

Chunli Bai

Scanning Tunneling Microscopy and Its Applications

Second, Revised Edition
With 208 Figures



Springer

SHANGHAI
SCIENTIFIC & TECHNICAL
PUBLISHERS

Contents

1. Introduction	1
1.1 Advantages of STM Compared with Other Techniques	1
1.2 From Optical Microscopy to Scanning Tunneling Microscopy	3
1.2.1 Electron Microscopes	3
1.2.2 Field Ion Microscope	5
1.2.3 Scanning Tunneling Microscope	5
1.3 Overview	7
2. The Tunneling Effect	11
2.1 Historical Remarks	12
2.2 Tunneling-Current Theory	17
2.2.1 Tunneling Current	18
2.2.2 Practical Tip and Surface Wave Functions	22
2.3 Tip-Surface Interaction Model	25
2.3.1 Tunneling Current	25
2.3.2 Tunnel Conductance	29
2.3.3 Tunneling Active Orbital at the Tip	30
2.3.4 Double-Tip and Interference Effects	32
3. Spectroscopy, and Spectroscopic Imaging	37
3.1 Concepts of Tunneling Spectroscopies	38
3.1.1 Solid-State-Barrier Tunneling	38
3.1.2 Metal-Vacuum-Metal Tunneling	40
3.2 Experimental Modes	42
3.2.1 Current-Voltage Characteristics	43
3.2.2 Current-Separation and Separation-Voltage Characteristics	44
3.2.3 Constant-Current Topography	46
3.2.4 Current-Imaging Tunneling Spectroscopy	46
3.3 Energy Resolution	47
3.4 Examples	49
3.4.1 Surface States	50
3.4.2 Adsorbate-Covered Surfaces	56
3.4.3 Superconductivity	57
3.4.4 Outlook	60

a) Influence of the Tip	60
b) Interpretation of Spectroscopy Results	60
4. STM Instrumentation	63
4.1 The Vibration Isolation System	63
4.2 Mechanical Designs	67
4.2.1 Piezoelectric Ceramics	70
4.2.2 Three-Dimensional Scanners	71
4.2.3 Coarse Sample Positioning	74
4.2.4 STMs for Operation in Various Environments	76
4.3 Tip Preparation	80
4.3.1 Preparation of Tungsten Tips	80
4.3.2 Preparation of Pt-Ir Tips	84
4.3.3 Other Ways to Prepare STM Tips	87
4.3.4 Tip Treatment	89
4.4 Electronics	92
4.5 Computer Automation	96
4.5.1 Hardware	97
4.5.2 Software	98
4.5.3 Image Processing	100
a) Histogram Equalization	101
b) Convolution Filter	101
c) Statistical Differencing	102
d) Three-Dimensional Representation	102
5. Other Related Scanning Probe Microscopes	105
5.1 Atomic Force Microscope	105
5.1.1 The Force Sensor	107
5.1.2 Deflection Detection	112
5.1.3 Illustrating AFM Applications	114
5.2 Other Scanning-Force Microscopies	121
5.2.1 Lateral Force Microscope	121
5.2.2 Force Microscope Operating in the Noncontact Mode	112
5.2.3 Force Microscope Operating in the Tapping Mode	126
5.2.4 Magnetic Force Microscope	127
5.2.5 Electrostatic Force Microscope	130
5.3 Ballistic-Electron-Emission Microscopy	133
5.3.1 The Principle of BEEM	133
5.3.2 The BEEM Experiment	135
5.3.3 The Application of BEEM	136
5.3.4 Ballistic-Hole Spectroscopy of Interfaces	140
5.3.5 Interfacial Modification with BEEM	144
5.4 Scanning Ion-Conductance Microscope	145
5.5 Scanning Thermal Microscope	147

5.6	Scanning Tunneling Potentiometry and Scanning Noise Microscopy	149
5.7	Photon Scanning Tunneling Microscopy and Scanning Plasmon Near-Field Microscopy	151
5.8	Near-Field Scanning Optical Microscopy and Spectroscopy . .	153
5.8.1	Principles of Near-Field Optics	155
5.8.2	Optical Probes for Near-Field Optics	156
5.8.3	NSOM Operation	157
5.8.4	Near-Field Scanning Optical Spectroscopy	158
5.8.5	Near-Field Optical Chemical Sensors	161
5.8.6	Scanning Exciton Microscopy	162
5.8.7	Single-Molecule Detection by Near-Field Optics	163
6.	STM Studies of Clean Surfaces	165
6.1	Metal Surfaces	165
6.1.1	Geometric Structures	166
6.1.2	Electronic Structures	168
6.1.3	Surface Diffusion	172
6.2	Elemental Semiconductor Surfaces	173
6.2.1	The Si(111) Surface	173
a)	Si(111)- 7×7	173
b)	Si(111)- 2×1	175
6.2.2	The Si(001) Surface	177
a)	Geometric Structure	178
b)	Electronic Structure	180
c)	The $2 \times n$ Structure	182
6.2.3	Other Silicon-Surface Structures	183
6.2.4	The Ge Surfaces	184
a)	Ge(111)	184
b)	Ge(001)	185
6.2.5	The GeSi(111) Surface	186
6.3	Compound Semiconductors and Layered Compounds	187
6.3.1	GaAs Surfaces	188
a)	GaAs(110)	188
b)	GaAs(100)	190
c)	GaAs(111) and GaAs($\bar{1}\bar{1}\bar{1}$)	191
d)	GaAs-AlGaAs	192
6.3.2	Layered Compounds	193
6.3.3	Charge-Density Waves in Compound Semiconductors . .	195
a)	CDW Phases of 1T-TaS ₂	196
b)	Charge-Density Wave Defects	200
6.3.4	High-T _c Oxides	200

7. Surface Adsorbates and Surface Chemistry	205
7.1 Adsorption on Metal Surfaces	205
7.1.1 Cu(110)-O	206
7.1.2 Cu(100)-O	208
7.1.3 Dynamics	209
7.1.4 Ag(110)-O	211
7.1.5 Ni(110)-H and Ni(111)-H	213
7.1.6 Sulfur Adsorption	215
7.1.7 Cu(111)-S	216
7.1.8 Ni(111)-S	219
7.1.9 Cu(110)-S	221
7.1.10 Ni(110)-S	224
7.1.11 Mo(001)-S and Re(0001)-S	227
7.1.12 Other Non-metal Adsorbates on Metals	228
7.1.13 Metallic Adsorbates	228
7.2 Adsorption on Semiconductor Surfaces	229
7.2.1 Ag/Si(111)	230
7.2.2 Au/Si(111)	231
7.2.3 Cu/Si(111)	232
7.2.4 Group-III Metals on Si(111)	233
7.2.5 B/Si(111)	234
7.2.6 Cl/Si(111)	235
7.2.7 Bi on Si(100) and Si(111) Surfaces	235
7.2.8 Na/Si(111)	236
7.2.9 Na/GaAs(110) and Cs/GaAs(110)	238
7.2.10 Alkali Metals on Si(100)-2×1	241
7.3 Molecules, and Molecular Adsorbates	242
7.3.1 Molecular Crystals	242
7.3.2 Chemisorbed Aromatic Molecules in Ultrahigh Vacuum	243
7.3.3 Physisorbed Molecules in Ultrahigh Vacuum	245
7.3.4 Physisorbed Long-Chain Molecules	246
7.3.5 Chemisorption of Long-Chain Molecules	249
7.3.6 Fullerenes	252
a) C ₆₀ on GaAs(110)	252
b) C ₆₀ on Si(100)	254
c) C ₆₀ on Si(111)	254
d) C ₆₀ on MoS ₂ (0001)	254
e) C ₆₀ on Cu(111)	255
f) C ₆₀ on Au(111) and Ag(111)	255
7.3.7 Langmuir-Blodgett Films	256
7.4 Observation of Clusters	257
7.4.1 Metal Clusters	257
7.4.2 Semiconductor Clusters	260
7.5 Nucleation and Growth	260

7.5.1	Epitaxial Growth of Metal Films	261
7.5.2	Growth of Si on Si(001)	262
7.6	Chemical Reactions on Metals	265
7.6.1	Reaction on Ni(110)	265
7.6.2	Reaction on Cu(110)	268
7.6.3	Chemical Identity with STM	269
7.7	Chemical Reaction on Semiconductors	271
7.7.1	Reaction of NH_3 with Si(111)- 7×7 Surfaces	271
7.7.2	Reaction of NH_3 with B/Si(111)- $\sqrt{3}\times\sqrt{3}$ Surface	273
7.7.3	Reaction of NH_3 with Clean Si(001) Surface	274
7.7.4	Si(111)- 7×7 Oxidation	274
7.7.5	Si(100)- 2×1 Oxidation	276
7.7.6	Reaction of H with Si(111)- 7×7	276
7.7.7	Reaction of Sb_4 with Si(100)	277
8.	Biological Applications	279
8.1	Advantages and Problems	279
8.1.1	Substrates	280
8.1.2	Fixation of Samples onto Substrates	280
8.1.3	Flexibility of Biological Samples	281
8.1.4	Identification and Interpretation of STM Images	281
8.2	Preparation	282
8.2.1	Dispersion of Samples on Substrates	282
8.2.2	Fixation of Samples	283
	a) Sample Coatings	283
	b) Covalently Binding Samples with Strongly Absorbent Groups	283
	c) Binding Samples to the Substrate Covalently	284
8.2.3	STM Imaging in Aqueous Solutions	284
8.2.4	Hopping Technique	284
8.2.5	STM Directed by an Optical Microscope	286
8.3	Nucleic Acids	287
8.3.1	DNA in Air and in Vacuum	287
8.3.2	DNA Studies Under Water with an Electrolyte	289
8.3.3	DNA-Protein Complex	292
8.3.4	DNA Bases	292
8.3.5	DNA Sequencing by Scanning-Probe Microscopes	294
8.4	Proteins	296
8.4.1	Amino Acids and Peptides	296
8.4.2	Structural Proteins	298
8.4.3	Functional Proteins	299
8.5	Biological Membranes	301
8.6	Imaging Cells and Other Applications	302
8.7	Force Spectrum Analysis of Biological Materials	306

9. Surface Modification	309
9.1 Overview	309
9.2 Direct Indentation with the Tunneling Tip	310
9.2.1 Modification of Metal Surfaces	311
9.2.2 Modification of Semiconductor Surfaces	317
9.3 Nanolithography on Resist Films	321
9.4 Nanofabrication in Solution and in Gaseous Environments	324
9.4.1 Nanofabrication in Solution	324
9.4.2 Nanofabrication in Gaseous Environments	325
9.5 Atomic-Scale Manipulation	327
9.5.1 Manipulation of Atoms	327
a) Xenon Atoms	327
b) Iron Atom	330
c) Silicon Atom	331
d) Sulfur Atoms	333
9.5.2 Manipulation of Molecules and Clusters	333
a) Carbon Monoxide	333
b) Antimony Molecules	333
c) Decaborane and Other Organic Molecules	336
d) H ₂ O Molecules	336
9.6 Quantization of Conductance in Nano-Contacts Produced by STM	338
9.7 Fabrication with Other Scanning-Probe Microscopes	339
9.7.1 Machining Thin Films	339
9.7.2 Charge Storage	340
9.7.3 Magnetic Structures and Writing into an Interface	343
9.8 The Future	343
References	345
Subject Index	367