Nanoscale Science and Technology Division
Room B113 - Session NS+2D+EM+MN+SS-TuM

Scanning Probe Microscopy

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Fernando Castro**, National Physical Laboratory, U.K.

8:00am **NS+2D+EM+MN+SS-TuM-1 AVS Medard W. Welch Award Talk: Microscopy is All You Need: The Rise of Autonomous Science***, **Sergei Kalinin**[1],* University of Tennessee Knoxville **INVITED**

Making microscopes automated and autonomous is a North Star goal for areas ranging from physics and chemistry to biology and materials science – with the dream applications of discovering structure-property relationships, exploring physics of nanoscale systems, and building matter on nanometer and atomic scales. Over the last several years, increasing attention has been attracted to the use of AI interacting with physical system as a part of active learning – including materials discovery and optimization, chemical synthesis, and physical measurements. For these active learning problems, microscopy arguably represents an ideal model application combining aspects of materials discovery via observation and spectroscopy, physical learning with relatively shallow priors and small number of exogenous variables, and synthesis via controlled interventions. I introduce the concept of the reward-driven experimental workflow planning and discuss how these workflows can be implemented via domain-specific hyper languages. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. The real-time image analysis allows spectroscopic experiments at the predefined features of interest and atomic manipulation and modification with preset policies. I further illustrate ML methods for autonomous discovery, where the microstructural elements maximizing physical response of interest are discovered. Complementarily, I illustrate the development of the autonomous physical discovery in microscopy via the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed. These concepts and methods can be extended from microscopy to other areas of automated experiment.

8:40am **NS+2D+EM+MN+SS-TuM-3 Dielectric Constant Measurement Sensitivity in Electrostatic Force and Force Gradient Microscopy-Based Modes***, **Gheorghe Stan**,* National Institute of Standards and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines

Understanding of the nanoscale electrostatic interaction between a conductive atomic force microscopy (AFM) probe and a dielectric film is central to the operation of various nanoscale dielectric microscopies and determination of dielectric properties of the film. There is no simple analytical description of the electrostatic interaction generated in the confined probe-sample geometry of neither the static nor dynamic AFM modes used for dielectric measurements. An accurate description of the involved physics is obtained only by means of a finite element analysis modeling of the system. However, the alternative of using numerical analysis is not very popular being slower and requiring relatively high computation resources. In this work we revised the contributions from different parts of the AFM probe to the probe-sample capacitance by both analytical and numerical methods. We tried to reconciliate the two approaches and observed the differences as a function of geometry and material parameters. Under various noise levels, the efficiency of an analytical model was tested against finite element analysis that captures in detail the electrostatic interaction in AFM-based dielectric measurements. The investigation was performed in both spectroscopic force-distance curves and constant height scans with measurements for the deflection and frequency of the AFM probe. The obtained measurement sensitivities are relevant in selecting the optimal scanning mode and its operational parameters for given film thicknesses and dielectric constants but are also showing the critical role of the numerical analysis to the correct interpretation of the measurements.

9:00am **NS+2D+EM+MN+SS-TuM-4 Measuring and Understanding the Nanomechanical Properties of Halide Perovskites and Their Correlation to Structure***, I. Rosenhek-Goldian,* Dept. of Chemical Research Support, Weizmann Inst. of Science, Israel*; I. Buchine, N. Prathibha Jasti,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ., Israel*; D. Ceratti,* Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel & CNRS, UMR 9006, IPVF, Institut Photovoltaïque d'Ile-de-France*; S. Kumar,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. Ramat Gan Israel. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; D. Cahen,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; **Sidney R. Cohen**,* Dept. of Chemical Research Support, Weizmann Inst. of Science., Israel

Halide perovskites, HaP, and especially Pb-based ones exhibit a plethora of remarkable properties. Of these, their photovoltaic properties are the most widely studied due to the proven potential these materials hold for significant technological impact. In addition to photoresponse, this material class is characterized by interesting physical properties, of which mechanical properties enjoy special attention, not only because of potential use in flexible devices, but also from a fundamental science point of view. The mechanical response can shed light on the materials' behavior including dynamic processes and strain-related effects on optoelectronic behavior.

In the context of these studies, particular emphasis has been placed on environmental factors which can alter, especially degrade, material functionality and device performance. Exposure to humidity, light, and oxygen rank prominently amongst these factors.

In this study we measure the humidity influence on the mechanical properties, i.e., elastic modulus (E) and hardness (H), for two series of lead halide perovskite single crystals, varying either by cation or by anion type. Our conclusions are based on comparing results obtained from several different nano-indentation techniques, which separate surface modulus from that of the bulk, and probe different manifestations of the hardness. These studies reveal the different crystalline parameters governing influence of humidity on the mechanics at the surface and in the bulk.

An atypical inverse correlation between E and H was measured (as seen in the supplementary figure a). Furthermore, humidity influenced these two properties in opposite fashion – humidity exposure led to lower H, but to higher E (supplementary figure b). This trend is opposite to that found in most materials where hydration lowers both E and H. We suggest a link between dynamic disorder, self-healing, and the intriguing relation between E and H.

9:20am **NS+2D+EM+MN+SS-TuM-5 3D Nanoprinting of Advanced AFM Nano-Probes***, **Harald Plank**, M. Brugger-Hatzl, R. Winkler, L. Seewald,* Graz University of Technology, Austria

The demand for correlative microscopy is still increasing, as it enables a superior ensemble of information by using various methods to combine individual strengths. The highest level of that approach are hybrid microscopes, which enable individual characterization at the very same spot in a consecutive or even parallel way. With that, however, comes the demand of a conflict-free integration of different microscopes, which require a radical redesign of the instrumentation. A major step in that direction is a recently introduced dual system called FUSIONScope, which is a deeply integrated scanning electron microscopy (SEM) and atomic force microscopy (AFM) solution. While the former enables high-resolution guidance towards the region of interest, the latter complements SEM capabilities by true quantitative 3D surface information, which together exploit their full potential by the possibility to precisely land the AFM tip on highly exposed regions. Even more importantly, advanced AFM modes such as conductive AFM (CAFM), magnetic force microscopy (MFM), electrostatic / Kelvin force microscopy (EFM/KFM), scanning thermal microscopy (SThM) or mechanical mapping, provide functional information beyond SEM capabilities. For that, special nano-probes are required, which typically achieve their intended functionality by additional thin film coatings, which contains two main disadvantages. First, they increase the apex radii and limit the lateral resolution, which is in conflict with the still decreasing feature sizes. Secondly, coatings are prone to delamination during operation, which affects resolution, lateral correlation and reliability. Therefore, to exploit the full potential of advanced AFM modes, it is of great interest to develop new approaches for the fabrication of functional nano-probes. Following that motivation, we joined forces with industry and apply the additive direct-write technology focused electron beam induced

[1] **Medard W. Welch Award Winner**

deposition (FEBID) for the development of novel 3D nano-probe concepts with industrial relevance. In this contribution, we briefly discuss the 3D nano-printing process and then go through a variety of advanced, FEBID-based tip concepts for CAFM, EFM, MFM and SThM. The joint element for all probes is the coating-free character, which eliminates the aforementioned risks during operation. Additionally, the apex regions are routinely in the sub-10 nm regime, which allows for high-resolution imaging. Aside of comparisons to traditionally used nano-probes, which reveal the superior performance of FEBID-based nano-tips, we discuss on currently ongoing research towards multi-functional AFM tips, based on FEBIDs flexibility.

11:00am **NS+2D+EM+MN+SS-TuM-10 Chemical, Mechanical, and Morphological Evolution of Nanostructures on the Surfaces of Asphalt Binders***, L. Lyu, J. Pei,* Chang'an University, China*; E. Fini,* Arizona State University*; L. Poulikakos,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; **Nancy Burnham,*** Worcester Polytechnic Institute

Bitumen (asphalt binder) holds roads together. It is a complex, dynamic, nanostructured material that comes from the bottom of an oil refinery stack—a non-renewable resource. It ages, and it ages more quickly under the influence of heat and light. Can additives made from waste materials increase the longevity of bitumen, and thus roads?

In this study, atomic force microscopy (topography, phase imaging, PF-QNM) and its combination with infrared spectroscopy (AFM-IR) were used to explore the chemical, mechanical, and morphological evolution of the surface of bitumen without and with additives. Aging is assumed to begin at the surface.

Samples of bitumen were made with and without introducing bio-modified rubber additives. Each sample was exposed to several thermal and UV aging protocols. Evolution of surface under aging was studied. Depending on the additive and type of aging (thermal, UV, or combined), the nanostructures changed their chemistry, mechanical properties, and size. Furthermore, the matrices and phases immediately surrounding the nanostructures evolved differently upon aging than the included nanodomains. In general, carbonyl and sulfoxide IR bands became more prevalent, the samples became stiffer and less adhesive, and the phase immediately surrounding the nanostructures became smaller. One additive made from two different waste materials was found to enhance the stability of the surfaces.

By understanding the evolution of asphalt binders and which additives promote their stability, longer lasting roads might be designed and built, thereby lowering the need for a non-renewable resource.

11:20am **NS+2D+EM+MN+SS-TuM-11 Identifying Potential Carbon Sources for Direct Carbon Material Production by AI Assisted HR-AFM***, **Percy Zahl,*** Brookhaven National Laboratory*; Y. Zhang,* ExxonMobil Technology and Engineering Company*; S. Arias,* Brookhaven National Laboratory

High-resolution Atomic Force Microscopy (HR-AFM) has proven to be a valuable and uniquely advantageous tool for studying complex mixtures such as petroleum, biofuels/chemicals, and environmental or extraterrestrial samples. However, the full potential of these challenging and time-consuming experiments has not yet been fully realized. To overcome these bottlenecks and enable further research into solutions for the energy transition and environmental sustainability, automated HR-AFM in conjunction with machine learning and artificial intelligence will be crucial [1].

In this study, we focus on identifying potential carbon sources suitable for more direct carbon material production by analyzing various pitch fractions based on their solubility in toluene. Specifically, we present the first comprehensive AI-assisted study of hydrocarbon fractions derived from petroleum and coal tar pitch, using and refining our previously introduced "Automated HR-AFM" tools. We explored four classes derived from Petroleum Pitch (PP) and Coal Pitch Tar (CPT), separated into toluene soluble (TS) and toluene insoluble (TI) fractions. Our analysis revealed differences in the structural characteristics of the molecules, which we binned based on the number of aromatic rings.

(Please see also the in our supplemental document included figures 1 and 2)

Overall, our results demonstrate the potential of automated HR-AFM and AI-assisted analysis for understanding complex mixtures and identifying potential carbon sources for direct carbon material production. This work represents an important step towards more sustainable and environmentally-friendly energy solutions.

Reference:

[1] Yunlong Zhang, Energy & Fuels 35(18), 14422 (2021)

11:40am **NS+2D+EM+MN+SS-TuM-12 Automated Microscopy for Physics Discovery: From High-Throughput to Hypothesis Learning-Driven Experimentation***, **Yongtao Liu,*** *R. Vasudevan, M. Ziatdinov, S. Kalinin,* Oak Ridge National Laboratory

In this work, we explore the ferroelectric polarization switching in relation to the applied pulse bias including bias voltage and time in scanning probe microscopy (SPM). We perform two types of automated and autonomous experiments. First, we conduct automated high-throughput experimentation to gain a comprehensive understanding of the relationship between pulse biases and ferroelectric domain growth. Second, we employ an autonomous experimentation driven by machine learning (ML) algorithm to optimize experimental conditions based on real-time experiment results.

SPM has proven to be a powerful tool for manipulating and visualizing ferroelectric domains at the nanoscale. Investigations of ferroelectric domain size and stability can advance our knowledge of ferroelectrics application in memory devices, such as operating time, retention time, and bit size. However, conventional SPM measurements have been time-intensive and dependent on experienced researchers to perform repetitive tasks and make real-time decisions regarding measurement parameters. For example, researchers determine and manually tune the parameters for next iteration of experiment according to the previous results.Here, we perform automated and autonomous experiments in SPM to explore the mechanism of ferroelectric polarization. The first experiment is a high-throughput experiment of applying various bias pulse conditions to write ferroelectric domains followed by imaging domain structure using piezoresponse force microcopy. In this automated experiment, we systematically adapt the bias pulse parameters to gain a comprehensive understanding of their relationship with the resulting domain structures. We discovered different polarization states that show up upon different bias conditions. In the second experiment, we implement a hypothesis active learning (HypoAL) algorithm based on structured Gaussian process to control the SPM for ferroelectric domain writing. The HypoAL analyzes the relationship between the bias pulse conditions and the written domain size in real-time experiments, and determines the bias pulse parameters for the next iteration. The goal of HypoAL is to establish the best physical hypothesis for the material's behaviour within the smallest number of experiment step.The HypoAL identifies that the domain growth in a $BaTiO_3$ film is governed by kinetic control. The approaches developed here have the potential to be extended to other experiments beyond SPM in the future to accelerate the discovery of new materials and advances in physics.

Author Index

Bold page numbers indicate presenter