

Contents

Preface *XI*

1	Fundamentals of Porous Silicon Preparation	1
1.1	Introduction	1
1.2	Chemical Reactions Governing the Dissolution of Silicon	2
1.2.1	Silicon Oxides and Their Dissolution in HF	3
1.2.2	Silicon Oxides and Their Dissolution in Basic Media	3
1.2.3	Silicon Hydrides	4
1.3	Experimental Set-up and Terminology for Electrochemical Etching of Porous Silicon	5
1.3.1	Two-Electrode Cell	6
1.3.2	Three-Electrode Cell	6
1.4	Electrochemical Reactions in the Silicon System	7
1.4.1	Four-Electron Electrochemical Oxidation of Silicon	8
1.4.2	Two-Electron Electrochemical Oxidation of Silicon	9
1.4.3	Electropolishing	10
1.5	Density, Porosity, and Pore Size Definitions	11
1.6	Mechanisms of Electrochemical Dissolution and Pore Formation	13
1.6.1	Chemical Factors Controlling the Electrochemical Etch	16
1.6.2	Crystal Face Selectivity	18
1.6.3	Physical Factors Controlling the Electrochemical Etch	18
1.7	Resume of the Properties of Crystalline Silicon	19
1.7.1	Orientation	19
1.7.2	Band Structure	20
1.7.3	Electrons and Holes	21
1.7.4	Photoexcitation of Semiconductors	22
1.7.5	Dopants	23
1.7.6	Conductivity	24
1.7.7	Evolution of Energy Bands upon Immersion in an Electrolyte	24
1.7.8	Charge Transport at p-Type Si Liquid Junctions	26

1.7.9	Idealized Current–Voltage Curve at p-Type Liquid Junctions	26
1.7.10	Energetics at n-Type Si Liquid Junctions	28
1.7.11	Idealized Current–Voltage Curve at n-type Liquid Junctions	28
1.8	Choosing, Characterizing, and Preparing a Silicon Wafer	28
1.8.1	Measurement of Wafer Resistivity	29
1.8.2	Cleaving a Silicon Wafer	34
1.8.3	Determination of Carrier Type by the Hot-Probe Method	36
1.8.4	Ohmic Contacts	36
1.8.4.1	Making an Ohmic Contact by Metal Evaporation	39
1.8.4.2	Making an Ohmic Contact by Mechanical Abrasion	40
	References	40

2 Preparation of Micro-, Meso-, and Macro-Porous Silicon Layers 43

2.1	Etch Cell: Materials and Construction	43
2.2	Power Supply	44
2.3	Other Supplies	48
2.4	Safety Precautions and Handling of Waste	48
2.5	Preparing HF Electrolyte Solutions	50
2.6	Cleaning Wafers Prior to Etching	51
2.6.1	No Precleaning	51
2.6.2	Ultrasonic Cleaning	51
2.6.3	RCA Cleaning	52
2.6.4	Removal of a Sacrificial Porous Layer with Strong Base	52
2.7	Preparation of Microporous Silicon from a p-Type Wafer	53
2.8	Preparation of Mesoporous Silicon from a p ⁺⁺ -Type Wafer	57
2.9	Preparation of Macroporous, Luminescent Porous Silicon from an n-Type Wafer (Frontside Illumination)	59
2.9.1	Power Supply Limitations	63
2.10	Preparation of Macroporous, Luminescent Porous Silicon from an n-Type Wafer (Back Side Illumination)	64
2.11	Preparation of Porous Silicon by Stain Etching	68
2.12	Preparation of Silicon Nanowire Arrays by Metal-Assisted Etching	73
	References	75

3 Preparation of Spatially Modulated Porous Silicon Layers 77

3.1	Time-Programmable Current Source	78
3.1.1	Time Resolution Issues	79
3.1.2	Etching with an Analog Source	80
3.1.3	Etching with a Digital Source	82
3.2	Pore Modulation in the z-Direction: Double Layer	83
3.3	Pore Modulation in the z-Direction: Rugate Filter	83
3.3.1	Tunability of the Rugate Spectral Peak Wavelength	88
3.3.2	Width of the Spectral Band	92

- 3.4 More Complicated Photonic Devices: Bragg Stacks, Microcavities, and Multi-Line Spectral Filters 94
 - 3.4.1 Bragg Reflector 96
 - 3.4.2 Multiple Spectral Peaks-“Spectral Barcodes” 100
- 3.5 Lateral Pore Gradients (in the x - y Plane) 104
- 3.6 Patterning in the x - y Plane Using Physical or Virtual Masks 108
 - 3.6.1 Physical Masking Using Photoresists 109
 - 3.6.2 Virtual Masking Using Photoelectrochemistry 112
- 3.7 Other Patterning Methods 114
- References 114

- 4 Freestanding Porous Silicon Films and Particles 119**
 - 4.1 Freestanding Films of Porous Silicon-“Lift-offs” 120
 - 4.2 Micron-scale Particles of Porous Silicon by Ultrasonication of Lift-off Films 120
 - 4.3 Core-Shell (Si/SiO₂) Nanoparticles of Luminescent Porous Silicon by Ultrasonication 126
 - References 130

- 5 Characterization of Porous Silicon 133**
 - 5.1 Gravimetric Determination of Porosity and Thickness 134
 - 5.1.1 Errors and Limitations of the Gravimetric Method 137
 - 5.2 Electron Microscopy and Scanned Probe Imaging Methods 138
 - 5.2.1 Cross-Sectional Imaging 138
 - 5.2.2 Plan-View (Top-Down) Imaging 139
 - 5.3 Optical Reflectance Measurements 139
 - 5.3.1 Instrumentation to Collect Reflectance Data 139
 - 5.3.1.1 Reflectance Optics 140
 - 5.3.1.2 Wavelength Calibration 142
 - 5.3.2 Principles of Fabry-Pérot Interference 143
 - 5.3.3 Analyzing Fabry-Pérot Interference Spectra by Fourier Transform: the RIFTS Method 150
 - 5.3.3.1 Preparation of Spectrum for Fast Fourier Transform 151
 - 5.3.3.2 Interpretation of the Fast Fourier Transform 153
 - 5.3.4 Thickness and Porosity by the Spectroscopic Liquid Infiltration Method (SLIM) 154
 - 5.3.4.1 Bruggeman Effective Medium Approximation 155
 - 5.3.4.2 Determination of Thickness and Porosity by SLIM 156
 - 5.3.4.3 Determination of Index of Refraction of the Porous Skeleton 156
 - 5.3.4.4 Effect of Skeleton Index on Porosity Determined by SLIM 158
 - 5.3.5 Comparison of Gravimetric Measurement with SLIM for Porosity and Thickness Determination 159
 - 5.3.6 Analysis of Double-Layer Structures Using RIFTS 162

- 5.4 Porosity, Pore size, and Pore Size Distribution by Nitrogen Adsorption Analysis (BET, BJH, and BdB Methods) 167
- 5.5 Measurement of Steady-State Photoluminescence Spectra 170
 - 5.5.1 Origin of Photoluminescence from Porous Silicon 170
 - 5.5.1.1 Tunability of the Photoluminescence Spectrum 171
 - 5.5.1.2 Mechanisms of Photoluminescence 171
 - 5.5.2 Instrumentation to Acquire Steady-State Photoluminescence Spectra 173
- 5.6 Time-Resolved Photoluminescence Spectra 173
 - 5.6.1 Long, Nonexponential Excited State Lifetimes 173
 - 5.6.2 Influence of Surface Traps 175
- 5.7 Infrared Spectroscopy of Porous Silicon 176
 - 5.7.1 Characteristic Group Frequencies for Porous Silicon 176
 - 5.7.2 Measurement of FTIR Spectra of Porous Silicon 178
 - 5.7.2.1 Transmission Mode Measurement Using the Standard Etch Cell 179
- References 181

- 6 Chemistry of Porous Silicon 189**
 - 6.1 Oxide-Forming Reactions of Porous Silicon 190
 - 6.1.1 Temperature Dependence of Oxidation Using Gas-Phase Oxidants 190
 - 6.1.2 Thermal (Air) Oxidation 191
 - 6.1.3 Ozone Oxidation 192
 - 6.1.4 High-Pressure Water Vapor Annealing 193
 - 6.1.5 Oxidation in Aqueous Solutions 193
 - 6.1.5.1 Aqueous Oxidation Induced by Cationic Surfactants 194
 - 6.1.6 Electrochemical Oxidation in Aqueous Mineral Acids 194
 - 6.1.7 Oxidation by Organic Species: Ketones, Aldehydes, Quinones, and Dimethylsulfoxide 195
 - 6.1.8 Effect of Chemical Oxidation on Pore Morphology 196
 - 6.2 Biological Implications of the Aqueous Chemistry of Porous Silicon 198
 - 6.3 Formation of Silicon–Carbon Bonds 200
 - 6.3.1 Thermal Hydrosilylation to Produce Si–C Bonds 200
 - 6.3.2 Working with Air- and Water-Sensitive Compounds—Schlenk Line Manipulations 201
 - 6.3.3 Classification of Surface Chemistry by Contact Angle 203
 - 6.3.4 Microwave-Assisted Hydrosilylation to Produce Si–C Bonds 204
 - 6.3.5 Chemical or Electrochemical Grafting to Produce Si–C Bonds 206
 - 6.4 Thermal Carbonization Reactions 208
 - 6.4.1 Thermal Degradation of Acetylene to form “Hydrocarbonized” Porous Silicon 208

6.4.2	Thermal Degradation of Polymers to Form “Carbonized” Porous Silicon	209
6.5	Conjugation of Biomolecules to Modified Porous Silicon	211
6.5.1	Carbodiimide Coupling Reagents	211
6.5.2	Attachment of PEG to Improve Biocompatibility	212
6.5.3	Biomodification of “Hydrocarbonized” Porous Silicon	213
6.5.4	Silanol-Based Coupling to Oxidized Porous Silicon Surfaces	215
6.6	Chemical Modification in Tandem with Etching	217
6.7	Metallization Reactions of Porous Silicon	218
	References	219

Appendix A1. Etch Cell Engineering Diagrams and Schematics

Standard or Small Etch Cell-Complete	229
Standard Etch Cell Top Piece	230
Small Etch Cell Top Piece	231
Etch Cell Base (for Either Standard or Small Etch Cell)	232
Large Etch Cell-Complete	232
Large Etch Cell Top Piece	233
Large Etch Cell Base	233

Appendix A2. Safety Precautions When Working with Hydrofluoric Acid

Hydrofluoric Acid Hazards	235
First Aid Measures for HF Contact	236
Note to Physician	238
HF Antidote Gel	239
Further Reading	239

Appendix A3. Gas Dosing Cell Engineering Diagrams and Schematics

Gas Dosing Cell Top Piece	242
Gas Dosing Cell Middle Piece	243
Gas Dosing Cell Bottom Piece	244

Index	245
--------------	-----

