Contents

 $\begin{array}{ll} \textbf{List of Contributors} & XI \\ \textbf{Foreword} & XVII \\ \textbf{Introduction} & XIX \\ \end{array}$

Part I	Principles of Multiphoton Absorption	1
--------	--------------------------------------	---

1	Rapid Laser Optical Printing in 3D at a Nanoscale 3
	Albertas Žukauskas, Mangirdas Malinauskas, Gediminas Seniutinas, and
	Saulius Juodkazis
1.1	Introduction 3
1.2	3D (Nano)polymerization: Linear Properties 4
1.2.1	Photocure and Thermal Cure of Photoresists 5
1.2.2	Tight Light Focusing 6
1.2.3	Optical Properties at High Excitation: From Solid to Plasma 8
1.2.4	Heat Accumulation 10
1.3	3D (Nano)polymerization: Nonlinear Properties 13
1.3.1	Strongest Optical Nonlinearities 13
1.3.2	Avalanche Versus Multiphoton Excitation 15
1.4	Discussion 17
1.5	Conclusions and Outlook 18
	Acknowledgments 19
	References 19
2	Characterization of 2PA Chromophores 25
	Eric W. Van Stryland and David J. Hagan
2.1	Introduction 25
2.2	Description of Nonlinear Absorption and Refraction Processes 26
2.2.1	Two-Photon Absorption and Bound-Electronic Nonlinear
	Refraction 26
2.2.2	Excited-State Absorption and Refraction 28
2.3	Methods for Measurements of NLA and NLR 31
2.3.1	Direct Methods 31
2.3.1.1	Nonlinear Transmission 31

٧ı	Contents	
	2.3.1.2	Z-Scan 32
	2.3.1.3	Determining Nonlinear Response from Pulse-width Dependence of Z-Scans 39
	2.3.1.4	White-Light-Continuum Z-Scan (WLC Z-Scan) 41
	2.3.1.5	Other Variants of the Z-Scan Method 43
	2.3.2	Indirect Methods 45
	2.3.2.1	Excitation – Probe Methods 45
	2.3.2.2	White-Light-Continuum (WLC) Excite – Probe Spectroscopy 48
	2.3.2.3	Degenerate Four-Wave Mixing (DFWM) 51
	2.3.2.4	Two-Photon-Absorption-Induced Fluorescence Spectroscopy 53
	2.3.2.5	Fluorescence Anisotropy 55
	2.4	Examples of Use of Multiple Techniques 55
	2.4.1	Squaraine Dye 56
	2.4.2	Tetraone Dye 57
	2.5	Other Methods 59
	2.6	Conclusion 60
		Acknowledgments 60 References 60
		References 60
	3	Modeling of Polymerization Processes 65
		Alexander Pikulin and Nikita Bityurin
	3.1	Introduction 65
	3.2	Basic Laser Polymerization Chemistry and Kinetic Equations 66
	3.3	Phenomenological Polymerization Threshold and Spatial
		Resolution 69
	3.4	Effect of Fluctuations on the Minimum Feature Size 75
	3.5	Diffusion of Molecules 83
	3.5.1	Diffusion of the Growing Chains 84
	3.5.2	Diffusion of Inhibitor: Diffusion-Assisted Direct Laser Writing 86
	3.6	Conclusion 90
		Acknowledgements 91 References 91
		References 91
		Part II Equipment and Techniques 95
	4	Light Sources and Systems for Multiphoton Lithography 97
		Ulf Hinze and Boris Chichkov
	4.1	Laser Light Sources 97
	4.2	Ultrashort-Pulse Lasers 98
	4.3	Laboratory Systems and Processing Strategy 100
	4.4	Further Processing Considerations 105
		References 108
	5	STED-Inspired Approaches to Resolution Enhancement 111
		John T. Fourkas
	5.1	Introduction 111

<i>-</i> 2	Chimalatad Fasicai an Doubting Flagues William 112
5.2	Stimulated Emission Depletion Fluorescence Microscopy 113
5.3	Stimulated Emission Depletion in Multiphoton Lithography 117
5.4	Photoinhibition 122
5.5	Inhibition Based on Photoinduced Electron Transfer 123
5.6	Absorbance Modulation Lithography 126
5.7	Challenges for Two-Color, Two-Photon Lithography 127
5.8	Conclusions 128
	Acknowledgments 128
	References 128
	Part III Materials 133
6	Photoinitiators for Multiphoton Absorption Lithography 135
<i>(</i> 1	Mei-Ling Zheng and Xuan-Ming Duan
6.1	Introduction for Photoinitiators for Multiphoton Absorption
< 1.1	Lithography 135
6.1.1	Multiphoton Absorption Lithography 135
6.1.2	Photoinitiators for Multiphoton Absorption Lithography 135
6.1.2.1	History of the Design of Two-Photon Initiators 135
6.1.2.2	Property of Two-Photon Initiators 136
6.1.3	Characterization of Two-Photon Initiators 137
6.1.4	Molecular Design for Photoinitiators 140
6.2	Centrosymmetric Photoinitiators 141
6.3	Noncentrosymmetric Photoinitiators 153
6.4	Application of Photoinitiators in Multiphoton Absorption
	Lithography 156
6.5	Conclusion 162
	Acknowledgment 163
	References 163
7	Hybrid Materials for Multiphoton Polymerization 167
	Alexandros Selimis and Maria Farsari
7.1	Introduction 167
7.2	Sol–Gel Preparation 168
7.3	Silicate Hybrid Materials 169
7.4	Composite Hybrid Materials 171
7.5	Surface and Bulk Functionalization 173
7.6	Replication 175
7.7	Conclusions 176
	References 176
8	Photopolymers for Multiphoton Lithography in Biomaterials and
	Hydrogels 183
	Mark W. Tibbitt, Jared A. Shadish, and Cole A. DeForest
8.1	Introduction 183

VIII	Contents	
·	8.2	Multiphoton Lithography (MPL) for Photopolymerization 186
	8.3	MPL Equipment for Biomaterial Fabrication 188
	8.4	Chemistry for MPL Photopolymerizations 189
	8.4.1	Photopolymerization 189
	8.4.2	Photoinitiator Selection 191
	8.4.3	Photopolymer Chemistries 193
	8.4.3.1	Macromer Chemistries 193
	8.4.3.2	Photochemical Polymerization and Degradation 194
	8.5	Biomaterial Fabrication 202
	8.6	Biomaterial Modulation 203
	8.7	Biological Design Constraints 206
	8.8	Biologic Questions 208
	8.9	Outlook 209
		References 210
	9	Multiphoton Processing of Composite Materials and Functionalization
		of 3D Structures 221
		Casey M. Schwarz, Christopher N. Grabill, Jennefir L. Digaum,
		Henry E. Williams, and Stephen M. Kuebler
	9.1	Overview 221
	9.2	Polymer – Organic Composites 225
	9.2.1	Fluorescent-Dye-Doped Organic Microstructures 225
	9.2.2	Organic Composites for Lasing Microstructures 227
	9.2.3	Organic Composites for Electrically Conductive
		Microstructures 227
	9.2.4	Other Optically Active Microstructures 229
	9.3	Multiphoton Processing of Oxide-Based Materials 230
	9.3.1	Titanium Dioxide 231
	9.3.2	Zinc Oxide 231
	9.3.3	Zirconium Dioxide 232
	9.3.4	Iron Oxide 232
	9.3.5	Tin Dioxide 233
	9.3.6 9.3.7	Germanium Dioxide 234 Silicon Dioxide 234
	9.4 9.4.1	Multiphoton Processing of Metallic Composites and Materials 235 Thermal Evaporation 236
	9.4.2	Thermal Evaporation 236 e-Beam Evaporation 236
	9.4.3	Magnetron Sputtering 236
	9.4.4	Chemical Vapor Deposition 237
	9.4.5	Functionalization by Attachment of Nanoparticles 238
	9.4.6	Electroless Metallization from Solution 239
	9.4.7	Multiphoton Lithography of Nanoparticles Supported in a Polymer
		Matrix 242
	9.4.8	Direct Writing of Continuous-Metal Microstructures 244
	9.4.9	Metal Backfilling by Electroplating 245

9.5	Multiphoton Processing of Semiconductor Composites and
0.5.1	Materials 246
9.5.1	Structures Functionalized with Nanoparticles 246 Structures Functionalized using NP – Polymer Composites 246
9.5.2	Structures runctionalized doing 112 207,1112
9.5.3	Structures Functionalized by In Situ NP Formation 247
9.5.4	Structures Functionalized by NP Coating 248
9.5.5	Structures Functionalized by Silicon Inversion 250
9.5.6	Functional Structures Fabricated in Bulk Chalcogenide Glasses 252
9.5.7	Structures Fabricated in ChG Film 252
9.5.8	Structures Fabricated in ChG-NP Composites 254
9.6	Conclusion 254
	Acknowledgments 255
	References 255
	Part IV Applications 265
10	Fabrication of Waveguides and Other Optical Elements by
	Multiphoton Lithography 267
	Samuel Clark Ligon, Josef Kumpfmüller, Niklas Pucher, Jürgen Stampfl, and
	Robert Liska
10.1	Introduction 267
10.2	Acrylate Monomers for Multiphoton Lithography 268
10.3	Thiol – Ene Resins 277
10.4	Sol – Gel-Derived Resins 280
10.5	Cationic Polymerization and Stereolithography 284
10.6	Materials Based on Multiphoton Photochromism 287
10.7	Conclusions 292
	Acknowledgments 292
	References 292
11	Fabricating Nano and Microstructures Made by Narrow Bandgap
	Semiconductors and Metals using Multiphoton Lithography 297
	Min Gu, Zongsong Gan, and Yaoyu Cao
11.1	Introduction 297
11.2	Fabrication of 3D Structures Made by PbSe with Multiphoton
	Lithography 298
11.2.1	Challenges of Multiphoton Lithography with Top-Down Approach
	for Narrow Electronic Bandgap Semiconductors 298
11.2.2	Photoresin Development 299
11.2.3	Two-Photon Lithography of PbSe Structures 302
11.2.4	Confirmation of PbSe Formation 303
11.3	Fabrication of Silver Structures with Multiphoton Lithography 304
11.3.1	Principle of Resolution Improvement by Increasing Photosensitivity
	in Photoreduction 305
11.3.2	Photosensitivity Enhancement by Tuning Laser Wavelength 305

x	Contents	
	11.3.3	Dot Size Model Based on Photosensitivity 308
	11.3.4	Further Increase the Photosensitivity with an Electron Donor 310
	11.4	Conclusions 310
		Acknowledgments 312
		References 312
	12	Microfluidic Devices Produced by Two-Photon-Induced
		Polymerization 315
		Shoji Maruo
	12.1	Introduction 315
	12.2	Fabrication of Movable Micromachines 316
	12.3	Optically Driven Micromachines 320
	12.4	Microfluidic Devices Driven by a Scanning Laser Beam 325
	12.5	Microfluidic Devices Driven by a Focused Laser Beam 327
	12.6	Microfluidic Devices Driven by an Optical Vortex 330
	12.7	Future Prospects 331 References 332
		References 332
	13	Nanoreplication Printing and Nanosurface Processing 335
		Christopher N. LaFratta
	13.1	Introduction: Limitations of Multiphoton Lithography 335
	13.2	Micro-transfer Molding (μTM) 336
	13.3	μTM of Complex Geometries 338
	13.4	Nano-replication of Other Materials 339
	13.5	Nanosurface Metallization Processing 342
	13.6	Nanosurface Structuring via Ablation 344
	13.7	Conclusion and Future Directions 349
		References 351
		Part V Biological Applications 353
	14	Three-Dimensional Microstructures for Biological Applications 355
		Adriano J. G. Otuka, Vinicius Tribuzi, Daniel S. Correa, and
		Cleber R. Mendonça
	14.1	Introduction 355
	14.2	3D Structures for Cells Studies 357
	14.3	Biocompatible Materials 363
	14.4	Scaffolds for Bacterial Investigation 368
	14.5	Microstructures for Drug Delivery 371
	14.6	Final Remarks 374
		References 374

Index 377