

NANO SCIENCE AND TECHNOLOGY

NANO SCIENCE AND TECHNOLOGY

Series Editors:

P. Avouris B. Bhushan K. von Klitzing H. Sakaki R. Wiesendanger

The series NanoScience and Technology is focused on the fascinating nano-world, mesoscopic physics, analysis with atomic resolution, nano and quantum-effect devices, nano-mechanics and atomic-scale processes. All the basic aspects and technology-oriented developments in this emerging discipline are covered by comprehensive and timely books. The series constitutes a survey of the relevant special topics, which are presented by leading experts in the field. These books will appeal to researchers, engineers, and advanced students.

Nanoelectrodynamics

Electrons and Electromagnetic Fields
in Nanometer-Scale Structures

Editor: H. Nejo

Single Organic Nanoparticles

Editors: H. Masuhara, H. Nakanishi,
K. Sasaki

Epitaxy of Nanostructures

By V.A. Shchukin, N.N. Ledentsov,
D. Bimberg

Applied Scanning Probe Methods I

Editors: B. Bhushan, H. Fuchs,
S. Hosaka

Nanostructures

Theory and Modeling
By C. Delerue, M. Lannoo

**Nanoscale Characterisation
of Ferroelectric Materials**

Scanning Probe Microscopy Approach
Editors: M. Alexe, A. Gruverman

**Magnetic Microscopy
of Nanostructures**

Editors: H. Hopster, H.P. Oepen

Silicon Quantum Integrated Circuits

Silicon-Germanium Heterostructure
Devices: Basics and Realisations
By E. Kasper, D.J. Paul

The Physics of Nanotubes

Fundamentals of Theory, Optics
and Transport Devices
Editors: S.V. Rotkin, S. Subramoney

**Single Molecule Chemistry
and Physics**

An Introduction

By C. Wang, C. Bai

**Atomic Force Microscopy, Scanning
Nearfield Optical Microscopy
and Nanoscratching**

Application
to Rough and Natural Surfaces
By G. Kaupp

Applied Scanning Probe Methods II

Scanning Probe Microscopy
Techniques

Editors: B. Bhushan, H. Fuchs

Applied Scanning Probe Methods III

Characterization

Editors: B. Bhushan, H. Fuchs

Applied Scanning Probe Methods IV

Industrial Application

Editors: B. Bhushan, H. Fuchs

Nanocatalysis

Editors: U. Heiz, U. Landman

**Roadmap 2005
of Scanning Probe Microscopy**

Editor: S. Morita

Scanning Probe Microscopy

Atomic Scale Engineering
by Forces and Currents

By A. Foster, W. Hofer

A. Foster W. Hofer

Scanning Probe Microscopy

Atomic Scale Engineering by Forces
and Currents

With 116 Figures



Springer

Adam Foster
Laboratory of Physics
Helsinki University of Technology
Helsinki, Finland
asf@fyslab.hut.fi

Werner Hofer
Surface Science Research Centre
The University of Liverpool
Liverpool L69 3BX
Britain
whofer@liverpool.ac.uk

Series Editors:

Professor Dr. Phaedon Avouris
IBM Research Division
Nanometer Scale Science & Technology
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598, USA

Professor Dr. Bharat Bhushan
Ohio State University
Nanotribology Laboratory for
Information Storage and MEMS/NEMS
(NLIM)
Suite 255, Ackerman Road 650
Columbus, Ohio 43210, USA

Professor Dr. Dieter Bimberg
TU Berlin, Fakultät
Mathematik/Naturwissenschaften
Institut für Festkörperphysik
Hardenbergstr. 36
10623 Berlin, Germany

Professor Dr., Dres. h. c. Klaus von
Klitzing
Max-Planck-Institut für
Festkörperforschung
Heisenbergstr. 1
70569 Stuttgart, Germany

Professor Hiroyuki Sakaki
University of Tokyo
Institute of Industrial Science
4-6-1 Komaba, Meguro-ku
Tokyo 153-8505, Japan

Professor Dr. Roland Wiesendanger
Institut für Angewandte Physik
Universität Hamburg
Jungiusstr. 11
20355 Hamburg, Germany

ISSN 1434-4904

ISBN-10 0-387-40090-7
ISBN-13 978-0387-40090-7

Library of Congress Control Number: 2005936713

© 2006 Springer Science+Business Media, LLC

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America.

9 8 7 6 5 4 3 2 1

springer.com

Preface

This monograph on scanning probe microscopes (SPM) has three aims: to present, in a coherent way, the theoretical methods necessary to interpret experiments; to demonstrate how experimental results are in fact enhanced by theoretical analysis; and to describe the physical processes in solids that can be analyzed by this experimental method. In all these aims we focus on high-resolution experiments as the cutting edge in SPM, offering access to physical phenomena at the atomic scale.

The presentation is directed at an audience of practitioners in the field and newcomers alike. For one group, it presents an overview of methods, which are found in a widely disparate range of publications. Moreover, the immediate relevance for the physics of scanning probe microscopes is not usually obvious. For these practitioners, we aim at providing them with a toolbox that can be used in conjunction with existing numerical methods in solid state physics. For the other group, we seek to define the range of phenomena in solid state physics where scanning probe microscopes provide the best analytical tool at present. We also aim at demonstrating, in a step-by-step fashion, how physical problems in this field can be treated experimentally, and clarified with the help of state-of-the-art theoretical methods.

The monograph has four distinct parts: Part I, which includes Chapters 1 and 2, covers the basic physical principles and the experimental implementation of the instrument. Part II, Chapters 3–5, contains the core of the theoretical framework. Part III, Chapters 6–9, explains how the theoretical results can be used to analyze experimental data. We conclude the presentation with an outlook on the field, as it presents itself today, and try to estimate its potential development in the near future.

A systematic study of the present state in scanning probe microscopy is impossible without help from a large number of experimenters and theorists. In this respect the authors are grateful to their collaborators over the years in the field, and for the insights gained in many discussions. In particular we would like to thank the following individuals:

Wolf Allers, Andres Arnau, Clemens Barth, Alexis Baratoff, Roland Bennewitz, Richard Berndt, Flemming Besenbacher, Matthias Bode, Harald Brune, Giovanni Comelli, Pedro Echenique, Sam Fain, Roman Fasel, Andrew Fisher, Fernando Flores, Andrey Gal, Aran Garcia-Lekue, Franz Giessibl, Sebastian Gritschneider, Peter Grutter, Claude Henry, Regina Hoffmann, Lev Kantorovich, Josef Kirschner, Jeppe Lauritsen, Petri Lehtinen, Alexander Livshits, Christian Loppacher, Nicolas Lorente, Edvin Lundgren, Ernst Meyer, Rodolfo Miranda, Herve Ness, Risto Nieminen, Georg Olesen, Riku Oja, Olli Pakarinen, Krisztian Palotas, Ruben Pérez, John Pethica, John Polanyi, Josef Redinger, Michael Reichling, Jeff Reimers, Neville Richardson, Federico Rosei, Alexander Shluger, Alexander Schwarz, Udo Schwarz, Peter Sushko, Peter Varga, Matt Watkins, Roland Wiesendanger, and Robert Wolkow.

A first draft of the book was sent out to several colleagues for their comments, criticism, and suggestions for possible improvements. Their feedback was invaluable for improving and clarifying the presentation, both from a theoretical angle, and from the viewpoint of experiments. We would like to thank them particularly for the time and effort they devoted to this careful reading.

Contents

Preface	v
Mathematical Symbols	xiii
1 The Physics of Scanning Probe Microscopes	1
1.1 Experimental methods	2
1.2 Theoretical methods	3
1.3 Local probes	4
1.3.1 Principles of local probes	6
1.3.2 Surface preparation	7
1.4 Summary	8
References	9
2 SPM: The Instrument	11
2.1 SPM Setups	11
2.1.1 STM setup	12
2.1.2 SFM setup	12
2.1.3 Tip and surface preparation	16
2.2 Experimental development	17
2.2.1 STM Case 1: Au(110) and Au(111)	19
2.2.2 STM Case 2: Resolution of Spin States	21
2.2.3 SFM Case 1: silicon (111) 7×7	26
2.2.4 SFM case 2: cubic crystals	29
References	33
3 Theory of Forces	37
3.1 Macroscopic forces	37
3.1.1 Van der Waals force	37
3.1.2 Image forces	40
3.1.3 Capacitance force	40
3.1.4 Forces due to tip and surface charging	42

3.1.5	Magnetic forces	43
3.1.6	Capillary forces	43
3.2	Microscopic forces	44
3.2.1	Theoretical methods for calculating the microscopic forces	45
3.3	Forces due to electron transitions	48
3.4	Summary	52
	References	53
4	Electron Transport Theory	55
4.1	Conductance channels	55
4.2	Elastic transport	58
4.2.1	The scattering matrix	58
4.2.2	Transmission functions	60
4.2.3	A brief introduction to Green's functions	63
4.2.4	Green's functions and scattering matrices	69
4.2.5	Scattering matrices for multiple channels	70
4.2.6	Self-energies Σ	72
4.3	Nonequilibrium conditions	77
4.3.1	Finite-bias voltage	78
4.3.2	Spectral functions and charge density	79
4.3.3	Spectral functions and contacts	81
4.3.4	Self-energy Σ again	82
4.3.5	Nonequilibrium Green's functions	88
4.3.6	Electron transport in nonequilibrium systems	89
4.4	Transport within standard DFT methods	92
4.4.1	Green's function matrix	92
4.4.2	General self-consistency cycle	94
4.4.3	Self-energy of the leads	94
4.4.4	Hartree potential and Hamiltonian of the interface	96
4.4.5	Self-energies of the interface	96
4.4.6	Nonequilibrium Green's functions of the interface	98
4.4.7	Calculation of nonequilibrium transport properties	98
4.5	Summary	100
	References	101
5	Transport in the Low Conductance Regime	103
5.1	Tersoff–Hamann(TH) approach	104
5.1.1	Easy modeling: applying the Tersoff–Hamann model	104
5.2	Perturbation approach	106
5.2.1	Explicit derivation of the tunneling current	107
5.2.2	Tip states of spherical symmetry	109
5.2.3	Magnetic tunneling junctions	110
5.3	Landauer–Büttiker approach	113
5.3.1	Scattering and perturbation method	115

5.4	Keldysh–Green’s function approach	116
5.5	Unified model for scattering and perturbation	117
5.5.1	Scattering and perturbation	117
5.5.2	Green’s function of the vacuum barrier	118
5.5.3	Zero-order current	120
5.5.4	First-order Green’s function	123
5.5.5	Interaction energy	125
5.6	Electron–phonon interactions	127
5.7	Summary	130
	References	130
6	Bringing Theory to Experiment in SFM	133
6.1	Tip–surface interactions in SFM	133
6.2	Modeling the tip	136
6.2.1	Silicon-based models	137
6.2.2	Ionic models	138
6.3	Cantilever dynamics	140
6.3.1	SFM at small amplitudes	144
6.3.2	Atomic-scale dissipation	145
6.4	Simulating images	146
6.4.1	Test system	146
6.4.2	Microscopic interactions	148
6.4.3	Tip convolution	152
6.5	Summary	155
	References	156
7	Topographic images	159
7.1	Setting up the systems	159
7.1.1	Ru(0001)-O(2×2)	160
7.1.2	Al(111)	162
7.2	Calculating tunneling currents	165
7.2.1	Ru(0001)-O(2×2)	166
7.2.2	Al(111)	170
7.2.3	Cr(001)	176
7.2.4	Fe(001)	177
7.2.5	Metal alloys: PtRh(001)	178
7.2.6	Magnetic surfaces: Mn/W(110)	179
7.3	Silicon (001)	182
7.3.1	Saturation of Si(001) by hydrogen	183
7.4	Adsorbates on Si(001)	184
7.4.1	Acetylene C ₂ H ₂ on Si(001)	185
7.4.2	Benzene C ₆ H ₆ on Si(001)	187
7.4.3	Maleic anhydride C ₄ O ₃ H ₂ on Si(001)	189
7.5	Titanium dioxide (110)	190
7.5.1	Simulations of ideal and defective surfaces	191

7.5.2 Acid adsorption on the TiO ₂ (110) surface	192
7.6 Calcium difluoride (111)	194
7.7 Summary	203
References	203
8 Single-Molecule Chemistry	207
8.1 Introduction	207
8.2 Manipulation of atoms	208
8.2.1 Modeling atomic manipulation	210
8.3 Phonon excitation	213
8.3.1 Theoretical procedure	215
8.3.2 Applications	215
8.4 Summary	218
References	220
9 Current and Force Spectroscopy	221
9.1 Current spectroscopy	221
9.1.1 Differential tunneling spectroscopy simulations	223
9.1.2 Differential spectra on noble metal surfaces	229
9.1.3 Spectra on magnetic surfaces	235
9.1.4 Present limitations in current spectroscopy	242
9.2 Force spectroscopy	246
9.2.1 Silicon 7 × 7 (111) surface	247
9.2.2 Calcium Difluoride (111) surface	249
9.2.3 Potassium bromide (100) surface	252
9.3 Summary	254
References	255
10 Outlook	259
10.1 Challenges	259
10.2 The future	263
References	263
Appendix	265
A.1 Green's functions in the interface	265
A.1.1 Green's function and spectral function	265
A.1.2 Contacts	266
A.1.3 Electron density	266
A.1.4 Zero-order Green's function	267
A.1.5 Consistency check: Schrödinger equation	267
A.1.6 Consistency check: definition of Green's functions	268
A.2 Transmission probability	268
A.2.1 Contacts	268
A.2.2 Tunneling current of zero order	269
A.3 First-order Green's function	270

A.4	Recovering the Bardeen matrix elements	271
A.5	Interaction energy	272
A.6	Trace to first order	274
A.6.1	Term A	274
A.6.2	Term B	276
A.6.3	Term C	277
A.6.4	Taking the decay into account	278
Index	279

Mathematical Symbols

Symbol	Name	Unit	Chapter
V	Bias potential	volt (V)	4
B	Magnetic field	tesla (T) = V s/m ²	3
μ	Magnetic moment	$\mu_B = e\hbar/2mc$	3
	Chemical potential	eV	4
H	Hamiltonian	eV	3
ψ_{μ}, χ_{ν}	Eigenvector	(1/Å) ^{3/2}	3
$\Gamma_{\mu\nu}$	Transition rate	1/s	3
Γ	Contact	eV	4
$I, I_{\mu\nu}$	Current	ampere (A)	3
E_{μ}, E_{ν}	Eigenvalues	eV	3
E_F	Fermi energy	eV	4
σ	Broadening	eV	3
$\rho(\mathbf{r}), n(\mathbf{r})$	Electron density	(1/Å) ³	3
k	Electron wavevector, mode	1/Å	4
k_F	Fermi wavevector	1/Å	4
$f(E)$	Fermi distribution	unity	4
v_k	Electron velocity	m/s	4
R_C	Contact resistance	ohm(Ω)	4
G, σ	Conductance	Ω ⁻¹	4
Σ	Self energy	eV	4
T	Transmission	unity	4
S	Scattering matrix	unity	4
t	Transmission coefficient	unity	4
r	Reflection coefficient	unity	4
\bar{T}	Transmission function	unity	4

Symbol	Name	Unit	Chapter
G_{in}, G_{out}	Incoming and outgoing Green's function	(eV) $^{-1}$	4
$G^R (= G_{out})$	Retarded Green's function (GF)	(eV) $^{-1}$	4
$G^A (= G_{in})$	Advanced Green's function (GF)	(eV) $^{-1}$	4
ϵ_i	Eigenvalue	eV	4
U	Potential	eV	4
Σ^R	Retarded self-energy (SE)	eV	4
Σ^A	Advanced self-energy (SE)	eV	4
Γ_R	Retarded contact	eV	4
Γ_A	Advanced contact	eV	4
A	Spectral function	(eV) $^{-1}$	4
$\Sigma^{<}$	Nonequilibrium SE (less)	eV	4
$\Sigma^{>}$	Nonequilibrium SE (more)	eV	4
$G^{<}$	Nonequilibrium GF (less)	(eV) $^{-1}$	4
$G^{>}$	Nonequilibrium GF (more)	(eV) $^{-1}$	4
D	Phonon correlation function	eV	4
\mathbf{J}	Current density	A/m 2	4
f	Force	newton (N)	3
V	Potential	electron volt (eV)	3
E	Energy	eV = 1.6 $\times 10^{-19}$ joule	3
C	Capacitance	farad (F)	3
k	Cantilever spring constant	(N/m)	6
ω_0, f_0	Cantilever equilibrium frequency	(s $^{-1}$)	6
A_0, A	Cantilever amplitude	(m)	6
Q	Quality factor	unity	6
U_{bias}	Compensating bias in SFM	(V)	6
H	Hamaker constant	(joule)	6
R	Tip radius	(m)	6
h	Equilibrium height of cantilever	(m)	6
Δf	Frequency shift	(Hz)	6
γ_0	Normalized frequency shift	(fN \sqrt{m})	6