Contents

Preface \( xi \)

Part I  Electrical Conductive Materials: General Aspects  1

1.1  The Compromise Between Conductivity and Transparency  3
  Alicia de Andrés, Félix Jiménez-Villacorta, and Carlos Prieto
  1.1.1  Introduction  3
  1.1.2  Relevant Parameters for Transparent Electrodes  5
  1.1.2.1  Transmittance  5
  1.1.2.2  Transmittance and Absorption Coefficient: Experimental Aspects  6
  1.1.2.3  Electronic Transport Parameters  7
  1.1.2.4  Figure of Merit  9
  1.1.3  Spectroscopies  11
  1.1.3.1  Raman and Infrared Spectroscopies  11
  1.1.3.2  X-ray Absorption Spectroscopies  13
  1.1.3.3  UPS and XPS  15
  1.1.4  Transparent Conducting Materials  17
  1.1.4.1  Oxide Electrodes: Amorphous Films  17
  1.1.4.2  Metallic Nanowires and Grids  18
  1.1.4.3  Graphene and Graphene Oxide  19
  1.1.4.4  Graphene Doping with Atoms and Nanoparticles  21
  1.1.5  Conclusions and Forecast  24
  References  25

Part II  Inorganic Conductive Materials  31

2.1  Metallic Oxides (ITO, ZnO, SnO\(_2\), TiO\(_2\))  33
  Klaus Ellmer, Rainald Mientus, and Stefan Seeger
  2.1.1  Introduction  33
  2.1.2  Basic Bulk Properties  35
  2.1.2.1  ITO  38
  2.1.2.1.1  Crystallographic Structure  38
2.1.2.1.2 Electrical Properties 39
2.1.2.1.3 Optical Properties 40
2.1.2.2 ZnO 42
2.1.2.2.1 Crystallographic Structure 43
2.1.2.2.2 Electrical Properties 44
2.1.2.2.3 Optical Properties 46
2.1.2.3 SnO₂ 47
2.1.2.3.1 Crystallographic Structure 48
2.1.2.3.2 Electrical Properties 48
2.1.2.3.3 Optical Properties 48
2.1.2.4 TiO₂ 50
2.1.2.4.1 Crystallographic Structure 50
2.1.2.4.2 Electrical Properties 53
2.1.2.4.3 Optical Properties 55
2.1.3 Thin Film Properties 57
2.1.3.1 ITO 57
2.1.3.2 ZnO 59
2.1.3.3 SnO₂ 60
2.1.3.4 TiO₂ 63
2.1.4 Conclusions 67
References 68

2.2 Chemical Bath Deposition 81
Peter Fuchs, Yaroslav E. Romanyuk, and Ayodhya N. Tiwari
2.2.1 Introduction 81
2.2.2 Principles of Chemical Bath Deposition 81
2.2.3 Material Examples 82
2.2.3.1 ZnO 82
2.2.3.2 SnO₂ 90
2.2.3.3 In₂O₃ 92
2.2.3.4 CdO 93
2.2.4 Low-temperature Post-deposition Treatment 93
2.2.5 Implementation of CBD TCOs in Devices 94
2.2.6 Conclusions and Outlook 96
References 97

2.3 Metal Nanowires 105
Chao Chen and Changhui Ye
2.3.1 Synthesis of Metal Nanowires 108
2.3.2 Fabrication of Transparent Conductive Films on the Basis of Metal Nanowires 110
2.3.3 Patterning Metal Nanowire Transparent Conductive Films 112
2.3.4 Performance of Metal Nanowire Transparent Conductive Films 114
2.3.4.1 Transparency and Conductivity 115
2.3.4.2 Haze Factor 117
2.3.4.3 Color 119
2.3.4.4 Uniformity 120
Part III Organic Conductive Materials 133

3.1 Carbon Nanotubes 135
Félix Salazar-Bloise
3.1.1 Introduction 135
3.1.2 Some Simple Carbon Structures 136
3.1.3 Graphene in the Context of Nanotubes 137
3.1.4 Fundamentals of Nanotubes 142
3.1.4.1 Structure of Carbon Nanotubes 142
3.1.4.2 Electronic Properties of Carbon Nanotubes 146
3.1.5 Mechanical Properties 151
3.1.6 Thermal Properties 152
3.1.7 Some Techniques for Producing Nanotubes 155
3.1.7.1 Arc-discharge Method 155
3.1.7.2 Laser Ablation 156
3.1.7.3 Chemical Vapor Deposition (CVD) 156
References 156

3.2 Graphene 165
Judy Z. Wu
3.2.1 Introduction 165
3.2.2 Physical Properties of Intrinsic Graphene Transparent Conductors (GTCs) 167
3.2.3 Synthesis and Characterization of Graphene Transparent Conductors 169
3.2.3.1 Synthesis of Graphene 169
3.2.3.1.1 Solution Synthesis of Graphene 169
3.2.3.1.2 Chemical Vapor Deposition of Graphene on Metal Foils 170
3.2.3.1.3 Direct Growth of Graphene on Dielectric Substrates 171
3.2.3.2 Characterization of GTC Properties 174
3.2.3.3 GTC Interface with Other Materials in Heterostructures 175
3.2.3.3.1 Engineering Work Function of Graphene 175
3.2.3.3.2 Efficient Charge Transfer Across van der Waals Heterojunction Interface 176
3.2.4 Applications of Graphene Transparent Conductors 178
3.2.4.1 Photodetectors 178
3.2.4.2 Photovoltaics 180
3.2.4.2.1 Dye Sensitizer Solar Cells on GTC 180
3.2.4.2.2 Organic Solar Cells on GTC 181
3.2.4.2.3 Inorganic PV on GTC 182
3.2.4.3 Other Applications 182
3.2.5 Conclusion and Future Remarks 183
Acknowledgments 183
References 183

3.3 Transparent Conductive Polymers 193
Jose Abad and Javier Padilla

3.3.1 Introduction 193
3.3.1.1 About the Figure of Merit (FoM) 194
3.3.2 Polyaniline (PANI) and Polypyrrole (PPy) 195
3.3.2.1 Polyaniline (PANI) 196
3.3.2.2 Polypyrrole (PPy) 198
3.3.2.3 Other Polymers 198
3.3.3 Poly(3,4-dioxythiophene)–PEDOT 200
3.3.3.1 Oxidative Polymerization 200
3.3.3.2 In Situ Polymerization 200
3.3.3.3 Vapor-phase Polymerization (VPP) 201
3.3.3.4 Oxidative Chemical Vapor Deposition (o-CVD) 201
3.3.3.5 Electrochemical Polymerization 201
3.3.4 PEDOT:PSS 202
3.3.4.1 Solvents and Additives 203
3.3.4.2 Acids 204
3.3.4.3 Salts, Ionic Liquids, and Zwitterions 204
3.3.4.4 Other Approaches 207
3.3.4.5 PSS Substitution 207
3.3.5 Polymer–Metal Composites 208
3.3.5.1 Ag Grid/PEDOT:PSS 208
3.3.5.2 AgNW/PEDOT:PSS 210
3.3.5.3 Other Film Composites 212
3.3.6 Carbon-based Composites 212
3.3.6.1 Carbon Nanotubes (CNTs) 213
3.3.6.2 Graphene Oxide (GO) and Graphene (G) 215
3.3.7 Applications 216
3.3.8 Summary and Perspectives 217
References 219

Part IV Characterization of Transparent Conductive Films 245

4.1 Characterizations of Electrical Properties by the van der Pauw Method 247
Yuichi Sato and Toru Matsumura

4.1.1 Introduction 247
4.1.2 Measurements of Electrical Properties by the van der Pauw Method 248
4.1.3 Effects of Positions, Sizes, and Shapes of the Electrical Contacts Mounted on Various Shapes of Measuring Samples on the van der Pauw Measurement Values 249
4.1.3.1 Effect of Positions and Sizes of the Electrical Contacts Mounted on a Circular Shape Measuring Sample 249
4.1.3.2 Effects of Conditions of the Electrical Contacts in Square-shaped Measuring Samples 250
4.1.4 Effect of Inhomogeneity Existing in Measuring Samples on the van der Pauw Measurement Values 252
4.1.4.1 Estimations of Errors in the van der Pauw Measurement Values Concerning Inhomogeneous Materials 254
4.1.4.2 Incorrect Determinations of the Carrier Type in the van der Pauw Measurements of Inhomogeneous ZnO 259
4.1.5 Conclusions 260
References 261

Part V Applications 263

5.1 Electrochromic Oxide-based Materials and Devices for Glazing in Energy-efficient Buildings 265
Claes G. Granqvist
5.1.1 Introduction 265
5.1.2 Characterization of Optical Properties 267
5.1.3 Functional Principles and Materials 268
5.1.4 The Role of Nanostructure 270
5.1.5 Optical Properties 272
5.1.6 Case Study: Flexible Electrochromic Foil 275
5.1.7 Recent Development: Durability Assessment and Rejuvenation of Electrochromic Thin Films 282
5.1.8 Some Conclusions and Perspectives 285
References 286

5.2 Transparent Electrodes for Organic Light-emitting Diodes 301
Shigeki Naka
5.2.1 Introduction 301
5.2.2 Transparent Electrodes for Anode 303
5.2.3 Conducting Polymers 304
5.2.4 Dielectric/Metal/Dielectric Electrodes 304
5.2.5 Buffer Layer for Anode 308
5.2.6 Transparent Electrodes for Cathode 309
5.2.7 Buffer Layer for Cathode 310
5.2.8 Carrier Injection at Organic/Electrode Interface 311
5.2.9 Issue of Transparent Electrode for OLEDs 312
5.2.10 Conclusions 314
References 314
5.3 Dye-sensitized Devices: Photovoltaic and Photoelectrolytic Applications
José A. Solera-Rojas, Marisol Ledezma-Gairaud, and Leslie W. Pineda

5.3.1 Introduction

5.3.2 Properties of Titanium Dioxide
5.3.2.1 Structural Properties
5.3.2.2 Electronic Considerations
5.3.2.3 Optical Features
5.3.3 Surface Modification of TiO₂
5.3.3.1 Chemical Modifications
5.3.3.1.1 Doping
5.3.3.1.2 Chemical Modification at the TiO₂ Surface
5.3.3.1.3 Organometallic Dyes for Sensitization
5.3.4 Bridge-like Molecules to Immobilize Sensitizer Molecules in Nanoparticulate TiO₂
5.3.5 Applications for the Development of Photoelectrochemical Cells in Water Oxidation Reaction
5.3.6 Concluding Remarks
Acknowledgments
References

5.4 Smart Windows Based on Liquid Crystal Dispersions
Erick Castellón and David Levy

5.4.1 Introduction
5.4.2 Liquid Crystals
5.4.3 Liquid Crystal Dispersion Materials as Smart-window Devices
5.4.4 Parameters of Electrooptical Performance in LC-dispersion-based Smart Windows
5.4.5 Polymer-dispersed Liquid Crystals
5.4.5.1 Colloidal Method
5.4.5.2 Solvent-induced Phase Separation
5.4.5.3 Temperature-induced Phase Separation
5.4.5.4 Polymerization-induced Phase Separation
5.4.6 Polymer-stabilized Liquid Crystals
5.4.7 Gel-glass-dispersed Liquid Crystals
5.4.7.1 Sol–Gel Chemistry
5.4.7.2 Liquid Crystal Dispersions in Sol–Gel Materials
5.4.8 Other Liquid Crystal-dispersion Devices
5.4.9 Conclusion
References

Concluding Remarks
Castellón Erick and David Levy

Index