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TECHNICAL REPORT

# Basic Science of Radiation Effects in Ferroelectric Multi-Functional MEMS/NEMS



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**14. ABSTRACT**

Developed underpinning theory of radiation effects in ferroelectrics, investigated radiationinduced defect interactions, and demonstrated healing strategies for irradiated PZT films, and high-response, radiation-hard alternatives to PZT.

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**Abstract**

Developed underpinning theory of radiation effects in ferroelectrics, investigated radiation-induced defect interactions, and demonstrated healing strategies for irradiated PZT films, and high-response, radiation-hard alternatives to PZT

- Confirmed fundamental role of the ferroelectric stack in radiation-degradation of piezoMEMS cantilevers and relays;
- Identified the hetero-interface between PZT and electrode to have a critical role in both the radiation–material interaction and the radiation damage healing.
- Demonstrated that the result of ionizing radiation (gamma radiation) mostly affects traps charges in oxygen vacancy sites, while heavy ion radiation ($Fe^{3+}$) induces more defects on Zr/Ti sites, relative to Pb sites. Both result in reduced extrinsic contributions and hence reduced dielectric and piezoelectric response, and ultimately degrading piezoMEMS functionality.
- Developed a phenomenological model to quantify defect-defect interactions and their effects on functional materials for TID studies of piezoMEMS devices. The model was shown to be universally valid for quantification of different type of point defects (substitutional chemical dopants, ion implantation, ionizing radiation induced) on the functional response of a range of functional oxides.
- Developed strategies for mitigation of radiation impact on ferroelectric material stack and MEMS devices, through chemical doping with Mn.
- Demonstrated recoverable functionality in irradiated PZT thin films' through thermal annealing
- Successfully demonstrated high-response, radiation-tolerant alternatives to PZT (PMN-PT and $Hf_{0.5}Zn_{0.5}O_2$) thin films for piezoMEMS actuator and memory devices.

Developed instrumentation for nanoscale (band-excitation) spectroscopic electromechanical characterization of thin films and bulk functional materials. The developed codes and approaches are implementable via open-access software for any atomic force microscopy tool:

Additionally developed machine learning methodologies for analysis of the resulting multispectral data sets. All codes are also available in open-access repositories for implementation on any multispectral data set.

**Cumulative People Involved**

- At Georgia Institute of Technology: 1 principal investigator, 7 graduate students, 4 undergraduate students, 3 high school students
- At North Carolina State University: 1 co-Principal investigator, 2 graduate students, 2 postdoctoral researchers,
- At Army Research Laboratory: 2 co-Principal investigators, 1 graduate student, 1 undergraduate student, 3 technicians
- At Naval Research Laboratory: 2 co-Principal investigators

**Resulting Doctoral Theses**

- **Brewer Steven, PhD Thesis, Georgia Institute of Technology:** https://smartech.gatech.edu/handle/1853/59217

- **Chin Evelyn, PhD Thesis, Georgia Institute of Technology:** https://smartech.gatech.edu/handle/1853/63647
- **Griffin Lee, PhD Thesis, Georgia Institute of Technology:** Currently under 1 year embargo for open publication, due to remaining manuscripts under review (see attachment)
- **Magagnin Gregoire** M.S. Ecole Centrale de Lyon (thesis work performed at Georgia Tech)
- **Hanhan Zhou, PhD Thesis, North Carolina State University:** https://repository.lib.ncsu.edu/handle/1840.20/36584

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    - Evelyn Chin, PhD Materials Science and Engineering 2020 (full time).[10, 11] Currently at Intel
    - Lee Griffin, PhD Electrical Engineering 2020 (part time).[5, 12-15] Currently postdoctoral researcher at Georgia Tech Research Institute
    - Yulian Yao, PhD Materials Science and Engineering 2020 (part time). Starting at Applied Materials in January 2021
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Other publications:[17-19]

**Resulting Peer-Reviewed Publications**


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## Executive Summary of Work Performed

# SUMMARY

In recent years, the continuous thrust toward developing microelectronic devices with greater autonomy, reduced footprint size, and large-scale interconnection has necessitated high-performance materials capable of fulfilling multiple functional roles. Ferroelectric materials, and specifically lead zirconate titanate (PZT), boast large dielectric, polarization, and electromechanical responses, making them ideal for microelectromechanical system (MEMS) sensors and actuators, energy harvesters, multilayer ceramic capacitors (MLCC), ferroelectric logic elements and relays, *etc.* However, many of the most compelling applications for these types of devices – space travel, satellite communications, nuclear energy, and unmanned reconnaissance – concurrently require sustained operation in extremely demanding radiation-hostile environments. Radiation, both ionizing and displacive, has been shown to substantially degrade the functional responses of ferroelectric thin films, thus rendering the development of techniques for increased radiation tolerance of these materials critically important.

In this work, a multifaceted investigation towards increasing radiation hardness was undertaken, focusing on an array of critical interfaces and interactions in the ferroelectric material. Generally, the presence of oxygen vacancies at these interfaces resulted in substantial degradation of measured functional responses. Oyxgen vacancy motion, accumulation, and self-ordering have long been associated with ferroelectric fatigue, which results in the suppression of polarization and pins domain walls in ferroelectric materials. Furthermore, the exposure of oxygen vacancies to ionizing radiation can trap charges, yielding a singly-charged species of increased mobility. The work in this thesis aims to

elucidate the fundamental interactions of radiation-induced defects with the ferroelectric at critical interfaces, and attempts to discover methods for mitigating potential damage resulting from these interactions.

First, the hetero-interface between the ferroelectric thin film and top electrode contact was investigated with exposure to 2.5 Mrad gamma radiation, concluding that $IrO_2$ top electrodes are more radiation hard than Pt top electrodes. $IrO_2$ top electrodes are conductive to ionic motion, especially that of mobile oxygen vacancies; on the other hand, accumulation of mobile oxygen vacancies at the interface between Pt top electrodes and PZT results in ferroelectric fatigue-like effects and greater degradation of functional properties. This critical interaction between radiation, oxygen vacancies, and the ferroelectric material lead to an array of investigations to elucidate its fundamental nature and methods for its mitigation.

While single-dose radiation studies provide a glimpse of material and device behavior in radiation-hostile settings, total ionization dose (TID) studies more adequately simulate real-world conditions by probing material behavior across a valuable range of exposure doses. However, comparison of functional properties for multiple design parameters across this range of radiation doses can become cumbersome. A phenomenological model was thus developed to quantify functional behavior with TID, relying on the fact that radiation induces defects and defect interactions that modify functional material response. Fitting of functional response trends as a function of TID with the phenomenological model yields two important parameters describing (i) the global susceptibility to radiation-induced degradation by induced defects and (ii) the rate of defect saturation in the material. Extraction and comparison of these parameters allows for quantification of defect interactions as a function of microstructural and compositional variations in ferroelectric thin films. Furthermore, the model was applied other functional materials, such as those used for solid oxide fuel cells (SOFCs) and high-temperature superconductors; as well as methods for manipulating defect populations, *e.g.*, radiation, ion implantation, chemical doping, *etc.*

The derived model was employed to study multiple changes to the ferroelectric material stack, including variations in PZT thin film microstructure and crystallization interface frequency, whose effects are closely intertwined and dependent on thermal processing histories of the films. First, investigations comparing PZT thin films with columnar and equiaxed grains showed that, generally, samples with smaller, more uniformly-oriented columnar grains were more resistant to radiation-induced degradation of domain wall motion, and exhibited reduced rates of defect saturation with respect to samples with equiaxed grains. Greater grain boundary in the columnar samples resulted in greater defect accumulation at grain boundaries, effectively acting as defect sinks for mobile oxygen vacancies and potentially reducing their deleterious effects with respect to equiaxed-grained samples. The defects created were concluded to be of relatively low pinning energy, and overcome at elevated electric field.

Studies of crystallization interface periodicity from a functional response enhancement perspective showed that microstructural discontinuity, compositional fluctuations, crystallographic phase, and potential flexoelectric effects play critical roles in determining the extent of intrinsic and extrinsic contributions to the functional response. This investigation was expanded to include TID studies on the effects of layer crystallization interfaces in PZT thin films showed that samples with greater frequency of crystallization through the thickness of the film and more discrete interfaces were more susceptible to radiation-induced degradation, again due to mobile oxygen vacancy accumulation at more numerous internal interfaces. Interestingly, PZT thin films annealed after every one and every three layers both showed small enhancements of dielectric, polarization, and piezoelectric responses at low radiation doses, likely due to the effects of radiation-induced charging on internal bias in the films. Samples with greater frequency of crystallized layers demonstrated greater enhancements and reduced susceptibility to degradation of polarization and piezoelectric responses across the TID range, potentially resulting from increased radiation-induced symmetry of internal bias in samples with more even distribution of layer interfaces through the thickness of the film.

Given the prominent effects of oxygen vacancy concentration on radiation-induced degradation of functional properties in PZT thin films, methods for reducing as-fabricated oxygen vacancy populations were investigated. Mn acceptor-doping of the PZT solid solution can effectively consume oxygen vacancies, resulting in a "hard" PZT composition and dramatically increasing radiation tolerance relative to undoped PZT samples. Defect dipoles formed between substituted Mn ions and oxygen vacancies pin domain wall motion and reduce overall sample response before irradiation, but diminish the population of mobile oxygen vacancies (relative to undoped PZT), thus increasing radiation hardness of Mn-doped samples across all gamma doses studied.

Finally, components of the lower material stack were studied in order to evaluate their potential effects on ferroelectric functional properties and their tolerance to radiation. The elastic layer and substrate do not directly contact the ferroelectric layer in the material stack, yet modification thereof resulted in substantial impact to functional response.

Changes to the elastic layer thickness and material produced notable changes in radiation-induced degradation trends, suggesting that residual stress generated in the ferroelectric thin film can significantly affect defect motion and eventual radiation tolerance. Related preliminary work to selectively release the PZT thin film from the substrate via backside plasma etching of the Si substrate demonstrated substantial modification of stress in the ferroelectric material and accompanying changes to its functional response – enormous enhancements to electromechanical properties and minor local modifications to dielectric and ferroelectric response. These results, coupled with those from TID studies on elastic layer variations, suggest that components of the material stack have significant effects on residual stress and film clamping, and thus are likely to affect radiation and defect interactions with the ferroelectric material.

The studies presented in this thesis serve magnify the fundamental scientific understanding of the interaction of radiation with ferroelectric thin films. Such understanding is leveraged to develop direct engineering approaches to mitigate radiation-induced degradation in ferroelectric thin films. Modification of critical interfaces in the ferroelectric material stack can have dramatic effects on the interaction of radiation with the material, defect generation, defect-ferroelectric and defect-defect interactions, and the eventual effects on functional response. This knowledge of radiation-induced defect interactions is beneficial for further development of approaches to fabrication of radiation-tolerant ferroelectric thin film material stacks for use in MEMS and microelectronics devices.

# SUMMARY

Ferroelectric materials have switchable, spontaneous polarization. Additionally, they exhibit large dielectric, pyroelectric and piezoelectric properties, making them ideal for numerous microelectronic devices, including mechanical logic elements, optical sensors and transducers, precision positioners, energy harvesting units, nonvolatile memory storage, and microelectromechanical systems (MEMS) sensors and actuators. Due to their radiation tolerance, ferroelectric materials have also become attractive for use in devices for radiation-hostile environments such as in aerospace, medical physics, x-ray/high energy source measurement tools, and nuclear monitoring systems.

A common ferroelectric material for many microelectronic applications, including piezoelectric MEMS devices and ferroelectric memory devices, due to its high functional properties is lead zirconate titanate (PZT). However increasing demand for smaller device footprint has pushed research efforts on PZT towards its limitations, creating a need for new material systems to exceed the current standards. Of particular interest among these for piezoelectric MEMS applications is $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$, PMN-PT, a relaxor-ferroelectric solid solution, which in bulk crystalline form exhibits even larger electromechanical response than ceramic PZT. Furthermore, PMN-PT's increased chemical heterogeneity promises even greater radiation hardness with respect to PZT films. In this work, PMN-PT thin films are defect engineered through the variation of processing parameters via chemical solution deposition. Total ionization dose (TID) studies are performed by irradiating films with a $^{60}Co$ source to explore PMN-PT's radiation tolerance. The role of grain morphology, porosity, and crystallization interfaces on the radiation

tolerance of PMN-PT are also studied. The PMN-PT thin films exhibited equivalent to superior radiation tolerance than PZT while maintaining higher functional response. While the microstructure has a strong effect on the overall functional response of the material, it has little to no effect on the radiation tolerance of PMN-PT, suggesting that the radiation tolerance of PMN-PT is largely due to its inherent properties.

$HfZrO_2$ (HZO) is another alternative ferroelectric material of particular interest for use in non-volatile memory applications, where their nanometer thin films as well as CMOS compatibility allows for fabrication of small and complex 3D structures to optimize for both device size and efficiency. In this work, TID studies are performed on plasma-enhanced atomic layer deposited (PEALD) films and thermal atomic layer deposited (THALD) films to identify which has greater radiation tolerance, and to further identify the differences in defects which dictate the ferroelectricity of the films. While both showed significant degradation from aging, the PEALD films exhibited more stable functional response after gamma-radiation doses up to 5 Mrad(Si).

Radiation studies on these alternative material systems in relation to processing-structure-property provides a better understanding of the mechanisms responsible for both functional response and radiation tolerance. The studies illustrate different pathways for concomitant enhanced functionality and higher radiation tolerance in ferroelectric thin films.

# ABSTRACT

ZHOU, HANHAN. Effects of Radiation on Ferroelectric Thin Film Materials (Under the direction of Jacob L. Jones).

Ferroelectric materials have been considered ideal candidates for actuators, sensors, logic switches, microelectromechanical systems (MEMS), etc. Among ferroelectric materials, lead zirconate titanate (PZT) material system has been studied extensively because of its superior functional properties. With technology development in outer space, nuclear stations, and other radiation rich environments, one important area of research focuses on studying the effects of radiation on the properties and performance of ferroelectric based devices. The fundamental effects of radiation are involved with introducing displacement events which are composed of Frenkel pairs, and ionization events. Thus, these introduced defects can accumulate at the grain boundaries, film-substrate interfaces, etc., and act as pinning sites of domain wall motion, and degrade the performance of the devices.

In outer space, the radiation source is majorly composed of protons (up to 95%), electrons and heavy ions. The effects of 3 MeV proton irradiation at several fluence levels on PZT thin films with and without a top electrode were studied. In both sets of films, no significant changes in the surface morphology and texture of the irradiated films were observed from Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), respectively. The strain distribution was further quantitatively analyzed in both set films before and after irradiation, through the use of $\sin^2\psi$ measurements. The results indicate that radiation had altered the strain states in both sets of films relative to their virgin states. The change of defect types and their concentrations were further examined using Doppler Broadening Spectroscopy (DBS). Coupled with simulated radiation damage results and the estimated radiation induced vacancy concentration, it is shown that PZT films are radiation tolerant under 3 MeV proton irradiation.

In order to understand effects of another major source of radiation, heavy ions, on PZT material system, 4 MeV $Fe^{3+}$ particles were implanted with various fluence levels. Variation in sample fabrication methods, types of top electrodes capped on PZT thin films, and the introduction of dopants are also incorporated for a more systematic study. The material system studied in this dissertation is based on PZT, fabricated by the Army Research Lab or Sandia

National Lab, with or without Mn dopants, capped with a metal oxide ($IrO_2$) or metallic (Pt) top electrode. Before elucidating the effects of radiation on the thin film materials with different combinations, the microstructure of the non-irradiated films was first studied with Transmission Kikuchi Diffraction (TKD), to explore effects of the fabrication routes, top electrode, and dopants on the structures of PZT films. TKD was first introduced by Keller and colleagues in 2011. Because of the novelty of this technique, TKD was first applied to a less complex oxide material system, $CeO_2$, to explore the essential conditions for successful experiments. The results obtained from TKD suggest that the microstructure of PZT is greatly influenced by fabrication routes and the introduction of Mn dopant. Furthermore, by analyzing the collected Kikuchi patterns from TKD experiments in both undoped and Mn-doped films, their local strain distributions were estimated. The results suggest that at a local scale, the strain distribution in the films, with and without dopants is comparable, though there are large differences in their microstructure and elemental distribution.

The effects of Mn dopants on the structures of PZT films were further studied using *in situ* XRD under electric field. The collected XRD patterns under electric field indicate that a different response to external stimuli exists between undoped and Mn-doped PZT films, suggesting Mn dopant has the capability to modify the performance of the devices in real applications.

The effects of $Fe^{3+}$ irradiation on texture and changes in the defect concentrations in undoped and Mn-doped PZT films capped with $IrO_2$ or Pt top electrodes were explored using XRD and DBS, respectively. The XRD results suggest that even though the texture of the films in the four combinations remain the same, the PZT unit cell volume increases with an increasing fluence level, as a consequence of increasing amount of radiation induced defects. The DBS results further indicate that the heavy ion radiation induces more defects on Zr/Ti sites, relative to Pb sites, in all four types of films. Additionally, through the comparison of the DBS results on the four types of films which experienced the same levels of radiation, changes in the defect types and concentration are further correlated with the type of the top electrodes and the dopants.

# SUMMARY

Due to their exceptional piezoelectric properties, ferroelectric materials are extensively used for electromechanical applications, ranging from medical ultrasound transducers, to speakers, micro and nano-positioners, etc.. In particular, solid solutions of ferroelectric perovskites are the most widely used materials, due to their order of magnitude larger response when compared to other ferroelectrics. The large response of these materials is attributed to a wide range of physical and chemical phenomena, including: the influence of a morphotropic phase boundary (MPB), the presence of chemical and polar heterogeneties, extrinsic contributions from ferroelectric domain walls and phase boundaries, and more. While these individual phenomena have been studied for decades, much about them remains poorly understood.

Concurrently, increasing computational power has brought to prominence a set of complex statistical approaches commonly referred to as machine learning (ML) techniques. In recent years, these ML approaches have been combined with advanced *in-situ* characterization techniques, capable of producing unprecedented amounts of data, to accelerate the assessment of ferroelectrics and many other functional materials. However, the shortcomings of ML, such as their “interpretability” and lack of physical constraints, have become increasingly apparent and hindered many ML based studies.

This work addresses the electromechanical response of ferroelectric perovskite solid solutions and the effectiveness of ML techniques applied to this field. In particular, lead zirconate titanate (PZT) and lead manganese niobate-lead titanate (PMN-xPT), which exhibit some of the largest reported piezoelectric properties, are investigated. Characterization is achieved *via* piezoresponse force microscopy (PFM), and an open-source wide bandwidth PFM variant is developed to expand the capabilities of the technique. Insight into the obtained data is achieved with a variety of unsupervised ML approaches, the limitations of which are addressed through use of a quantitative methodology developed here.

First, the local piezoresponse of (1-x)PMN-xPT is investigated as a function of space, time, applied electric-field, and for a range of compositions at x=0, 0.28, 0.40. Due to a lack of physical and/or chemical constraints, ML analysis of such a multi-parameter characterization is difficult, as behaviors cannot be correlated across the various parameters. To facilitate such an analysis, dimensional stacking, a method for imposing constraints and allowing for correlation of the various measurement parameters, was developed. With this approach, the evolution of time- and voltage-dependent electromechanical behaviors were tracked across different chemical compositions and a glassy phase associated with the relaxor end member was identified. Furthermore, the glassy relaxor-like behavior was shown to persist into compositions with large amounts of the ferroelectric end-member, including those traditionally considered simply “ferroelectric”.

Expounding upon dimensional stacking, a scientifically consistent procedure for applying ML was developed. This procedure utilizes constraints provided by dimensional stacking, but also minimizes user bias and the effects of overfitting by advocating a quantitative and reproducible approach to model selection. The procedure was demonstrated on previously reported data characterizing the voltage-dependent piezoresponse in PZT films over a micron-scale area. The results were compared to two previous ML-based reports assessing this data, which identified exotic physical phenomena. We demonstrate that the experimental data are well-described by classical ferroelectric theory and that limitations with the data set and biased application of previously reported ML-methodologies can result in substantial misinterpretation of data and analysis output.

Lastly, the voltage-dependence of the local piezoresponse in 0.60PMN-0.40PT was investigated, probing the effect of ferroelectric domain walls. Ferroelectric domain walls contribute from 40 to 80% of the overall piezoelectric response in ferroelectric solid solutions, however it is unclear if such contributions persist at smaller length scales. Through application of ML approaches, proximity to domain walls was not found to impact the piezoresponse. Yet, when traditional statistical analysis was applied to the same data a limited impact was identified, highlighting an unavoidable limitation in ML: comparatively weak statistical trends can be ignored. This weak dependence of the switching behavior on domain walls was suggested to be due to underlying material heterogeneities acting as nuclei for polarization reversal, effectively curtailing the impact of domain walls. These results suggest that future work should concentrate on controlling these heterogeneities as opposed to the traditional approach of domain engineering.

The studies presented in this thesis highlight the power and limitations of "off-the-shelf" ML-based analysis applied to materials science. Through development of the instrumentation and the application of ML methodologies discussed here (namely, systematic clustering and dimensional reduction approaches augmented by data set stacking guided through physical and chemical understanding of the existing phenomena), significant contributions to the scientific understanding of the electromechanical response in complex ferroelectric oxides were achieved. Namely, new understandings of how composition and a glassy domain state affect the piezoresponse behavior in PMN-xPT were discovered and a composition previously purely considered to be "ferroelectric" was shown to exhibit glassy relaxor-like behavior. However, physically meaningful and unbiased results were found to require appropriate methodology and physical/chemical constraints. Additionally, the final study underscored a remaining limitation in these off-the-shelf ML approaches, specifically: these approaches can be limited when attempting to identify complex and statistically weak behavior. However, by supplementing ML with traditional statistical techniques, the final study also highlighted that increased sub-micron heterogeneities could reduce the impact of domain walls.

## Summary

This thesis describes the optimization of piezoelectric $PbZr_xTi_{1-x}O_3$ (PZT) thin films on flexible stainless steel foils for various types of mechanical piezoelectric microelectromechanical systems (MEMS), including sensors or energy harvesters. The piezoelectric film is deposited on metal foils by chemical solution deposition (CSD). Full utilization of the potential of PZT films on metal foils requires control of the film crystallographic texture in the [100] direction through control of the deposition parameters.

In this study, (100) textured PZT thin films are grown by chemical solution deposition on stainless steel foils. Highly oriented films were successfully deposited on stainless steel with an intermediate $LaNiO_3$ seed layer (for orientation) using also chemical solution deposition. The $LaNiO_3$ film is optimized to have a high (100) orientation and a good conductivity (bulk resistivity of 70 m$\Omega$.cm on platinized stainless steel). The (100) oriented PZT film achieve a vertical piezoelectric displacement $d_{33,f}$ of 80 pm/V on a $100$ $\mu$m electrode and a dielectric permittivity of 790 at 1 kHz.