

*Michael Köhler and Wolfgang Fritzsche*

# **Nanotechnology**

An Introduction to Nanostructuring Techniques

Second, Completely Revised Edition



WILEY-VCH Verlag GmbH & Co. KGaA

## Contents

- 1 Introduction 1**
  - 1.1 The Way into the Nanoworld 1
    - 1.1.1 From Micro- to Nanotechniques 1
    - 1.1.2 Definition of Nanostructures 2
    - 1.1.3 Insight into the Nanoworld 3
    - 1.1.4 Intervention into the Nanoworld 4
  - 1.2 Building Blocks in Nanotechnology 5
  - 1.3 Interactions and Topology 7
  - 1.4 The Microscopic Environment of the Nanoworld 9
  
- 2 Molecular Basics 13**
  - 2.1 Particles and Bonds 13
    - 2.1.1 Chemical Bonds in Nanotechnology 13
    - 2.1.2 Van der Waals Interactions 14
    - 2.1.3 Dipole–Dipole Interactions 14
    - 2.1.4 Ionic Interactions 16
    - 2.1.5 Metal Bonds 16
    - 2.1.6 Covalent Bonds 17
    - 2.1.7 Coordinative Bonds 19
    - 2.1.8 Hydrogen Bridge Bonds 20
    - 2.1.9 Polyvalent Bonds 20
  - 2.2 Chemical Structure 23
    - 2.2.1 Binding Topologies 23
    - 2.2.2 Building Blocks of Covalent Architecture 24
    - 2.2.3 Units for a Coordinative Architecture 27
    - 2.2.4 Building Blocks for Weakly Bound Aggregates 27
    - 2.2.5 Assembly of Complex Structures through the Internal Hierarchy of Binding Strengths 28
  - 2.2.6 Reaction Probability and Reaction Equilibrium 29
  
- 3 Microtechnological Foundations 33**
  - 3.1 Planar Technology 33
  - 3.2 Preparation of Thin Layers 37

3.2.1	Condition and Preprocessing of the Substrate Surface	37
3.2.2	Layer Deposition from the Gas Phase	39
3.2.3	Evaporation	42
3.2.4	Sputtering	43
3.2.5	Chemical Vapor Deposition	46
3.2.6	Galvanic Deposition	48
3.2.7	Deposition by Spinning (Spin Coating)	50
3.2.8	Shadow-mask Deposition Techniques	53
3.3	Preparation of Ultrathin Inorganic Layers and Surface-bound Nanoparticles	54
3.3.1	Ultrathin Layers by Vacuum Deposition Processes	54
3.3.2	Deposition of Ultrathin Films from the Liquid Phase	55
3.3.3	In Situ Generation of Ultrathin Inorganic Films by Chemical Surface Modification	56
3.3.4	In Situ Formation of Ultrathin Inorganic Layers on Heteroorganic Materials	57
3.3.5	Immobilization of Nanoparticles	58
3.3.6	In Situ Formation of Inorganic Nanoparticles	59
3.4	Structure Generation and Fabrication of Lithographic Masks	59
3.4.1	Adhesive Mask Technique	59
3.4.2	Role of Resist in Photolithography	63
3.4.3	Serial Pattern Transfer	64
3.4.4	Group Transfer Processes	67
3.4.5	Maskless Structure Generation	68
3.4.6	Soft Lithography	68
3.5	Etching Processes	70
3.5.1	Etching Rate and Selectivity	70
3.5.2	Isotropic and Anisotropic Etching Processes	71
3.5.3	Lithographic Resolution in Etching Processes	72
3.5.4	Wet Etching Processes	73
3.5.5	Dry Etching Processes	76
3.5.6	High-resolution Dry Etching Techniques	78
3.5.7	Choice of Mask for Nanolithographic Etching Processes	80
3.6	Packaging	80
3.7	Biogenic and Bioanalogue Molecules in Technical Microstructures	84
<b>4</b>	<b>Preparation of Nanostructures</b>	<b>87</b>
4.1	Principles of Fabrication	87
4.1.1	Subtractive and Additive Creation of Nanostructures	87
4.1.2	Nanostructure Generation by Lift-off Processes	89
4.1.3	Principles of Nanotechnical Shape-definition and Construction	91
4.2	Nanomechanical Structure Generation	96
4.2.1	Scaling Down of Mechanical Processing Techniques	96
4.2.2	Local Mechanical Cutting Processes	97
4.2.3	Surface Transport Methods	97

4.2.4	Reshaping Processes	98
4.2.5	Soft Lithography for Nanopatterning and Nanoimprinting	101
4.3	Nanolithography	105
4.3.1	Structure Transfer by Electromagnetic Radiation	105
4.3.2	DUV- and Vacuum-UV Lithography	108
4.3.3	EUV and X-ray Lithography	110
4.3.4	Multilayer Resist Techniques with Optical Pattern Transfer	113
4.3.5	Near-field Optical Micropatterning Techniques	114
4.3.6	Energetic Particles in Nanolithographic Structure Transfer	116
4.3.7	Electron Beam Lithography	117
4.3.8	Ion Beam Lithography	124
4.3.9	Atomic Beam Lithography	126
4.3.10	Molecular and Nanoparticle Beam Lithography	126
4.3.11	Direct Writing of Structures by a Particle Beam	127
4.3.12	Nanostructure Generation by Accelerated Single Particles	130
4.3.13	Patterning by Local Chemical Conversion	132
4.3.14	Nanofabrication by Self-structuring Masks	132
4.4	Nanofabrication by Scanning Probe Techniques	133
4.4.1	Mechanical Surface Modifications based on Scanning Force Microscopy (SFM)	134
4.4.2	Manipulation by a Scanning Tunneling Microscopy (STM)	135
4.4.3	Thermo-mechanical Writing of Nanostructures	137
4.4.4	Electrically Induced Structure Generation by Scanning Probe Techniques	138
4.4.5	Chemical Induced Scanning Probe Structure Generation	143
4.4.6	Nanostructure Generation by Optical Near-field Probes	145
4.4.7	Scanning Probe Methods for Nanoscale Transfer	146
4.5	Reduction of Feature Sizes by Post-Lithographic Processing	146
4.5.1	Narrowing of Nanogaps by Material Deposition	146
4.5.2	Size Reduction by Thermally Induced Reshaping	147
4.5.3	Size Reduction by Sidewall Transfer	148
4.5.4	Formation of Nanodots by Dewetting	148
<b>5</b>	<b>Nanotechnical Structures</b>	<b>149</b>
5.1	Nanostructures and Nanomaterials	149
5.2	Inorganic Solids	150
5.2.1	Influence of Material Morphology on Nanoscale Pattern Processes	150
5.2.2	Inorganic Dielectrics	150
5.2.3	Metals	152
5.2.4	Semiconductors	154
5.3	Carbon Nanostructures	156
5.4	Organic Solids and Layer Structures	158
5.4.1	Solids Composed of Smaller Molecules	158
5.4.2	Organic Monolayer and Multilayer Stacks	158
5.4.3	Synthetic Organic Polymers	160

5.4.4	Biopolymers	161
5.5	Molecular Monolayer and Layer Architectures	162
5.5.1	Langmuir–Blodgett Films	162
5.5.2	Self-assembled Surface Films	164
5.5.3	Binding of Molecules on Solid Substrate Surfaces	165
5.5.4	Secondary Coupling of Molecular Monolayers	167
5.5.5	Categories of Molecular Layers	168
5.5.6	Molecular Coupling Components (Linkers) and Distance Components (Spacers)	171
5.5.7	Definition of Binding Spots on Solid Substrates	172
5.6	Molecular Architectures	174
5.6.1	Single Molecules as Nanostructures	174
5.6.2	Strategies of Molecular Construction	178
5.6.3	Biogenic and Bio-analogous Nanoarchitectures	182
5.6.4	DNA Nanoarchitectures	185
5.6.5	Synthetic Supramolecules	192
5.6.6	Nanoparticles and Nanocompartments	200
5.7	Combination of Molecular Architectures and Nanoparticles With Planar Technical Structures	202
<b>6</b>	<b>Characterization of Nanostructures</b>	<b>211</b>
6.1	Geometrical Characterization	211
6.1.1	Layer Thickness and Vertical Structure Dimensions	211
6.1.2	Lateral Dimensions	215
6.1.3	Structures that Assist Measurement	216
6.2	Characterization of Composition of Layers and Surfaces	217
6.2.1	Atomic Composition	217
6.2.2	Characterization of the Chemical Surface State	220
6.3	Functional Characterization of Nanostructures	223
<b>7</b>	<b>Nanotransducers</b>	<b>225</b>
7.1	Design of Nanotransducers	225
7.2	Nanomechanical Elements	227
7.2.1	Nanomechanical Sensors	227
7.2.2	Nanometer-precision Position Measurements with Conventional Techniques	228
7.2.3	Electrically Controlled Nanoactuators	228
7.2.4	Chemically Driven Nanoactuators	230
7.2.5	Rigidity of Nanoactuators	234
7.3	Nanoelectronic Devices	235
7.3.1	Electrical Contacts and Nanowires	235
7.3.2	Nanostructured Tunneling Barriers	240
7.3.3	Quantum Dots and Localization of Elementary Particles	242
7.3.4	Nanodiodes	243
7.3.5	Electron Islands and Nanotransistors	244

7.3.6	Nanoswitches, Molecular Switches and Logic Elements	251
7.3.7	Particle-Emitting Nanotransducers	253
7.4	Nanooptical Devices	254
7.4.1	Nanostructures as Optical Sensors	254
7.4.2	Nanostructured Optical Actuators	255
7.4.3	Nanooptical Switching and Conversion Elements	257
7.5	Magnetic Nanotransducers	258
7.6	Chemical Nanoscale Sensors and Actuators	260
7.8	Nanochannels and Nanofluidic Devices	265
7.8.1	Nanochannel Arrays	267
7.8.2	Nanofluidic Electrospraying	269
7.8.3	Liquid Transport in Nanotubes	269
7.8.4	Nanofluidic Actuators for Optical Application	269
7.8.5	Functional Molecular Devices for Nanofluidics	269
<b>8</b>	<b>Technical Nanosystems</b>	<b>271</b>
8.1	What are Nanosystems?	271
8.2	Systems with Nanocomponents	272
8.3	Entire Systems with Nanometer Dimensions	273
<b>Table of Examples</b>		<b>279</b>
<b>References</b>		<b>283</b>
<b>Index</b>		<b>307</b>