## Contents

### Preface

Preface xi

### Acknowledgments

Acknowledgments xiii

### Frequently Used References

Frequently Used References xv

### 1. Introduction

1.1 Silicon-Based Chemical Sensors 2
1.2 Semiconducting Metal Oxide Sensors 5
1.3 Catalysis 7
1.4 Solid Electrolyte Sensors 8
1.5 Membranes 10

### 2. Solid State Background

2.1 Semiconductors 13
  2.1.1 The Bulk 13
  2.1.2 The Surface 23
2.2 Solid Electrolytes 37
  2.2.1 The Bulk 37
  2.2.2 Use of a Solid Electrolyte as a Membrane 44

### 3. Solid / Gas Interfaces

3.1 Physisorption and Chemisorption 67
3.2 Ionosorption 72
3.3 Electrical Effects of Adsorbed Gases:
   Models for Semiconductor Gas Sensors 74
3.4 Introduction of Bulk Defects from the Surface 83
  3.4.1 Electrical Behavior of Defects 83
  3.4.2 Reduction, Oxidation and Dissociation of Oxides 87
3.5 Development of a Surface Phase 98
3.6 Adsorption of Water Vapor from Air 101

4. Solid / Liquid Interfaces 105
  4.1 The Metal/Liquid Interface 105
    4.1.1 Electrode Reactions 105
    4.1.2 Diffusion-Limited Electrode Reactions 113
    4.1.3 Electron-Transfer-Limited Electrode Reaction 137
  4.2 The Semiconductor/Liquid Interface 142
  4.3 The Insulator/Liquid Interface 143
  4.4 The Solid Electrolyte/Liquid Interface 147
  4.5 Hydration of the Solid 150

5. Catalysis Background 159
  5.1 Mechanisms 160
    5.1.1 Need for Activation 160
    5.1.2 Sites for Activation of Oxygen 161
    5.1.3 Sites for Activation of Organic Molecules or Hydrogen 167
    5.1.4 Heterogeneity 171
    5.1.5 Promoters 174
  5.2 Supported Catalysts 178
    5.2.1 Support/Catalyst Interactions: Spillover and Fermi Energy Control 179
    5.2.2 Dispersion of Catalysts 187
    5.2.3 Examples of the Use of Supported Catalysts 188
    5.2.4 Deactivation of the Supported Catalyst 190

6. Membrane Background 197
  6.1 Membrane Cell Fundamental Characteristics 199
    6.1.1 Donnan Potential 199
    6.1.2 Liquid Junctions 202
    6.1.3 The Selectivity Coefficient 205
    6.1.4 The Ion-Exchange Current Density 211
6.2 Types of Membranes and Their Most Important Properties 215
   6.2.1 Ion-Exchange Membranes 216
   6.2.2 Neutral-Carrier Membranes 226
   6.2.3 Charged Carriers 241
   6.2.4 Lifetime, Selectivity and Immobilization of Polymer-Supported Membrane Components 243
   6.2.5 Drug and Detergent ISEs 246
   6.2.6 Types of Polymer Matrices for Membranes 251
   6.2.7 Solid-State Membrane Electrodes 252
   6.2.8 Sensitized ISEs (Composite Systems) 256
   6.2.9 Response Time of ISEs 259
6.3 Asymmetric Membrane Configurations 264

7. Biosensor Principles 277
   7.1 Biosensor Characteristics 278
   7.2 Enzyme Electrodes 285
   7.3 Cell-Based Sensors (Microbial Sensors) 294
   7.4 Immunosensors 297
   7.5 Very Thin Membranes—Bilayer Lipid Membranes—Langmuir-Blodgett Films 304
   Glossary of Biosensor Terminology 315

8. Principles of ChemFET Operation 325
   8.1 Electronics Considerations 326
   8.2 Chemical Considerations 332
      8.2.1 Thermodynamic Analysis of an Electrochemical Cell Incorporating an Insulator 333
      8.2.2 pH Dependency of $\psi_0$, the Potential Drop in the Electrolyte at the Interface Insulator/Electrolyte 337
      8.2.3 Site-Binding Theory 340
   8.3 Application of the Site-Binding Model to Various Semiconductor Liquid Interfaces 346
   8.4 Polarizable and Nonpolarizable Interfaces—Esin-Markov Coefficient 349
8.5 Bulk Model to Explain pH Sensitivity 353  
8.6 Dynamic Range of a ChemFET 354  
8.7 Charge Groups on Spacer Arms 355  

9. Silicon-Based Chemical Sensors 359  
9.1 Potentiometric Devices 360  
9.1.1 Type of Device—A Question of Signal Line Length 361  
9.1.2 Overview of Inorganic Gate Materials 396  
9.1.3 Overview of Organic-Gate Materials 404  
9.2 Amperometric Devices—A New Start 409  

10. Thin-Film Gas Sensors 419  
10.1 Schottky Barrier Diode (MIS) Structures as Gas Sensors 420  
10.2 Sensors Using Films of Metal Oxide 424  
10.2.1 Single-Crystal “Thin-Film” Sensors 424  
10.2.2 Thin-Film Oxide Sensors 426  
10.2.3 Catalysts and Selectivity with Thin-Film Sensors 430  
10.3 Thin-Film Sensors for Hydrogen Sulfide 431  
10.4 Organics as Gas Sensors 432  

11. Solid Electrolytes—Devices 437  
11.1 Candidate Ionic Conductors for Incorporation in Sensors 437  
11.1.1 ZrO₂ 440  
11.1.2 Alternative Oxide Ion Conductors for Oxygen Sensing 445  
11.1.3 Nonoxides for Oxygen Sensing 445  
11.1.4 Proton Conductors 448  
11.1.5 Polymer Salt Complexes 458  
11.2 Microionic Structures 459  
11.2.1 Microionic ZrO₂ Sensor 459  
11.2.2 Microionic HUP Sensor 461  
11.2.3 Fluoride-Based Microionic Sensors 462  
11.2.4 All-Solid-State Reference Electrodes 468  
11.2.5 An Ac-Driven Microionic Sensor 470
11.2.6 A TiO₂-Based Microionic Device
11.2.7 An IrO₂-Based Microionic pH Sensor— A Mixed Conductor Ion Sensor

12. Gas Sensors Based on Semiconductor Powders

12.1 Practical Details
12.1.1 Construction of Sensors
12.1.2 Experimental Testing Methods
12.2 Sensors for Reducing Agents
12.2.1 Choice of Semiconductor and Operating Temperature
12.2.2 Selectivity by Selective Filters or Reactants
12.2.3 Selectivity and Activity Using Catalysts and Promoters
12.2.4 Reproducibility and Stability in Semiconductor Gas Sensors
12.3 Sensors for Humidity, CO₂ and Oxidizing Agents
12.3.1 Humidity and CO₂ Sensors
12.3.2 Sensors of Oxidizing Agents

13. Application of Solid-State Chemical Sensors

13.1 Commercial Solid-State Gas Sensors
13.1.1 Current Use of Commercial Solid-State Gas Sensors
13.1.2 Problems with Semiconductor Sensors
13.1.3 Potential of Commercial Use of Semiconductor Sensors
13.2 Electrochemical- and FET-Based Gas Sensors
13.2.1 ISFET
13.2.2 Gas MOSFET
13.2.3 Hybrid Devices and Miniature ISEs
13.2.4 EGFET
13.3 Markets for Chemical Sensors
13.3.1 Current Sensor Applications
13.3.2 Emerging Sensor Applications

Index