

Farzad Nasirpour

# Electrodeposition of Nanostructured Materials

# Contents

<b>1 An Overview of Nanostructured Materials</b> . . . . .	1
1.1 Introduction to Materials Science . . . . .	1
1.2 Physics of Solid State Materials . . . . .	2
1.2.1 Atoms and the Periodic Table of Elements . . . . .	2
1.2.2 Atomic Bonds and Condensed Matter . . . . .	5
1.2.3 The Band Theory of Solids . . . . .	15
1.3 Thermodynamics of Materials . . . . .	24
1.3.1 Nucleation and Growth of Solids . . . . .	25
1.4 Kinetics of Materials . . . . .	29
1.5 Nanostructures and Bulk Nanostructured Materials . . . . .	31
1.5.1 Dimensionality in Nanomaterials . . . . .	32
1.5.2 Two-Dimensional (2D) Nanostructures . . . . .	34
1.5.3 One-Dimensional Nanostructures (Quantum Wires or Tubes) . . . . .	38
1.5.4 Zero-Dimensional Nanostructures . . . . .	40
1.5.5 Bulk Nanostructured Materials . . . . .	40
References . . . . .	42
<b>2 An Overview to Electrochemistry</b> . . . . .	43
2.1 Introduction to Electrochemistry in Materials Science . . . . .	43
2.2 Principles of Electrochemistry . . . . .	44
2.3 Equilibrium Electrochemistry . . . . .	44
2.3.1 Ions: Formation, Thermodynamics and Interactions . . . . .	44
2.3.2 Electrochemical Cells . . . . .	49
2.4 Ion Transport . . . . .	50
2.4.1 Migration . . . . .	50
2.4.2 Diffusion of Ions . . . . .	53
2.5 Dynamic Electrochemistry: Processes at Electrodes . . . . .	54
2.5.1 The Electrode Double Layer . . . . .	55
2.5.2 Zeta Potential ( $\zeta$ ) . . . . .	57
2.5.3 Electrode Potentials . . . . .	59

2.5.4	The Rate of Charge Transfer: Electrode Kinetics and the Butler-Volmer Equation . . . . .	61
2.5.5	Polarisation . . . . .	65
2.6	Electrochemical Instrumentation and Techniques . . . . .	66
2.6.1	Electrochemical Cell . . . . .	66
2.6.2	Electrochemical Tests and Techniques . . . . .	68
	References. . . . .	73
<b>3</b>	<b>Fundamentals and Principles of Electrode-Position . . . . .</b>	<b>75</b>
3.1	Introduction . . . . .	75
3.2	Electrolysis . . . . .	76
3.2.1	Electrolysis Cell . . . . .	76
3.2.2	Electrodeposition Cells and Reactions. . . . .	77
3.2.3	Electrodeposition Electrolytes . . . . .	78
3.2.4	Electrodeposition Techniques and Classification . . . . .	81
3.2.5	Electrodeposition Kinetics: Potential-Current Relationship . . . . .	81
3.2.6	Co-electrodeposition of Various Ions . . . . .	85
3.3	Nucleation and Growth of Electrodeposits . . . . .	90
3.3.1	Atomistic View . . . . .	90
3.3.2	Thermodynamics of Nucleation. . . . .	91
3.3.3	Kinetics of Electrocrystallisation . . . . .	93
3.3.4	Surface Morphology and Roughness . . . . .	102
3.4	Characterisation of Initial Stages of Electrodeposition Process . . . . .	107
3.4.1	Scanning Probe Microscopy (SPM) Techniques . . . . .	107
3.4.2	Electrochemical Quartz Crystal Microbalance (EQCM). . . . .	111
3.4.3	Oblique Incidence Reflectivity Difference . . . . .	113
3.5	Modified Electrodeposition Processes Under External Forces . . . . .	114
3.5.1	Magnetic Electrodeposition . . . . .	114
3.5.2	Sono-Electrodeposition . . . . .	116
	References. . . . .	118
<b>4</b>	<b>Electrodeposition of 2D and 3D Meso and Nanostructures . . . . .</b>	<b>123</b>
4.1	Introduction . . . . .	123
4.2	UPD and OPD: General Consideration. . . . .	124
4.2.1	Underpotential Deposition (UPD) . . . . .	125
4.2.2	UPD and OPD in Electrodeposited Lead (Pb) on Copper (Cu). . . . .	126
4.2.3	UPD and OPD in Electrodeposited Lead (Pb) on Gold (Cu). . . . .	134
4.3	Three Dimensional (3D) Growth of Electrodeposits . . . . .	139
4.3.1	3D Nuclei as Free Standing Meso- and Nano-Structures . . . . .	140
4.3.2	Multiple 3D Nuclei and Coalescence for Film Growth . . . . .	158
4.3.3	3D Faceted Core-Shell Mesocrystals . . . . .	178

4.3.4	Hexagonal and Polyhedral Ag Core-Ni Shell Mesocrystals . . . . .	178
4.3.5	Truncated Icosahedral and Pyramidal Ag Core-Ni Shell Mesocrystals . . . . .	181
	References. . . . .	183
<b>5</b>	<b>Template Electrodeposition of Nanowires Arrays . . . . .</b>	<b>187</b>
5.1	Introduction . . . . .	187
5.2	Template. . . . .	188
5.2.1	Track-Etched Templates . . . . .	188
5.2.2	Anodic Aluminum Oxide (AAO) Templates. . . . .	190
5.3	Electrodeposition into Template . . . . .	205
5.3.1	Template Electrodeposition: Electrochemical Consideration . . . . .	206
5.3.2	Template Electrodeposition: Techniques . . . . .	209
5.4	Magnetic Nanowires. . . . .	215
5.4.1	Regular Metal and Alloy Magnetic Nanowires . . . . .	216
5.4.2	Core-Shell Nanowire Arrays . . . . .	232
5.4.3	Multilayered Nanowires . . . . .	240
5.4.4	Diameter Modulated Nanowires . . . . .	253
	References. . . . .	254
<b>6</b>	<b>Electrodeposited Nanocrystalline Films and Coatings . . . . .</b>	<b>261</b>
6.1	Introduction . . . . .	261
6.2	Electrodeposition of Nanocrystalline Films. . . . .	261
6.3	Pulse Electrodeposition. . . . .	262
6.3.1	Electrochemical Implications of Pulse Current Technique . . . . .	262
6.3.2	Principles of Pulse Electrodeposition. . . . .	264
6.3.3	Electrochemical Aspects of Pulse Electrodeposition . . . . .	266
6.3.4	Pulse Electrodeposition Conditions for Nanocrystalline Films. . . . .	271
6.4	Electrodeposited Nanocrystalline Nickel Films. . . . .	272
6.4.1	Surface Morphology and Roughness of Nanocrystalline Ni Films . . . . .	274
6.4.2	Crystallite Size and Crystallographic Texture . . . . .	277
6.4.3	Microhardness of Nanocrystalline Nickel Films . . . . .	281
6.4.4	Magnetic Properties of Nanocrystalline Nickel Films . . . . .	281
6.4.5	Corrosion Behaviour of Nanocrystalline Nickel Films . . . . .	283
	References. . . . .	287

<b>7 Electrodeposited Nanocomposite Films</b> . . . . .	289
7.1 Introduction . . . . .	289
7.2 Principles of Electrodeposition of Nanocomposites. . . . .	290
7.2.1 Electrochemical Aspects of Co-electrodeposition of Nanocomposites . . . . .	290
7.2.2 Models . . . . .	290
7.3 Effective Factors in Co-electrodeposition of Nanocomposites. . . . .	294
7.3.1 Electrodeposition Control Technique. . . . .	294
7.3.2 Particle Properties . . . . .	298
7.3.3 Electrolyte Parameters. . . . .	299
7.4 Properties of Nanocomposite Coatings . . . . .	304
7.4.1 Mechanical Properties of Ni-CNT Nanocomposite Films. . . . .	304
7.4.2 Corrosion Behavior of Ni-MWCNT Coatings in 3.5% NaCl . . . . .	306
References. . . . .	309
<b>8 Miscellaneous Electrodeposited Nanostructures</b> . . . . .	311
8.1 Scanning-Tunneling Assisted Electrodeposition of Nanostructures . . . . .	311
8.2 Lithographically Patterned Nanowire Electrodeposition . . . . .	314
8.3 Electrodeposited Mesoporous Nanostructures by Lyotropic Liquid Crystals. . . . .	315
8.4 Nanostructures by Galvanic Displacement . . . . .	316
References. . . . .	318
<b>Index</b> . . . . .	319