541.377 HAN

CONTENTS

CHAPTER		PAGE
FOREWORD		v
PREFACE		vii
ACKNOWLEDGMENT		ix
PRINCIPAL SYMBOLS		xi
VALUES OF FUNDAMENTAL CONSTANTS		xiv
CONVERSION FACTORS FOR VARIOUS UNITS OF ENERGY		xiv
1. SEMICONDUCTOR PRINCIPLES.	N. B. *Hannay*	1
Introduction		1
Electrons and Holes		2
Energy Bands		4
Free Atom Approach to Energy Bands		5
Free Electron Approach to Energy Bands		9
Semiconduction		15
Intrinsic Semiconduction		16
Donors and Acceptors		17
Impurity Semiconductors		17
Nonstoichiometry		20
Energy Levels of Donors and Acceptors		21
Equilibrium of Electrons and Holes		24
Fermi-Dirac Distribution Law		24
Fermi-Dirac Statistics Applied to Semiconductors		27
Carrier Behavior		34
Electrical Conductivity		34
Hall Effect		36
Seebeck Effect		40
Comparison of Hall and Seebeck Effects		42
Nonequilibrium Carrier Behavior		43
Junctions		45
The *p-n* Junction		45
The Junction Transistor		48
2. SURVEY OF SEMICONDUCTOR CHEMISTRY.	*J. J. Lander*	50
Introduction		50
Intrinsic Semiconductors		51
The Main Group		54
d-Band Semiconductors		59
Organic Semiconductors		60

Electronic Conduction in Substances which Normally Exhibit Ionic Conduction . . . 60
Applications . . . 63
Kinds of Imperfections . . . 64
Electrons and Holes . . . 67
Lattice Vacancies . . . 68
Interstitials . . . 73
Lattice Substitutions . . . 74
Interactions of Imperfections; Complex Imperfections . . . 76
Survey of Chemical Theory of Imperfections . . . 80
Equilibria in Complex Systems . . . 82
Chemistry at Surfaces and Dislocations . . . 84

3. SEMICONDUCTOR CRYSTAL GROWING, M. *Tanenbaum* . . . 87
Introduction . . . 87
Growth from the Melt . . . 88
General Considerations . . . 89
Growth in a Containing Crucible . . . 95
Crystal Pulling . . . 101
Growth without a Crucible . . . 113
Growth from Solution . . . 125
General Considerations . . . 125
Solution Techniques . . . 127
Crystal Growth from the Vapor Phase . . . 132
General Considerations . . . 132
Direct Growth from the Vapor . . . 134
Growth from a Vapor Phase by Chemical Reaction . . . 138

4. CONTROL OF COMPOBITION IN SEMICONDUCTORS BY FREEZING METHODS, *C. D. Thurmond* . . . 145
Introduction . . . 145
Liquid and Solid Phases at Equilibrium . . . 146
Ideal Binary Liquid and Solid Solutions . . . 146
Ideal Dilute Solid Solutions and Ideal Liquid Solutions . . . 148
Distribution Coefficient and Liquidus and Solidus Curves Near the Melting Point . . . 151
Distribution Coefficient as a Function of Temperature and Composition . . . 152
Distribution Coefficient Correlations . . . 155
Liquid and Solid Phases Not at Equilibrium: Freezing . . . 157
Freezing of a One-Component Liquid . . . 157
Freezing of a Two-Component Liquid . . . 160

The Influence of Liquid and Solid Phase Transport Processes on Composition ... 161
Equilibrium Freezing-in ... 161
Simple Freezing-in ... 162
Diffusion Controlled Freezing-in ... 163
The Influence of the Freezing Method on Solid Phase Composition. 165
Normal Freezing ... 165
Zone Melting ... 166
Conservative Freezing Methods ... 168
Nonconservative Freezing Methods ... 171
Applications ... 173
Purification ... 173
Uniform Solid Phase Compositions ... 177
Nonuniform Impurity Distributions ... 180

5. Defect Interactions in Semiconductors. *C. S. Fuller* ... *192*
Introduction ... 192
Theoretical Background ... 193
Heterogeneous Equilibria ... 194
Defects as Species ... 195
Defect Equilibria in Semiconductors ... 195
Analogies between Semiconductor and Aqueous Solutions ... 195
Solubility Equilibria—Effect of Hole-Electron Equilibrium ... 199
Solubility Equilibria—Effect of Ion Pairing on Solubility ... 203
Ion Pair Processes and Kinetics ... 206
Ion Pairs Involving Lithium ... 207
Ion Pairing Relaxation ... 207
Interaction of Ion Pairs with Carriers ... 210
Ion Triplets ... 212
Pairing of Substitutional Ions ... 213
Other Association Complexes ... 215
Vacancy-Vacancy Pairing ... 215
Vacancy-Atom and Vacancy-Ion Complexes ... 215
Compound Formation in Semiconductors ... 216
Reactions between Donor and Acceptor Atoms ... 217
Reactions in Silicon Containing Oxygen ... 217

6. Diffusion Processes in Germanium and Silicon. *Howard Reiss and C. S. Fuller* ... *222*
Introduction ... 222
Fundamentals of Diffusion Processes ... 222
Concept of Diffusion Coefficient ... 222
Boundary Value Problems in Diffusion ... 224

Chemical Potentials and Diffusion 224
Kinetics of Diffusion 225
Measurement of Diffusion in Semiconductors 228
Total Conductance Methods 228
Sheet Conductance 230
p-n Junction Methods 231
Capacitance Method 232
Other Electrical Methods 233
Diffusion Studies in Germanium and Silicon 234
Diffusion of Hydrogen and Helium in Ge and Si 234
Diffusion of Lithium in Ge and Si 235
Diffusion of Copper in Ge and Si 238
Diffusion of Group III and Group V Elements in Ge and Si 242
Diffusion of Other Elements 246
Surface Effects 247
Internal Fields in Macroscopic Diffusion 248
Diffusion of Oxygen in Si 252
Diffusion-Controlled Reactions 253
Annealing of Radiation Damage 254
Precipitation of Copper, Nickel, and Lithium in Ge and Si 256

7. THE CHEMISTRY OF SOME COMPOUND SEMICONDUCTORS, D. G. Thomas 269
Introduction 269
Generalized Treatment of Crystal Imperfections 270
Nomenclature 270
Equilibrium between the Vapor and a Crystal Displaying Frenkel Disorder 271
Simplifications that Arise from Complete Ionization 274
Incorporation of Foreign Atoms 277
Application to Experiment 280
Lead Sulfide 280
Interstitial Copper in Lead Sulfide 287
Cadmium Sulfide 290
Barium Oxide 293
Zinc Oxide 300
Sintered Zinc Oxide 310

8. GROUP IV SEMICONDUCTORS, T. H. Geballe 313
Introduction 313
Intrinsic Electrical Properties of Silicon and Germanium 314
Energy Bands 314

Lattice Vibrational Spectra . . . 326
Intrinsic Conductivity and the Energy Gap . . . 329
The Effect of Impurities and Imperfections . . . 333
"Shallow" Impurity Levels . . . 334
The Ionization Equilibrium . . . 336
Deep-Lying Impurity Levels . . . 340
Isothermal Transport Properties . . . 344
General Experimental Procedure . . . 345
Conductivity and Mobility . . . 346
Lattice Scattering for p-Type Materials . . . 355
The Effects of Impurities . . . 357
Magnetoresistance in n-Type Material . . . 364
Piezoresistance . . . 366
Thermal Transport Properties . . . 369
Experimental Procedures . . . 369
Thermoelectricity . . . 369
Thermomagnetic Effects . . . 376
Thermal Conduction . . . 376
Other Properties of Germanium and Silicon . . . 378
Non-ohmic Behavior at High-Electric Fields—"Hot Electrons" . . . 378
Thermodynamic Quantities . . . 380
Magnetic Susceptibility . . . 381
Other Group IV Semiconductors . . . 382
Diamond . . . 382
Silicon Carbide . . . 383
Germanium-Silicon Alloys . . . 384
Gray Tin . . . 384
Liquid Phases . . . 384

9. PROPERTIES OF SOME COVALENT SEMICONDUCTORS. J. M. *Whelan* 389
Introduction . . . 389
The Group III-V Compounds . . . 389
Indium Antimonide . . . 391
Indium Arsenide . . . 405
Indium Phosphide . . . 409
Gallium Antimonide . . . 410
Gallium Arsenide . . . 411
Aluminum Antimonide . . . 416
Other III-V Compounds . . . 417
Group V-VI Compounds . . . 418
Group II-IV Compounds . . . 424
Tellurium, Selenium, and Boron . . . 426

10. INFRARED ABSORPTION OF SEMICONDUCTORS, H. J. *Hrostowski* . . 437
Introduction . . . 437
Experimental Methods . . . 437
Electronic Transitions between Bands . . . 438
The Absorption Edge of Silicon and Germanium . . . 438
The Absorption Edge of Si-Ge Alloys . . . 445
The Absorption of Indium Antimonide . . . 446
Oscillatory Magneto-Absorption . . . 448
Temperature and Pressure Effects on E_g . . . 450
Interband Transitions . . . 451
Lattice Absorptions . . . 453
Free Charge Carrier Absorption . . . 457
Determination of Effective Mass . . . 459
Electrical Susceptibility . . . 459
Infrared Cyclotron Resonance . . . 461
Impurity States . . . 462
Theory of Shallow Impurity States . . . 466
Comparison of Theoretical and Experimental Results . . . 470
Optical Ionization Energies . . . 472
Deep Levels . . . 473
Electrically Inactive Impurities . . . 474
Photoconductivity . . . 478

11. RECOMBINATION AND TRAPPING, R. G. *Shulman* . . . 482
Introduction . . . 482
Recombination . . . 482
Chemical Origin of Recombination Centers in Ge . . . 487
Crystalline Imperfections as Recombination Centers in Ge . . . 489
Recombination in Silicon and InSb . . . 490
Temperature Dependence of Lifetime . . . 491
Methods of Measuring Lifetime . . . 493
Radiative Recombination . . . 500
Trapping of Minority Carriers . . . 502
Chemical Origin of Trapping Centers . . . 504

12. EFFECT OF IMPERFECTIONS ON GERMANIUM AND SILICON, J. N. *Hobstetter* . . . *508*
Introduction . . . 508
Classes of Defects . . . 508
Point Defects . . . 509
Line Defects . . . 509
Surface Defects . . . 512

Elements of Dislocation Theory . . . 513
Plastic Deformation . . . 513
Dislocation Motions . . . 515
Dislocation Sources . . . 516
Elastic Interaction of Dislocations . . . 518
Dislocation Combination . . . 521
Dislocation Jogs . . . 521
Work Hardening . . . 522
Interaction with Point Defects . . . 523
Dislocations in Germanium and Silicon . . . 524
Geometry of Dislocations . . . 524
Deformation of Germanium and Silicon . . . 527
Detection of Dislocations . . . 527
Confirmation of Dislocation Theory . . . 531
Effect of Defects on Properties . . . 533
Effect of Bombardment . . . 533
Effect of Quenching . . . 534
Effect of Deformation . . . 534
Effect of Annealing . . . 535
Effect of Dislocations on Number of Carriers . . . 536
Effect of Dislocations on Mobility . . . 538
Effect of Dislocations on Lifetime . . . 538

13. SEMICONDUCTING PROPERTIES OF SOME OXIDES AND SULFIDES.
A. R. *Hutson* . . . 541
Introduction . . . 541
Idiosyncracies of Non-Single-Crystal Samples . . . 542
Electrical Conductivity . . . 543
Hall Effect . . . 546
Thermoelectric Power . . . 546
Dielectric Constant . . . 547
Pore Conductivity . . . 548
The Role of Lattice Polarization . . . 551
Polar Vibrational Modes and Conduction Electrons and Holes . . . 551
The Coupling Constant . . . 556
Optical Mode Scattering . . . 558
Polarons and Bound States . . . 560
Effective Ionic Charge . . . 561
Alkaline-Earth Oxides . . . 563
Magnesium Oxide . . . 563
Barium Oxide . . . 569
Calcium Oxide and Strontium Oxide . . . 576

Wurtzite-Zinc Blende Compounds. 577
Zinc Oxide. 580
Cadmium Sulfide. 585
Cadmium Telluride. 587
Other Compounds—CdO. 590
Lead Sulfide, Selenide, and Telluride. 590

14. OXIDES OF THE 3*d* TRANSITION METALS, F. J. Morin. 600
Introduction. 600
Antiferromagnetism. 602
Atomic Orbitals and the Crystal Field. 606
The 3*d* Band. 612
TiO_2. 612
TiO. 614
Ti_2O_3 and V_2O_3. 614
Relative Energies of the 4*s*, 3*d*, and 2*p* Levels. 616
Nickel Oxide—NiO. 621
Iron Oxide Fe_2O_3. 628
Transport in the 3d Levels. 631

15. ORGANIC SEMICONDUCTORS, C. G. B. Garrett. 634
Introduction. 634
Survey of Experimental Techniques. 636
Measurements on Powders and Evaporated Films. 638
Semiconductivity—Single Crystals. 644
Anthracene. 646
Naphthalene. 647
Phthalocyanine and Metal Phthalocyanines. 649
Pyrene. 650
p-Terphenyl. 650
trans-Stilbene and Phenylstilbenes. 650
Photoconductivity—Single Crystals. 651
The Role of Impurities. 654
Other Experimental Information. 655
Crystallographic Data. 656
Thermoelectric Measurements. 657
Magnetic Properties. 657
Spectroscopic Data. 657
Ionization Potentials and Electron Affinities. 659
The Evidence Against Electrolysis. 659
Dielectric Properties. 659
Point-Contact Rectification. 660

Summary of Experimental Results 661
Theoretical Considerations 662
The Future 670

16. SEMICONDUCTOR SURFACES. *J. T. Law* **676**
Introduction 676
The Surface of a Semiconductor 677
Definition of Terms 677
The Metal-Semiconductor System 681
The Gas or Vacuum-Semiconductor System **683**
Carrier Mobility in the Space-Charge Region 684
Surface States 685
Summary 688
Adsorption on Semiconductors 688
Theory 688
Experiment 692
Thick Oxide Films 694
Oxide Films 695
Photo Effects 696
Catalysis 696
Photocatalysis on Semiconductors 702
Electrical Properties of Semiconductor Surfaces 703
General Remarks 703
Electrical Measurements on Clean Surfaces 704
Electrical Measurements on Etched Surfaces of Elemental Semiconductors 709
Compound Semiconductors 720

17. SEMICONDUCTOR ELECTRODES. *J. F. Dewald* **727**
Introduction 727
The Equilibrium Condition 727
The Potential Drop Across the Boundary Layer 728
The Charge-Distribution in the Region of the Interface 730
Charge-Transfer Processes 733
Quasi-Equilibrium Electrode Kinetics 737
The Supply of Holes and Electrons 737
The Phenomenological Equations 739
The Germanium Electrode 741
Other Reactions at the Germanium Electrode 747
Other Semiconductor Electrodes 748
Corrosion Kinetics—Etching 748
INDEX 753