

## Contents

<b>Series Preface</b>	<i>IX</i>
<b>Volume Preface</b>	<i>XI</i>
<b>List of Contributors</b>	<i>XIII</i>

<b>1</b>	<b>Valve Metal, Si and Ceramic Oxides as Dielectric Films for Passive and Active Electronic Devices</b>	<b>1</b>
	<i>Alexander Michaelis</i>	
1.1	Introduction	1
1.1.1	Experimental Approaches	2
1.2	Fundamentals and Experimental Details	5
1.2.1	Electrochemical Oxide Layer Formation on Valve Metals	5
1.2.2	The $C(U)$ Curve of a Valve Metal Electrode	7
1.2.3	Application of Lasers in Electrochemistry	8
1.2.3.1	Thermal Effects	9
1.2.4	Electrochemical Photocurrent Measurements (Optical/Electrical Method Class), Introduction of a New Model	10
1.2.4.1	Photocurrent Model for Ultra-thin, Amorphous Films With $\text{TiO}_2$ as an Example	11
1.3	Valve Metal Systems	15
1.3.1	Ti/ $\text{TiO}_2$ System	15
1.3.1.1	Experimental Details	15
1.3.1.2	Determination of Ti Substrate Grain Orientation by SAME	17
1.3.1.3	Photocurrent Spectra and $i_{\text{ph}}(U)$ Measurements on Single Ti/ $\text{TiO}_2$ Grains	18
1.3.1.4	Microscopic Modification of the $\text{TiO}_2$ Films by Means of Laser Scanning	19
1.3.1.5	Characterization of the Modified $\text{TiO}_2$ Films	21
1.3.1.6	Photoresist Microelectrochemistry (Nanoliter Droplet Method)	25
1.3.1.7	Applications of Photoresist Microelectrodes	28
1.3.1.8	Summary and Conclusions for the Ti/ $\text{TiO}_2$ System	36

1.3.2	Zr/ZrO <sub>2</sub> and Hf/HfO <sub>2</sub> Systems	37
1.3.2.1	Zr/ZrO <sub>2</sub>	37
1.3.2.2	Hf/HfO <sub>2</sub>	46
1.3.3	Systems: Nb/Nb <sub>2</sub> O <sub>5</sub> , Ta/Ta <sub>2</sub> O <sub>5</sub> and Al/Al <sub>2</sub> O <sub>3</sub>	48
1.3.3.1	Nb/Nb <sub>2</sub> O <sub>5</sub> System	49
1.3.3.2	Al/Al <sub>2</sub> O <sub>3</sub> System	53
1.3.3.3	Ta/Ta <sub>2</sub> O <sub>5</sub> System	54
1.3.4	Application of Valve Metals in Electrolytic Capacitor Manufacturing	57
1.3.4.1	Capacitor Fundamentals	57
1.3.4.2	Capacitor Device Types and Production of Ta Capacitors	62
1.3.4.3	Current Development Trends for Ta Capacitors and Research Issues Involved	65
1.3.4.4	Effect of Oxygen Content and Sinter Conditions on Dislocation Formation	67
1.3.4.5	Thermal Runaway	70
1.4	Si/SiO <sub>2</sub> System	74
1.4.1	Application of the Si/SiO <sub>2</sub> System	77
1.4.1.1	Si/SiO <sub>2</sub> in MOSFETs	77
1.4.1.2	Si/SiO <sub>2</sub> in DRAMs	80
1.4.1.3	DRAM Storage Capacitor (Deep Trench)	82
1.4.2	Alternative Dielectric Materials	90
1.4.2.1	Ta <sub>2</sub> O <sub>5</sub>	92
1.4.2.2	Ti/TiO <sub>2</sub>	95
1.5	Summary and Conclusions	96
	References	99
<b>2</b>	<b>Superconformal Film Growth</b>	<b>107</b>
	<i>Thomas P. Moffat, Daniel Wheeler, and Daniel Josell</i>	
2.1	Introduction	107
2.2	Destabilizing Influences	108
2.3	Stabilization and Smoothing Mechanisms	110
2.3.1	Geometric Leveling	110
2.3.2	Inhibitor-based Leveling	110
2.3.3	Brightening by Grain Refinement	111
2.3.4	Catalyst-derived Brightening	112
2.3.5	Stabilization Across Length Scales	112
2.4	Additive Processes	113
2.4.1	Adsorption Kinetics	117
2.4.2	Surface Segregation versus Consumption Processes	117
2.4.2.1	Adsorbates Segregated onto Growing Surface	118
2.4.2.2	Adsorbates Incorporated into Growing Deposit	119
2.4.2.3	Deactivation of Adsorbate	121
2.4.3	Adsorbate Evolution	121
2.4.4	Impact on Microstructure	122
2.4.5	Quantifying Adsorbate Inhibition of Metal Deposition	125

2.4.6	Co-adsorption Effects	130
2.4.7	Catalysis of Metal Deposition	134
2.4.8	Activation of Blocked Electrodes by Competitive Adsorption of a Catalyst	135
2.4.9	Catalyst Function and Consumption	138
2.4.10	Quantifying the Effects of Competitive Adsorption on Metal Deposition	141
2.4.10.1	Site Dependence of Charge Transfer Kinetics	142
2.4.10.2	Catalyst Evolution	143
2.4.10.3	SPS Adsorption from the Electrolyte	143
2.5	Interface Motion and Morphological Evolution	146
2.5.1	Shape Change Simulations	146
2.5.2	Geometric Leveling	150
2.5.3	Inhibitor-based Leveling	153
2.5.3.1	Feature Filling	153
2.5.3.2	Stability Analysis	160
2.5.4	Catalyst-derived Brightening	161
2.5.4.1	Feature Filling	161
2.5.4.2	Stability Analysis	173
2.5.5	Bridging the Length Scales	176
2.6	Conclusions and Outlook	179
	References	179
<b>3</b>	<b>Transition Metal Macrocycles as Electrocatalysts for Dioxygen Reduction</b>	<b>191</b>
	<i>Daniel A. Scherson, Attila Palencsár, Yuriy Tolmachev, and Ionel Stefan</i>	
3.1	Introduction	191
3.1.1	Electrocatalysis	192
3.1.2	Dioxygen Reduction in Aqueous Electrolytes: General Aspects	193
3.1.3	Transition Metal Macrocycles	199
3.1.3.1	General Characteristics	199
3.1.3.2	Electrocatalytic Properties Toward Oxygen Reduction	201
3.2	Homogeneous Electrocatalysis	204
3.2.1	Intrinsic Properties of Solution Phase Transition Metal Macrocycles	204
3.2.1.1	Formal Redox Potentials and Diffusion Coefficients	204
3.2.1.2	Molecular Speciation	209
3.2.1.3	Rates of Heterogeneous Electron Transfer Reactions	211
3.2.2	Macrocyclic-Mediated Reduction of Dioxygen in Aqueous Electrolytes	212
3.2.2.1	Model Systems	212
3.3	Heterogeneous Electrocatalysis	219
3.3.1	Adsorption Isotherms	220
3.3.2	Chemically Modified Electrodes	221
3.3.2.1	Preparation and Electrochemical Characterization	221

3.3.2.2	<i>In situ</i> Spectroscopic Characterization	226
3.3.3	Redox Active Chemically Modified Electrodes	232
3.3.3.1	Thermodynamic Aspects	232
3.3.3.2	Redox Speciation	235
3.3.3.3	Redox Dynamics	238
3.3.4	Electrocatalytic Aspects of Dioxygen Reduction	241
3.3.4.1	Theoretical Considerations	241
3.3.4.2	Model Systems	244
3.4	Thermal Activation of Transition Metal Macrocycles	269
3.4.1	Brief Introduction	269
3.4.2	Electrochemical Characterization	269
3.4.2.1	Cyclic Voltammetry	270
3.4.2.2	Oxygen Reduction Polarization Curves	271
3.4.3	Spectroscopic and Structural Characterization	273
3.4.3.1	Pyrolysis-Mass Spectrometry	273
3.4.3.2	Mossbauer Effect Spectroscopy	277
3.4.3.3	X-ray Absorption Fine Structure	278
3.4.3.4	X-ray Photoelectron Spectroscopy	281
3.4.4	<i>In Situ</i> and Quasi <i>In Situ</i> Spectroscopic Characterization	281
3.4.5	Concluding Remarks	283
	References	285
<b>4</b>	<b>Multiscale Modeling and Design of Electrochemical Systems</b>	<b>289</b>
	<i>Richard D. Braatz, Edmund G. Seebauer, and Richard C. Alkire</i>	
4.1	Introduction	289
4.2	Background and Motivation	291
4.2.1	Multiscale Simulation	291
4.2.2	Electrochemical Systems	293
4.2.3	Microelectronic Applications	295
4.2.4	Nanoscale Science and Technology	296
4.2.5	Other Electrochemical Applications	297
4.3	Trend Toward Atomistic/Molecular Simulation	298
4.3.1	Integrated Circuit Example	298
4.3.2	Continuum Methods	300
4.3.3	Molecular Simulation Methods	300
4.3.4	Coarse-grained Simulation Methods	303
4.4	Multiscale Simulation	304
4.5	Challenges and Requirements of Multiscale Modeling	310
4.6	Addressing the Challenges in Multiscale Modeling	311
4.7	Design Based on Multiscale Models	315
4.8	Concluding Remarks	322
	References	324
	<b>Index</b>	<b>335</b>