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Preface to Special Topic: Piezoresponse Force Microscopy

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Almost two decades beyond the inception of piezoresponse force microscopy (PFM) and the seminal papers by Güthner and Dransfeld[1] and Gruverman *et al.*,[2] the technique has become the prevailing approach for nanoscale functional characterization of polar materials and has been extended to the probing of other electromechanical effects through the advent of electrochemical strain microscopy (ESM).[3] This focus issue celebrates some of the recent advances in the field and offers a wider outlook of polar materials and their overall characterization. Covered topics include discussions of the properties of traditional ferroelectrics, such as lead zirconate titanate (PZT) and lithium niobate, relaxor-ferroelectrics, as well as more "exotic" ferroelectric oxides such as hafnia, ferroelectric biological matter, and multiferroic materials. Technique-oriented contributions include papers on the coupling of PFM with other characterization methods such as x-ray diffraction (XRD) and superconducting quantum interface device (SQUID), as well as considerations on the open questions on the electromechanical response in biased scanning probe microscopy (SPM) techniques, including the effects of the laser spot placement on the readout cantilever displacement, the influence of the tip on the creation of the domain shapes, and the impact of ionic and electronic dynamics on the observed nanoscale hysteretic phenomena.

A common thread among many of the papers presented in this issue is the correlation between nanoscale electromechanical and polar phenomena, and domain size. Volk *et al.* use electron beam irradiation to induce domains in $LiNbO_3$ crystals and show that the domain size depends on the irradiation conditions and is related to a modified defect structure in a thin layer at the surface. Turygin *et al.* investigate domain size, switching, and relaxation behavior for $BaZr_{0.2}Ti_{0.8}O_3$ and $Ba_{0.7}Ca_{0.3}TiO_3$ solid solutions. These lead-free ferroelectrics follow the previously reported[4] square root dependence of domain size on grain size. Coexistence of rhombohedral and tetragonal phases is directly correlated with ease of switching, while the larger concentration of defects at the grain boundaries results in distortion of the piezoresponse hysteresis curves. The paper by Vasudevan *et al.* reports on the local electromechanical response in $0.72Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.28PbTiO_3$ solid solution single crystals, a prototypical relaxor-ferroelectric. A combination of the large data analytics and multi-dimensional spectroscopic PFM technique unravels relaxation behavior variability in the tens of nanometers scale, creating a disorder map of the material.

Modification of the properties of the material through doping and creation of solid solutions is also pursued by Alikin *et al.*, reporting on the nanoscale origins of the enhanced piezoelectric response of the Sm-doped $BiFeO_3$. Sm-$BiFeO_3$ ceramics with compositions close to the morphotropic phase boundary are probed by XRD and PFM to determine the phase composition, consisting of the coexistence of a polar *R3c* phase and an antipolar *Pbam* phase. PFM is then used for mapping of the two phases detected by XRD, and the relative content of the two phases determined by both techniques shows a good agreement. Ye *et al.* study the domain structure and evolution in multiferroic $(1-x)[0.9BiFeO_3$–$0.1DyFeO_3]$-$xPbTiO_3$ ceramics through combined PFM-SQUID characterization techniques, illustrating specific polarization directions as well as thermally induced magnetic transitions.

Moving yet further from the "traditional" ferroelectric compositions, such as those presented above, a clear trend emerges towards more "exotic" ferroelectric compositions. And while hafnia thin films are certainly not exotic in the field of semiconductor devices, these binary oxides have been subject of fierce debate and continuous investigations over the last few years. PFM-based techniques remain at the forefront of their characterization, given the inherent limitations for macroscopic characterization, set by the film thicknesses and sizes where the ferroelectric phenomena are observed. Schroeder *et al.* elucidate the importance of the oxide-electrode interface and illustrate how interface oxidation of the electrodes during annealing results in a different density of oxygen vacancies in Gd:HfO_2 films, which is ultimately responsible for the stabilization of the ferroelectric phase in these materials.

More "exotic," albeit substantially less so for biologists, are the reports on ferroelectricity in thymine (one of the four nucleobases of DNA) and β-glycine (the smallest amino acid) by Bdikin *et al.* and Seyedhosseini *et al.*, respectively. The former paper leverages PFM to demonstrate the presence of local piezoelectricity and apparent ferroelectricity in synthetic thymine microcrystals, while the latter shows that β-glycine is ferroelectric at room temperature with switchable polarization, controllable domains, and charged domain walls responsible for the properties of this amino acid.

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The above studies highlight the large breadth of the field of applications of PFM, specifically to probe ferroelectric phenomena and domain structure and evolution. With a view towards the future of the field, however, we need to ask the question of what is next for PFM. This question can be answered in three parts: advanced data analysis, reproducibility and quantification of signals, and investigation of electromechanically active non-ferroelectrics.

Working towards the first thrust, Vasudevan *et al*. demonstrate advanced statistical data analysis methods for extraction of correlations in the measured data and expose "hidden" results, which would not have been easily discernible by human eye. Statistical analysis of the data is set to become an important tool in the future developments of many characterization techniques and specifically, biased-tip scanning probe microscopy, aiding in extraction of physical phenomena from experimental data.

While statistical analysis can enable discovery of trends otherwise non-easily apparent and/or quantifiable, data reproducibility, and response quantification remain two of the major challenges to overcome for PFM and ESM techniques. PFM signal amplitude, for example, strongly depends on the tip choice; can vary from tip to tip; and is often not comparable between different research groups. Therefore, the instrumentation's influence on the measured PFM signal remains a hot topic in the field. The articles by Karapetian *et al*. and Starkov *et al*. report in detail about the electric fields created around a point charge provided by a PFM tip and how the tip itself can influence the shape of the resulting switched domain, respectively. As a consequence, PFM results may vary depending on the exact tip geometry, which highlights the need of a higher quality control for commercial tips. Additionally, the vibrating cantilever has a strong effect on the measured piezoelectric response. Proksch *et al*. demonstrate how crucial the placement of the laser spot on the cantilever beam is for surface displacement measurements. Since the placement of the laser spot is typically performed manually, there is a strong variation of experimental values. Eventual artifacts can be so severe that electromechanical hysteresis is observed even in non-hysteretic materials. Quantification of response therefore hinges on automated or more precise methods for recording data in a more systematic way, and development of procedures to remove instrumentation effects.

In addition to the role of instrumentation, the knowledge of sample properties is just as important in identifying eventual artifacts. As shown exemplarily by Yamada *et al*., the sample polarization can be strongly altered by clamping effects depending on the crystallographic texturing of PZT thin films. While the reported work is based on time-resolved synchrotron XRD, the results clearly impact scanning probe-based results, as the same clamping effects can affect PFM experiments. In a second example, Balke *et al*. show how surface charges, charge injection, and sample conductivity—i.e., charge flow during local measurement—can alter the experimental PFM response and hysteresis loop shape.

With the increasing ease in obtaining PFM data, it is therefore of increasing importance to identify alternative signal origins, beyond ferroelectricity, and in biased-tip scanning probe techniques. While examples of electrostatic forces acting between tip and sample, and Joule heating are discussed in the article by Balke *et al*., many additional signal origins can be identified. Foremost among these is ionic motion, where ionic concentration is correlated to the sample volume through the Vegard law and can be probed through ESM techniques. In the article by Kim *et al*., the electromechanical responses induced by ionic motion and by piezoelectricity are compared in ionic-conductive ceramics with piezoelectric inclusions, an important step towards understanding nanoscale electrochemical strain. This experimental work is directly complemented by the theoretical work by Morozovska *et al*. discussing the frequency dependence of ion-induced electromechanical response for mixed ionic-electronic conductors, paving the path for quantitative investigations of Li-based solid electrolytes and electrodes, materials with resistive switching, and electroactive ferroelectric polymers through ESM. The recent developments of PFM-like techniques beyond ferroelectricity have in fact important practical applications, especially in the field of energy-related materials, as shown by the work of Luchkin *et al*., leveraging ESM for investigation of aging behavior in a commercial Li-ion battery electrode. Pannala *et al*. give a thorough overview of the diverse characterization techniques used for investigation of these systems.

In summary, this special issue highlights how advances in data analysis and work towards quantification of not only piezoelectricity but also other electromechanical effects will strongly enhance the quality and reproducibility of PFM experiments and expand the applications of PFM-type characterization techniques to a wider range of materials. These advancements require continued efforts in identifying instrumental effects on the measured surface displacements and persistent endeavors towards identification and quantification of various sources of electromechanical response contributing to the measured sample response. This research thrust is of paramount importance in many materials systems where the electromechanical and electrochemical responses are correlated and both contributing to the overall functional response of the material. Such is the case even for "traditional" ferroelectric materials, where skin layers and surface charges are of increasing importance in determining the effective material properties at smaller length-scales.

Advanced data analysis will help to identify the physical origins of local response variability and will become increasingly important to transition from free-standing PFM-type techniques to multi-technique approaches. This can be realized by combining SPM with other techniques focusing on electrical, magnetic, and optical sample characterization. First steps towards this goal have been historically made by Shur *et al*.[5] in combining PFM and Raman spectroscopy. The combination of SQUID and PFM presented by Ye *et al*. provides a further step forward towards this goal. Such multi-technique approach will be of special interest not only for the investigation of ferroelectrics but also even more so for multiferroic materials—where combination of different order parameters will benefit from multiple characterization techniques—as well as any material where multi-stimuli/

responses of electro-chemo-mechanical systems are relevant. First and foremost among these will be (Li-)ion battery materials, where many techniques, such as infrared spectroscopy, neutron imaging, and micro-Raman mapping, have been already leveraged to characterize the material properties as highlighted by Pannala *et al*.

We would like to thank all the participants in the 2014 PFM Workshop and Conferences, and specially the authors contributing to this special issue. The field of the bias-top scanning probe microscopy is still in strong growth mode, as evidenced by the important attendance at the meetings and the quality of the research being performed. We would like to thank Dr. Andre Anders, Ms. Ania Bukowski, and the leadership in the American Institute of Physics for their continuous support in the dissemination of our community's scientific efforts, and we look forward to the future discoveries and exciting contributions to come.

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