Bharat Bhushan
(Editor)

Scanning Probe Microscopy in Nanoscience and Nanotechnology

With 453 Figures

Springer
Contents

Part I Scanning Probe Microscopy Techniques

1 Time-Resolved Tapping-Mode Atomic Force Microscopy ................. 3
   Ali Fatih Sarioglu and Olav Solgaard
   1.1 Introduction .................................................. 3
   1.2 Tip-Sample Interactions in TM-AFM .............................. 5
       1.2.1 Interaction Forces in TM-AFM ............................ 5
       1.2.2 Cantilever Dynamics and Mechanical
            Bandwidth in TM-AFM .................................. 6
   1.3 AFM Probes with Integrated Interferometric
       High Bandwidth Force Sensors ................................. 8
       1.3.1 Model .................................................. 9
       1.3.2 Interferometric Grating Sensor .......................... 13
       1.3.3 Sensor Mechanical Response & Temporal Resolution ... 19
       1.3.4 Fabrication ............................................ 21
       1.3.5 Detection Schemes ..................................... 23
       1.3.6 Characterization and Calibration ......................... 26
       1.3.7 Time-Resolved Force Measurements ....................... 27
   1.4 Imaging Applications ........................................... 30
       1.4.1 Nanomechanical Material Mapping ......................... 31
       1.4.2 Imaging of Molecular Structures in Self
            Assembled Monolayers .................................. 32
       1.4.3 Imaging Microphase Separation
            in Triblock Copolymer ................................... 33
   1.5 Conclusion ..................................................... 34
   References .......................................................... 35

2 Small Amplitude Atomic Force Spectroscopy ............................... 39
   Sissi de Beer, Dirk van den Ende, Daniel Ebeling,
   and Frieder Mugele
   2.1 Introduction .................................................. 39
   2.2 Small Amplitude Spectroscopy .................................. 42
       2.2.1 Actuation Techniques ................................. 43
       2.2.2 Effect Frequency Dependent Damping .................... 53
5.2 Detailed Description of the Near-field Microwave Microscope

5.2.1 Probe-Tip for NFMM

5.2.2 Dipole–Dipole Interaction

5.2.3 Tip–sample Distance Control in NFMM

5.2.4 The Basic Experimental Setup of NFMM

5.3 Theory of Near-field Microwave Microscope

5.3.1 Transmission Line Theory

5.3.2 Perturbation Theory

5.3.3 Finite-Element Model

5.4 Electromagnetic Field Distribution

5.4.1 Probe-tip–fluid Interaction

5.4.2 Probe-tip–photosensitive Heterojunction Interaction

5.4.3 Probe-Tip–Ferromagnetic Thin Film, Magnetic Domain Interaction

5.5 Experimental Results and Images Obtained by Near-Field Microwave Microscope

5.5.1 NFMM Characterization of Dielectrics and Metals

5.5.2 NFMM Characterization of Semiconductor Thin Films

5.5.3 NFMM Characterization of DNA Array, SAMs, and Mixture Fluids

5.5.4 Biosensing of Fluids by a NFMM

5.5.5 NFMM Characterization of Solar Cells

5.5.6 NFMM Characterization of Organic FET

5.5.7 NFMM Characterization of Magnetic Domains

References

6 Single Cluster AFM Manipulation: a Specialized Tool to Explore and Control Nanotribology Effects

Guido Paolicelli, Massimo Rovatti, and Sergio Valeri

6.1 Introduction

6.2 Manipulation and Friction Effects Explored by Dynamic AFM

6.2.1 Experimental Evidences

6.2.2 Controlled Movements

6.2.3 Depinning and Energy Dissipation

6.3 The Problem of Contact Area in Nanotribology Explored by AFM Cluster Manipulation

6.4 Conclusion

References

Part II Characterization

7 Cell Adhesion Receptors Studied by AFM-Based Single-Molecule Force Spectroscopy

Robert H. Eibl

7.1 Introduction

7.2 AFM-Based Single-Molecule Force Spectroscopy
7.3 Receptor–Ligand Interactions ............................................ 203
7.4 Cell Adhesion Interactions on Living Cells .......................... 204
7.5 Limitations of the AFM Method ........................................ 212
References ........................................................................... 213

8 Biological Application of Fast-Scanning Atomic Force
Microscopy ................................................................. 217
Yuki Suzuki, Masatoshi Yokokawa, Shige H. Yoshimura,
and Kunio Takeyasu
8.1 Introduction ..................................................................... 217
8.2 Principles of Biological Fast-Scanning AFM ................. 219
  8.2.1 Hansma’s Fast-Scanning AFM ................................. 219
  8.2.2 Miles’ Fast-Scanning AFM ...................................... 219
  8.2.3 Ando’s Fast-Scanning AFM ..................................... 220
8.3 Effects of a Scanning Probe and Mica Surface
  on Biological Specimens ................................................. 221
  8.3.1 Experimental Conditions Required
    for Fast-Scanning AFM Imaging ............................... 221
  8.3.2 Effects of High-Speed Scanning
    on the Behavior of DNA in Solution .......................... 222
  8.3.3 Effects of High-Speed Scanning on Protein Movement .... 222
8.4 Application to Biological Macromolecule Interactions ........ 225
  8.4.1 Application to Protein–Protein Interaction .......... 225
  8.4.2 Application to DNA–Protein Interaction .............. 229
8.5 Mechanisms of Signal Transduction
  at the Single-Molecule Level ........................................... 233
  8.5.1 Conformational Changes of Ligand-Gated
    Ion Channels .......................................................... 235
  8.5.2 Conformational Changes of G-protein
    Coupled Receptors .................................................. 235
  8.5.3 Direct Visualization of Albers–Post Scheme
    of P-Type ATPases ................................................ 236
8.6 Conclusion ..................................................................... 238
References ........................................................................... 238

9 Transport Properties of Graphene with Nanoscale Lateral
Resolution ................................................................. 247
Filippo Giannazzo, Vito Raineri, and Emanuele Rimini
9.1 Introduction ..................................................................... 248
9.2 Transport Properties of Graphene ...................................... 252
  9.2.1 Electronic Bandstructure and Dispersion Relation .... 252
  9.2.2 Density of States .................................................... 256
  9.2.3 Carrier Density ........................................................ 256
  9.2.4 Quantum Capacitance ............................................. 258
9.2.5 Transport Properties: Mobility, Electron Mean Free Path .................................................. 259

9.3 Local Transport Properties of Graphene by Scanning Probe Methods ........................................... 269

9.3.1 Lateral Inhomogeneity in the Carrier Density and in the Density of States ................................. 269

9.3.2 Nanoscale Measurements of Graphene Quantum Capacitance .............................................. 273

9.3.3 Local Electron Mean Free Path and Mobility in Graphene .................................................. 275

9.3.4 Local Electronic Properties of Epitaxial Graphene/4H-SiC (0001) Interface ............................. 278

9.4 Conclusion .......................................................................................................................... 281

References ................................................................................................................................ 282

10 Magnetic Force Microscopy Studies of Magnetic Features and Nanostructures .................................. 287

Lanping Yue and Sy-Hwang Liou

10.1 Magnetic Force Microscopy .................................................................................................. 287

10.1.1 Introduction ..................................................................................................................... 287

10.1.2 MFM Basic Principles .................................................................................................... 288

10.1.3 MFM Image Contrast ...................................................................................................... 289

10.1.4 Magnetic Imaging Resolution .......................................................................................... 290

10.2 High-Resolution MFM Tips ................................................................................................ 291

10.3 Magnetic Domains ............................................................................................................. 296

10.4 Patterned Nanomagnetic Films ............................................................................................ 301

10.4.1 FIB Milled Patterns ........................................................................................................ 301

10.4.2 Arrays of Magnetic Dots by Direct Laser Patterning .................................................... 303

10.5 Template-Mediated Assembly of FePt Nanoclusters ............................................................. 309

10.6 Interlayer Exchange-Coupled Nanocomposite Thin Films ...................................................... 310

10.6.1 (Co/Pt)/NiO/(CoPt) Multilayers with Perpendicular Anisotropy ........................................ 311

10.6.2 Co/Ru/Co Trilayers with In-Plane Anisotropy .................................................................... 313

10.7 Conclusion (Outlook) .......................................................................................................... 314

References ................................................................................................................................ 315

11 Semiconductors Studied by Cross-sectional Scanning Tunneling Microscopy .................................. 321

J.K. Garleff, J.M. Ulloa, and P.M. Koenraad

11.1 Introduction ......................................................................................................................... 321

11.2 Cleaving Methods and Geometries ....................................................................................... 322

11.3 Properties of Cleaved Surfaces ............................................................................................ 327

11.3.1 The (111) Surface of Silicon and Germanium .................................................................... 327

11.3.2 The (110) Surface of Silicon ............................................................................................ 329

11.3.3 The (110) Surface of III–V Semiconductors ..................................................................... 329

11.3.4 The (110) Surface of II–VI Semiconductors ..................................................................... 330
11.4 Semiconductor Bulk Properties ...........................................330
  11.4.1 Ordering in Semiconductor Alloys ..............................330
  11.4.2 Phase Separation Effects .........................................332
11.5 Low-Dimensional Semiconductor Nanostructures ..................332
  11.5.1 Quantum Wells ...................................................333
  11.5.2 Quantum Dots ....................................................337
11.6 Impurities in Semiconductors ...........................................344
  11.6.1 Impurity Atoms in Silicon .......................................345
  11.6.2 Impurity Atoms in III–V and II–VI Semiconductors ..........346
References ..................................................................................349

12 A Novel Approach for Oxide Scale Growth
Characterization: Combining Etching with Atomic Force Microscopy ............................................355
V. Presser, A. Loges, and K.G. Nickel
12.1 Introduction .................................................................356
12.2 Oxidation of Silicon Carbide ...........................................357
12.3 Silica: Growth and Crystallization ...................................358
12.4 Etching .................................................................362
12.5 Scale and Interface Morphology .......................................363
12.6 Kinetics: Details and Overall Model .................................371
12.7 Conclusion and Outlook ...............................................377
References ..................................................................................378

13 The Scanning Probe-Based Deep Oxidation Lithography
and Its Application in Studying the Spreading of Liquid
n-Alkane .................................................................385
Yuguang Cai and Lingbo Lu
13.1 Introduction .................................................................385
13.2 Part 1. The Chemical Patterning Method for Alkane
  Spreading Study .............................................................386
    13.2.1 Octadecyltrichlorosilane as the Substrate
    for Pattern Fabrication ...............................................386
    13.2.2 Fabricating Hydrophilic Chemical Patterns
    on OTS: The Scanning Probe Deep Oxidation
    Lithography ..............................................................388
    13.2.3 The Structure and Chemistry of the OTSpd Pattern ....390
    13.2.4 The Depth of the OTSpd Pattern ..........................391
    13.2.5 OTSpd Is Terminated with Carboxylic Acid Group ....393
    13.2.6 The Two-Step Patterning Method for Liquid
    Spreading Studies .......................................................395
    13.2.7 The Validity of the Two-Step Patterning Approach ....395
    13.2.8 The Time Scale of the Heating–Freezing
    Cycle and the Time Scale of the Spreading ..................396
## 13 Part 2. Structures of Long-Chain Alkanes on Surface

### 13.3 Alkane Structures on Hydrophilic Surfaces and on Hydrophobic Surfaces

### 13.3.2 The Multiple Domains Within a Seaweed-Shaped Layer

### 13.4 Part 3. The Role of Vapor During the Spreading of Liquid Alkane

### 13.4.1 The Stability of the Parallel Layer During the Spreading

### 13.5 Conclusion

## References

## 14 Self-assembled Transition Metal Nanoparticles on Oxide Nanotemplates

Emanuele Cavaliere, Stefano Agnoli, Gaetano Granozzi, and Luca Gavioli

### 14.1 Introduction

### 14.2 The Structure of the UT Oxide Layers

#### 14.2.1 TiOx/Pt(111)

#### 14.2.2 Al2O3/Ni3Al(111)

#### 14.2.3 FeO/Pt(111)

### 14.3 The Oxide Layers as Nanotemplates for Metal NPs

#### 14.3.1 Au and Fe on z'-TiOx-Pt(111)

#### 14.3.2 Metals on Al2O3/Ni3Al(111)

#### 14.3.3 Au on FeO/Pt(111)

### 14.4 Conclusions

## References

## 15 Mechanical and Electrical Properties of Alkanethiol Self-Assembled Monolayers: A Conducting-Probe Atomic Force Microscopy Study

Frank W. DelRio and Robert F. Cook

### 15.1 Introduction

### 15.2 Order, Orientation, and Surface Coverage

### 15.3 Conducting-Probe Atomic Force Microscopy

### 15.4 Theoretical Framework

#### 15.4.1 Elastic Adhesive Contact

#### 15.4.2 Effective Elastic Modulus of a Film–Substrate System

#### 15.4.3 Electron Tunneling Through Thin Insulating Films

### 15.5 Mechanical Properties

### 15.6 Electrical Properties

### 15.7 Conclusions and Future Directions

## References
16 Assessment of Nanoadhesion and Nanofriction Properties
of Formulated Cellulose-Based Biopolymers by AFM ..........473
Maurice Brogly, Ahmad Fahs, and Sophie Bistac
16.1 Introduction ...........................................473
16.2 Application of Cellulose-Based Biopolymers
in Pharmaceutical Formulations ...............................474
16.3 General Composition of Pharmaceutical Film Coatings ......475
16.3.1 Plasticizers ..............................................475
16.3.2 Surfactants and Lubricants ...............................476
16.4 Structure and Bulk Properties of HPMC Biopolymers ..........477
16.4.1 Chemical Structure of HPMC ............................477
16.4.2 Physicochemical Properties ...............................478
16.5 Physicochemical Properties of HPMC-Formulated Films ......481
16.5.1 Materials ................................................481
16.5.2 Pure HPMC Film Formation ..............................482
16.5.3 Formulation of HPMC–Stearic Acid Films
and HPMC–PEG Films ........................................482
16.5.4 Thermomechanical Properties of HPMC–PEG Films ......483
16.5.5 Thermo-Mechanical Properties of HPMC–SA Films ......483
16.6 Surface Properties of HPMC-Formulated Films Adhesion ....486
16.6.1 Surface Topography and Morphologies by AFM ..........486
16.6.2 AFM Force–Distance Experiments .......................490
16.6.3 LFM Nanofriction Experiments ..........................496
16.7 Conclusions ................................................502
References ......................................................503

17 Surface Growth Processes Induced by AFM Debris
Production. A New Observable for Nanowear ..................505
Mario D’Acunto
17.1 Introduction ................................................505
17.2 Single Asperity Nanowear Experiments .......................507
17.2.1 Surface Growth Processes Induced by AFM
Tip: Experimental Results ....................................511
17.3 A Model for Wear Debris Production in a UHV AFM
Scratching Test ...............................................513
17.3.1 Localisation of the Free Energy Changes
Due to Stressing AFM Tip ....................................514
17.3.2 Flux of Adatoms Induced by the AFM
Stressing Tip ................................................516
17.3.3 Evaluation of Number Cluster Density
via Nucleation Theory ........................................519
17.4 Continuum Approach for the Surface Growth Induced
by Abrasive Adatoms ..........................................523
17.5 Conclusions and Future Perspectives ........................529
References ......................................................530
18 Frictional Stick-Slip Dynamics in a Deformable Potential ........................................ 533
Djuidjé Kenmoé Germaine and Kofané Timoléon Crépin
18.1 Introduction .............................................................................................................. 533
18.2 The Model and Equation of motion ......................................................................... 535
  18.2.1 Potential and geometry ...................................................................................... 535
  18.2.2 Frictional Force and Static Friction as a Function of the Shape Parameter .... 537
  18.2.3 Equation of Motion ............................................................................................ 538
18.3 Numerical Results ..................................................................................................... 540
  18.3.1 Phase Space and Stroboscopic Observation ..................................................... 540
  18.3.2 Stick-Slip Phenomena ....................................................................................... 541
  18.3.3 Influence of the Shape Parameter on the Transition from Stick-Slip Motion to Modulated Sliding State .............................................................. 544
18.4 Pure Dry Friction ....................................................................................................... 545
18.5 Conclusion .................................................................................................................. 548
References ......................................................................................................................... 548

19 Capillary Adhesion and Nanoscale Properties of Water ........................................... 551
Michael Nosonovsky and Bharat Bhushan
19.1 Introduction .............................................................................................................. 551
19.2 Metastable Liquid Capillary Bridges ....................................................................... 553
  19.2.1 Negative Pressure in Water ............................................................................... 553
  19.2.2 Negative Pressure in Capillary Bridges in AFM Experiments ....................... 555
  19.2.3 Disjoining Pressure ............................................................................................ 557
  19.2.4 Calculating Pressure in Capillary Bridges ....................................................... 558
19.3 Capillarity-Induced Low-Temperature Boiling .......................................................... 561
19.4 Room Temperature Ice in Capillary Bridges ............................................................ 563
  19.4.1 Humidity Dependence of the Adhesion Force ................................................. 563
  19.4.2 Ice in the Capillary Bridges ............................................................................. 565
  19.4.3 Water Phase Behavior Near a Surface and in Confinement ......................... 566
19.5 Conclusions ............................................................................................................... 568
References ......................................................................................................................... 568

20 On the Sensitivity of the Capillary Adhesion Force to the Surface Roughness .............. 573
Michael Nosonovsky, Seung-Ho Yang, and Huan Zhang
20.1 Introduction .............................................................................................................. 573
20.2 Capillary Force Between Rough Surfaces ................................................................ 575
  20.2.1 Shape of the Meniscus ..................................................................................... 576
  20.2.2 Capillary Force .................................................................................................. 578
20.3 Case-Study: Two-Tiered Roughness ........................................................................ 581
20.4 Experimental Data .................................................................................................... 582
20.5 Conclusions .............................................................................. 585
References ......................................................................................... 586

Part III Industrial Applications

21 Nanoimaging, Molecular Interaction, and Nanotemplating of Human Rhinovirus .......................................................... 589
Markus Kastner, Christian Rankl, Andreas Ebner,
Philipp D. Pollheimer, Stefan Howorka, Hermann J. Gruber,
Dieter Blaas, and Peter Hinterdorfer
21.1 Introduction ............................................................................. 589
21.2 Contact Mode AFM Imaging .................................................. 590
21.3 Dynamic Force Microscopy Imaging ...................................... 593
21.3.1 Magnetic AC Mode (MAC mode) AFM Imaging ............... 594
21.4 Introduction to Molecular Recognition
Force Spectroscopy ........................................................................ 596
21.4.1 AFM Tip Chemistry ............................................................... 597
21.4.2 Applications of Molecular Recognition
Force Spectroscopy ........................................................................ 600
21.4.3 Topography and Recognition Imaging ............................. 603
21.5 Nanolithography ..................................................................... 605
21.5.1 Applications of Nanolithography ....................................... 605
21.5.2 Native Protein Nanolithography ....................................... 611
21.6 Imaging and Force Measurements of Virus–Receptor
Interactions ...................................................................................... 612
21.6.1 Virus Particle Immobilization and Characterization .......... 613
21.6.2 Virus–Receptor Interaction Analyzed
by Molecular Recognition Force Spectroscopy ......................... 619
21.6.3 Virus Immobilization on Receptor Arrays ....................... 624
References ......................................................................................... 633

22 Biomimetic Tailoring of the Surface Properties
of Polymers at the Nanoscale: Medical Applications ..................... 645
Valeria Chiono, Emiliano Descrovi, Susanna Sartori,
Piergiorgio Gentile, Mirko Ballarini, Fabrizio Giorgis,
and Gianluca Ciardelli
22.1 Introduction ............................................................................. 645
22.1.1 Biomimetic Material Design Criteria
for Biomedical Applications .......................................................... 645
22.1.2 Techniques for the Characterization
of Surfaces at the Nanoscale ......................................................... 648
22.2 Realization of Biomimetic Surfaces by Coating Strategies ....... 653
22.2.1 Generalities .......................................................................... 653
22.2.2 Coating Methods ............................................................... 655
22.3 Realization of Biomimetic Surfaces by Chemical Modification

22.3.1 Introduction of Functional Groups on Polymer Surfaces by Irradiation and Chemical Techniques

22.3.2 Immobilization of Bioactive and Biomimetic Compounds

22.3.3 Not-Conventional Approaches Towards Nanoscale Tailoring of Biomimetic Surfaces

22.4 Scanning Probe Techniques for Optical and Spectroscopic Characterization of Surfaces at High Resolution

22.4.1 Dynamic-Mode AFM for the Characterization of Organosilane Self-Assembled Monolayers

22.4.2 SNOM for Fluorescence Imaging

22.4.3 TERS for Chemical Mapping at the Nanoscale

22.5 Conclusions

References

23 Conductive Atomic-Force Microscopy Investigation of Nanostructures in Microelectronics

Christian Teichert and Igor Beinik

23.1 Introduction

23.2 Technical Implementation of C-AFM

23.3 C-AFM to Study Gate Dielectrics

23.3.1 Local Current-Voltage Characteristics, Dielectric Breakdown, and Two-Dimensional Current Maps

23.3.2 Investigation of High-k Dielectrics

23.4 Conductivity Measurements of Phase-Separated Semiconductor Nanostructures

23.4.1 Exploration of Supported Nanowires and Nanodots

23.4.2 Investigation of Defects in Ternary Semiconductor Alloys

23.5 C-AFM Investigations of Nanorods

23.6 Application of C-AFM to Electroceramics

23.7 Outlook to Photoconductive AFM

23.8 Overall Summary and Perspectives

References

24 Microscopic Electrical Characterization of Inorganic Semiconductor-Based Solar Cell Materials and Devices Using AFM-Based Techniques

Chun-Sheng Jiang

24.1 Introduction

24.2 AFM-Based Nanoelectrical Characterization Techniques

24.2.1 Scanning Probe Force Microscopy

24.2.2 Scanning Capacitance Microscopy

24.2.3 Conductive AFM

References
24.3 Characterization of Junctions of Solar Cells ..........................732
24.3.1 Junction Location Determination ..................................732
24.3.2 Electrical Potential and Field on Junctions ......................745
24.4 Characterization of Grain Boundaries
of Polycrystalline Materials..............................................758
24.4.1 Carrier Depletion and Grain Misorientation
on Individual Grain Boundaries
of Polycrystalline Si Thin Films .......................................759
24.4.2 Electrical Potential Barrier on Grain
Boundaries of Chalcopyrite Thin Films ...............................765
24.5 Localized Structural and Electrical Properties
of nc-Si:H and a-Si:H Thin Films and Devices .....................771
24.5.1 Localized Electrical Properties of a-Si:H
and nc-Si:H Mixed-Phase Devices ..................................772
24.5.2 Doping Effects on nc-Si:H Phase Formation ..................779
24.6 Summary .....................................................................784
References .......................................................................786

25 Micro and Nanodevices for Thermoelectric Converters ..........791
J.P. Carmo, L.M. Gonçalves, and J.H. Correia
25.1 Introduction ..............................................................791
25.1.1 Macrodevices .........................................................792
25.1.2 Microdevices ........................................................793
25.1.3 Nanodevices and Superlattices .................................795
25.2 Thermoelectric Converters Models ................................797
25.2.1 Peltier Effect on Hot and Cold Sides .........................800
25.2.2 Joule Heating .........................................................801
25.3 Thin-Films Technology for Thermoelectric Materials .........802
25.3.1 Bismuth and Antimony Tellurides Depositions ............804
25.3.2 Optimization of Thermoelectric Properties .................808
25.4 Superlattices for Fabrication of Thermoelectric
Converters .......................................................................809
25.4.1 Why Superlattices? .................................................809
25.4.2 Materials and Properties .......................................810
25.4.3 Fabrication ..........................................................810
References .......................................................................811
Index ...............................................................................813