

Preface

Scanning probe microscopy (SPM) has become a mainstream technique of nanoscience and nanotechnology by providing easy to use methodology for non-invasive imaging and manipulation on the nanometer and atomic scales. Beyond topographic imaging, SPM techniques have found an extremely broad range of applications in probing electrical, magnetic, optical and mechanical properties – often at the level of several tens of nanometers [1, 2], opening the way to an understanding material functionality and interactions at their fundamental length scales [3].

For more than a decade after the introduction of the first commercial microscopes in late 1980s, SPM evolved as a primarily qualitative imaging method. The surface topographic and functional (e.g., magnetic, electrostatic, or mechanical) images were acquired in parallel and were interpreted by an observer. A common feature for these measurements was that only a single or a small number of parameters describing the local properties were obtained; furthermore, information contained in complementary images was usually ignored (or interpreted solely within the limits of a cursory examination). These limitations stemmed primarily from the inherent limits of data processing electronics available at the time, the dearth of well-characterized probes, relative novelty of the field, and only a small number of available microscopic platforms. Nevertheless, even qualitative imaging capabilities have provided multiple opportunities in research for almost a decade. Ironically, this multitude of research opportunities has somewhat shifted the focus of research and development away from further technological advances in SPM.

In contrast, the last several years have seen tremendous progress in force-based SPMs. The emergence of digital control and field-programmable gate array electronics have greatly increased the data acquisition and processing speed, allowing multiple information channels to be acquired without compromising image acquisition speed or quality. Similarly, recent advances in the theoretical understanding of contrast mechanisms in SPM and increasing market competition have lead to the rapid emergence of multimodal and spectroscopic SPM methods, including dual excitation frequency SPM (Asylum) [4–6], HarmoniX (Veeco) [7, 8], and configurable multiple frequency lock-ins by Agilent [9] and Nanonis [10]. This progress in fast data acquisition electronics and signal processing in SPM has allowed multiple information channels to be collected in the 1–10 ms range of a single pixel. This development in turn enabled several families of rapid multimodal and spectroscopic

imaging SPM techniques. Examples include band excitation [11] and digital lock-in [12] SPM, which allow rapid sampling of a response–frequency curve at each location on a surface, switching spectroscopy PFM [13] for mapping the ferroelectric behavior, rapid force–volume imaging [14] modes ushered in by small (high frequency) cantilever technology, torsional resonance imaging for mechanical property characterization [7], and many others.

Advances in ultra-stable STM platforms resulted in a resurgence of STM-based spectroscopic methods, such as continuous imaging tunneling spectroscopy (CITS), dI/dV (density of states), dI/dz (work function), and d^2I/dv^2 (vibrational) imaging [15]. It is not an exaggeration to say that most of the recent advances in nanoscale science and condensed matter physics have been linked to the development of particular spectroscopic imaging modes – including imaging high-temperature superconductivity by Davies [16] and Yazdani [17], optically assisted SPM introduced by Ho [18], mechanical HarmoniX imaging introduced by Sahin [7, 8], and many others.

In parallel with these instrumental developments, significant progress was achieved in development of SPM methods that combine novel experimental modalities, including thermal and mass-spectrometry assisted methods, novel electrical characterization modes, and combinations between SPM and beam techniques including focused X-ray and electron microscopy. Common to all of these methods is the acquisition of complex multidimensional data sets, typically comprised local spectroscopic responses of materials to external stimuli, or multiple parallel channels of information. At the same time, this allows not only the visualization of the structure of surfaces on the nanometer scale, but also insight into their functionalities.

In this book, we aim to provide an overview of several notable recent developments in the field of functional SPM enabled by the advances in sample preparation and platform development, ultra-high resolution imaging, novel combined imaging modes, signal detection, data interpretation, and novel dynamic modes.

In Chap. 1, Maksymovych delineates the applications of scanning tunneling microscopy and spectroscopy for probing chemical processes on a single-molecule level. While applications of STM for imaging surface structures on the molecular and atomic level has become common, he illustrates how STM can provide insight into chemical functionality of molecular systems. These range from tip-induced surface chemical reactions including long-range hot-electron induced phenomena to time spectroscopies of single molecule transformations to the minute details of the vibrational spectra probed by inelastic electron spectroscopy.

High-resolution studies of biological functionality are addressed in the contribution by Malkin and Plomp (Chap. 2). Creatively combining the insights from the crystallization theory and high resolution atomic force microscopy imaging, the authors demonstrate that the molecular structure of the biological objects such as bacterial spores and viruses contains a wealth of information on their functionality and life cycle. Beyond providing a highly illuminating and often spectacular view of microscopic structure of these systems, these studies can be used to identify individual strains of bacterial systems, and establish their developmental pathways in response to changes in environment, chemical stimulants, and therapeutics.

The recent advances in spectroscopic and multimodal SPMs enabled by novel data acquisition and analysis methods are summarized in Chaps. 3–6. Holscher et al. provide an in-depth description of dynamic force spectroscopy and microscopy in ambient conditions. Based on the precise measurements of the dynamic response of the cantilever, the complete force–distance curve and associated mechanical functionalities can be extracted. This topic is further developed in the contribution by Hurley (Chap. 4) who discusses probing mechanical functionality on the nanoscale, including mechanical properties and adhesive behavior, using Atomic Force Acoustic Microscopy-based methods. The signal formation mechanisms, detailed data interpretation, and multiple experimental examples are discussed.

The new paradigm in dynamic SPMs – multiple frequency methods – is discussed in Chap. 5 by Proksch. While the classical SPMs utilize purely sinusoidal excitation signals corresponding to a single frequency in the Fourier domain, the use of multiple excitation and detection frequencies allows systematic mapping of frequency dispersion of the signal. Strategies for nanoscale mapping of dissipative interactions via multifrequency detection are discussed in detail.

Finally, in Chap. 6 Sahin describes the tensional resonance method for probing dynamic mechanical properties. Utilizing decoupling between the flexural and torsional oscillation modes and difference in the corresponding resonant frequencies, the dynamic probing of the force–distance curve at each spatial pixel is possible. This approach is demonstrated for multiple applications, including phase transitions in polymers and high-resolution imaging of biological systems.

The contribution by Ovchinnikova in Chap. 7 discusses in depth the rapidly emerging chemical imaging methods based on the combination of SPM and mass-spectrometry. While SPM is renowned for high spatial resolution, the amount of chemical information is typically limited. At the same time, modern mass-spectrometry methods provide ultimate information on the chemical structure of complex biological and pharmaceutical systems, often using minute amounts of material. The SPM-MS approach combines local thermal or optical excitation directed by an SPM tip, with subsequent pick-up of locally emitted products by the mass spectrometer, thus allowing local chemical identification. Critical for broad implementation of this approach is mass spectrometry at atmospheric pressures, and these methods are reviewed in detail.

SPM methods for probing thermal phase transitions locally are summarized in the contribution by Nikiforov and Proksch (Chap. 8). Recent advances in SPM tip fabrication lead to the development of heated SPM probes with high heating–cooling rates. These probes enable a broad spectrum of thermal imaging methods. In one approach, the SPM tip concentrates the thermal field within the material, while the resulting surface deformation is detected by SPM electronics. The onset of melting transition below the probe results in probe penetration in the material, allowing the transition temperature to be identified. The combination of periodic heating and dynamic driving modes allows mapping of the glass transition temperatures as well. Beyond thermomechanical effects, these methods can be extended to probing local sample temperatures and heat conductivity, suggesting broad applicability for high-energy density material and devices.

The applications of SPM methods to probing electrical and electromechanical functionalities are discussed at length in Chaps. 9–13. In Chap. 9, Magonov et al. extend multiple frequency SPM to in-depth quantitative studies of electrical properties of semiconductors, ferroelectrics and self-assembled monolayers. Along with the overview of Kelvin Probe Force Microscopy and Electric Force Microscopy applications they discuss how frequency modulation realized in these modes can overcome uncertainties related to various mechanisms of response signal formation and improve spatial resolution in functional imaging.

The contribution by Tian et al. (Chap. 10) describes the quantitative measurements of ferroelectric polarization distribution on the nanoscale by piezoresponse force microscopy (PFM). The force-based SPM signals scale linearly with tip-surface contact area resulting in a dearth of quantitative measurement capabilities in the range from molecular to mesoscopic (~ 100 nm) length scale. At the same time, the electromechanical signal in continuous approximation does not depend on the contact radius, enabling quantitative measurements of ferroelectric properties in the PFM mode. Using finite element simulation of the electric and elastic fields for various tip-sample interaction models, Tian et al. show that the real domain wall thickness can be extracted from experimental PFM line profiles across domain walls.

This topic of PFM characterization of ferroelectrics is further developed by Huey and Nath in Chap. 11, who systematize a broad range of experimental studies of domain switching dynamics in ferroelectric thin films. By introducing high speed PFM, the rapid mapping of instantaneous domain patterns is possible at a rate of at least 100 times over standard PFM imaging. This is one of the most promising approaches in overcoming the PFM limitation in revealing the parameters of nucleation and fast domain wall motion as the basic mechanisms of polarization reversal in ferroelectric-based devices (notably ferroelectric memories) and understanding the role of structural defects in the thermodynamics of ferroelectric switching.

The polar structure and polarization dynamics in relaxor ferroelectrics, one of the most mysterious classes of ferroic materials, are discussed in Chap. 12 by Shvartsman et al. The nanoscale ferroelectric ordering in relaxors presents a significant exploratory challenge but at the same time makes them the textbook example materials for demonstrating the superior capabilities of PFM in discerning the relationship between the polar structure and the unconventional dielectric properties. A detailed review of the PFM studies of several important groups of relaxors is presented highlighting experimental observation of temperature-induced transformation between ferroelectric and relaxor states.

In Chap. 13, Ruediger reviews a complex problem of PFM image interpretation stemming from the tensorial nature of the electromechanical response, asymmetry in the local field distribution due to the sample defect structure or tip shape, surface modification and cantilever mechanics. Understanding these contributions allows one to avoid image misinterpretation and identify imaging artifacts while providing additional means for structural and electrical characterization of electronic materials.

The novel functional SPM methods are discussed in Chaps. 14–17. In Chap. 14, Rose et al. discuss the perspectives of combined STM-focused X-ray measurements. The X-ray methods have evolved to provide in-depth information on the crystallographic structures and chemical identity of the surfaces, often with extremely high temporal resolution. However, spatial resolution is limited to several tens of nanometers. At the same time, STM-based methods routinely yield atomic spatial resolution, but are limited by 10–100 kHz bandwidth of amplifiers and are limited in chemical sensitivity. The potential for X-ray-STM combination and corresponding operational mechanism are discussed.

The scanning ion conductance microscopy and its application for mapping surface structures and biological systems are discussed in detail by Rheinlander and Schäffer in Chap. 15. This method allows mapping ionic flows through the microcapillary and is ideally suited for studying the biological and electrochemical systems. This topic is further extended by Beyder and Sachs (Chap. 16), who describe the techniques that combine classical patch-clamp and AFM methods to probe electrophysiological properties on the cellular and subcellular levels.

The contribution by Rodriguez et al. (Chap. 17) discusses in detail the novel problems that appear in the context of analysis of the multicomponent spectral data, and illustrates their applications for the voltage and time spectroscopies in PFM. The direct functional fits methods are discussed and compared with multivariate statistical methods including principal component analysis and correlation function analysis. Finally, the contribution by Gruverman (Chap. 18) reviews recent advances in probing and understanding polarization dynamics in ferroelectric capacitors. Although the PFM capability to detect the polarization state through the top electrode allows for direct studies of the dynamics of domain structure under the uniform field conditions, a major limitation was low time resolution. Discussion of the approach to extend the PFM studies into the 100 ns range is presented. The role of inhomogeneous domain nucleation and measurements of the switching parameters in conjunction with microstructural and scaling effects is discussed.

Taken together, this book aims to give a prospective of new directions in functional SPM imaging. Many of the applications described in the book have appeared only in the last several years, and the future will undoubtedly see the emergence of a number of SPM modes for addressing materials functionality at the nanoscale.

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