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B.I. Shklovskii A.L. Efros

Electronic Properties of Doped Semiconductors



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With 106 Figures

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Preface

First-generation semiconductors could not be properly termed “doped” — they were simply very impure. Uncontrolled impurities hindered the discovery of physical laws, baffling researchers and evoking pessimism and derision in advocates of the burgeoning “pure” physical disciplines. The eventual banishment of the “dirt” heralded a new era in semiconductor physics, an era that had “purity” as its motto. It was this era that yielded the successes of the 1950s and brought about a new technology of “semiconductor electronics”. Experiments with pure crystals provided a powerful stimulus to the development of semiconductor theory. New methods and theories were developed and tested: the effective-mass method for complex bands, the theory of impurity states, and the theory of kinetic phenomena.

These developments constitute what is now known as semiconductor physics. In the last fifteen years, however, there has been a noticeable shift towards impure semiconductors — a shift which came about because it is precisely the impurities that are essential to a number of major semiconductor devices. Technology needs impure semiconductors, which unlike the first-generation items, are termed “doped” rather than “impure” to indicate that the impurity levels can now be controlled to a certain extent.

New problems have arisen in the theory of the electronic states of doped semiconductors. They concern electrons located not in an ordered field of crystal atoms, but in the chaotic field of impurities, and the potential energy of the latter is by no means small. At low temperatures a doped semiconductor crystal becomes a disordered system, which in its general characteristics resembles an amorphous system. This is true for both lightly and heavily doped semiconductors: the lighter the doping, the lower the temperature at which these characteristics are exhibited.

The aim of this book is to present in logical fashion the theory of electronic states and conduction in doped semiconductors at low temperatures, that is, in the region where the properties of the electronic states differ most from those of Bloch waves.

Depending on the doping, the electronic states of a semiconductor at zero temperature may be localized or delocalized. An important advance in the theory of disordered systems was the so-called Anderson theorem, which posits the existence of strictly localized states under certain conditions. A discussion of this question (Chap. 2) begins our exposition of the theory of electronic states, which differs from that for ideal crystals in that it must account

for electron-electron interaction even at the lowest electron concentrations. To this end, a nonlinear screening theory was developed, based on the self-consistent field method (Sect. 3.4). This method does not, however, work in the vicinity of the Fermi level, where the density of states has interesting and peculiar features (Chap. 10).

If the Fermi level is in the localized-state region, then conduction is due to electron hopping and is exponentially dependent on temperature and the impurity concentration. The hopping conduction phenomenon was identified long ago, but several major advances have taken place in the last decade. A theory was developed which describes the temperature, concentration and magnetic field dependences quantitatively. This theory is based on a new mathematical discipline known as "percolation theory". Today, the percolation method is as essential to the study of low-temperature conduction as the kinetic equation method is for band conduction; the term "percolation level" is as frequent in the relevant literature as "relaxation time". Good reviews of the percolation theory do exist — we cite many in Chap. 5 — but these were written relatively long ago and are inappropriate to the study of hopping conduction. For this reason we found it necessary to write a separate chapter detailing the main tenets of percolation theory (Chap. 5), replete with bibliography on the topic.

In all chapters devoted to hopping conduction there is a thorough comparison of theory and experiment, a comparison that we find, on the whole, favorable. We have tried to point out discrepancies and theoretical problems that in our view remain unsolved.

Although the book is devoted to crystalline semiconductors, many of the ideas and methods also apply to amorphous semiconductors, so much so that "amorphous digressions" are an integral part of the text. Occasionally (see Chap. 9) we use experimental data on amorphous semiconductors to support certain concepts.

Our book is not intended solely as a specialists' monograph, but also as an extension of an ordinary course in semiconductor theory that touches on a new range of problems. Chapter 1 and Sects. 4.1 and 11.1 serve to connect this book with standard courses in the theory of "pure" semiconductors. The book is aimed at a wide readership: theoretical and experimental physicists, graduate students, and engineers acquainted with the basics of solid-state physics. An easier version of our book can be obtained by omitting Sects. 1.3, 2.3–2.5, 5.4, 5.5, 8.3, 10.1, 10.2, 11.3, 12.3, 13.4. It is useful to keep in mind that as a rule all questions are discussed twice, first qualitatively and then quantitatively. For the reader not interested in mathematical detail the qualitative explanation should suffice; sections which may be omitted are usually designated as such in the text.

We substantially updated the book for the English edition, adding new results in percolation theory and hopping conduction. During the five years since we had written our book, several significant developments had occurred in the physics of disordered systems. One of these was the creation in 1979 of

the scaling theory of localization by Anderson with coworkers and Thouless. We have incorporated this theory, as we understand it, into Chapter 2 of the present edition.

New ideas have also emerged in the understanding of electron-electron interaction in disordered systems. In 1975 we proposed the idea that a Coulomb gap may form in the vicinity of the Fermi level, which if correct would make it necessary to revise Mott's law for variable-range hopping conduction. In the Russian edition we timidly devoted only one section to this question (in Chapter 10), but since then, a number of authors have made both theoretical and experimental contributions to this subject, and we felt compelled to write a whole new chapter for the present edition (Chapter 14). It describes computer modelling of the Coulomb gap, the impurity-band structure, and hopping conduction.

In 1979–1982 Al'tshuler and Aronov published a series of remarkable papers devoted to the role of electron-electron interaction in disordered systems with delocalized states. We were not able to consider these concepts in detail – otherwise we would have had to write a new book. One reason not to do so was furnished by Al'tshuler and Aronov themselves, who discuss these topics in a chapter of the volume entitled *Electron-Electron Interaction in Disordered Systems* ed. by A. L. Efros and M. Pollak (North-Holland, Amsterdam 1984). Other contributions to that volume also substantially complement our book.

It is a pleasure to us that Springer-Verlag has undertaken to publish the English translation of our book. We thank Professor Mike Pollak, our long-time friend, and Dr. Serge Luryi for their hard and selfless labor in preparing this edition. We are grateful to our foreign colleagues B. N. Butcher, J. Chroboczek, E. Guyon, J. J. Hauser, S. Kirkpatrick, Y. Imry, P. A. Lee, R. Mansfield, N. F. Mott, G. A. Thomas, H. E. Stanley, J. P. Straley, and many others who regularly send us reprints of their works, thus keeping us abreast with the latest developments.

Leningrad, December 1983

B. I. Shklovskii · A. L. Efros

Semiconductor Technology

Ion Implantation Techniques

Lectures given at the Ion Implantation School in Connection with the Fourth International Conference on Ion Implantation: Equipment and Techniques, Berchtesgaden, Federal Republic of Germany, September 13–15, 1982

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Ion Implantation: Equipment and Techniques

Proceedings of the Fourth International Conference Berchtesgaden, Federal Republic of Germany, September 13–17, 1982

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Very Large Scale Integration (VLSI)

Fundamentals and Applications

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With contributions by numerous experts
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147 figures. XI, 302 pages (Springer Series in Electrophysics, Volume 5). ISBN 3-540-11368-1

Contents: Introduction. – VLSI Device Fundamentals. – Advanced Lithography. – Computer Aided Design for VLSI. – GaAs Digital Integrated Circuits for Ultra High Speed LSI/VLSI. – VLSI Architecture. – VLSI Applications and Testing. – VHSIC Technology and Systems. – VLSI in Other Countries. – Addenda. – Subject Index.

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Editor: **H.-J. Queisser**

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(Topics in Applied Physics, Volume 22).
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Contents: Introduction: Structure and Structuring of Solids. – High Brilliance X-Ray Sources. – X-Ray Lithography. – X-Ray and Neutron Interferometry. – Section Topography. – Live Topography.

Insulating Films on Semiconductors

Proceeding of the Second International Conference, INFOS 81, Erlangen, Federal Republic of Germany, April 27–29, 1981

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Contents: Si-SiO₂ Interface. – Thin Insulating Films. – Charge Injection Into Insulators. – Multilayer Structures. – Interface Characterization Techniques. – Breakdown and Instability of the SiO₂-Si System. – Technology. – Laser Processing. – Transport Properties in Inversion Layers. – Films on Compound Semiconductors. – Index of Contributors.



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Contents

Part I Lightly Doped Semiconductors

1. The Structure of Isolated Impurity States	2
1.1 Shallow Impurities	2
1.2 Impurity Levels Near a Nondegenerate Band	4
1.2.1 Extremum at the Center of the Brillouin Zone	5
1.2.2 Several Equivalent Extrema	8
1.3 Impurity Levels Near a Point of Band Degeneracy	11
1.4 Asymptotic Behavior of the Impurity-State Wave Functions ...	19
2. Localization of Electronic States	25
2.1 Narrow Bands and the Mott Transition	26
2.2 Anderson Transition	30
2.3 Examples of Transition from Localized to Delocalized States. Conductivity Near the Transition Point	35
2.4 The Scaling Theory of Localization	39
2.5 Localization in the Lifshitz Model	46
3. The Structure of the Impurity Band for Lightly Doped Semiconductors	52
3.1 General Remarks	52
3.2 The Impurity Band at Low Degrees of Compensation	55
3.3 Long-Range Potential at Low Degrees of Compensation	62
3.4 The Impurity Band at High Degrees of Compensation	65
4. A General Description of Hopping Conduction in Lightly Doped Semiconductors	74
4.1 Basic Experimental Facts	74
4.2 The Resistor Network Model Proposed by Miller and Abrahams	82
5. Percolation Theory	94
5.1 Lattice Problems	94
5.2 Continuum Problems	107
5.3 Random Site Problems	111

5.4	Theory of Critical Exponents	118
5.5	Electric Conductivity of Random Networks of Conducting Bonds. Infinite Cluster Topology	123
5.5.1	Dead Ends	125
5.5.2	The Nodes and Links Model	126
5.5.3	The Scaling Hypothesis and Calculation of the Conductivity $\sigma(x)$	129
5.6	Percolation Theory and the Electric Conductivity of Strongly Inhomogeneous Media	130
6.	Dependence of Hopping Conduction on the Impurity Concentration and Strain in the Crystal	137
6.1	Resistivity ρ_3 for Semiconductors with Isotropic Impurity Wave Functions	137
6.2	Resistivity ρ_3 for Semiconductors with Anisotropic Impurity Wave Functions	144
7.	Hopping Conduction in a Magnetic Field	155
7.1	The Elementary Resistance R_{ij} in a Magnetic Field	156
7.2	Evaluation of the Magnetoresistance and Discussion of Experimental Data	163
8.	Activation Energy for Hopping Conduction	180
8.1	Activation Energy ε_3 at Low Degree of Compensation	180
8.2	Activation Energies ε_1 and ε_3 at High Compensation	186
8.3	The Perturbation Method in Percolation Theory. General Theory of the Activation Energy ε_1	191
9.	Variable-Range Hopping Conduction	202
9.1	Mott's Law	202
9.2	Magnetoresistance in the Region of Variable-Range Hopping Conduction	210
9.3	The Dependence of Hopping Conduction in Amorphous Films on Film Thickness	216
9.4	The Preexponential Factor in Hopping Conductivity	222
10.	Correlation Effects on the Density of States and Hopping Conduction	228
10.1	Coulomb Gap in the Density of States	228
10.1.1	The Theory of the Coulomb Gap	228
10.1.2	Possible Manifestations of the Coulomb Gap	238
10.2	Many-Body Correlations in Hopping Conduction	244
10.2.1	Hubbard Current Correlations	246
10.2.2	Coulomb Correlations	250

Part II Heavily Doped Semiconductors

11. Electronic States in Heavily Doped Semiconductors	255
11.1 Linear Screening Theory	255
11.2 Density of States Near the Bottom of the Conduction Band	259
11.3 Derivation of the Quasiclassical Formula for the Density of States	264
12. The Density-of-States Tail and Interband Light Absorption	268
12.1 The Optimum Fluctuation Method	268
12.2 The Uniformly Charged Sphere Approximation. The Spectrum of the Majority Carriers	270
12.3 Exact Distribution of Impurities in Optimum Fluctuations	277
12.3.1 Derivation of Basic Equations	277
12.3.2 Derivation of (12.2.12)	279
12.3.3 Density-of-States Asymptotics in the Absence of Impurity Correlations	281
12.4 The Spectrum of the Minority Carriers	283
12.4.1 Classical Case ($\gamma \gg E_s$)	284
12.4.2 Quantum Case ($\gamma \ll E_s$)	285
12.5 The Theory of Interband Light Absorption	287
12.5.1 On the Relation Between the Density of States and the Interband Light Absorption Coefficient (ILAC)	287
12.5.2 Light Absorption Induced by Gaussian Fluctuations in the Absence of Carrier Degeneracy	289
12.5.3 Discussion of Experimental Results	293
13. The Theory of Heavily Doped and Highly Compensated Semiconductors (HDCS)	295
13.1 Uncorrelated Impurity Distribution	295
13.1.1 Qualitative Discussion	295
13.1.2 Basic Equations and the Asymptotic Properties of the Potential	299
13.2 Correlated Impurity Distribution	303
13.3 Kinetic Properties of HDCS	305
13.4 Completely Compensated Semiconductor	309

Part III Computer Modelling

14. Modelling the Impurity Band of a Lightly Doped Semiconductor and Calculating the Electrical Conductivity	316
14.1 Minimization of the Total Energy and Calculation of the Density of States	318
14.2 Density of States and the Fermi Level	322

14.2.1 Intermediate Degrees of Compensation	324
14.2.2 Strong Compensation ($1 - K \ll 1$)	326
14.2.3 Low Compensation	328
14.3 Distribution of Electric Fields on Neutral Donors	329
14.4 Activation Energy of Hopping Conduction	333
14.5 Variable-Range Hopping Conduction	341
14.6 Activation Energy ε_1 of Band Conduction	344
14.7 Some Other Applications of the Minimization Program	350
Appendix	353
References	359
Subject Index	387

Part I

Lightly Doped Semiconductors

1. The Structure of Isolated Impurity States

This chapter is a brief introduction to the theory of impurity centers in semiconductors. The reader interested in more detail is recommended a review by *Kohn* [1.1], the more recent one by *Bassani et al.* [1.2], and the book by *Bir and Pikus* [1.3].

1.1 Shallow Impurities

At low temperatures most of the electronic properties of semiconductors are determined by impurities. An impurity can be of either donor or acceptor type. A donor impurity can be comparatively easily ionized in the crystal medium by donating an electron to the conduction band. These electrons can then participate in transport processes while the impurity centers become positively charged. Donors give rise to the electronic type of conductivity in semiconductors. When the impurity concentration is not too large, electrons are captured by donors at a sufficiently low temperature and become neutral. This phenomenon is sometimes called the "freezing-out" of conduction electrons.

The most important characteristic of an impurity is its ionization energy, i.e., the energy necessary to move one electron from the donor level to the bottom of the conduction band. The freeze-out temperature is mainly determined by this energy. On the energy-level diagram of a semiconductor the donor levels are located in the forbidden gap (Fig. 1.1).

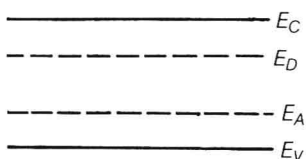


Fig. 1.1. Band diagram of a semiconductor. E_C and E_V are, respectively, the edges of the conduction and the valence bands; E_D and E_A are the energies of the donor and acceptor levels

A donor impurity is called shallow if its level is close to the bottom of the conduction band, i.e., when the ionization energy is small compared to the energy gap. Shallow impurities play a special role in semiconductor physics. As we shall see below, their properties permit a universal description. Both in this chapter and in the rest of the book we shall deal primarily with shallow impurities.

An acceptor impurity has the property of capturing one electron from the crystal. The impurity center becomes negatively charged while a hole appears in the valence band. Acceptors in semiconductors are responsible for conductivity by holes, or *p*-type conductivity. At low temperatures holes are frozen out, each hole being localized near an acceptor. Acceptor levels are also located in the forbidden gap (cf. Fig.1.1). Shallow acceptors are those whose levels are close to the top of the valence band.

Whether a given impurity is a donor or an acceptor is determined in many cases merely by its position in the periodic table. Thus, for example, in semiconductors of Group IV (Ge, Si), impurities which belong to Group V (P, Sb, As) are generally donors. This rule is related to the tetrahedral lattice structure of the Group IV semiconductors. Each atom is bound to its four nearest neighbors with covalent chemical bonds formed by four sp^3 orbitals. The elements of Group V have five valence electrons, and when placed in a tetrahedral host structure, these atoms easily lose the excess electron, i.e., become donors. In contrast, Group III elements lack one electron, which they can easily capture from the host, giving rise to a mobile hole in the valence band of the latter. Therefore in germanium and silicon the Group III elements (B, Al, Ga, and In) become acceptors. We note that the type of impurity is not always determined by properties of the impurity atom itself. For example, in gallium arsenide an atom of Ge or Si can become either a donor or an acceptor, depending on whether it substitutes for gallium or arsenic.¹

There is a situation in which the structure and energy of an impurity state are almost independent of its particular chemical nature. This occurs in the very important and common case of shallow impurities. To be specific we shall discuss this situation in the instance of donors, while bearing in mind that for acceptors the argument is similar. The proximity of a donor level to the bottom of the conduction band implies that an excess electron is weakly bound to the donor center, and located far from it on the average. This means that the atomic structure of the impurity center has little influence on the state of the extra electron, which is bound to the center only because of the positive charge on the center. We can therefore regard the impurity center as a point charge and assume a central potential for the electron motion, viz.

$$U(r) = e^2/\kappa r, \quad (1.1.1)$$

where e is the electron charge, r the distance to the center, and κ the dielectric permittivity of the lattice. It is permissible to use κ when the radius of an impurity state greatly exceeds the lattice constant. In low-symmetry crystals κ is a tensor. We note that since an impurity center does not move,

1. It is possible for a single atom to have many impurity levels of either kind, e.g., gold in germanium has three acceptor levels and one donor level in the forbidden energy gap. However, these are not shallow impurities (translator's note).