Keynote Talk Abstracts

Reconfigurable 2D Electron Gases in Ferroelectric Domain Walls

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For the last 10 years, domain wall conductivity (DWC) in ferroelectrics has become a very attractive and prospective field of research. We intensively explore DWs in bulk and thin-film LiNbO3 (LNO) single crystals, a material that is known for its large bandgap of ~4 eV, optical endurance, and excellent CMOS compatibility, with the help of dedicated scanning force-microscopy (SPM) methods (i.e. AFM, cAFM, FFM, KPFM, etc.). Nevertheless, when engineering domains across such crystals, domain walls (DWs), i.e. the tiny region that separates adjacent areas of opposite or non-collinear dielectric polarization, show, to our great surprise, excellent metallic-like properties. When applying a small voltage of ±10 V across such a wall, extremely large DWCs of up to ±1 mA per DW are recorded, and this even at room temperature. Mandatory for this to happen, however, are low injection barriers as well as optimized electron (hopping) transport properties along such DWs, as is experimentally mediated by slightly inclining DWs with respect to the polar LNO axes. In this talk, I will provide clear proof for the existence of this 2-dimensional electron gas (2DEG) in these DWs by exploring Hall-transport properties, excited both with and without external photo-illumination. In addition, I will show how to follow and track the effective trajectory of electrons when flowing along the DW; the latter is achieved by applying a novel type of non-linear optical microscopy, so-called Che- renkov Second Harmonic Microscopy, a method that then reveals a 3-dimensional profile of individual domain walls across the bulk, excellently complementing our SPM surface data. Most interestingly, these large DWCs allow for fabricating nanoelectronics devices, making use of the reconfigurable 2DEG in these DWs.

Mysteries of the chemical bond revealed by atomic force microscopy

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The imaging process in AFM rests on the temporary chemical bonds that are created and broken during the imaging process. CO terminated AFM tips have been shown to provide outstanding spatial resolution on organic molecules, metallic clusters and other samples. Experimental evidence and calculations show that the CO tip is chemically inert and probes organic molecules mainly by Pauli repulsion. Thus, images of organic molecules, graphene etc. observed with a CO tip can be interpreted as a map of the absolute charge density of the sample. The total charge density of a single adatom is approximately given by a Gaussian peak. While single silicon adatoms appear similar to a Gaussian peak when imaged by AFM with a CO terminated tip, copper and iron adatoms adsorbed on Cu(111) and Cu(110) appear as tori. Initially, we explained these images by szp hybridization of the valence electrons of the adatoms. Recent experiments and DFT calculations show that the total charge density of Cu and Fe adatoms is approximately Gaussian – in contrast to the hybridization theory. The bounding strength between the AFM tip and the atoms of the sample depends not only on the chemical identity but also on the coordination - corner atoms in clusters are more reactive than center atoms.

References:

Hybrid electrochemical scanning probe microscopy (SPM) – Physical and electrochemical characterization of interfaces

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Hybrid scanning probe techniques such as scanning ion conductance microscopy (SICM) – scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM)-SECM have gained tremendous importance in physical and electrochemical characterization of interfaces [1]. Our research team has pioneered combined AFM-SECM using AFM-tip integrated electrodes, which are not in direct contact with the sample surface [2], and therefore allow simultaneous mapping of physical and electrochemical properties at electrified interfaces in contrast to other approaches based on metallic/metallized AFM tips [3,4]. Recently, we introduced a new type of electrochemical scanning probe tip for combined AFM-SECM measurements providing instead of a conventional AFM tip, a conductive colloid sphere attached to an otherwise insulated cantilever [5]. Such conductive spherical probes may consist of boron-doped diamond [6], a highly attractive electrode material, or may be electrochemically modified, e.g., with polymers, highly suitable for force spectroscopic measurements such as adhesion measurements under potential control. Within this contribution, selected examples of combined electrochemical and nanomechanical mapping will be presented and discussed along with experimental challenges. In addition, electrochemical force spectroscopic measurements with polydopamine (PDA)-modified colloidal probes will be presented taking advantage of the fact that the surface functionality of PDA and hence the force interaction can be altered by oxidation or reduction of functional groups.

References:
Recent studies have emphasized the critical role that local mechanical stress can play on the functionality of ferroelectric materials. For instance, stress applied from an atomic force microscope (AFM) tip has been shown to induce polarization reversal through the flexoelectric effect in ultrathin films, where the strain gradients can permeate through the film thickness [1]. In addition, local stress can alter electric field-induced switching behavior, affecting hysteresis loop shape, coercive field, and remnant polarization [2]. The mixed phase form of epitaxially-strained BiFeO3 thin films, having a coexistence of rhombohedral-like R phase, comprising needle-like structures, within a tetragonal-like T phase matrix, meanwhile show a particular susceptibility to applied stress. The effects include transitions between phases, with the resulting boundaries demonstrating enhanced conductivity [3], and stress-induced alterations to electric field-induced hysteresis [4].

In this work, a loading-force dependent evolution of strain effects is reported, from structural phase changes at low forces (< 1 µN) to nanomechanical machining at higher forces (~ 1 µN). Switching behavior and switching currents are also found to be affected by force, with coercive fields decreasing with increasing loading force. Notably, mechanically-induced currents increase with applied force and may enable polarization state determination in ferroelectric memory applications. Lastly, at high forces > 10 µN, a moving tip can be used to remove material. Through a systematic investigation of a range of AFM parameters, including force, we demonstrate that AFM-based machining is an effective tool for rapid and precise modification of local regions of the film, as well as for the fabrication of several different nanostructures, including nanocapacitor arrays with individually addressable ferroelectric elements. AFM-based machining of ferroelectric nanostructures offers advantages over established techniques, such as bottom-up approaches and focused ion beam milling, in select cases where low damage and low-cost modification of already-fabricated thin films are required.

References:

Correlated surface potential and electrochemical activity on 2D materials
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The AFM is a versatile tool to investigate a large and still growing number of systems, in particular in combination with fluorescence microscopy. Here I will first show how unique insights into polymer physics can be obtained by single molecule force spectroscopy. Temperature dependent experiments combined with molecular dynamics simulations could quantify entropic and energetic contributions to the elasticity of polymers and showed that neither PEG nor PNIPAM are pure entropic chains [1]. Then I will show how the mobility within polymer coatings can be determined with AFM-based scratching experiments. This mobility can be surprisingly high in crosslinked coatings.

Next I will show how a combination of AFM based indentation and fluorescence microscopy is used to correlate nanomechanical properties with the organization of chondrocytes in osteoarthritic cartilage [2]. This correlation is further extended towards the organization of the collagen networks using AFM based fast force-mapping.

Finally I will present an outlook on the characterization of 3D-printed micrometer scale auxetic elastic structures, which underlines the great versatility of today's AFM-based research.

References:
Quantification of nanoscale electromechanical responses

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Surface electromechanics at the nanoscale are typically studied by Piezoresponse Force Microscopy (PFM), based on the inverse piezoelectric effect. As a first approach, generally only homogeneous responses are taken into account, but it has been realized that the effect of gradients in electro-mechanical phenomena at the nanoscale can become dominating: the generation of electrical signals after the application of mechanical strain gradients with an AFM tip has been proved, and it has been shown that it is possible to write ferroelectric domains [1] or to move oxygen vacancies and charges.

In this talk, I will review several different phenomena that directly affects quantification of piezoelectric response at the nanoscale, that is, the determination of the d33 effective piezoelectric coefficient. First, I will show how gradient-based electromechanical effects couples and interferes with PFM measurements. I will start by demonstrating the asymmetry in mechanical properties induced by the coupling of flexoelectricity to ferroelectricity leading to ferroelectrics as smart mechanical materials [2], and opening new opportunities to mechanically read ferroelectric polarization states in both, thin films and single crystals, on the base of Contact Resonance Frequency AFM mode. Then, I will put the light in another new aspect: converse flexoelectric effect [3] due to the presence of strong local electric field gradients at the tip end can induce a mechanical strain of the sample in dielectric centrosymmetric materials with magnitudes comparable to piezoelectric d33 coefficient. Finally I will go over the effect of Schottky barriers on the determination of the d33 coefficient of piezoelectric semiconductors, and show how the metal-insulator junctions can induce non-linear and multiharmonic electromechanical responses [4].

References
[4] Lozano, E; Catalan, G; Esteve, J; Murillo, G; Domingo, N; Non-linear and Multiharmonic Nanoscale Piezoresponse of Single ZnO nanowires with Schottky Junctions. (under review)
Nanorheological measurement based on AFM is reviewed with showing several examples of polymeric materials. Dynamic modulus determination, such as storage ($E'$), loss ($E''$) moduli and loss tangent with wide-frequency range is now realized by this technique. [1, 2]

The first example uses its capability of wide frequency measurement and its temperature control function to validate time-temperature superposition (TTS) principle. We used styrene-butadiene rubber (SBR) vulcanize of which glass-rubber transition temperature, $T_g$ is $-27^\circ$C. [3] It was confirmed that the viscoelastic values of a pure SBR vulcanize were quantitatively equivalent to bulk DMA results. TTS holds even at nanoscale if just viewing “average,” while some breakdown occurs due to heterogeneous nature of GR transition.

As the second example, we applied this technique to silica-filled SBR to investigate the nature of the interfacial rubber region. [4] Its dynamics properties were different from those of matrix rubber regions. The master curve obtained by this technique perfectly coincided with that by bulk DMA.

However, by examining the frequency-dependent change of $E''$, we found that this transition does not occur uniformly depending on spatially heterogeneous polymer segmental dynamics. The miscibility between two polymer species is the third example. Nanorheological AFM was utilized to investigate the nature of a SBR/butadiene rubber (BR) partially miscible blend. The blend seemed to be immiscible according to SEM and conventional AFM techniques. However, when both $E'$ and $E''$ for the blends were compared with those for the homopolymers, values for both the SBR-rich and BR-rich regions did not coincide with those for the pure components as shown in Fig. 1. In particular, the BR-rich region, exhibited a dynamic heterogeneity, where the frequency responses were much more complicated than those of the BR homopolymer, though DSC could not detect it as the change of $T_g$.

References:

Figure 1. (a) Loss tangent map of SBR/BR blend by nanorheological AFM ($f$ = 20 kHz). The scan size is 2.0 µm. (b) Frequency dependence of loss tangent for both SBR/BR blend and each homopolymers.
Three-dimensional nano-architectures in energy, bio-medical, electronic and sensing applications – optimization based on correlative microscopy and spectroscopy and machine learning

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Complex nano-architectures of various material combinations (e.g. Si-nanostructures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications. In this context we will show nano-material choices e.g. for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in e.g. electronic nose devices based on resistors or field-effect transistors.

Materials and device optimization will rely on advanced, scale bridging correlated electron- ion-, optical- and x-ray microscopy and spectroscopy (CORRMIC) including atom probe techniques. The application of nanoGPS to enable true correlation with nanoscale precision between different techniques in different machines is essential and respective workflows will be demonstrated. In addition, we will show the application of machine learning strategies to aforementioned heterogeneous data to further exploit optimization of materials and device performance.