Nanoscale Stress-induced Functionality in Ferroelectric and Functional Oxides via Writing and Patterning Using the AFM

Primary Supervisor: Amit Kumar

Secondary Supervisors: Raymond McQuaid and Marty Gregg

Summary: With the recent development of high-stiffness Atomic Force Microscope (AFM) cantilevers, previously unobtainable extremely high stress levels to be applied to specific localised nanoscale regions can now be achieved. In this project, we seek to explore how the delivery of such intense site-specific stress might be used to progress AFM-enabled high-resolution patterning, 3D tomography and nanoscale phase and microstructure control in functional oxides (such as ferroelectric-ferroelastics and materials undergoing metal-insulator phase transitions).

Background and Context:
As all-diamond AFM probes have evolved and become capable of applying significantly high stress in GPa regime, tip induced stress has begun to be used as a really effective tool to study intriguing aspects of stress-induced phenomena in ferroelectrics and functional oxides. Mechanical switching of phases in mixed phase ferroelectrics, stress mediated phase competition and resulting microstructures with enhanced conductivities [1], and stress-enabled tunability of coercive field and switching behaviour in ferroelectrics [2] are some of the clear examples in this context. Localised stress also could offer a dynamic way to inject and manipulate ferroelastic domain microstructures[3] and can be particularly effective in harnessing wall/domain related functionalities in systems where other field variables like electric field are ineffective. The possibility of confining even larger stresses and stress gradients under stiffer tips hints towards more direct opportunities in terms of controlling metal-insulator phase transitions (such as those in VO_2) on the nanoscale. The challenge lies in employing such large localised stresses to generate heterogeneous functionality in a deterministic manner and this could even provide pathways towards stress-imprinted nanocircuitry and practical nanoscale devices. Stress confined under a nanoscale tip can also enable precise material removal (milling and machining) in ferroelectric oxides and metallic electrodes[4]. AFM-based milling and Tomographic atomic force microscopy (TAFM, involving layer-by-layer material removal) exploit the remarkably high stiffness and hardness of custom-made tips to enable tip-mediated milling and simultaneous or interleaved functional imaging. TAFM can be used to unveil 3D functional information and more crucially novel physics in functional oxides which was previously inaccessible[5], with unprecedented resolution and ease. Moreover, opportunities exist to employ AFM milling towards precise milling of oxides and metallic electrodes to fabricate nanostructures such as ferroelectric nanocapacitors as shown by us. The above discussion illustrates the exciting avenues emerging in terms of nanoscale stress-induced functionality and tomography but significant challenges/opportunities exist in terms of establishing the underpinning physics and optimisation of involved experimental geometries and engineering methodologies. This project aims to address selected aspects of these challenges.

This Project: We will investigate the capabilities of the high-stiffness probes to access stress-induced phase transformations in functional oxides and create local microstructural alterations (with implications for spatially resolved heterogeneous functionality such as nano-circuitries). Using the localised tip stress, we will aim to perform 3D tomographic imaging in increased volumes and at greater speeds than achieved till date and compare the approach with focussed ion beam milling approaches. Such 3D tomography could help unveil novel aspects of physics in materials of interest such as uniaxial ferroelectrics (e.g. lead germanate) and rare-earth hexagonal manganites. We will also aim to ascertain the capability of stiff probes to increase patterning rates and allow greater depths of patterns when compared to more conventional probes. The nanostructures prepared via tip-assisted milling will be compared with other conventional approaches to evaluate mill resolutions and geometric limitations. The project is linked to EPSRC activity and will be supported via two current US-Ireland grants with international collaborations hovering around the core themes of nanofabrication and ferroelectrics.

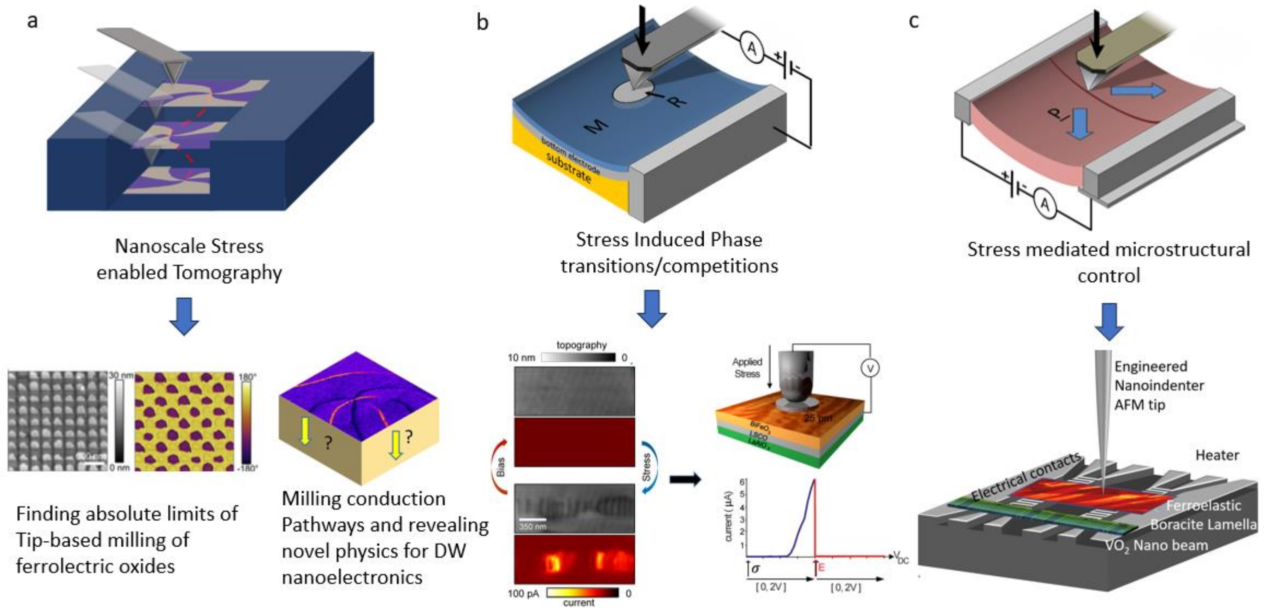

Figure 1: Three key aspects of nanoscale stress enabled phenomena (a) Nanoscale stress-enabled tomography can allow precise nanopatterning competing with parallel approaches and also allow 3D mapping of functionality revealing novel physics (b) Tip stress mediated phase transitions and competitions can induce functional states in ferroelectrics and materials undergoing metal-insulator transitions with implications for practical devices (c) Stress induced via a tip can be used to deterministically inject functional microstructures in ferroelastic oxides and could be used as a means to generate stress mediated nano-circuitry.

References:

[1] Edwards et al., "Giant resistive switching in mixed phase BiFeO3 via phase population control" *Nanoscale.* **10**, 17629 (2018).

[2] Edwards et al., "Local probing of ferroelectric and ferroelastic switching through stress-mediated piezoelectric spectroscopy" *Advanced Materials Interfaces* 3, 1500470 (2016).

[3] McQuaid et al., "Injection and controlled motion of conducting domain walls in improper ferroelectric Cu-Cl boracite" *Nature Communications* 8, 15105 (2017).

[4] Zhang et al., "Investigation of AFM-based machining of ferroelectric thin films at the nanoscale" *Journal of Applied Physics* **127**, 034103 (2020).

[5] Tikhonov et al., "Polarisation topology at the nominally charged domain walls in uniaxial Ferroelectrics" *Advanced Materials* 34, 2203028 (2022).