Contents

PREFACE xvii

PART I INTRODUCTION TO MATERIAL SCIENCE 1

   A. Different Types of Materials / 3
   B. Uses of Materials / 6
   C. Approaches to Producing New Materials, New Properties, and Uses / 8
   D. Devices and Machines / 10
   E. The Role of Chemistry in Materials Science / 11
   F. A Broader Perspective / 13
   G. Terminology / 15
   H. Example Journals Where Materials Science Publications Can be Found / 15
   I. Study Questions / 15

2. Fundamental Principles that Underlie Materials Chemistry 17
   A. Why Are Different Materials Different / 17
   B. The Role of Different Elements / 17
   C. Different Types of Chemical Bonds / 19
      1. Van der Waals Forces and the Lennard-Jones Potential / 20
      2. Covalent Bonds / 21
      3. Coordinate Bonds / 30
CONTENTS

4. Ionic Assemblies / 30
5. Metallic Bonding / 31

D. Size of Molecular Units / 32
E. Different Shapes of Component Molecules and Influence of Solid-State Structure / 34

F. Suggestions for Further Reading / 37
G. Study Questions / 38

3. Basic Synthesis and Reaction Chemistry 40

A. Underlying Principles / 40
B. Starting Points for Materials Synthesis—Isolation of Elements / 41
C. Principles that Underlie Materials Synthesis / 44
1. Importance of Halides in Materials Synthesis / 44
2. Acidic Hydroxides and Condensation Reactions / 46
3. Metathetical Exchange Reactions / 47
4. Nucleophilic Substitution / 48
5. Electrophilic Substitution / 49
6. Coordination Chemistry / 50
7. Branching and Crosslinking / 50
8. Polymerization–Depolymerization Equilibria / 52

D. Illustrative Chemistry of Selected Nonmetallic Elements / 52
1. Carbon Chemistry / 52
2. Silicon Chemistry / 56
3. Boron Chemistry / 60
4. Phosphorus Chemistry / 63
5. Interelement Compounds / 66
6. Small Rings, Cages, and Short Chains / 66

E. Suggestions for Further Reading / 66
F. Study Questions / 67

4. Structure Determination and Special Techniques for Materials Characterization 68

A. Purpose / 68
B. Analysis of Bulk Materials / 68
1. Elemental Microanalysis / 68
2. Infrared–Raman Spectroscopy / 69
3. Solid-State Nuclear Magnetic Resonance Spectroscopy / 69
4. Thermal Analysis / 70
5. Stress–Strain and Impact Analysis / 74
6. X-Ray Diffraction / 75
7. Refractive Index and Chromatic Dispersion / 79
8. Magnetic Susceptibility / 80
9. Electrical Conductivity / 82
10. Transmission Electron Microscopy / 83

C. Surface and Thin-Film Analysis Techniques / 83
   1. Scanning Electron Microscopy / 83
   2. Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) / 85
   3. X-Ray Photoelectron Spectroscopy (XPS) / 88
   4. Total Internal Reflection Infrared Spectroscopy / 90
   5. Ellipsometry / 90
   6. Contact Angles / 91

D. Solution Analysis Techniques / 92
   1. General Comments / 92
   2. Solution NMR Spectroscopy / 92
   3. Solution-State Light Scattering / 92
   4. Gel Permeation Chromatography / 92

E. Suggestions for Further Reading / 93
F. Study Questions / 93

PART II  DIFFERENT TYPES OF MATERIALS 95

5. Small Molecules in Solids 97
   A. Importance of Small-Molecule Materials / 97
   B. Packing of Small Molecules in the Solid State / 98
      1. Shape-Fitting / 98
      2. Dipolar or Charged Molecules / 99
      3. Hydrogen Bonding / 99
   C. Self-Assembly by Crystallization / 100
   D. Spherical Molecules Such as Fullerenes in the Solid State / 100
   E. Disk-Shaped Molecules and Other Flat Structures / 101
      1. Liquid Crystallinity from Disk- or Wafer-Shaped Molecules / 101
      2. Electronic Phenomena from Disk-Shaped Molecules in the Solid State / 102
   F. Rod-Shaped Molecules / 107
   G. Charge Transfer Complexes / 107
   H. Clathrates—Molecular Inclusion Adducts / 108
      1. Clathrates of Water Ice / 110
      2. Urea and Thiourea / 111
      3. Perhydrotriphenylene / 112
      4. Cyclophosphazenes / 112
      5. Hofmann and Werner-Type Complexes / 114
      6. Cyclodextrins, Cryptates, and Crown Ethers / 114
   I. Suggestions for Further Reading / 115
   J. Study Questions / 116
6. Polymers

A. Overview / 118
B. Synthesis of Polymers / 119
   1. General Principles / 119
   2. Addition Polymerization / 119
   3. Condensation Polymerization / 130
   4. Ring-Opening Polymerization / 132
   5. Electrochemical Polymerization / 133
   6. Secondary Reactions / 133
C. Structure–Property Relationships and Polymer Design / 135
   1. Influence of Molecular Architecture / 135
   2. Molecular Weights and Distributions / 137
   3. Chain Flexibility / 138
   4. Influence of Different Skeletal Elements and Backbone Bonding / 139
   5. Specific Influence of Different Side Groups / 139
   6. Effects of Crosslinking / 140
D. Polymers in the Solid State / 140
   1. Chain Entanglement / 140
   2. Crystallinity / 141
   3. Liquid Crystallinity / 141
E. Fabrication of Polymers / 143
   1. Solution Casting of Films / 143
   2. Melt-Fabrication of Films / 144
   3. Fabrication of Fibers / 144
   4. Injection Molding / 144
   5. Thermoforming / 145
   6. Blow Molding / 145
   7. Sintering / 145
   8. Polymerization Combined with Fabrication / 145
F. Example Polymeric Materials / 146
   1. Polymers Produced by Addition Reactions / 146
   2. Polyurethanes / 147
   3. Polymers Produced by Condensation Reactions / 148
   4. Polymers Produced by Ring-Opening Polymerizations / 150
G. Future Challenges in Polymeric Materials Science / 154
H. Suggestions for Further Reading / 154
I. Study Questions / 155

7. Glasses and Ceramics

A. Overview / 157
B. Oxide Ceramics and Glasses Obtained or Produced Directly from Mineralogical Materials / 159
   1. General Observations / 159
2. Silica, Silicates, and Aluminosilicates—General Characteristics / 160
3. Aluminosilicate Clays and Related Minerals—Properties and Structure / 164
4. Chrysotile and Other Forms of Asbestos / 169
5. Glasses / 170

C. Oxide Ceramics from Small-Molecule Inorganic and Organometallic Precursors / 173
1. Optical Waveguides (Optical Fibers) / 174
2. The Sol–Gel Process for Low-Temperature Ceramic Formation / 174
3. Zeolites / 178
4. Calcium Hydroxyapatite / 179

D. Nonoxide Ceramics / 180
1. General Aspects / 180
2. Carbon Fiber / 181
3. Silicon Carbide / 185
4. Silicon Nitride / 186
5. Boron Nitride and Other Boron-Containing Ceramics / 188
6. Aluminum Nitride / 189
7. Other Ceramics Formed by the Preceramic Polymer Process / 190

E. Fabrication of Ceramics and Glasses / 190
1. General Comments / 190
2. Sculpting / 191
3. Melting, Extrusion, and Molding / 191
4. Powder Sintering / 191
5. Sol–Gel Fabrication / 192

F. Future Challenges in Ceramics and Glass Science / 192
G. Suggestions for Further Reading / 193
H. Study Questions / 194

8. Metals

A. Important Aspects of Metal Science and Technology / 195
1. Background / 195
2. Advantages and Disadvantages of Metals as Materials / 196
3. Scope of This Chapter / 196

B. Isolation of Specific Metals from Their Ores / 197
1. Iron and Steel / 197
2. Nickel / 199
3. Chromium / 200
4. Aluminum / 200
5. Magnesium / 201
CONTENTS

6. Titanium / 201
7. Tin / 201
8. Copper / 202
9. Silver / 202
10. Gold / 203

C. Corrosion / 203

D. Solid-State Structure of Metals and Alloys / 205
   1. Packing of Spheres / 206
   2. Alloys / 207

E. Electrical Conductivity / 208

F. The Color of Metals / 211

G. Thermal Conductivity of Metals / 212

H. Magnetic Properties of Metals / 213

I. Mechanical Properties of Metals / 214

J. Fabrication of Metals / 214

K. Future Challenges in Metallic Materials / 215

L. Suggestion for Further Reading / 215

M. Study Questions / 215

9. Alloys, Composites, and Defects / 217

A. Overview / 217
   1. Important Mechanical Properties / 217
   2. Homogeneous versus Heterogeneous Solids / 218
   3. Different Types of Composite Materials / 219
   4. Defects in Solids / 219

B. Pure Materials and Homogeneous Solid Solutions / 221
   1. Slip Planes, Dislocations, and Grain Boundaries in Metals / 221
   2. Homogeneous Metallic Alloys / 224
   3. Polymer Alloys—Blends / 224
   4. Interpenetrating Polymer Networks / 225
   5. Ceramic–Polymer “Alloys” (Ceramers) / 226

C. Heterophase Materials / 227
   1. General Observations / 227
   2. Reasons for Phase Segregation / 228
   3. Phase-Separated Metals / 229
   4. Heterophase Mineralogical Materials / 229
   5. Microcrystalline Polymers / 229
   6. Heterogeneous Ceramic–Polymer Composites / 230
   7. Phase-Separated Polymer–Polymer Composites / 230
   8. Phase-Separated Block Copolymers / 231
   9. Laminates / 233
   10. Filled Thermoplastics and Thermosetting Materials / 234
D. Suggestion for Further Reading / 234
E. Study Questions / 234

PART III MATERIALS IN ADVANCED TECHNOLOGY 237

10. Semiconductors and Related Materials 239

A. Importance of Semiconductors / 239
B. Semiconductor Theory / 240
C. Preparation of Semiconductor-Grade Silicon and Compound Semiconductors / 242
   1. Semiconductor-Grade Silicon / 242
   2. Amorphous Semiconductor Silicon / 243
   3. Preparation of Compound Semiconductors / 244
D. Organic Polymer Semiconductors / 244
   1. Background—Polyacetylene / 244
   2. Poly(phenylene vinylene) / 246
   3. Poly(p-phenylene) / 247
   4. Polypyrrole and Polythiophene / 247
   5. Polyaniline / 247
E. Photolithography and Microlithography / 248
   1. Principles of Semiconductor Fabrication / 248
   2. Overview of the Semiconductor Manufacturing Process / 250
   3. Equipment / 253
F. Photoresists / 255
   1. General Features of Resists / 255
   2. Novolac Positive Tone Resists / 255
   3. Chemical Amplification / 256
   4. Poly(4-hydroxystyrene) Resists / 257
   5. Multilayer Lithography / 257
   6. All-Dry Resists / 258
G. Electron Beam Lithography / 258
H. X-Ray Lithography / 258
I. Circuit Wiring / 258
J. Semiconductor Devices / 259
   1. Devices Based on Presence of a Single Semiconductor / 259
   2. The Transistor and the Metal Oxide Integrated Circuit / 260
   3. Phenomena Based on a p–n Junction / 261
K. Unsolved Problems in Semiconductor Materials Science / 267
L. Suggestions for Further Reading / 267
M. Study Questions / 268
11. Superconductors 269
   A. Overview / 269
   B. Nomenclature / 271
   C. Synthesis of High-Temperature Superconductors / 272
   D. Solid-State Structure / 274
   E. Theories of Superconduction / 277
   F. Other Superconducting Systems / 278
   G. Current and Proposed Uses for Superconductors / 279
   H. Challenges for the Future / 280
   I. Suggestions for Further Reading / 280
   J. Study Questions / 280

   A. General Observations / 282
   B. Fuel Cell Materials / 284
      1. Background / 284
      2. General Principles / 284
      3. Polymer Electrolyte Membrane (PEM) Fuel Cells / 285
      4. Phosphoric Acid Fuel Cells / 290
      5. Alkaline Fuel Cells / 291
      6. Molten Carbonate Fuel Cells / 292
      7. Solid Oxide Fuel Cells / 293
   C. Battery Electrolyte Materials / 295
      1. Background / 295
      2. Lithium Ion (“Rocking Chair”) Batteries / 295
      3. Principles behind Lithium Ion Transport Membranes / 296
      4. Metallic Lithium/Solid Polymer or Gel Electrolyte Batteries / 298
      5. Example Polymers for Lithium Battery Applications / 299
      6. Lithium–Seawater Batteries / 300
   D. Capacitors and Supercapacitors / 301
   E. Challenges for the Future / 303
      1. Challenges for Materials in Fuel Cells / 303
      2. Challenges in Battery Science and Technology / 304
      3. Challenges for Capacitors and Supercapacitors / 304
   F. Suggestions for Further Reading / 305
   G. Study Questions / 306

13. Membranes 307
   A. Background / 307
   B. Porous Membranes / 308
      1. Mechanism of Operation / 308
3. Photochromic Materials / 341
4. Nonlinear Optical Materials / 343
5. Electrochromic Devices / 350
6. Thermochromism / 351
7. Light-Emitting Materials / 352

D. Challenges for the Future / 352
E. Final Comments / 352
F. Suggestions for Further Reading / 353
G. Study Questions / 353

15. Surface Science of Materials

A. Perspective / 355
B. Summary of Characterization Methods / 356
C. Surfaces of Metals / 356
   1. Important Aspects / 356
   2. Etching of Metal Surfaces / 357
   3. Heterogeneous Catalysis by Metals / 357
   4. Metal Surfaces and Vapor Deposition, Sputtering, or Solution Reactions / 357
D. Ceramic Surfaces / 358
   1. Oxide Ceramic Surfaces / 358
   2. Chemical Modification of Glass Surfaces / 359
   3. Nonoxide Ceramic Fiber Surfaces / 359
   4. Ceramic Decomposition by Pollutants / 359
E. Polymer Surfaces / 360
   1. General Aspects of Polymer Surfaces / 360
   2. Unusual Characteristics of Polymer Surfaces / 360
   3. Chemical Modification of Polymer Surfaces / 360
   4. Polymer Surfaces in Offset Lithography Printing / 361
   5. Plasma Modification of Polymer Surfaces / 362
   6. Influence of Polymer Fabrication Method / 362
   7. Micro- and Nanofiber Surfaces / 363
   8. Role of Block Copolymers at Surfaces / 364
F. Surfaces of Semiconductors / 364
   1. Oxidation of Semiconductor Silicon / 364
   2. High-Surface-Area Semiconductors / 364
G. Assembly of Molecules on Surfaces / 366
   1. Langmuir–Blodgett Techniques / 366
   2. Self-Assembly on Gold Surfaces / 366
   3. Layer-by-Layer Assembly / 368
   4. Surface Patterning by AFM / 368
H. Adhesion and Surface Chemistry / 368
   1. General Characteristics of Adhesion / 368
   2. Chemical Bonding as a Source of Adhesion / 368
   3. Physical Bonding of Surfaces / 369
I. Relationship to Other Materials Topics / 369
   1. Soft Contact Printing / 369
   2. Biomedical Materials Surfaces / 370
J. Suggestions for Further Reading / 371
K. Study Questions / 372

16. Biomedical Materials
   A. Special Requirements for Biomedical Materials / 373
   B. Traditional Biomedical Materials / 375
      1. Metals / 375
      2. Ceramics / 376
      3. Polymers / 376
   C. Materials for Specific Medical Applications / 382
      1. Cardiovascular Materials / 382
      2. Surgical Sutures, Clips, and Staples / 386
      3. Orthopedic Materials / 386
      4. Optical Materials in Medicine / 387
      5. Controlled Drug and Vaccine Delivery / 387
      6. Tissue Engineering / 391
   D. Fabrication and Testing of Biomedical Materials / 393
      1. Fabrication / 393
      2. Testing of Biomedical Materials / 393
   E. Unsolved Problems in Biomedical Materials Science / 394
   F. Suggestions for Further Reading / 395
   G. Study Questions / 396

17. Materials in Nanoscience and Nanotechnology
   A. Background and Motivation / 398
   B. Synthesis and Fabrication of Nanostructures / 400
      1. “Top–Down” Nanostructure Preparations / 400
      2. “Bottom–Up” Synthesis Methods / 401
   C. Examples of Nanostructures / 402
      1. Nanofibers / 402
      2. Nanowires / 403
      3. Nanoscale Particles / 404
      4. Nanochannels and Nanotubes / 406
      5. Nanoscale Features in Electronics and Photonics / 409
      6. Nanomachines / 409
   D. Major Challenges in Nanoscience and Technology / 410
   E. Suggestions for Further Reading / 410
   F. Study Questions / 411

GLOSSARY 413
INDEX 419