

Semiconductor Statistics

J. BLAKEMORE

SEMICONDUCTOR STATISTICS

by

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PREFACE

MANY observed effects in semiconducting materials are determined in part by the densities of electrons and holes in the various bands and levels. A carrier density cannot of course be measured directly; the magnitude of an observed quantity is always concerned with other attributes of carriers as well as their density. (Thus electrical conductivity depends on the densities of electrons *and* on their mobilities.) Several recently published books (e.g. 1953:4, 1958:9, 1960:19) dwell at length on the relationships between carrier densities and transport effects, and the subject matter of this volume is complementary to that topic.

The book is divided into two parts. Part I, of three chapters, provides introductory material on the electron theory of solids and then discusses carrier statistics for semiconductors in thermal equilibrium. Of course a solid cannot be in true thermodynamic equilibrium if any electrical current is passed; but when currents are reasonably small the distribution function is but little perturbed, and the carrier distribution for such a "quasi-equilibrium" condition is inappreciably different from that of thermal equilibrium itself. Thus the results of Part I are not invalidated when the properties of a semiconductor are measured using small current densities.

The seven chapters of Part II consider non-equilibrium statistics, for semiconductors with appreciable excess carrier densities. The various kinds of recombination mechanism are considered in turn, and the consequences discussed for steady state and transient situations. No attempt is made to expose the special problems of semiconductor contacts and junctions, since these have been treated so extensively in other recent volumes (e.g. 1957:32, 1960:17).

The subject matter of this book is deliberately restricted in scope so that the volume may be of maximum value to scientists with an active interest in the basic properties of semiconducting materials. The introductory material of Chapter 1 should help to make the book useful to those who are approaching semiconductors as a new field of

specialization. Appreciation of Chapter 1 is aided by some awareness of basic quantum-mechanical principles, but a detailed knowledge of that subject is certainly not necessary in order to make use of the results presented here.

Dr. Henisch first suggested the writing of this book in 1952, and I have been conscious since that time of his encouragement. Enough is now known about recombination processes to permit a hope that this volume might remain useful for some time.

I should like to express my appreciation of the help given by a number of other colleagues and friends. My first interest in thermal equilibrium carrier statistics was stimulated by Mr. G. King, Mr. T. R. Scott and Mr. A. C. Sim. It is a pleasure to acknowledge the encouragement given by Dr. V. W. Beringer and Dr. F. J. Larsen to basic recombination studies at Honeywell. In both the experimental and theoretical aspects of these studies I have enjoyed a close collaboration with Dr. K. C. Nomura, and many of the ideas in Chapters 8 and 10 were developed jointly with Dr. Nomura. His comments on this manuscript, and those of Dr. S. R. Morrison, Dr. A. Nussbaum, and Professor P. T. Lansberg have helped in the elimination of many errors and obscurities. The difficult task of typing the manuscript has been undertaken by Mrs. C. Lehr, and that of preparing the figures by Mrs. V. Squier; hearty thanks are due to both. My wife, June Blakemore, has been forced into the role of an observer as the writing process has enveloped her husband's existence for many months; her faith and constant encouragement have indeed been appreciated.

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CONTENTS

Preface	xi
Part I. SEMICONDUCTORS IN THERMAL EQUILIBRIUM	1
Chapter I. BASIC CONCEPTS IN THE ELECTRON THEORY OF SOLIDS	3
1.1 Classical Theories of Metallic Conduction	3
1.1.1 Drude's Model	3
1.1.2 Lorentz's Model	4
1.2 Quantum Statistics and the Free Electron Theory	5
1.2.1 \mathbf{p} -Space and \mathbf{k} -Space. The Density of States	5
1.2.2 Pauli's Exclusion Principle and Fermi-Dirac Statistics	10
1.2.3 Degeneracy of an Electron Distribution. Sommerfeld's Model	12
1.3 The Band Theory of Solids	16
1.3.1 Schrödinger's Equation—One-electron Functions	17
1.3.2 The Energy-Wave-Vector Relationship. Brillouin Zones	21
1.3.3 Filling of Energy Bands—Metals and Insulators	26
1.3.4 Thermal Excitation in Semiconductors	27
1.3.5 Validity of the Band Model	30
1.4 The Effective Mass of Charge Carriers	35
1.4.1 Phase and Group Velocities	36
1.4.2 The Reduced Zone	36
1.4.3 The Effective Mass	39
1.4.4 The Density of States	44
1.4.5 Mass Renormalization in Band Theory	46
1.4.6 Magnetic Sub-bands	48
1.5 Band Shapes for Some Representative Semiconductors	53
1.5.1 The Band Structure of Silicon	58
1.5.2 Germanium	64
1.5.3 Indium Antimonide	68

1.6	Some Varieties of Impurity Center (Flaw)	71
1.6.1	Impurities in Elemental Semiconductors Such as Ge and Si	72
1.6.2	Donors and Acceptors in Compound Semiconductors	73

Chapter 2.	THE FERMI LEVEL—ELECTRON DENSITY EQUILIBRIUM	75
2.1	The Fermi-Dirac Integrals	79
2.1.1	Equivalence of Formalism for Electron and Hole Populations	80
2.2	Interrelation of Free Electron Density and Fermi Level	82
2.2.1	Temperature-independent Electron Density	84
2.2.2	The Effect of a Magnetic Field	87
2.3	Intrinsic Semiconductors	94
2.3.1	Non-degenerate Intrinsic Semiconductors	94
2.3.2	Degenerate Intrinsic Semiconductors	102
2.4	The Product $n_0 p_0$ and ϕ for Intrinsic and Extrinsic Situations	106
2.5	Spatial Fluctuations of Carrier Density	113
2.5.1	Spatial Fluctuations of the Intrinsic Gap	113
2.5.2	Spatial Fluctuations of Impurity Density	114
Chapter 3.	SEMICONDUCTORS DOMINATED BY IMPURITY LEVELS	117
3.1	Occupancy Factor for Impurity Levels	117
3.1.1	Impurity Level Spin Degeneracy	118
3.2	Semiconductors Controlled by a Single Monovalent Donor Species	120
3.2.1	Temperature Dependence of n_0 and ϕ for a Set of Simple Uncompensated Donors	121
3.2.2	The Realistic Case—Partly Compensated Impurities	130
3.2.3	The Influence of Excited States	140
3.2.4	Impurity Ground State Split in the Crystal Field	146
3.2.5	Impurity States Split by Anisotropic Elastic Strain	149
3.2.6	Effect of a Magnetic Field on Impurity States	151
3.2.7	Some Comments in Summary	152
3.3	Semiconductors Dominated by Several Localized Levels	153
3.3.1	Several Independent Types of Monovalent Donor	153
3.3.2	Electron Distribution Over a Set of Multivalent Flaws	156
3.3.3	Amphoteric Impurities	160

3.4	The Influence of Lattice Defects	162
3.4.1	Non-stoichiometric Compounds	162
3.4.2	Irradiation Effects	164
3.5	Impurity Bands and the Behavior of an Impurity Metal	166
3.5.1	Weak Impurity Metals	169
3.5.2	Strong Impurity Metals	172
3.5.3	Occupancy of Weakly Interacting Impurities	174

Part II. SEMICONDUCTORS CONTAINING EXCESS CARRIERS

Chapter 4.	FACTORS AFFECTING CARRIER TRANSITION RATES	179
4.1	Reciprocity of Transition Probabilities	179
4.1.1	The Principle of Detailed Balance	180
4.1.2	Electrochemical Potentials and Mean Capture Coefficients	183
4.2	The Continuity Equations	189
4.2.1	Some Definitions of Carrier Lifetime	191
4.3	Band-to-Band and Band-to-Flaw Transitions	193
4.3.1	Transitions Across the Intrinsic Gap	193
4.3.2	Transitions to a Localized State (Flaw)	194
4.3.3	Relative Importance of Recombination Processes	195
Chapter 5.	RADIATIVE AND RADIATIONLESS RECOMBINATION	196
5.1	The Physics of The Two Processes	196
5.1.1	Radiative Recombination	196
5.1.2	Radiationless (Multiphonon) Recombination	203
5.2	Behavior of the Radiative Lifetime	203
5.2.1	Equivalence of All Definitions of Lifetime	204
5.2.2	Variation of Lifetime with Doping and Modulation	205
5.2.3	The Dependence on Excess Generation Rate	207
5.2.4	Transient Decay	209
5.2.5	Variation with Temperature	211
Chapter 6.	BAND-TO-BAND AUGER RECOMBINATION	214
6.1	Electron-Electron and Hole-Hole Collisions	215
6.1.1	The Model of Beattie and Landsberg	216
6.1.2	Net Recombination Rate in Non-equilibrium	219
6.2	Behavior of the Auger Lifetime when $m_e < m_h$	220
6.2.1	Dependence on Doping and Modulation	222
6.2.2	The Variation with Generation Rate	225
6.2.3	Transient Decay	226
6.2.4	Lifetime-Temperature Relationship	227

Chapter 7. FREE CARRIER CAPTURE BY FLAWS	237
7.1 Flaw Capture Mechanisms	237
7.1.1 Radiative Recombination	239
7.1.2 Phonon Recombination	241
7.1.3 Auger Recombination	242
7.1.4 Relative Probability of the Various Processes	243
7.2 Behavior of the Extrinsic Lifetime	244
7.2.1 For Phonon-aided Recombination	244
7.2.2 For Auger Recombination	246
7.3 Interaction with Both Bands	248
Chapter 8. RECOMBINATION THROUGH A SET OF MONOVALENT FLAWS	250
8.1 The Two Continuity Equations	250
8.1.1 Capture Cross-sections and Capture Coefficients	250
8.1.2 Balance Between Generation and Recombination	254
8.1.3 Adoption of a Dimensionless Notation	256
8.1.4 Steady State and Transient Decay Equations	257
8.2 The Criteria of Trapping	258
8.2.1 Class I and Class II Situations	258
8.2.2 Electron and Hole Trapping	259
8.2.3 The Excess Carrier Ratio	260
8.3 Lifetime for a Small Flaw Density (The S-R Model)	262
8.3.1 Small-modulation Lifetime	263
8.3.2 Variation of Lifetime with Modulation	269
8.3.3 Variation of Excess Density with Steady State Excitation Rate	271
8.3.4 Transient Decay	274
8.4 Steady State Conditions for Arbitrary Flaw Density	277
8.4.1 Small-modulation Lifetime	278
8.4.2 Finite Modulation	279
8.5 Transient Decay for Arbitrary Flaw Density	283
8.5.1 The Initial Stages of Decay	284
8.5.2 The Final Stages of Decay	288
8.5.3 The Course of Class I Decay	296
8.5.4 The Course of Class II Decay	302
Chapter 9. MORE COMPLICATED EXAMPLES OF FLAW RECOMBINATION	305
9.1 Multivalent Flaws	305
9.2 More Than One Kind of Flaw	309
9.3 The Haynes-Hornbeck Trapping Model	310
9.3.1 Flaws Which Do Not Capture Holes	310

CONTENTS

ix

9.3.2	Small-modulation Decay	311
9.3.3	Finite Modulation Trapping Solution	315
9.3.4	Solution When There is Some Hole Capture	315
9.4	Recombination and Trapping at Dislocations	316
Chapter 10.	SPATIAL DISTRIBUTION OF EXCESS CARRIERS	319
10.1	Approach to the Space-dependent Problem	319
10.1.1	The Continuity Equations	319
10.1.2	Assumption of a Constant Lifetime	320
10.2	Situations Involving Junctions and Contacts	321
10.2.1	Inhomogeneous Semiconductors	321
10.2.2	Contact Effects	322
10.3	Residual Spatial Influences in Homogeneous Samples	322
10.3.1	Surface Recombination	323
10.3.2	Spatial Distribution of Generation	326
10.4	Lifetime in Filaments	330
10.4.1	Homogeneous Equation. Decay Modes	331
10.4.2	The Amplitudes of Decay Modes	336
10.4.3	Inhomogeneous Equation. Green's Function Method	341
APPENDIXES		
Appendix A.	THE FERMI-DIRAC DISTRIBUTION LAW	343
Appendix B.	TABLES OF THE FERMI-DIRAC INTEGRALS	346
Appendix C.	SOME APPLICATIONS AND PROPERTIES OF THE FERMI-DIRAC INTEGRALS	354
C.1.	Fermi-Dirac Integrals and Transport Properties	354
C.2.	Fermi-Dirac Integrals for Non-standard Bands	355
C.3.	Analytic Properties of the Fermi Integrals, and Asymptotic Expansions for Non-degenerate and Degenerate Cases	357
REFERENCES		366
INDEX		375

PART I.

*SEMICONDUCTORS IN THERMAL
EQUILIBRIUM*

Chapter 1

BASIC CONCEPTS IN THE ELECTRON THEORY OF SOLIDS

1.1 CLASSICAL THEORIES OF METALLIC CONDUCTION

CONSIDERABLE insight into the nature and behavior of semiconductors (and metals) comes from an examination of the band theory of solids. This theory can be regarded as arising naturally from the broadening of the discrete quantized energy levels of an isolated atom, but it is also useful to observe the development of band theory from the so-called collective electron point of view. We accordingly start with a review of the classical and quantized free electron models of metallic conduction. This discussion serves to introduce in historical sequence the important ideas which led to the band model and to an explanation of the distinction between metals, semiconductors and insulators.

1.1.1 DRUDE'S MODEL

Not long after the discovery of the electron, the suggestion was first made that the outer electrons of each atom in a metal might not be tightly bound to their individual atomic cores, but might rather form a free electron gas, collectively owned by the entire set of atoms which make up a crystal. That electrons should be free to move anywhere in a crystal seems reasonable in view of the validity of Ohm's law; and that their density might be comparable with that of atoms is indicated by the very large electrical and thermal conductivities of metals. Drude (1904:1) investigated the consequences of a simple model in which all the free electrons moved with a classical momentum $\bar{p} = (3m_0kT)^{1/2}$ and were presumed to be scattered in random directions

by the positive ion cores. The model did not have any features from which the absolute strength of this scattering could be determined, thus conductivities could be quoted only in relative terms. Drude's model did, however, give a result for the ratio of thermal to electrical conductivities:

$$\frac{\kappa}{\sigma} = 3 \left(\frac{k}{e} \right)^2 T \quad (111.1)$$

which was in surprisingly good agreement with the experimental law of Wiedemann and Franz (1853:1).

1.1.2 LORENTZ'S MODEL

Attempts were made by Lorentz (summarized in 1909:1) to improve upon Drude's model, particularly in recognizing that not all free electrons will move with the same speed and momentum. Of course, from general thermodynamic principles it is evident that if a system contains a large number of particles (such as electrons), then the particles will normally tend to find positions of lowest energy. At the same time, for any temperature other than absolute zero, particles are continually receiving and emitting energy in a way which tends to oppose the process of settling towards minimum energy.

Lorentz assumed that electron velocities and momenta varied in accordance with the classical Maxwell-Boltzmann distribution law. For a classical population of \mathcal{N} free electrons in thermal equilibrium, the number with momenta in an infinitesimal range $d\mathbf{p}$ is

$$dN = \frac{4\pi\mathcal{N}p^2}{(2\pi m_0 kT)^{3/2}} \cdot \exp\left[\frac{-p^2}{2m_0 kT}\right] \cdot d\mathbf{p} \quad (112.1)$$

The Lorentz theory considered the deformation of this distribution in applied fields, and the manner in which a perturbed distribution tends to return to normal. By an ironic chance, these sophisticated calculations yielded apparently less satisfactory results than Drude's crude model in several respects:

(a) Drude had obtained a ratio of thermal to electrical conductivity of $3(k/e)^2 T$, in good agreement with the experimental law of Wiedemann and Franz. Lorentz's result was one-third smaller.

(b) The more elaborate theory made it impossible to explain the actual temperature dependence of conductivities in ordinary metals if scattering was based on any central law of force, elastic or inelastic!

(c) Lorentz was able to predict values for other metallic properties such as thermoelectric, magnetoresistive and Hall coefficients. The Hall effect expression

$$R = -3\pi/8ne \quad (112.2)$$

confirmed that free electrons are as numerous in metals as atoms—yet this served only to deepen the mystery that the free electron gas does not give metals a large additional specific heat.

From the foregoing, it will be seen that classical theory could do little to account for electronic behavior in metals—let alone semi-conductors, whose existence was barely noted at the beginning of this century. It was not until the 1920's that any significant advances were made by the application of quantum ideas to the problem.

1.2 QUANTUM STATISTICS AND THE FREE ELECTRON THEORY

Arnold Sommerfeld (1928:1) retained a number of the important features in Drude's and Lorentz's earlier theories. Thus, like them, he assumed that free electrons enjoy a constant potential energy $-W$ inside a metal. (Whereas the potential experienced by an electron must actually depend on its relationship to other free electrons and to the periodic array of positively ionized atomic cores.) Also he was forced to accept that some form of scattering takes place to set the absolute value of the resistivity, yet he could not cite the specific cause of this scattering. Even so, a number of mysteries on the classical theories were easily explained by Sommerfeld's model, based on quantum statistics.

1.2.1 **p**-SPACE AND **k**-SPACE. THE DENSITY OF STATES

Consider a space for which the co-ordinates are the x , y and z components of electron momentum (Fig. 12.1). An electron of any momentum \mathbf{p} can be represented by the vector from 0 to some point in \mathbf{p} -space. This electron has kinetic energy $E = p^2/2m_0$, and it is evident that a sphere centered on the origin of \mathbf{p} -space will be a constant energy

surface.† Applying the concept of \mathbf{p} -space to the classical distribution (112:1), it can be seen that the density of electrons in \mathbf{p} -space for a given energy is

$$\begin{aligned} \frac{dN}{4\pi p^2 \cdot dp} &= \frac{N}{(2\pi m_0 kT)^{3/2}} \exp\left[\frac{-p^2}{2m_0 kT}\right] \\ &= \frac{N}{(2\pi m_0 kT)^{3/2}} \exp\left[\frac{-E}{kT}\right] \end{aligned} \quad (121.1)$$

when classical conditions hold.

In expressing the result (121:1), it is assumed that an electron may have any momentum and energy. This does not hold true when the

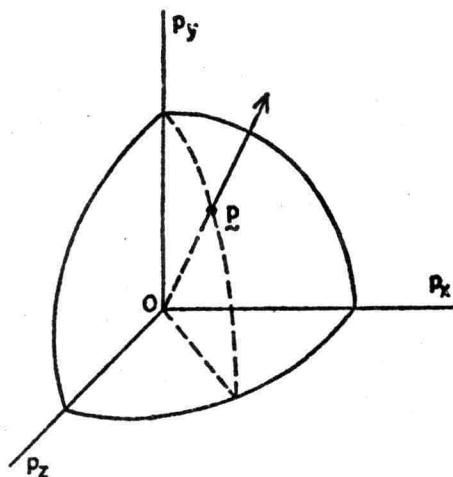


FIG. 12.1. Momentum space. The vector \mathbf{p} represents the momentum of a particle, $p = \sqrt{(p_x^2 + p_y^2 + p_z^2)}$. Thus any sphere centered on the origin of momentum space is a surface of constant kinetic energy.

additional postulates of quantum theory are taken into account. According to quantum theory, when the motion of an electron is restricted by boundary conditions (as it is for an electron moving within

† In discussing the free electron model, the origin of energy is arbitrarily set as that of zero electronic kinetic energy. This is convenient for our present purposes since we are concerned only with differences of kinetic energies, and do not discuss problems of thermionic emission, contact potential, etc. (for which the height W of the surface potential barrier would be important). In discussions of the more complicated band models later in the book, different criteria of the most convenient origin for energy are encountered, and adopted where appropriate.

a crystal of finite size), there is a finite number of possible electron states (distinguishable patterns of electron behavior) within any specified range of energy and momentum.

In order to determine how many separate quantum states there are within a range of momentum, it is convenient to recall that—in quantum-mechanical terms—a free electron of momentum \mathbf{p} can be represented by a wave of wavelength $\lambda = h/p$, or wave-vector $\mathbf{k} = \mathbf{p}/\hbar$. Thus as a companion to \mathbf{p} -space, we can construct the corresponding \mathbf{k} -space (Fig. 12.2), in which a vector \mathbf{k} shows the direction and periodicity of the wave representing an electron of component momenta

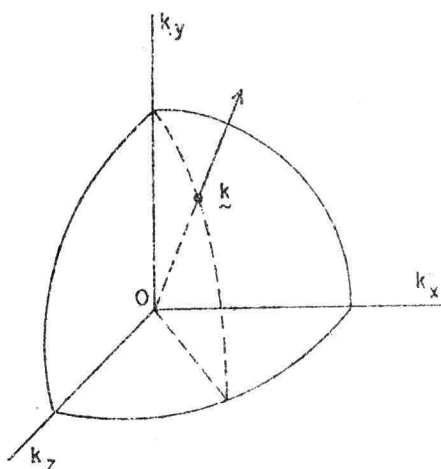


FIG. 12.2. \mathbf{k} -space. The vector \mathbf{k} represents the periodicity and direction of the wave representing an electron for which $k_x = (p_x/\hbar)$, $k_y = (p_y/\hbar)$, $k_z = (p_z/\hbar)$. For free electrons a sphere of radius k , centered on the origin, is a surface of constant energy.

$p_x = \hbar k_x$, $p_y = \hbar k_y$, and $p_z = \hbar k_z$. The kinetic energy of such an electron can be written

$$E = \frac{\hbar^2}{2m_0}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m_0} \quad (121.2)$$

It is necessary to be temporarily concerned not only with the energies but also with the wave-functions ψ of electrons. According to wave-mechanical principles [for a very readable account see (1957:1)], ψ is