# Contents

Preface to the Second Edition XI

v

Preface XIII

### 1 Principles of Semiconductor Physics 1

- 1.1 Crystal Structure 1
- 1.2 Energy Levels in Solids *3*
- 1.3 Optical Properties 8
- 1.4 Density of States and Carrier Concentrations 11
- 1.4.1 Intrinsic Semiconductors 14
- 1.4.2 Doped Semiconductors 15
- 1.5 Carrier Transport Phenomena 17
- 1.6 Excitation and Recombination of Charge Carriers 19
- 1.7 Fermi Levels under Nonequilibrium Conditions 21

### 2 Semiconductor Surfaces and Solid–Solid Junctions 23

- 2.1 Metal and Semiconductor Surfaces in a Vacuum 23
- 2.2 Metal–Semiconductor Contacts (Schottky Junctions) 26
- 2.2.1 Barrier Heights 26
- 2.2.2 Majority Carrier Transfer Processes 31
- 2.2.3 Minority Carrier Transfer Processes 35
- 2.3 p-n Junctions 38
- 2.4 Ohmic Contacts 41
- 2.5 Photovoltages and Photocurrents 42
- 2.6 Surface Recombination 46

### 3 Electrochemical Systems 49

- 3.1 Electrolytes 49
- 3.1.1 Ion Transport in Solutions 49
- 3.1.2 Interaction between Ions and Solvent 52
- 3.2 Potentials and Thermodynamics of Electrochemical Cells 53
- 3.2.1 Chemical and Electrochemical Potentials 53
- 3.2.2 Cell Voltages 56

VI Contents

3.2.3	Reference Potentials 59
3.2.4	Standard Potential and Fermi Level of Redox Systems 60
А	Experimental Techniques 65
4 4 1	Electrode Preparation 65
4.2	Current-Voltage Measurements 65
421	Voltametry 65
422	Photocurrent Measurements 67
4.2.3	Rotating Ring Disk Electrodes 68
4.2.4	Scanning Electrochemical Microscopy (SECM) 69
4.3	Measurements of Surface Recombination and Minority Carrier
	Injection 70
4.4	Impedance Measurements 72
4.4.1	Basic Rules and Techniques 72
4.4.2	Evaluation of Impedance Spectra 74
4.4.3	Intensity Modulated Photocurrent Spectroscopy (IMPS) 78
4.5	Surface Conductivity Measurement 80
4.6	Flash Photolysis Investigations 82
4.7	Surface Science Techniques 82
4.7.1	Spectroscopic Methods 83
4.7.2	<i>In situ</i> Surface Microscopy (STM and AFM) 85
5	Solid–Liquid Interface 89
5.1	Structure of the Interface and Adsorption 89
5.2	Charge and Potential Distribution at the Interface 91
5.2.1	The Helmholtz Double Layer 92
5.2.2	Gouy Layer in the Electrolyte 93
5.2.3	Space Charge Layer in the Semiconductor 94
5.2.4	Charge Distribution in Surface States 101
5.3	Analysis of the Potential Distribution <i>102</i>
5.3.1	Germanium Electrodes 102
5.3.2	Silicon Electrodes 109
5.3.3	Compound Semiconductor Electrodes 111
5.3.4	Flatband Potential and Position of Energy Bands at the Interface
5.3.5	Unpinning of Energy Bands during Illumination 118
5.4	Modification of Semiconductor Surfaces 123
6	Electron Transfer Theories 127
6.1	The Theory of Marcus 127
6.1.1	Electron Transfer in Homogeneous Solutions 127
6.1.2	The Reorganization Energy 132
6.1.3	Adiabatic and Nonadiabatic Reactions 134
6.1.4	Electron Transfer Processes at Electrodes 134
6.2	The Gerischer Model 138
6.2.1	Energy States in Solution 138

114

Contents VII

6.2.2 Electron Transfer 143 6.3 Ouantum Mechanical Treatments of Electron Transfer Processes 145 146 6.3.1 Introductory Comments Nonadiabatic Reactions 149 6.3.2 6.3.3 Adiabatic Reactions 156 6.4 The Problem of Deriving Rate Constants 165 6.5 Comparison of Theories 167 Charge Transfer Processes at the Semiconductor–Liquid Interface 169 7 7.1 Charge Transfer Processes at Metal Electrodes 169 7.1.1 Kinetics of Electron Transfer at the Metal–Liquid Interface 169 7.1.2 Diffusion-controlled Processes 178 7.1.3 Investigations of Redox Reactions by Linear Sweep Voltametry 182 Criteria for Reversible and Irreversible Reactions 183 7.1.4 7.2 Qualitative Description of Current-Potential Curves at Semiconductor Electrodes 185 7.3 One-step Redox Reactions 186 7.3.1 The Energetics of Charge Transfer Processes 186 Quantitative Derivation of Current–Potential Curves 189 7.3.2 7.3.3 Light-Induced Processes 194 7.3.4 Majority Carrier Reactions 198 7.3.5 Minority Carrier Reactions 211 7.3.6 Electron Transfer in the "Inverted Region" 222 7.4 The Quasi-Fermi-Level Concept 225 7.4.1 Basic Model 225 7.4.2 Application of the Concept to Photocurrents 229 7.4.3 Consequences for the Relation between Impedance and IMPS Spectra 233 7.4.4 Quasi-Fermi-Level Positions under High-Level Injections 237 7.5 Determination of the Reorganization Energy 240 7.6 Two-step Redox Processes 244 7.7 Photoluminescence and Electroluminescence 249 7.7.1 Kinetic Studies by Photoluminescence Measurement 250 7.7.2 Electroluminescence Induced by Minority Carrier Injection 255 7.8 Hot Carrier Processes 258 7.9 Catalysis of Electrode Reactions 262 Electrochemical Decomposition of Semiconductors 267 8 8.1 Anodic Dissolution Reactions 267 8.1.1 Germanium 267 8.1.2 Silicon 271 Compound Semiconductors 279 8.1.3 8.2 Cathodic Decomposition 283 8.3 Dissolution under Open Circuit Conditions 283 8.4 Energetics and Thermodynamics of Corrosion 285

VIII

Contents	
8.5	Competition between Redox Reaction and Anodic Dissolution 288
8.6	Formation of Porous Semiconductor Surfaces 293
9	Photoreactions at Semiconductor Particles 295
9.1	Quantum Size Effects 295
9.1.1	Quantum Dots 296
9.1.2	Single Crystalline Quantum Films and Superlattices 303
9.1.3	Size Quantized Nanocrystalline Films 305
9.2	Charge Transfer Processes at Semiconductor Particles 306
9.2.1	Reactions in Suspensions and Colloidal Solutions 306
9.2.2	Photoelectron Emission 313
9.2.3	Comparison between Reactions at Semiconductor Particles and at Compact Electrodes 316
9.2.4	The Role of Surface Chemistry 317
9.2.5	Enhanced Redox Chemistry in Quantized Colloids 318
9.2.6	Reaction Routes at Small and Big Particles 322
9.2.7	Sandwich Formation between Different Particles and between Particle and Electrode 324
9.3	Charge Transfer Processes at Quantum Well Electrodes (MQW, SOW) 327
9.4	Photoelectrochemical Reactions at Nanocrystalline Semiconductor Lavers 331
9.4.1	Impact Ionization and Carrier Multiplication 333
9.4.2	Hot Carrier Cooling and Exciton Multiplication in Quantum
9.4.3	Multiple Exciton Collection in a Sensitized Photovoltaic System 340
10	Electron Transfer Processes between Excited Molecules and Semiconductor Electrodes 343
10.1	Energy Levels of Excited Molecules 343
10.2	Reactions at Semiconductor Electrodes 349
10.2.1	Spectra of Sensitized Photocurrents 349
10.2.2	Dye Molecules Adsorbed on the Electrode and in Solution 352
10.2.3	Potential Dependence of Sensitization Currents 356
10.2.4	Sensitization Processes at Semiconductor Surfaces Modified by Dye Monolavers 357
10.2.5	Ouantum Efficiencies, Regeneration, and Supersensitization 364
1026	Kinetics of Electron Transfer between Dye and Semiconductor

- 10.2.6Kinetics of Electron Transfer between Dye and Semiconductor Electrode 366
- Sensitization Processes at Nanocrystalline Semiconductor 10.2.7 Electrodes 370
- 10.3 Comparison with Reactions at Metal Electrodes 375
- Production of Excited Molecules by Electron Transfer 376 10.4

- **11** Applications 379
- 11.1 Photoelectrochemical Solar Energy Conversion 379
- 11.1.1 Electrochemical Photovoltaic Cells 379
- 11.1.2 Photoelectrolysis 402
- 11.1.3 Photoreduction of  $CO_2$  424
- 11.2 Photocatalytic Processes 426
- 11.2.1 Photodegradation of Pollutants 427
- 11.2.2 Photocatalytic Reactions 429
- 11.2.3 Light-Induced Chemical Reactions 430
- 11.3 Etching of Semiconductors 431
- 11.4 Light-Induced Metal Deposition 433

## Appendices 437

- A.1 List of Major Symbols 437
- A.2 Physical Constants 440
- A.3 Lattice Parameters of Semiconductors 440
- A.4 Properties of Important Semiconductors 441
- A.5 Effective Density of States and Intrinsic Carrier Densities 441
- A.6 Major Redox Systems and Corresponding Standard Potentials 442
- A.6.1 Aqueous Solutions 442
- A.6.2 In Acetonitrile (vs Ag/AgCl) 442
- A.7 Potentials of Reference Electrodes 443

References 445

Index 465