

Edited by R. d'Agostino, P. Favia, Y. Kawai,  WILEY-VCH  
H. Ikegami, N. Sato, and F. Arefi-Khonsari

# Advanced Plasma Technology



## Contents

**Preface** *XV*

**List of Contributors** *XVII*

<b>1</b>	<b>Basic Approaches to Plasma Production and Control</b>	<b>1</b>
	<i>N. Sato</i>	
1.1	Plasma Production	2
1.1.1	Under Low Gas Pressure (<0.1 torr)	2
1.1.2	Under Medium Gas Pressure (0.1–10 torr)	4
1.1.3	Under High (Atmospheric) Gas Pressure (>10 torr)	6
1.2	Energy Control	7
1.2.1	Electron-Temperature Control	7
1.2.2	Ion-Energy Control	10
1.3	Dust Collection and Removal	11
	References	15
<b>2</b>	<b>Plasma Sources and Reactor Configurations</b>	<b>17</b>
	<i>P. Colpo, T. Meziani, and F. Rossi</i>	
2.1	Introduction	17
2.2	Characteristics of ICP	18
2.2.1	Principle	18
2.2.2	Transformer Model	19
2.2.3	Technological Aspects	20
2.2.3.1	Matching	20
2.2.3.2	Capacitive Coupling	22
2.2.3.3	Standing Wave Effects	22
2.3	Sources and Reactor Configuration	23
2.3.1	Substrate Shape	23
2.3.1.1	Flat Substrates	24
2.3.1.2	Complex Three-Dimensional Shapes	24
2.3.1.3	Large Area Treatment	26
2.4	Conclusions	31
	References	32

<b>3</b>	<b>Advanced Simulations for Industrial Plasma Applications</b>	<b>35</b>
	<i>S.J. Kim, F. Iza, N. Babaeva, S.H. Lee, H.J. Lee, and J.K. Lee</i>	
3.1	Introduction	35
3.2	PIC Simulations	37
3.2.1	Capacitively Coupled O <sub>2</sub> /Ar Plasmas	37
3.2.1.1	Gas Composition	38
3.2.1.2	Pressure Effect in Ar/O <sub>2</sub> Plasmas	41
3.2.2	Three-Dimensional (3D) Charge-up Simulation	42
3.2.2.1	Description of 3D Charge-up Simulations	42
3.2.2.2	Effects of Secondary Electron Emission	44
3.2.2.3	Negative Ion Extraction	45
3.3	Fluid Simulations	47
3.3.1	Capacitively Coupled Discharges	48
3.3.2	Large Area Plasma Source	49
3.4	Summary	51
	References	52
<b>4</b>	<b>Modeling and Diagnostics of He Discharges for Treatment of Polymers</b>	<b>55</b>
	<i>E. Amanatides and D. Mataras</i>	
4.1	Introduction	55
4.2	Experimental	56
4.3	Model Description	57
4.4	Results and Discussion	60
4.4.1	Electrical Properties	61
4.4.2	Gas-Phase Chemistry	66
4.4.3	Plasma–Surface Interactions	71
4.5	Conclusions	72
	References	73
<b>5</b>	<b>Three-Dimensional Modeling of Thermal Plasmas (RF and Transferred Arc) for the Design of Sources and Industrial Processes</b>	<b>75</b>
	<i>V. Colombo, E. Ghedini, A. Mentrelli, and T. Trombetti</i>	
5.1	Introduction	76
5.2	Inductively Coupled Plasma Torches	77
5.2.1	Modeling Approach	77
5.2.1.1	Modeling Assumptions	77
5.2.1.2	Governing Equations of the Continuum Phase	78
5.2.1.3	Governing Equations of the Discrete Phase	79
5.2.1.4	Computational Domain and Boundary Conditions	81
5.2.2	Selected Simulation Results	82
5.2.2.1	High-Definition Numerical Simulation of Industrial ICPTs	82

5.2.2.2	Numerical Simulation of the Trajectories and Thermal Histories of Powders Injected in Industrial ICPTs	84
5.3	DC Transferred Arc Plasma Torches	85
5.3.1	Modeling Approach	85
5.3.1.1	Modeling Assumptions	85
5.3.1.2	Governing Equations	86
5.3.1.3	Computational Domain and Boundary Conditions	87
5.3.2	Selected Simulation Results	89
5.3.2.1	Magnetically Deflected Transferred Arc	89
5.3.2.2	The Twin Torch	89
5.3.2.3	The Cutting Torch	94
	References	95
<b>6</b>	<b>Radiofrequency Plasma Sources for Semiconductor Processing</b>	<b>99</b>
	<i>F. F. Chen</i>	
6.1	Introduction	99
6.2	Capacitively Coupled Plasmas	99
6.2.1	Dual-Frequency CCPs	100
6.3	Inductively Coupled Plasmas	103
6.3.1	General Description	103
6.3.2	Anomalous Skin Depth	106
6.3.3	Magnetized ICPs	107
6.4	Helicon Wave Sources	109
6.4.1	General Description	109
6.4.2	Unusual Features	110
6.4.3	Extended Helicon Sources	114
	References	114
<b>7</b>	<b>Advanced Plasma Diagnostics for Thin-Film Deposition</b>	<b>117</b>
	<i>R. Engeln, M.C.M. van de Sanden, W.M.M. Kessels, M. Creatore, and D.C. Schram</i>	
7.1	Introduction	117
7.2	Diagnostics Available to the (Plasma) Physicist	118
7.3	Optical Diagnostics	118
7.3.1	Thomson–Rayleigh and Raman Scattering	118
7.3.2	Laser-Induced Fluorescence	121
7.3.3	Absorption Techniques	122
7.3.4	Surface Diagnostics	126
7.4	Applications	127
7.4.1	Thomson–Rayleigh Scattering and Raman Scattering	127
7.4.2	Laser-Induced Fluorescence	128
7.4.3	Absorption Spectroscopy	130
7.4.4	Surface Diagnostics	133
	References	134

- 8 Plasma Processing of Polymers by a Low-Frequency Discharge with Asymmetrical Configuration of Electrodes 137**  
*F. Arefi-Khonsari and M. Tatoulian*
- 8.1 Introduction 137
- 8.2 Plasma Treatment of Polymers 139
- 8.2.1 Surface Activation 139
- 8.2.2 Functionalization (Grafting) Reactions 139
- 8.2.3 Crosslinking Reactions 140
- 8.2.4 Surface Etching (Ablation) Reactions 142
- 8.2.4.1 Decarboxylation 142
- 8.2.4.2  $\beta$ -Scission 142
- 8.2.4.3 Plasma Cleaning/Etching Effect 142
- 8.3 Surface Treatment of Polymers in a Low-Frequency, Low-Pressure Reactor With Asymmetrical Configuration of Electrodes (ACE) 145
- 8.3.1 Surface Functionalization 147
- 8.3.2 Ablation Effect of an Ammonia Plasma During Grafting of Nitrogen Groups 148
- 8.3.3 Acid-Base Properties 151
- 8.3.3.1 Introduction 151
- 8.3.3.2 Contact Angle Titration Method 152
- 8.3.4 Aging of Plasma-Treated Surfaces 155
- 8.3.4.1 Aging of Ammonia Plasma-Treated PP 156
- 8.3.4.2 Stability of PP Treated in Plasmas of Mixtures of He + NH<sub>3</sub> for Improved Adhesion to Aluminum 157
- 8.4 Plasma Polymerization 158
- 8.4.1 Influence of the Chemical Composition of the Substrate on the Plasma Polymerization of a Mixture of CF<sub>4</sub> + H<sub>2</sub> 160
- 8.4.2 Plasma Polymerization of Acrylic Acid 165
- 8.5 Conclusions 169
- References 170
- 9 Fundamentals on Plasma Deposition of Fluorocarbon Films 175**  
*A. Milella, F. Palumbo, and R. d'Agostino*
- 9.1 Deposition of Fluorocarbon Films by Continuous Discharges 175
- 9.1.1 Active Species in Fluorocarbon Plasmas 176
- 9.1.2 Effect of Ion Bombardment 178
- 9.1.3 The Activated Growth Model 179
- 9.2 Afterglow Deposition of Fluorocarbon Films 181
- 9.3 Deposition of Fluorocarbon Films by Modulated Glow Discharges 183
- 9.4 Deposition of Nanostructured Thin Films from Tetrafluoroethylene Glow Discharges 185
- References 193

<b>10</b>	<b>Plasma CVD Processes for Thin Film Silicon Solar Cells</b>	<b>197</b>
	<i>A. Matsuda</i>	
10.1	Introduction	197
10.2	Dissociation Reaction Processes in $\text{SiH}_4$ and $\text{SiH}_4/\text{H}_2$ Plasmas	198
10.3	Film-Growth Processes on the Surface	199
10.3.1	Growth of a-Si:H	199
10.3.2	Growth of $\mu\text{c-Si:H}$	200
10.3.2.1	Nucleus Formation Process	201
10.3.2.2	Epitaxial-Like Crystal Growth	203
10.4	Defect Density Determination Process in a-Si:H and $\mu\text{c-Si:H}$	203
10.4.1	Growth of a-Si:H and $\mu\text{c-Si:H}$ with $\text{SiH}_3$ (H) Radicals	203
10.4.2	Contribution of Short-Lifetime Species	204
10.5	Solar Cell Applications	206
10.6	Recent Progress in Material Issues for Thin-Film Silicon Solar Cells	207
10.6.1	Control of Photoinduced Degradation in a-Si:H	207
10.6.2	High-Rate Growth of Device-Grade $\mu\text{c-Si:H}$	208
10.7	Summary	210
	References	210
<b>11</b>	<b>VHF Plasma Production for Solar Cells</b>	<b>211</b>
	<i>Y. Kawai, Y. Takeuchi, H. Mashima, Y. Yamauchi, and H. Takatsuka</i>	
11.1	Introduction	211
11.2	Characteristics of VHF $\text{H}_2$ Plasma	212
11.3	Characteristics of VHF $\text{SiH}_4$ Plasma	214
11.4	Characteristics of Large-Area VHF $\text{H}_2$ Plasma	219
11.5	Short-Gap VHF Discharge $\text{H}_2$ Plasma	222
	References	226
<b>12</b>	<b>Growth Control of Clusters in Reactive Plasmas and Application to High-Stability a-Si:H Film Deposition</b>	<b>227</b>
	<i>Y. Watanabe, M. Shiratani, and K. Koga</i>	
12.1	Introduction	227
12.2	Review of Cluster Growth Observation in $\text{SiH}_4$ HFCCP	228
12.2.1	Precursor for Cluster Growth Initiation	228
12.2.2	Cluster Nucleation Phase	230
12.2.3	Effects of Gas Flow on Cluster Growth	231
12.2.4	Effects of Gas Temperature Gradient on Cluster Growth	232
12.2.5	Effects of $\text{H}_2$ Dilution on Cluster Growth	233
12.2.6	Effects of Discharge Modulation on Cluster Growth	234
12.3	Cluster Growth Kinetics in $\text{SiH}_4$ HFCCP	235
12.4	Growth Control of Clusters	237
12.4.1	Control of Production Rate of Precursor Radicals	238
12.4.2	Control of Growth Reactions and Transport Loss of Clusters	238

- 12.5 Application of Cluster Growth Control to High-Stability a-Si:H Film Deposition 238
- 12.6 Conclusions 241  
References 241
- 13 Micro- and Nanostructuring in Plasma Processes for Biomaterials: Micro- and Nano-features as Powerful Tools to Address Selective Biological Responses 243**  
*E. Sardella, R. Gristina, R. d'Agostino, and P. Favia*
- 13.1 Introduction: Micro and Nano, a Good Point of View in Biomedicine 243
- 13.2 Micro- and Nanofeatures Modulate Biointeractions *In Vivo* and *In Vitro* 246
- 13.3 Micro- and Nano-fabrication Technologies 249
- 13.3.1 Photolithography: The Role of Photolithographic Masks 249
- 13.3.1.1 Role of Plasma Processes in Photolithography 253
- 13.3.1.2 Limits of Photolithography 255
- 13.3.2 Soft Lithography 255
- 13.3.2.1 Description of the Technique 255
- 13.3.2.2 Role of Plasma Processes in Soft Lithography 255
- 13.3.2.3 Limits of Soft Lithography 256
- 13.3.3 Plasma-Assisted Micropatterning: The Role of Physical Masks 256
- 13.3.3.1 Micropatterning 257
- 13.3.3.2 Nanopatterning 260
- 13.3.4 Novel Approaches in Plasma-Patterning Procedures 262
- 13.3.4.1 Plasma Polymerization and Patterning of “Smart” Materials 262
- 13.3.4.2 Deposition of Micro- and Nanostructured Coatings 263
- 13.4 Conclusions 264  
References 264
- 14 Chemical Immobilization of Biomolecules on Plasma-Modified Substrates for Biomedical Applications 269**  
*L. C. Lopez, R. Gristina, R. d'Agostino, and P. Favia*
- 14.1 Introduction 270
- 14.2 Immobilization of Biomolecules 274
- 14.2.1 Immobilization of PEO Chains (Unfouling Surfaces) 274
- 14.2.2 Immobilization of Polysaccharides 275
- 14.2.3 Immobilization of Proteins and Peptides 276
- 14.2.3.1 Immobilization of Collagen 277
- 14.2.3.2 Immobilization of Peptides 279
- 14.2.4 Immobilization of Enzymes 280
- 14.2.5 Immobilization of Carbohydrates 281
- 14.3 Conclusions 282

14.4	List of Abbreviations	283
	References	284
<b>15</b>	<b><i>In Vitro</i> Methods to Assess the Biocompatibility of Plasma-Modified Surfaces</b>	<b>287</b>
	<i>M. Nardulli, R. Cristina, R. d'Agostino, and P. Favia</i>	
15.1	Introduction	287
15.2	Surface Modification Methods: Plasma Processes and Biomolecule Immobilization	289
15.3	<i>In Vitro</i> Cell Culture Tests of Artificial Surfaces	290
15.4	Cytotoxicity Analysis	292
15.4.1	Viability Assays	292
15.4.2	Metabolic Assays	293
15.4.3	Irritancy Assays	294
15.5	Analysis of Cell Adhesion	294
15.6	Analysis of Cell Functions	298
15.7	Conclusions	299
	References	299
<b>16</b>	<b>Cold Gas Plasma in Biology and Medicine</b>	<b>301</b>
	<i>E. Stoffels, I.E. Kieft, R.E.J. Sladek, M.A.M.J. Van Zandvoort, and D.W. Slaaf</i>	
16.1	Introduction	301
16.2	Experiments	303
16.3	Plasma Characteristics	307
16.4	Bacterial Inactivation	311
16.5	Cell and Tissue Treatment	314
16.6	Concluding Remarks and Perspectives	317
	References	317
<b>17</b>	<b>Mechanisms of Sterilization and Decontamination of Surfaces by Low-Pressure Plasma</b>	<b>319</b>
	<i>F. Rossi, O. Kylián, and M. Hasiwa</i>	
17.1	Introduction	319
17.1.1	Overview of Sterilization and Decontamination Methods	320
17.1.1.1	Current Cleaning and Sterilization Processes	320
17.1.1.2	Low-Pressure Plasma-Based Method	322
17.2	Bacterial Spore Sterilization	322
17.3	Depyrogenation	324
17.4	Protein Removal	324
17.5	Experimental	325
17.5.1	Experimental Setup	325
17.5.2	Biological Tests	326
17.5.3	Pyrogen Samples Detection	326
17.5.4	Protein Removal Tests	327



17.6	Results	327
17.6.1	Sterilization	327
17.6.2	Depyrogenation	329
17.6.3	Protein Removal	331
17.7	Discussion	332
17.7.1	Plasma Sterilization	332
17.7.2	Depyrogenation	338
17.7.3	Protein Removal	338
17.8	Conclusions	338
	References	339
<b>18</b>	<b>Application of Atmospheric Pressure Glow Plasma: Powder Coating in Atmospheric Pressure Glow Plasma</b>	<b>341</b>
	<i>M. Kogoma and K. Tanaka</i>	
18.1	Introduction	341
18.2	Development of Silica Coating Methods for Powdered Organic and Inorganic Pigments with Atmospheric Pressure Glow Plasma	341
18.2.1	Experimental	342
18.2.2	Results and Discussion	343
18.2.3	Conclusion	347
18.3	Application to TiO <sub>2</sub> Fine Powder Coating with Thin Film of SiO <sub>2</sub> to Quench the Photosensitive Ability of the Powder	348
18.3.1	Experimental	348
18.3.2	Results and Discussion	349
18.3.2.1	XPS Analysis	349
18.3.2.2	TEM Analysis of Powder	350
18.3.2.3	GC/MS Spectrum of the Vapor from UV-Irradiated Squalene Oil That Mixed With the Powders	351
18.3.3	Conclusion	352
	References	352
<b>19</b>	<b>Hydrocarbon and Fluorocarbon Thin Film Deposition in Atmospheric Pressure Glow Dielectric Barrier Discharges</b>	<b>353</b>
	<i>F. Fanelli, R. d'Agostino, and F. Fracassi</i>	
19.1	Introduction	353
19.2	DBDs for Thin Film Deposition: State of the Art	354
19.2.1	Filamentary and Glow Dielectric Barrier Discharges	354
19.2.2	Electrode Configurations and Gas Injection Systems	356
19.2.3	Hydrocarbon Thin Film Deposition	357
19.2.4	Fluorocarbon Thin Film Deposition	359
19.3	Experimental Results	360
19.3.1	Apparatus and Diagnostics	360
19.3.2	Deposition of Hydrocarbon Films by Means of He-C <sub>2</sub> H <sub>4</sub> GDBDs	361

- 19.3.3 Deposition of Fluorocarbon Films by Means of He-C<sub>3</sub>F<sub>6</sub> and He-C<sub>3</sub>F<sub>8</sub>-H<sub>2</sub> GDBDs 364
- 19.4 Conclusion 366  
References 367
- 20 Remark on Production of Atmospheric Pressure Non-thermal Plasmas for Modern Applications 371**  
*R. Itatani*
- 20.1 Introduction 371
- 20.2 Why Atmospheric Pressure Non-thermal Plasmas Are Attractive 372
- 20.3 Origin of Activities of Plasmas 373
- 20.4 Limits of Similarity Law of Gas Discharge 373
- 20.5 Reduction of Gas Temperature 374
- 20.6 Examples of Realization of the Above Discussion 375
- 20.7 Large-Area Plasma Production 376
- 20.8 Summary of Evidence To Date to Obtain Uniform DBDs 376
- 20.9 Consideration to Realize Uniform Plasmas of Large Area 377
- 20.10 Factors to be Considered to Realize Uniformity of DBD Plasma 377
- 20.11 Remote Plasmas 378
- 20.12 Conclusion 379  
References 380
- 21 Present Status and Future of Color Plasma Displays 381**  
*T. Shinoda*
- 21.1 Introduction 381
- 21.2 Development of Color PDP Technologies 383
- 21.2.1 Panel Structure 383
- 21.2.2 Driving Technologies 387
- 21.3 Latest Research and Development 388
- 21.3.1 Analysis of Discharge in PDPs 388
- 21.3.2 High Luminance and High Luminous Efficiency 389
- 21.3.3 ALIS Structure 390
- 21.4 Conclusion 391  
References 391
- 22 Characteristics of PDP Plasmas 393**  
*H. Ikegami*
- 22.1 Introduction 393
- 22.2 PDP Operation 394
- 22.3 PDP Plasma Structure 395
- 22.4 Plasma Density and Electron Temperature 397
- 22.5 Remarks 399  
References 399

<b>23</b>	<b>Recent Progress in Plasma Spray Processing</b>	<b>401</b>
	<i>M. Kambara, H. Huang, and T. Yoshida</i>	
23.1	Introduction	401
23.2	Key Elements in Thermal Plasma Spray Technology	401
23.3	Thermal Plasma Spraying for Coating Technologies	402
23.3.1	Plasma Powder Spraying	403
23.3.2	Plasma Spray CVD	406
23.3.3	Plasma Spray PVD	407
23.3.4	Thermal Barrier Coatings	407
23.4	Thermal Plasma Spraying for Powder Metallurgical Engineering	414
23.4.1	Thermal Plasma Spheroidization	414
23.4.2	Plasma Spray CVD	415
23.4.3	Plasma Spray PVD	415
23.5	Thermal Plasma Spraying for Waste Treatments	416
23.6	Concluding Remarks and Prospects	417
	References	418
<b>24</b>	<b>Electrohydraulic Discharge Direct Plasma Water Treatment Processes</b>	<b>421</b>
	<i>J.-S. Chang, S. Dickson, Y. Guo, K. Urashima, and M.B. Emelko</i>	
24.1	Introduction	421
24.2	Characteristics of Electrohydraulic Discharge Systems	421
24.3	Treatment Mechanisms Generated by Electrohydraulic Discharge	422
24.4	Treatment of Chemical Contaminants by Electrohydraulic Discharge	424
24.5	Disinfection of Pathogenic Contaminants by PAED	429
24.6	Municipal Sludge Treatment	430
24.7	Concluding Remarks	432
	References	432
<b>25</b>	<b>Development and Physics Issues of an Advanced Space Propulsion</b>	<b>435</b>
	<i>M. Inutake, A. Ando, H. Tobari, and K. Hattori</i>	
25.1	Introduction	436
25.2	Performance of Rocket Propulsion Systems	437
25.3	Experimental Researches for an Advanced Space Thruster	440
25.3.1	Experimental Apparatus and Diagnostics	440
25.3.2	Improvement of an MPDA Plasma Using a Magnetic Laval Nozzle	442
25.3.3	RF Heating of a High Mach Number Plasma Flow	444
25.4	Summary	447
	References	448
	<b>Index</b>	<b>449</b>