarter of its length (Fig. 122.1). By reference to Fig. 122.2, drawn with a [111] direction vertical, it is evident that the (111) plane actually consists of a closely-spaced pair of planes, the set of planes,

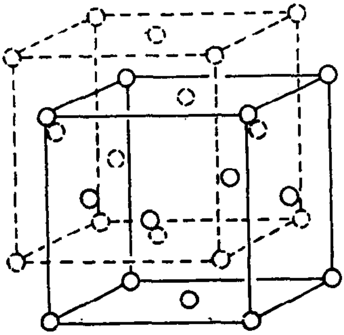

FIG. 122.1. Formation of the diamond lattice by two interpenetrating face-centred cubic lattices.

labelled *A*, *B*, *C*, . . ., belonging to one f.c.c. lattice and the set, labelled α, β, γ, . . ., belonging to the other f.c.c. lattice displaced from it by $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$. Each unit cell in the diamond lattice, therefore, contains 8 atoms in the positions 0 0 0, 0 $\frac{1}{2}$ $\frac{1}{2}$, $\frac{1}{2}$ 0 $\frac{1}{2}$, $\frac{1}{2}$ $\frac{1}{2}$ 0; $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$, $\frac{1}{4}$ $\frac{3}{4}$ $\frac{3}{4}$, $\frac{3}{4}$ $\frac{1}{4}$ $\frac{3}{4}$, $\frac{3}{4}$ $\frac{3}{4}$ $\frac{1}{4}$, or, in brief, written as 0 0 0, $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$, face-centred. The size of the unit cell, i.e. the lattice constant, *a*, is equal to 5·429 Å for silicon and 5·657 Å for germanium.

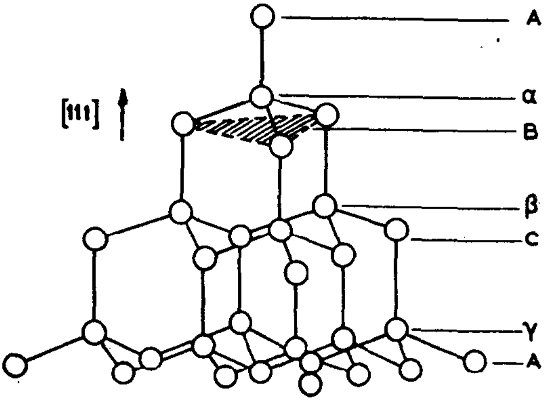

Fig. 122.2. The diamond lattice structure showing the arrangement of the pairs of (111) planes.

The atomic arrangement is such that each atom, with its valency of four, is surrounded by four equidistant neighbouring atoms, thus constituting a tetrahedral group. By the sharing of these valency electrons between neighbouring atoms, electron-pair or covalent bonds are formed parallel to the ⟨111⟩ directions and it is these shared electrons which play the significant role in semiconduction. Covalent bonding, however, is not unique to the group IV elements and many other substances, such as hydrogen, chlorine, copper, etc., composed of chemically identical and electrically neutral atoms, have this same type of bonding. A treatment of the physical laws which govern the interactions of the atoms lies outside the aims of this book. However, a simple picture of the interatomic forces involved will help in understanding how the atoms are held together in the solid state.

As the atoms are brought into the proximity of their respective fields of force, i.e. when the electron clouds which represent their outer valency electrons begin to overlap, strong attractive forces come into effect. However, at still closer distances of approach, repulsive forces predominate. These are the forces which are set up between the inner, filled electron shells of two neighbouring atoms as their respective electron clouds penetrate each other more deeply. Clearly, the potential energy curve associated with these forces will have a minimum, corresponding to the equilibrium separation between the atoms. This minimum determines the lattice spacing in a given solid material. Unlike the ionic bond, in which the electron charge density between neighbouring ions of the crystal is relatively small so that the valence electrons can be regarded as attached to the atoms, in the covalent bond the interaction between the wave functions of the valence electrons results in an accumulation of charge, binding the two adjacent atoms together. In other words, an electron from each atom participates in the bonding, the spins of the two electrons being antiparallel.

In general, the number of close neighbours to a given atom in a covalent material is given by $8-N$, where N is the number of molecular wave functions that can be created from the valency s and p states. Carbon, for example, with four valence electrons, i.e. two in the $2s$ orbital and two in the $2p$ orbital, can form electron pairs with four of its neighbours. The preferred directions of the tetrahedrally-directed bonds in the diamond structure are due to the fact that the p wave functions of the electrons are not spherically symmetrical and extend out in certain specific directions.

With such a regular arrangement of atoms and charge distribution, the perfect diamond structure would be electrically neutral and no conduction would occur. In fact, at very low temperatures, the resistivity of diamond is very high indeed. In reality, however, deviations from this ideal structure do occur, such as the presence of substituted impurity atoms, broken covalent bonds, lattice vacancies and interstitials. In real crystals of the group IV elements (real in the sense that they do not, and indeed cannot have perfect lattice structures) it is these defects and chemical impurities which are responsible for their semiconducting properties.

1.2.3 SEMICONDUCTION AND THE BAND MODEL

Most of our understanding of the electrical properties of semiconductors has come as the result of the quantum mechanical or band model of the solid state (Wilson, 1931:**3**) as mentioned in Section 1.1. According to this theory the electrons have certain energy ranges or