SEMICONDUCTORS

Edited by

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American Chemical Society
Monograph Series

REINHOLD PUBLISHING CORPORATION
NEW YORK

CHAPMAN & HALL, LTD., LONDON

Library of Congress Catalog Card Number: 59-7816

REINHOLD PUBLISHING CORPORATION

Publishers of Chemical Engineering Catalog, Chemical Materials Catalog, "Automatic Control," "Materials in Design Engineering," "Progressive Architecture"; Advertising Management of the American Chemical Society

Printed in the United States of America

General Introduction

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

FOREWORD

Chemistry is old enough to look backward as well as forward. The view is sobering, in a "space age" when it is often alleged that the rate of scientific progress is ever-quickening. For, a century ago, Clausius with the kinetic theory of gases and Kekulé with the tetravalence of carbon and the formation of carbon chains had established concepts of molecular identity, structure and valency. Further, Graham's distinction between colloids and crystalloids, and Mendelejeff's and Meyer's Periodic Law came soon afterward. But still, variances in chemical bonding among insulators, salts (both of which Faraday illuminated still earlier) and metals remained unspecified 50 years later. Only four decades ago was the electronic description of valency advanced. This deliberate, even labored, pace of progress in chemical science reminds us how rare, how elusive, are really new ideas. Happily, the chemistry of semiconductors has led to several important new concepts.

For example, the notions of the covalent molecule expanded into the covalent crystal (silicon, diamond) have been harmonized with evidence of ionic states coming from suitable defects or "impurities", (P in Ge, Al in Si, etc.) in the same crystal. Likewise, in both this case and the dramatic influences of imperfections (dislocations, etc.) on semiconductors, the classic ideas of geometry of bonds, or stereochemistry, have been rebuilt. Also, the partly-free, partly-bound electrons of semiconductor solids have liberated thinking about electron localization in organic molecules. Indeed, deep connections between organic and inorganic matter are appearing. Challenges for chemistry in this time include especially understanding of living tissue, which may ease man's life, and of metals (including the uranium families), which may be the means to keep free his life. Semiconductors are in between these kinds of matter, and are enriching the knowledge of both. For instance, dislocations have revitalized metallurgy; paramagnetic electrons have revealed new vistas in biochemistry and biology. Both were stimulated by semiconductor science.

Finally, the most elegant refinements of chemistry—its cultural badges of purity and identity—have come to new dimensions in semiconductor chemistry. Zone melting and refining have given the most nearly perfect and purest forms of matter processed by man. In such crystals of silicon and germanium the chemist's fanciful use of Avogadro's number (as number of atoms of a *certain kind* per cc) for the first time becomes literal, at least over a range of 10^{10}.

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PREFACE

The rapid growth of solid state physics and chemistry has been an outstanding feature of postwar science and technology. While tremendous strides have been taken in the last decade, there can be little doubt that many phases of solid state science are still in their infancy. The field that has progressed perhaps the farthest, largely because of the practical impetus given it in 1947 by the invention of the transistor, is the study of semiconductors. Since that date, the development and application of semiconductor devices have proceeded at a rapid pace. At the same time there has been an equally rapid increase both in the degree of control over the chemistry of the materials, and in the understanding of the basic physics and chemistry of semiconductor processes. The implications of these developments extend well beyond the field of semiconductors. Many phenomena which have been studied to particular advantage in semiconductors are of basic importance not only in other solid state systems, but in other branches of physics and chemistry as well. It is in this latter regard that much in chemistry can be clarified from studies of semiconductors, and it is one of the objectives of this book to facilitate this process.

The roles of the chemist and the physicist in solid state work frequently cannot be clearly differentiated, and likewise there is often no clear distinction between "semiconductor physics" and "semiconductor chemistry." The chemist has had to achieve, in single crystals of semiconductors, a degree of purity and a control over the addition and distribution of impurities as well as over the stoichiometry, far beyond that required in ordinary chemical systems. In addition, one seeks to relate the physical behavior of the semiconductor (for example, the electrical, optical, and magnetic properties) to the chemical composition, or the crystal chemistry. The points of view of both physics and chemistry are usually necessary in achieving this aim, and the contributions from the two disciplines are often inextricably bound up with one another. Accordingly, this book is intended to present the fundamental science of semiconductors from a chemical point of view. No attempt has been made, nor would we consider it desirable, to include only those subjects thought to be purely chemical in nature. Physical processes in semiconductors often depend directly upon the chemistry, contribute to the understanding of the chemistry, or are such an important part of the general field that their omission would give the reader a picture seriously out of balance.

In many of the chapters, heavy emphasis has been placed upon germanium and silicon. This does not represent mere prejudice on the part of the authors, but results from the fact that these two semiconductors are under far better control, and are much better understood, than any other. Germanium and silicon serve in many ways as models for the future understanding of these other materials. At the same time we have sought to select, from the voluminous literature on compound semiconductors that work which seemed to have the soundest basis, giving only references in the less well established cases.

This book was written with a desire to satisfy the requirements of two kinds of readers. The first group includes chemists, either graduate students or chemists whose major interests lie outside the particular subject of this book, who have a desire to learn something about a field which is rapidly absorbing the attention of more and more chemists. Secondly, there are the chemists, physicists and metallurgists who are actively working in the field, who may find illuminating a treatment of semiconductors which emphasizes the chemical aspects of the subject, and which includes certain topics not treated in other books on semiconductors.

The first two chapters give a general background of the physics and chemistry of semiconductors. Chapters 3–7 deal with the physical chemistry of semiconductor systems. In Chapters 8–15 the relationship between the chemistry and the electrical and optical properties of a number of semiconductors is discussed. Chapters 16–17 deal with properties associated with semiconductor surfaces.

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Murray Hill, New Jersey
February, 1959

ACKNOWLEDGMENT

The authors and the editor are very much indebted to a number of their colleagues at Bell Telephone Laboratories for their many helpful discussions and comments on the manuscript. We are also grateful to Dr. O. Simpson for a discussion of material in Chapter 15, to Dr. J. M. Wilson for details of previously unpublished crystal-growing methods described in Chapter 3, and to Professor George Jura and Dr. H. Ehrenreich for their comments on Chapters 1 and 8, respectively. We are indebted to Mrs. M. R. Higgins for her aid in preparing the manuscript.

A number of the figures have been taken from the literature. We would like to thank the authors and publishers of these for permission to reproduce the following figures:

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PRINCIPAL SYMBOLS

A	Helmholtz free energy
A, B	undetermined constants; components
b	ratio of electron to hole mobilities
c	velocity of light
C	concentration
D	diffusion coefficient
D_0	pre-exponential factor in the general diffusion equation
D, A	donor, acceptor
$\mathcal{E}$	electric field
e^-, e^+	electron, hole
E	energy; energy of quantum states
E_F	Fermi level
E_D, E_A	energy of donor, acceptor centers
E_t	energy of trap, recombination center
E_v, E_c	energy at valence, conduction band edge
E_i	Fermi level for intrinsic semiconductor
E_G	energy gap
f	Fermi distribution function
f	growth rate
f	flux density
F	foreign atom
F_I, F_S	foreign interstitial, substitutional
h	Planck's constant
$\hbar$	$h/2\pi$
H	heat content (enthalpy)
H	magnetic field intensity
i	$\sqrt{-1}$
I	interstitial
I_F	foreign interstitial
I	electrical current
I_s	saturation current
J	current density, flux density
k	Boltzmann's constant
k	rate constant
$\mathbf{k}$, k	wave vector
k, κ	equilibrium distribution coefficient, mole fraction equilibrium distribution coefficient
k	extinction coefficient
K	equilibrium constant

K	thermal conductivity
L	diffusion length
$\mathfrak{L}$	see Eq. (16.5)
m	mass of electron
m^*	effective mass
$m_n^{(N)}$, $m_p^{(N)}$	"density of states" effective mass for electrons, holes
M	metal; cation
M	ionic mobility
M_I, etc.	interstitial M atom, etc.
M_I^+, etc.	ionized interstitial M atom, etc.
M_S, etc.	substitutional M atom, etc.
M_S^+, etc.	ionized substitutional M atom, etc.
n	refractive index
n	density of electrons (number per cm^3)
n_i	intrinsic density of electrons, holes
n_D	density of electrons in donor states
n_o, p_o	equilibrium electron, hole densities
N	Avogadro's number
N	density of countable entities (number per cm^3)
N_v, N_c	density of states in valence, conduction bands
N_D, N_A	*total* density of donors, acceptors (ionized plus unionized)
N_I	density of imperfections
N_V, N_I	density of un-ionized lattice vacancies, interstitials
$N_{V_M^-} N_{V_{Pb}^-}$, etc.	density of ionized vacancies at M sites, lead sites, etc.
N_d	density of dislocations per cm^2
p	momentum
p	density of holes
p_A	density of holes in acceptor states
P	ion pair
P	pressure
q	electronic charge
$\mathbf{q}$, q	phonon wave vector
Q	thermoelectric power
Q_e	electronic contribution to thermoelectric power
Q_p	phonon-drag contribution to thermoelectric power
R	gas constant
R	Hall coefficient
s	surface recombination velocity
S	entropy
S	substitutional atom
t	time
T	ion triplet

T	absolute temperature
v	velocity; thermal velocity
V	voltage
V	volume
V	lattice vacancy
V_A, V_C	anion, cation vacancies
V_M, V_{Pb}, etc.	un-ionized vacancy at an M site, lead site, etc.
V_M^-, V_{Pb}, etc.	ionized vacancy at an M site, lead site, etc.
W	thermodynamic probability
W	work
x	mole fraction
X	anion
x, y, z	coordinates
y, Y	see Eq. (16.5), (16.6)
α	absorption coefficient
β	q/kT
δ	effective diffusion layer thickness
κ	dielectric constant
κ	equilibrium distribution coefficient
λ	wave length
λ	n_i/n_o
$\bar{\mu}$	electrochemical potential (Fermi level)
μ, μ_i	chemical potential, of the ith component
μ	mobility
μ_H, μ_n, μ_p	Hall mobility, electron and hole mobility
μ_L, μ_a, μ_o	lattice scattering, acoustical mode, optical mode mobilities
π	Peltier coefficient
ρ	charge density
ρ	resistivity
σ	conductivity
τ	lifetime; relaxation time
ν	frequency; jump frequency
$\bar{\nu}$	wave number $= \nu/c$
Φ_o	Fermi level ($q\Phi_o = E_F$)
Φ_s	separation between Fermi level and Ψ_s
Φ_n, Φ_p	quasi-Fermi levels (imrefs) for electrons, holes
Φ_{ns}, Φ_{ps}	surface quasi-Fermi levels for electrons, holes
Ψ	wave function
Ψ	electrostatic potential
Ψ_s	electrostatic potential at surface
Ψ_0	electrostatic potential in interior
ω	angular frequency $= 2\pi\nu$

VALUES OF FUNDAMENTAL CONSTANTS

	cgs units
Electronic charge q	4.80×10^{-10} esu (1.60×10^{-19} coul.)
Electronic mass m	9.11×10^{-28} g
Planck's constant h	6.62×10^{-27} erg sec
$\hbar = h/2\pi$	1.054×10^{-27} erg sec
Boltzmann's constant k	1.38×10^{-16} erg deg^{-1} (8.62×10^{-5} ev. deg^{-1})
Speed of light c	2.998×10^{10} cm sec^{-1}

CONVERSION FACTORS FOR VARIOUS UNITS OF ENERGY

1 ev = 1.60×10^{-12} erg = 23.053 kcal/mol

1 ev corresponds to:

(a) a temperature of 1.16×10^4 °K

(b) a wave number of 8.066×10^3 cm^{-1}

(c) a wave length of 1.24 micron

CONTENTS