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Introduction

Scanning Probe Microscopy Techniques for Electrical and Electromechanical Characterization

S.V. KALININ AND A. GRUVERMAN

Progress in modern science is impossible without reliable tools for characterization of structural, physical, and chemical properties of materials and devices at the micro-, nano-, and atomic scale levels. While structural information can be obtained by such established techniques as scanning and transmission electron microscopy, high-resolution examination of local electronic structure, electric potential and chemical functionality is a much more daunting problem. Local electronic properties became accessible after the development of Scanning Tunneling Microscopy by G. Binnig and H. Rohrer in 1981 at IBM Zurich 25 years ago—an invention that earned its authors the Nobel Prize in Physics five years later [1]. Based on the quantum mechanical tunneling between an atomically sharp metallic tip and conductive surface, scanning tunneling microscopy (STM) has become the first instrument to generate real-space images of surfaces with atomic resolution and has triggered development of new classes of STM-related techniques. In 1986, Binnig, Quate, and Gerber demonstrated atomic force microscope (AFM) based on the mechanical detection of the Van der Waals forces between the tip and the surface using a pliable cantilever [2]. It was almost immediately realized that AFM could be extended to map forces of various types, such as magnetic and electrostatic forces, as well as for probing chemical interactions. This dual capability of probing currents and forces at the nanometer and atomic level has led to a rapid growth of a variety of scanning probe microscopy (SPM) techniques over the last two decades. Techniques such as AFM, magnetic force microscopy (MFM), electrostatic force microscopy (EFM), scanning capacitance microscopy (SCM), near-field scanning optical microscopy (NSOM), and others have emerged to provide capability to access local electrical, magnetic, chemical, mechanical, optical, and thermal properties of materials on the nanometer scale. It has been demonstrated that the SPM approach allows not only imaging, but also control and modification of the local structure and material functionality at the nano- and atomic level. As a consequence, the last two decades have witnessed an explosive growth in application of SPM techniques in a wide spectrum of fields of science, ranging from condensed matter physics, chemistry and materials science to medicine and biology. It will not be an exaggeration to say that the rapid development of nanoscience and nanotechnology in the last two decades was strongly stimulated by the availability of SPM techniques, and in turn constantly stimulates development of novel SPM probes.

In parallel with the development of ambient SPM techniques, a significant progress was achieved in the development of high-resolution ultrahigh vacuum (UHV) SPM systems. Compared to ambient systems, UHV operation imposes major difficulties in the sample preparation and microscope operation. However, it provides a potential for true atomic resolution imaging both in STM and AFM modes. STM sensitivity to local electronic properties provided physicists with the tool to probe electronic phenomena such as edge states in quantum Hall systems, phase separation and charge ordering in strongly correlated oxides, and transport in mesoscopic conductors. In the context of surface science and catalysis, the capability to probe chemical and photochemical processes on the atomic level have emerged. Many ambient electrostatic and electromechanical probes can be implemented in UHV conditions as well. As such, UHV SPM paves the way to the investigation of fundamental electrical and mechanical properties of materials at the atomic level.

One of the primary challenges in the SPM applications to local electrostatic and electromechanical phenomena is quantitative analysis of the acquired signal. Indeed, a typical SPM image, were it a surface potential map, electromechnical activity map, capacitance distribution or a gate potential image, provides a quantitative measure of local surface properties. However, image formation mechanisms in most SPM techniques are extremely complex due to the geometry of tip-surface system and multitude of contributing interactions. For example, noticeable progress in understanding such well-established topographic imaging techniques as non-contact AFM or intermittent contact AFM was achieved only in the last few years. The problem of quantitative interpretation of the local property map is even more difficult; further progress requires thorough understanding of the image formation mechanisms through combination of first-principles methods to describe atomistic processes at tip-surface junction, continuum mechanics, and electrostatics to describe long-range interactions and cantilever dynamics. However, once achieved, this transforms SPM from a mere imaging tool into a quantitative probe of local physical phenomena on the nanoscale, realizing an age-old dream of precise measurements of physical and chemical properties on nanometer, molecular, and ultimately atomic levels.

Tremendous growth in SPM instrumentation, theory, and applications have resulted in a large number of monographs, books, and reviews addressing general aspects of SPM [3–12], including STM studies of atomic structure and electronic phenomena [13–16], electrochemical SPM [17], theoretical aspects of AFM [18] and STM [19], nanofabrication [20], application of SPM in biology and bioengineering [21–24]. However, there is a long-due need to bring together a permanently growing knowledge base on the practical and theoretical aspects of advanced electrical and electromechanical SPM techniques. The goal of this book is to provide a comprehensive reference on the nanoscale characterization of *electrical and mechanical properties of functional materials* by SPM techniques and to make readers aware of tremendous developments in the field in the last decade. This book provides a link between well-established ambient SPM techniques and UHV SPM, materials and device applications, and theoretical basis for interpretation of SPM data. While a number of SPM techniques have been used in a variety of scientific fields ranging from semiconductors to ferroelectrics to optics, in this book various aspects of these techniques will be presented on an interdisciplinary basis. By bringing together critical reviews written by the leading researchers from the different scientific disciplines relevant information will be conveyed that will allow readers to learn more about the fundamental and technological advances and future trends in the different fields of nanoscience.

The book comprises 35 chapters divided into four parts. Part I introduces the reader to the technical and instrumental features of SPM techniques for electrical, electromechanical, transport, near-field optical and microwave characterization. Part II deals with the SPM imaging at the resolution limit in molecular systems, complex oxides, and low-dimensional structures, as well as theoretical underpinnings of SPM. Part III illustrates application of SPM to electrical and electromechanical characterization of a broad spectrum of materials ranging from semiconductors to polymers to biosystems. Finally, Part IV discusses SPM-based devices and nanofabrication methods.

Chapter I.01 by A. P. Baddorf reviews technical aspects of Scanning Tunneling Potentiometry (STP), an extension of STM to transport measurements. The chapter discusses applications of STP to probe mesoscopic transport in low-dimensional systems, defect-induced scattering, and transport tin phase-separated strongly correlated oxides. Further prospects of transport imaging with nanometer and atomic resolution are discussed. Chapter I.02 by P. Eyben *et al.*, discusses implementation, probe choice, calibration, and theoretical aspects of Scanning Spreading Resistance Microscopy, the technique that has emerged as one of the primary tools for dopant profiling and device characterization and failure analysis on the nanoscale. Chapter I.03 by J. Kopanski discusses principles of SCM and its application to electrical characterization of semiconductors and dielectric films, integrated circuit failure analysis, quantitative dopant profiling, and optical pumping for carrier mobility measurements. Chapter I.04 by T. Glatzel *et al.*, discusses Kelvin Probe Force Microscopy (KPFM), introduces principles of amplitude and frequency detection in KPFM and relevant theory. The chapter describes in detail resolution theory and probe function determination in KPFM, paving the way for quantitative measurements of electrostatic surface potentials, photovoltaic phenomena, and work function distributions. Chapter I.05 by O'Hayre *et al* introduces two SPM techniques for probing frequency-dependent transport at the nanoscale. Nanoimpedance microscopy is a current-based technique combining conventional impedance spectroscopy with AFM. Scanning Impedance Microscopy (SIM) is a force-based technique in which AFM probe detects amplitude and phase of local voltage oscillations induced by lateral periodic bias applied through macroscopic electrodes. These methods are similar to conventional 4-probe resistance measurements, in which AFM tip is used as a moving electrode, providing advantage of high spatial resolution. Piezoresponse Force Microscopy (PFM) and its application for imaging, spectroscopy, and manipulation of ferroelectric domains are reviewed in Chapter I.06 by Kholkin *et al.* The chapter briefly discusses principles and image formation mechanism in PFM, as well as its application to imaging of polar nanodomains in ferroelectric relaxors, high-density data storage, and ferroelectric capacitor characterization. Near-Field Microwave Microscopy is described in Chapter I.07 by Anlage *et al.* The authors review the basic concepts of near-field interactions between a source and sample, present a historical overview and discuss quantitative approaches to interpretation of near-field microwave images. Chapter I.08 by A. Bouchelier and R. Bachelot discusses implementation and application of apertureless Near Field Optical Microscopy and related techniques. The tip enhancement of electromagnetic field allows imaging and spectroscopy of optical phenomena on the length scales well below optical wavelength. Application of SPM techniques to the study of electrochemical interfaces is discussed in Chapter I.09 by T. Smith and K. Stevenson. These techniques include Electrochemical Scanning Tunneling Microscopy (EC-STM), Electrochemical Atomic Force Microscopy (EC-AFM), and hybrid techniques such as Scanning Electrochemical Microscopy - Atomic Force Microscopy (SECM-AFM) and Local Electrochemical Impedance Spectroscopy - Atomic Force Microscopy (LEIS-AFM). Application of electrochemical SPM in the emerging areas of energy storage and conversion, corrosion, catalysis, and electrochemical deposition processes are described. Recent theoretical and instrumental developments in high-frequency near field probes are reviewed in Chapter I.10 by C. Paulsen and D. Van der Weide, providing a unified description of a broad range of optical, infrared, and microwave probes. The chapter also provides a theoretical framework for the interpretation of near-field experiments, as well as extensive literature survey and discussion of future potential of these techniques.

Part II of the book combines a number of reviews on experimental and theoretical aspects of fundamental electrical and electromechanical phenomena on the nano- and atomic scales and describes the recent instrumental and theoretical advances in high-resolution imaging of electrical, transport, and electromechanical properties on surfaces, low-dimensional systems, nanotubes and nanowires, and molecules. In Chapter II.01, M. Morgenstern describes applications of STM and AFM for probing transport phenomena in 2D electron systems in high-mobility III-V semiconductors. Imaging nanomagnetic and spin structure of materials with nanometer and atomic resolution by Spin–polarized STM (SpSTM) is described in chapter II.02 by W. Wulfhekel *et al.* Probe fabrication, one of the key components for successful SpSTM experiment, is discussed in detail. The principles and advantages of constant-current, spectroscopic, and differential magnetic modes of SpSTM are discussed. The applications for imaging ferromagnetic and antiferromagnetic surfaces of bulk materials and thin-film systems are illustrated. Approaches for fabrication and probing of molecular electronic devices are described in Chapter II.03 by K. Kelly and P. S. Weiss. Self-assembled monolayers are utilized to isolate molecules with various electronic properties to determine the fundamental transport mechanisms, and the relationships between molecular structure, environment, connection, coupling, and electrical functionality. STM of individual conjugated molecules inserted in alkanethiol SAM illustrates a rich gamut of electronic behavior, including reversible conductance switching. SPM imaging and control of charge transport in individual carbon nanotubes and carbon nanotube networks are discussed in Chapters II.04 and II.05. In Chapter II.04, C. Staii *et al.*, discuss the application of Scanning Gate Microscopy (SGM), EFM, SIM, and thermal SPM to probe electronic structure of individual defects in carbon nanotube circuits. Applications of high-frequency SGM and SIM and memory effects in nanotube circuits are presented. In Chapter II.05, M. Stadermann and S. Washburn describe the application of conductive SPM to networks of carbon nanotubes to map current paths and differentiate semiconducting and metallic nanotubes, as well as to probe conductance decay at nanotube junctions. In Chapter II.06, V. Meunier and P. Lambin apply a density functional theory to model STM images of carbon nanotubes and grain boundaries in graphene. The transport properties of single-wall nanotubes and tip-tube interactions in SGM and EFM are modeled using non-equilibrium Green's function theory. In Chapter II.07, S. Hasegawa discusses instrumentation and application of multiple-probe STM for surface transport studies. Precise positioning of conductive tips allows probing conductance through step edges and orientation dependence of conductance. Ultimately, this technique is being developed as a probe of a surface transport Green's function. Principles and application of Dynamic Force Microscopy (DFM), also referred to as Non-Contact Atomic Force Microscopy, are described in Chapter II.08 by U. Schwarz and H. Hölscher. Application of DFM for atomic-resolution imaging of conductors, semiconductors, and insulators are described. DFM probing of surface electrostatic properties including charge distributions around charged monoatomic vacancies and individual doping atoms in semiconductors are illustrated. Application of high-resolution STM to probe atomic and electronic structure and electronic inhomogeneities in manganites are described in Chapter II.09 by C. Renner and H. Ronnow. These studies illustrate the impact high-resolution probes can have on understanding the fundamental physical phenomena in strongly-correlated complex oxides including manganites, cuprates, and relaxors.

Part III includes a series of reviews on application of ambient SPM techniques for characterization of transport, electromechanical, optical, and electrical phenomena in materials, heterostructures, and devices. A number of topics, such as transport in semiconductor optoelectronic and electronic structures, imaging and quantification of electroactive grain boundaries, dislocations and interfaces, electromechanical imaging of biological systems, and photovoltaic phenomena in photosynthetic molecules are covered. In Chapter III.01, S. Kuntze *et al.*, describe application of Scanning Voltage Microscopy (SVM) and Scanning Differential Resistance Microscopy (SDRM) for *in-situ* imaging of operational electronic devices. Examples include direct observation of the current blocking breakdown in a buried heterostructure laser, effect of current spreading inside actively biased ridge waveguide lasers, origin of anomalously high series resistance encountered in ridge lasers and electron over-barrier leakage. Instrumentation and imaging mechanisms in SVM and SDRM are discussed and sources of artifacts (such as circuit time constants and photocurrent) are analyzed. Chapter III.02 by I. Lee and E. Greenbaum describes application of KPFM and EFM to probe photovoltaic activity in

Photosystem I (PSI) reaction centers, DNAs, protein microarrays on surfaces, and PSI at the air–liquid interfaces, providing insights into fundamental mechanisms of photosynthesis. In Chapter III.03, A. Gruverman *et al.*, describe application of Piezoresponse Force Microscopy (PFM) to probe the structure of biomaterials with nanometer scale spatial resolution, utilizing ubiquitous presence of piezoelectricity in biopolymers. Examples of bioelectromechanical imaging include human tooth, femur canine cartilage, deer antler, and butterfly *Vanessa Virginiensis* wing scales. A potential of PFM to study the internal structure and orientation of the protein microfibrils is illustrated. Application of SCM for failure analysis of semiconductor devices, carrier dynamics in FET channel during device operation, and visualization of radiation effects are described in Chapter III.04 by C. Nakakura *et al.* Extensive practical experimental details and a broad range of examples render this chapter extremely useful for SCM practitioners. Application of KPFM for local studies of surface band bending, defects, and grain boundaries in semiconductors are presented in Chapter III.05 by Rosenwaks *et al.* This chapter also reviews recent KPFM studies of local electronic phenomena in quantum wells and organic light-emitting devices, and develops KPFM framework for spectroscopic studies of surface states. Chapter III.06 by B. Rodriguez *et al.*, summarizes recent applications of SPM to nanoscale studies of the electric properties of III-nitride thin films, bulk crystals and heterostructures. The chapter illustrates the complementary application of techniques such as KPFM, conductive AFM, and PFM to probe charge defects and inversion boundaries in these materials. Measurement of surface polarity and the screening mechanism of III-nitrides using SPM and Photoelectron emission Microscopy are discussed. In Chapter III.07, S. Cohen gives a broad perspective on electron flow in molecular systems. This research is motivated by advent of molecular electronics, drive to understand a charge transfer in biological systems, and functionality and performance bottlenecks in devices such as organic light emitting diodes and dye-sensitized solar cells. SPM measurements of electron flow through DNA and STM measurements of isolated molecules on a semiconductor surface are discussed in detail. The principles and instrumentation for local conductance imaging of perovskite thin films are discussed in Chapter III.08 by C. Szot *et al.* Imaging of conductive paths in insulating oxides provides real-space information on electrical activity of defects and dislocations. The role of surface adsorbates on electrical and PFM imaging is discussed. In Chapter III.09, T. Ishida *et al.*, describe methods for evaluating the electric properties of conjugated molecules embedded in alkanethiol SAMs, including electrical conduction and barrier height measurements of SAMs and single molecules using STM and conductive AFM. Finally, in Chapter III.10, W. Silveira *et al.*, review application of high-sensitivity EFM to probe charge transport and local electronic properties in organic electronic devices. Instrumentation and contrast formation in EFM are also described in detail.

Part IV of the book is devoted to the SPM-based devices and nanofabrication methods. In Chapter IV.01, N. Naujoks *et al.*, describe application of charge lithography for fabrication of nanostructures. In this method, charged patterns deposited by an AFM tip are used to attract oppositely charged nanoparticles, resulting in a stable deposited pattern. Nano-oxidation of semiconductor and metal surfaces is described in Chapter IV.02 by J. Dagata. The author introduces the method, describes relevant technical and theoretical details, and discusses the potential and limitations of this nanofabrication technique. Nanofabrication on the atomic level is introduced in Chapter IV.03 by P. Albrecht *et al.* Development of the atomic-resolution hydrogen resist technique and its application to the templated self-assembly of molecular systems on silicon are described. A mechanism of tip-induced desorption is determined through isotope studies. An integration of carbon nanotubes with silicon and the III-V compound semiconductors is explored. Ferroelectric lithography is described in Chapter IV.04 by D. Li and D. Bonnell. Several methods, including contact electrode, SPM, and e-beam are used to pattern domains on ferroelectric surfaces in the absence of a top electrode. The domain specific reactivity in metal photodeposition process and domain patterning are combined into a fabrication process that is demonstrated for several classes of magnetic and optoelectronic nanostructures. Chapter IV.05 by M. Lewis *et al.* introduces several methods of nanopatterning in SAM systems. Additive, subtractive, and exchange approaches for SAM lithography are described. Finally, in Chapter IV.06, S. Hong and N. Park describe application of resistive SPM probes for data storage in ferroelectric medium, potentially opening the pathway for Tbit density storage.

Overall, the book is intended to present a unified outlook on all aspects of modern electrical and electromechanical probes and combine practical and theoretical aspects of these techniques and applications ranging from fundamental physical studies to device characterization and failure analysis to nanofabrication. We hope that this book will develop new educational advances by helping students and postdoctoral scientists significantly improve their knowledge on the new applications of SPM and on the nanoscale properties of a number of functional materials, such as electroactive polymers, biomolecules, piezoelectrics, and so on. It is our expectation that with SPM becoming a must-know technique in many scientific disciplines, this book will become a valuable source of information for interdisciplinary research that can be used as a reference handbook.

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