## Contents

*Preface*  page xv  
*List of acronyms*  xix  
*Introduction*  1  

### Part one

**Experimental methods and theoretical background of scanning probe microscopy and spectroscopy**

1 Scanning tunneling microscopy (STM)  11
   1.1 Historical remarks on electron tunneling  11
   1.2 Theoretical treatment of one-dimensional electron tunneling  12
      1.2.1 Elastic tunneling through a one-dimensional rectangular potential barrier using the time-independent approach ('wave-matching method')  15
      1.2.2 Elastic tunneling through a one-dimensional rectangular potential barrier using the time-dependent approach  17
      1.2.3 Elastic tunneling through a one-dimensional potential barrier of arbitrary shape using the WKB approximation  20
      1.2.4 Elastic tunneling in planar metal–insulator–metal junctions  21
      1.2.5 Field emission or Fowler–Nordheim regime and Gundlach oscillations  25
      1.2.6 Tunneling including the image potential  25
      1.2.7 Band structure effects in elastic tunneling  28
      1.2.8 Resonant tunneling  30
      1.2.9 Traversal time for tunneling  34
Contents

1.3 Elastic tunneling experiments with planar metal–insulator–metal junctions 35
  1.3.1 Giaever tunneling 36
  1.3.2 Josephson tunneling 44
  1.3.3 Coulomb blockade and single-electron tunneling 47
  1.3.4 Spin-polarized tunneling 49
1.4 Inelastic electron tunneling in planar metal–insulator–metal junctions 55
  1.4.1 Inelastic tunneling involving excitation within the insulating barrier 55
  1.4.2 Inelastic tunneling involving excitation in the metal electrodes or metal–insulator interfaces 61
1.5 Semiconductor (p–n) junctions: Esaki tunnel diodes 63
1.6 Metal–semiconductor junctions: Schottky barrier tunneling 66
1.7 Point contact spectroscopy (PCS) 68
1.8 Vacuum tunneling before the invention of the STM 73
1.9 The birth of STM 81
1.10 STM design and instrumentation 83
  1.10.1 Vibration isolation 84
  1.10.2 Positioning devices 87
  1.10.3 Scanning units 91
  1.10.4 Electronics 97
  1.10.5 Computer automation 98
  1.10.6 Sensor tip preparation and characterization 99
  1.10.7 Combined analysis instruments 106
1.11 Topographic imaging by STM 109
  1.11.1 Constant current imaging (CCI) 109
  1.11.2 Constant height imaging (CHI) or variable current mode 128
  1.11.3 Differential tunneling microscopy (DTM) 130
  1.11.4 Tracking tunneling microscopy (TTM) 130
  1.11.5 Scanning noise microscopy (SNM) 130
  1.11.6 Nonlinear alternating-current tunneling microscopy 131
1.12 Local tunneling barrier height 131
  1.12.1 Local tunneling barrier height measurements at fixed surface locations 134
  1.12.2 Spatially resolved local tunneling barrier height measurements 135
Contents

1.12.3 Anomalous barrier heights 139

1.13 Tunneling spectroscopy (TS)
1.13.1 Voltage-dependent STM imaging 142
1.13.2 Scanning tunneling spectroscopy (STS) at constant current 145
1.13.3 Local I–U measurements at constant separation 147
1.13.4 Current imaging tunneling spectroscopy (CITS) 148
1.13.5 Variable-separation spectroscopy 149
1.13.6 Assessment of tunneling spectroscopy compared with other spectroscopical techniques 152

1.14 Spin-polarized scanning tunneling microscopy (SPSTM)
1.14.1 Concepts of SPSTM 157
1.14.2 Spin-polarized scanning tunneling spectroscopy (SPSTS) 158
1.14.3 Other spin-sensitive STM experiments 163

1.15 Inelastic electron tunneling (IET) in STM
1.15.1 Phonon spectroscopy by IET 164
1.15.2 Molecular vibrational spectroscopy by IET 165
1.15.3 Photon emission by IET 166

1.16 Tunneling-induced luminescence microscopy and spectroscopy 166

1.17 STM with laser excitation
1.17.1 Thermal effects 172
1.17.2 Rectification, frequency mixing and laser-driven STM 173
1.17.3 Generation and detection of surface plasmons 176
1.17.4 Photovoltaic effects and photoassisted tunneling spectroscopy 177

1.18 Scanning tunneling potentiometry (STP) 179

1.19 Ballistic electron emission microscopy (BEEM) and spectroscopy (BEES) 183

1.20 Scanning field emission microscopy (SFEM) and spectroscopy (SFES)
1.20.1 Field emission resonances (FER) and electron interferometry at surfaces and interfaces 190
1.20.2 Field emission scanning microscopy 193
1.20.3 Other field emission experiments 197
1.21 Transition to point contact 198
1.22 Forces in STM 204

2 Scanning force microscopy (SFM)
2.1 Historical remarks on surface force measurements and surface profilometry 210
2.1.1 Surface force apparatus (SFA) 210
2.1.2 Surface profilometers 213
2.2 The birth of SFM 214
2.3 SFM design and instrumentation 216
2.3.1 Force sensors 216
2.3.2 Cantilever deflection measurement techniques 221
2.4 Topographic imaging by SFM in the contact mode 226
2.4.1 Constant force imaging (CFI) 226
2.4.2 Variable deflection imaging (VDI) 230
2.4.3 Differential force microscopy (DFM) 230
2.5 Frictional force microscopy (FFM) 231
2.6 Force spectroscopy (FS) 235
2.6.1 Local force spectroscopy (LFS) 236
2.6.2 Scanning force spectroscopy (SFS) 239
2.7 Non-contact force microscopy 241
2.7.1 Van der Waals (VDW) force microscopy 245
2.7.2 Electrostatic force microscopy (EFM) 246
2.7.3 Magnetic force microscopy (MFM) 251

3 Related scanning probe methods 265
3.1 Scanning near-field optical microscopy (SNOM) 267
3.1.1 SNOM with nanometer-size aperture probes 268
3.1.2 Photon scanning tunneling microscopy (PSTM) 270
3.1.3 Scanning plasmon near-field microscopy (SPNM) 272
3.2 Scanning near-field acoustic microscopy (SNAM) 273
3.3 Scanning near-field thermal microscopy (SNTM) 275
3.3.1 Scanning thermal profiler (STHP) 276
3.3.2 Tunneling thermometer (TT) 278
3.4 Scanning capacitance microscopy (SCAM) 279
3.5 Scanning electrochemical microscopy (SECM) 283
3.6 Scanning micropipette microscopy (SMM) 284
3.6.1 Scanning ion conductance microscopy (SICM) 284
3.6.2 Scanning micropipette molecule microscopy (SMMM) 286
Part two
Applications of scanning probe microscopy and spectroscopy

4 Condensed matter physics 291
   4.1 Surface science 292
      4.1.1 Semiconductors 292
      4.1.2 Metals 357
      4.1.3 Layered materials 387
      4.1.4 Insulators 417
   4.2 Magnetism 422
      4.2.1 Micromagnetic configurations 423
      4.2.2 Magnetic storage media 430
   4.3 Superconductivity 431
      4.3.1 Local energy gap 434
      4.3.2 Spatially resolved energy gap 439
      4.3.3 Phonon density of states 441
      4.3.4 Abrikosov flux lattice 443
   4.4 Charge density waves (CDW) 452
      4.4.1 CDW in quasi-two-dimensional materials 454
      4.4.2 CDW defects 457
      4.4.3 CDW domains 461
      4.4.4 CDW energy gap 464
      4.4.5 CDW in quasi-one-dimensional materials and CDW dynamics 464

5 Chemistry 468
   5.1 Surface reactions 468
      5.1.1 Chemical reactions at semiconductor surfaces 470
      5.1.2 Chemical reactions at metal surfaces 478
   5.2 Electrochemistry 481
      5.2.1 Electrochemical oxidation and reduction of surfaces 485
      5.2.2 Potential-dependent reconstruction at electrochemical surfaces 487
      5.2.3 Electrochemical deposition under potentiostatic control 488

6 Organic material 493
   6.1 Thin molecular layers 495
      6.1.1 Chemisorbed molecules on metal substrates 496
      6.1.2 Liquid crystal molecules 501
      6.1.3 Alkanes and alkane-derived molecules 511
      6.1.4 Langmuir–Blodgett (LB) films 512
      6.1.5 Polymers 518
6.1.6 Fullerene films 518
6.2 Molecular crystals 521
6.3 Biomacromolecules 525
  6.3.1 Nucleic acids 528
  6.3.2 Proteins 529
  6.3.3 Membranes 534

7 Metrology and standards 537
  7.1 Nanometrology 537
  7.2 Quantum standards 539

8 Nanotechnology 542
  8.1 Fabrication of nanometer-scale structures 543
    8.1.1 Mechanical surface modifications 545
    8.1.2 Chemical surface modifications 551
    8.1.3 Electric-field-induced surface modifications 558
    8.1.4 Thermally induced surface modifications 562
    8.1.5 Electrostatic surface modifications 567
    8.1.6 Magnetic surface modifications 569
  8.2 Nanometer-scale electronic devices 571
  8.3 Scanning probe methods combined with microfabrication 574
    8.3.1 Microfabrication of SPM sensors 575
    8.3.2 Microfabrication of multiple sensor tips 575
    8.3.3 Microfabrication of SPM instruments 576
    8.3.4 Field emission microprobe system 576
    8.3.5 Microfabrication of SPM-based sensors 579
  8.4 Conclusion 580

References 581
Index 625