Iridium Oxide (IrO2) as a Top Electrode for Ferroelectric Micro-Electro-Mechanical Systems (MEMS) Devices for Radiation Rich Environments

Manuel Rivas

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Iridium Oxide (IrO₂) as a Top Electrode for Ferroelectric Micro-Electro-Mechanical Systems (MEMS) Devices for Radiation Rich Environments

Manuel Rivas, PhD
University of Connecticut, 2018

The multifunctional properties of ferroelectric materials make them ideal components for numerous applications including for extreme environments such as space. Iridium oxide (IrO₂) electrodes have been demonstrated to improve the lifetime of ferroelectric memory devices, however little is known about its influence on the electromechanical properties important for ferroelectric microelectromechanical systems (MEMS). The performance of thin film lead zirconate titanate (PZT) based MEMS is affected by the processing conditions, composition, device design, electrode materials, and the environment. This work details the development and characterization of iridium oxide electrodes for PZT based microelectromechanical and pyroelectric-harvesting systems, fabrication induced defects, and design of clamped vs unclamped devices. This work also considers the influence of iridium oxide top electrodes on the properties of PZT films and MEMS devices subjected to gamma and heavy ion radiation for applications in space and for evaluating nuclear material where human exposure must be kept to a minimum.

Using single point force measurements with an atomic force microscope, this work presents the first known experimental value of Young’s modulus for thin film IrO₂ ($E_{IrO_2} = 262$ GPa). It was discovered that iridium oxide films of different morphologies are produced by manipulating the reactive gas flow rate in a sputtering process. Planar IrO₂ for piezoelectric applications was optimized at 60 sccm O₂ flow rate deposited at 500°C. Nanostructured, 2D platelets are observed for high oxygen flow rates (100 sccm) producing a self-limiting dense columnar film as the base of the plate-like structures. While the plate-like region continues to grow with increased deposition
at a rate of \(~6\) nm/s, the dense film appears to reach a critical thickness of approximately \(60 \pm 10\). Devices with iridium oxide top electrode appear to be more radiation resistant when compared to identically fabricated devices with a platinum (Pt) top electrode, when exposed up to 10 Mrad(Si) of gamma rays from a \(^{60}\)Co source and an equivalent dose with \(\text{Fe}^{3+}\) ions.
Iridium Oxide (IrO$_2$) as a Top Electrode for Ferroelectric Micro-Electro-Mechanical Systems (MEMS) Devices for Radiation Rich Environments

Manuel Rivas

B.S., University of Texas-Pan American, 2012
M.S., University of Connecticut, 2018

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Iridium Oxide (IrO\textsubscript{2}) as a Top Electrode for Ferroelectric Micro-Electro-Mechanical Systems (MEMS) Devices for Radiation Rich Environments

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2018
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I was fortunate enough to spend fifteen years looking up to you, without realizing I was learning the foundation of what it is to be a great man by simply trying to imitate you. Ever since I can remember, I always tried to make you proud and continue to try to do so to this day. I was fifteen when I stood by your bed wondering what it was that you wanted to tell me before you slipped into your coma, the same weight I felt on my shoulders that day I still carry. I held your hand while making promises hoping you were able to listen. I’ll be able to take good care of the family now. I finally did it. Happy birthday dad. I love and miss you every day.

This dissertation is dedicated to my family:
my grandmother, my brother, my sister, my mother and my father.
May he rest in peace.
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Chapter 1

Introduction and Motivation

Ferroelectric thin films and devices are vital components for numerous applications such as non-volatile memory [1-4], sensors and actuators [5-7], RF devices [8, 9], and energy harvesting systems [10,11]. The multifunctional properties of ferroelectric materials make these ideal for microelectromechanical system (MEMS) devices. Of specific interest are lead zirconate titanate (PZT) thin films, which have been used for filters [12], pyroelectric infrared radiation detectors [13], mechanical logic relays [8], digital computation elements for low power systems [7, 8], energy harvesting systems [11], and millimeter-scale robotics [7, 8]. The large dielectric and piezoelectric response in PZT thin films depend crucially on grain boundaries, phase boundaries, and/or domain walls which are non-linearly mobile and hysteretic internal interfaces.

The performance of thin film PZT-based MEMS is affected by the processing conditions, composition, device design, electrode materials, and operating environment. Previous work has focused on identifying bottom electrodes to template specific texturing in ferroelectric crystal growth [14], reducing electric losses [15], understanding the domain nucleation at the interface [16]. In this work the focus is on IrO$_2$ top electrodes and the effects on the piezoelectric, pyroelectric, and ferroelectric performance enhancements that the top electrode imparts. The top electrode material can significantly affect the performance of PZT MEMS by manipulating the composite mechanical properties, quality factor, piezoelectric parameters, and changing electrical response such as polarization, resistivity, and tunability. This work also considers the influence of iridium oxide top electrodes on the properties of PZT films and MEMS devices subjected to
gamma and heavy ion radiation for applications in space, nuclear reactors, and for evaluating nuclear material where human exposure must be kept to a minimum.

This chapter provides a fundamental background of Piezoelectricity, Pyroelectricity, and Ferroelectricity, the material properties and effects that are investigated in this work. A background on Micro-Electro-Mechanical-Systems, Lead zirconate titanate (PZT), and the importance of top electrodes is given. A thorough background on radiation, its two types, and the different effects radiation has on materials is provided. Finally, the different tools used to characterize the ferroelectric devices and top electrode are given and explained.

1.1 Piezoelectricity

Piezoelectricity, first discovered by the Curie brothers in 1880, is the property of some materials to develop an electric charge when mechanical stress is applied (Eq. 1), known as the direct piezoelectric effect. After Lippman theoretically predicted thermodynamically the converse piezoelectric effect, i.e. a change in strain with an applied electric field (Eq. 2), the Curie brothers verified it the following year [17].

\[ D_i = d_{ijk} T_{jk} \quad \text{Equation 1} \]
\[ S_{jk} = d_{ijk} E_i \quad \text{Equation 2} \]

Where \( D_i \) is the induced electric displacement (Cm\(^{-2}\)), proportional to \( d_{ijk} \) - the piezoelectric coefficient (CN\(^{-1}\) or mV\(^{-1}\)) and \( T_{jk} \) - the applied stress (Nm\(^{-2}\)); \( S_{jk} \) is the induced strain (unitless) which is proportional to the piezoelectric coefficient and \( E_i \) - the applied electric field (Vm\(^{-1}\)).

The Curie brothers established some relationships between piezoelectricity and crystal structure but it was Woldemar Voigt in 1894 who determined which of the 32 crystal point groups could have piezoelectric properties. Due to the definition of the piezoelectric effect, all components
of the piezoelectric tensor vanish in crystals with a center of symmetry. Out of the 32 crystal point groups, as seen in Table 1, 21 are non-centrosymmetric, meaning they do not have a point reflection through the center. Out of these 21 non-centrosymmetric groups, 20 are found to be piezoelectric. The exception is the cubic class 432, because the piezoelectric charges which develop along the 111 polar axes cancel each other by definition.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>32 Crystallographic Point Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1 -1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2 m 2/m</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>222 mm2 mmm</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4 -4 4/m 422 4mm -42m 4/mmm</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3 -3 32 3m -3m</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6 -6 6/m 622 6mm -62m 6/mmm</td>
</tr>
<tr>
<td>Cubic</td>
<td>23 m3 432* -43m m3m</td>
</tr>
</tbody>
</table>

Table 1: Crystal Systems and Point Groups. Those that are centro-symmetric are in blue. Non-centrosymmetric and piezoelectric are in red, polar (pyroelectric) are in bold. * Denotes only exemption to non-centrosymmetric being piezoelectric.

Statistically, about 30% of all materials are non-centrosymmetric, with several hundred potentially possessing sufficient piezoelectric activity to be valuable for applications. But the absence of a center of symmetry is a necessary but not entirely sufficient requirement for the material to exhibit any sizeable piezoelectric effect [18]. Naturally occurring piezoelectric crystals include quartz, sucrose (table sugar), Rochelle salt, Topaz, Tourmaline group minerals, and the mineral macedonite (lead titanate). Piezoelectricity also occurs naturally in bone, tendon, silk,
wood (due to texture), enamel, dentin, DNA, and various proteins. Synthetic crystals such as Gallium orthophosphate (GaPO_4) and Langasite (La_3Ga_5SiO_14), as well as many ceramics including Barium titanate (BaTiO_3), Lead zirconate titanate (PZT), Lithium niobate (LiNbO_3), and many more, have been developed to exploit the coupling of electrical and mechanical energy of the piezoelectric effect. Numerous applications result, which can be grouped as follows:

1) Sensor applications – using the direct effect
2) Actuator applications – using the converse effect
3) Resonance applications – using both direct and converse effects
4) Energy conversion – direct effect

This body of work will partially focus on thin film actuator devices. The piezoelectric material is deposited between a top and bottom electrode. This is combined with an elastic layer to maximize the deformation using the transverse piezoelectric coefficient, d_{31}, as seen in Figure 1. Such thin film actuators are beneficial because they can operate with a relatively low actuation voltage and can apply a high contact force when maximally deformed.
These thin film actuators offer low actuation voltage and high contact force. The fabrication process for many of the large piezoelectric coefficient ceramics are complicated due to the temperature needed for the crystallization of the material [19].

1.2 Pyroelectricity

Of the 20 piezoelectric crystal point groups, 10 can further be classified as polar, meaning an electric dipole moment is present in the absence of an electric field. If this spontaneous polarization changes with temperature, the material is then also pyroelectric. The earliest description of the pyroelectric effect was by the Greek philosopher Theophrastus, in the fourth century BC, when he described the mineral today known as tourmaline as having the property of attracting straw and bits of wood. He especially observed these effects of electrostatic charges due to temperature changes in the mineral [20]. Centuries later, the first description of pyroelectricity in a scientific journal was by Louis Lemery, in 1717 [21]. In 1756, Dr. Aepinus observed that tourmaline became electrified by being warmed and pyroelectricity once again began to be of interest to the scientific community.
As seen in Eq. 3, the pyroelectric coefficient ($\Pi$ with units Cm$^{-2}$K$^{-1}$) is the change in net electrical polarization, $P$ (C/m$^2$), proportional to a change in temperature, $T$ (K). It can be applied in materials via the pyroelectric equation (Eq. 4):

$$\Pi = \frac{\partial P_{S,i}}{\partial T} \quad \text{Equation 3}$$

$$I_p = \Pi A \frac{dT}{dt} \quad \text{Equation 4}$$

where $I_p$ is the current (Amperes) produced by the relationship of the pyroelectric coefficient, $A$ – the area, temperature, and $t$ – time (s).

Due to the polarization being sensitive to temperature, the most popular use for pyroelectricity is the detection of radiation [22]. More applications have been found for pyroelectric materials such as Infrared (IR) detectors, solar energy conversion, pyrometry, thermometry, refrigeration [22, 23] and more recently wireless power transfer [24]. The most widespread application is sensing body heat for automatically opening doors, switching on lights, enabling HVAC systems, counting customers in lines (essentially crowd control/optimization), etc.[private communication, J. Mantese, United Technologies Research Center]

### 1.3 Ferroelectricity

Ferroelectric behavior, a subset of piezoelectricity and further of pyroelectricity, was first identified in Rochelle salt in the 1920’s. A ferroelectric material is not centrosymmetric like a piezoelectric, displays a spontaneous electric dipole moment like a pyroelectric, and finally this polarization can be re-oriented by an applied electric field. Most technologically important ferroelectric materials are perovskite structured oxides [25]. In the perovskite structure, ABO$_3$, the
A-site atom is a divalent ion located at the corners of the unit cell (0,0,0), the B-site is a tetravalent ion located in the body center position (1/2,1/2,1/2) and the oxygen atoms sit in the face center position (1/2,1/2,0) as seen in Figure 2.

Figure 2: Representation of cubic (Pm3m) perovskite ABO$_3$ structure below the $T_c$ (a) and tetragonal (P4mm) perovskite structure above the $T_c$ (b).

Above the perovskite material’s Curie temperature ($T_c$), the crystal structure is cubic with no dipole moment, making it a paraelectric. Below the $T_c$, the lattice is distorted as the ions shift to a lower energy configuration, specifically with one or more atoms shifting such that the lattice becomes non-centrosymmetric. This creates an internal dipole moment with magnitude and alignment according to the collective shifts of the ion positions. This dipole moment per unit cell can be observed because it can produce a net electrical polarization. This polarization is a vector, with both a magnitude and direction.
1.3.1 Ferroelectric Hysteresis

The most recognizable aspect of ferroelectricity is the polarization electric field hysteresis (PE) loop, seen in Figure 3. The PE loop results from the change in net polarization of the material as the applied electric field is changed.

![Figure 3: Schematic of polarization electric field hysteresis loop illustrating maximum polarization ($P_{max}$), saturation polarization ($P_{sat}$), remanent polarization ($P_r$), and coercive field ($E_c$).](image)

The maximum polarization, $P_{max}$, is the polarization which results under the most extreme applied electric fields (at the rail electric field). The saturation polarization, $P_{sat}$, is the linear extrapolation nearest $P_{max}$ back to the y-axis (polarization). The remnant polarization, $P_r$, is the actual polarization when the electric field is zero ($E=0$). The coercive field $E_c$, is the electric field where half of the switchable domains have switched, creating a net polarization of zero. While these
specific parameters for ferroelectrics are important, the shape and shift of the PE loop offers valuable information as well. The slope of the hysteresis loop at the coercive field is known as the hysteresis tilt. The higher the tilt, the more instantaneous repolarization occurs. The smaller the tilt, i.e. for flatter loops, suggests either a dielectric film with low permittivity between the ferroelectric material and the electrodes, defects pinning the domain wall motion restricting the switching, or a broad distribution of local coercive fields within the sampled volume usually related to a wide range of defects.

Thin film ferroelectrics were first developed and integrated into semiconductor chips in 1984 [26] and into silicon chips in the early 1990’s [27]. This allowed ferroelectrics to expand to broad areas of research and application i.e. substrate-film interfaces, ferroelectric random access memories (FeRAMs), dynamic random access memory (DRAM) capacitors, electron emitters, sensors, etc.[27].

1.4 MEMS

The demand for faster, smaller, cheaper, lower power consumption, mass producible, and especially functional and integrated devices has led to the development of micrometer-scale devices that integrate electrical and mechanical elements known as Micro-Electro-Mechanical-Systems (MEMS). In 2015, the MEMS market was valued at $13.0 billion and is projected to reach $26.8 billion by 2022 [28]. This is due to a wide range of applications, primarily driven by MEMS accelerometers and gyroscopes [29-31] that are increasingly ubiquitous in automobiles, smartphones, and other consumer products. They are also implemented in adaptive optics for improved imaging [32-34] and in projection displays [35]. They have enabled advances in DNA separation, biology, and medicine as MEMS implants to assist healing and enhance biological functions as well [8,36-40].
Piezoelectric materials are especially noteworthy. They are used for a variety of applications like pressure sensors [42] and energy harvesters [43]. MEMS microphones [44], inkjet head printers [7], and mm-scale robotics [8] all exploit the material’s high power density. They are used for communications for switches and tuning devices too. MEMS switches provide a low loss, low power alternative with a key advantage being their linearity [44]. Common piezoelectric materials used in MEMS devices include AlN, ZnO, and Lead Zirconate Titanate (PZT) [9].

1.5 Lead Zirconate Titanate (PZT)

PZT is one of the primary material used in thin film piezoelectric MEMS [45]. This is in part due to its large piezoelectric constant enabling it to generate large displacements and forces [46], its large electromechanical coupling factor, and its piezoelectric coefficient being tunable with voltage [47, 48]. All of these factors make PZT an ideal candidate for many piezoelectric applications: i.e. low voltage and low power switches, phase shifters, analog to digital converters, tunable passives, resonators, filters, and millimeter-scale robotics [7, 8, 47].

With the chemical formula Pb(Zr$\text{x}$Ti$_{1-x}$)O$_3$, PZT is a combination between PbZrO$_3$ and PbTiO$_3$ with different ferroelectric and piezoelectric properties dependent on the Zirconium to Titanium ratio. In 1954, Jaffe et al performed an investigation on the composition spread of PZT that led to the discovery of a morphotropic phase boundary. This MPB is a region where the rhombohedral and tetragonal phases become a two-phase mixture. In the case of PZT, the MPB is near the 52/48 ratio of Zr$^{4+}$/Ti$^{4+}$ as seen in the phase diagram in Figure 4.
Above the Curie temperature PZT is cubic. Below $T_c$, in the regions with higher ratio of Zr to Ti, the material should be rhombohedral. For Ti rich region below $T_c$, a Tetragonal structure should result, with the MPB intersecting these two phase regions. The structure of PZT in the tetragonal region, even for no applied electric field, therefore results in a net polarization per unit cell (Figure 5a). Upon application of an external electric field, the atom distorts further with a concomitant further expansion or contraction of the tetragonal unit cell (b) depending on the direction of the applied field. If the field exceeds the coercive field, the displaced B-site atom flips to the opposite half of the unit cell as shown, resulting in an inversion of the sign of the polarization.
Especially large piezoelectric effects and polarization are observed at the MPB. All of the PZT in this work is prepared at the MPB with a Zr/Ti ratio of 52/48.

1.6 Top Electrode

The electrode plays a vital role in PZT-based MEMS. Since device performance is affected by processing conditions, in particular relatively high temperatures, noble metal electrodes have been widely explored i.e. Ru, Ir, Au, Pt, Ag, Cu, Ni [50, 51, 52]. Research has also been conducted using metal alloys like AgPd [53] or Ag$_{0.97}$Pd$_{0.01}$Cu$_{0.02}$ [54], and conductive oxide electrodes including La$_{0.5}$Sr$_{0.5}$CoO$_3$, YBa$_2$Cu$_3$O$_{7-x}$, LaNiO$_3$, In$_2$O$_3$, RuO$_2$, IrO$_2$, SrRuO$_3$ [51, 55-60]. Combinations of noble metals with a metal oxide are considered as well, such as Pt/SRO [61].

In resonant MEMS devices, there are two primary factors for evaluating electrodes: resistivity, and mechanical quality factor. Resistivity can be extremely important for maintaining high performance resonant devices as electrical impedance can be a dominant loss mechanism for
The mechanical properties of the top electrode are most significant in terms of how they modify the collective mechanical properties of the completed device stack: elastic layer, bottom electrode, piezoelectric film, top electrode, and possibly also a final capping layer. Of particular importance is the composite modulus and neutral axis of a released (free-moving) device, which therefore is a function of the Young’s Modulus ($E$) of the top electrode material. It is also important to account for the fact that many properties of thin films deviate from their bulk counterparts [64, 65]. This deviation usually relates to critical dimensions (thickness or patterned feature sizes) approaching the dimensions of microstructural features, including grains, grain boundaries, strain and concentration gradients, dislocation networks, etc. [66].

1.6.1 Platinum

A commonly used electrode material in R&D for thin film lead zirconate titante (PZT) devices is platinum. Pt is used as a top and bottom electrode. The advantage of using Pt as a bottom electrode is it acts as a growth template for PZT because the lattice spacing in the (111) plane of Pt is closely matched to the (001) plane of PZT. Therefore proper growth can yield highly textured [001] oriented films with the polarization directed normal to the electrode surfaces [14]. Additionally, Pt is non-reactive, suppressing the formation of intermediate oxides between the electrode and the oxygen containing PZT during high temperature fabrication processes. The disadvantage is that PZT growth on Pt produces high angle grain boundaries which have been shown to cause aging and fatigue due to charge segregation and defect accumulation. Pt electrode devices are therefore problematic in terms of long term device performance and reliability [60, 67].
1.6.2 Iridium Oxide

Iridium Oxide (IrO$_2$) electrodes have been considered as a replacement for platinum (Pt) electrodes in memory devices since 1992, with the introduction of mass produced ferroelectric random access memory (FRAM) [68]. Iridium oxide (IrO$_2$) is a promising top electrode material for piezo and ferroelectric devices due to its thermal stability, reliability performance, relative low resistivity for a metal-oxide, and high charge injection capacity. It also has negligible reactivity with Si at high temperatures [59], can minimize hydrogen [68] and lead [59] diffusion, allows a reduction in the accumulation of oxygen vacancies at the electrode interface [69] believed to be caused by enabling oxygen vacancies to migrate across the already-oxide-based electrode interface. There have been several reports on different sputtering techniques of IrO$_2$ and how the parameters of partial pressure, temperature, and oxygen flow affect its properties [69-72]. Oxygen vacancy accumulation is thought to be the underlying mechanism for degradation in ferroelectric materials and is influential in radiation hardening [73].

For pyroelectric applications, the top electrode furthermore should be highly spectrally absorbing as well. Under high oxygen flow deposition conditions, IrO$_2$ has been shown to grow plate-like structures with a substantial increase in the surface area. This can dramatically increasing photon absorption, making it extremely attractive for ferroelectric-based pyroelectric sensors and energy harvesters.

While plate-like IrO$_2$ structures have been previously reported in literature [70-72], no detailed report has been made on their growth, microstructural evolution, or incorporation into real devices. Moreover, experimental Young’s modulus data for continuous or high-surface area IrO$_2$ thin films is hardly available, especially when compared to copious reports for Pt and other widespread electrode materials [74-76]. In fact, the most widely used data for $E_{IrO2}$ is a first-
principles calculation, computed with density functional theory within a generalized gradient density approximation [77]. Experimental verification is needed to increase the fidelity of piezoelectric actuator models where IrO$_2$ is the top electrode. Such insight into the measured mechanical properties of IrO$_2$, as well as the performance of pyroelectric devices based on high-surface-area plate-like IrO$_2$, are important novel contributions of this work to the functional device community.

1.7 Radiation

The advances in MEMS designs, materials, and fabrication, especially including size, functionality, and low power operation, suggest opportunities for space and military applications. In many such cases, performance and reliability as a function of radiation exposure is crucial. Space is a harsh environment that can have short and long term effects on electronics due to continual but also highly variable radiation exposure. Accumulated damage from high energy protons, electrons, and cosmic rays limit the performance, operation, and lifetime of most electronic systems in space [78]. Ferroelectric devices provide benefits over traditional materials in terms of radiation insensitivity. Accordingly, many ferroelectric-based applications have been explored for the extreme environment of space, including infrared sensors [79], actuators for micro-thrusters for satellites [80], and vital components for satellite systems.

Furthermore, aerospace systems generally rely on numerous sensors for military, intelligence, and scientific applications such as surveillance, fire control, target tracking and discrimination, and imaging. For operating stability and minimization of thermal noise, some of these systems must be cooled to extremely low temperatures, which presents significant challenges due to weight, power, cost, and maintenance [79]. PZT based MEMS have the potential to excel
in these challenges since they can miniaturize some of the functional components and therefore minimize heat loads for requisite cooling requirements.

A critical question for these applications is the actual effects of radiation on the devices themselves. Previous work has focused on evaluating the radiation effects on ferroelectric properties for ferroelectric memory [81-84], with little research reported about the influence of radiation on the electromechanical properties of these materials and assembled piezoelectric MEMS [85]. Such investigations are clearly important for the deployment of ferroelectric MEMS in radiation environments. IrO$_2$ is especially promising as an electrode material for MEMS in radiation environments because it reduces oxygen vacancy density at the electrode interface and oxygen vacancies are thought to be the underlying mechanism for radiation defects. This is the remaining primary focus of this work: broadening the fundamental understanding of radiation effects on functional properties of ferroelectric films, piezoMEMS devices.

1.7.1 Types of Radiation

To fully understand the effects of radiation on materials, one must first be familiar with the different types of radiation, their detrimental consequences referred to as radiation damage, and their mechanism for interaction with the various materials in any given device. The type of material also affects these parameters, so a fundamental understanding of the characteristics of the material are needed as well. Radiation can be categorized into two types: Ionizing, and Non-Ionizing.

Ionizing radiation, as the name implies, creates ions in the material by removing electrons from their atoms. This includes alpha and beta particles, protons, neutrons, as well as gamma and X-rays, see Table 2. Non-Ionizing radiation is radiation that will cause atoms to vibrate or excite
electrons to a higher energy state. This type of radiation includes the electromagnetic spectrum, from near ultraviolet and visible light to microwaves and low frequencies, thermal radiation, and black body radiation. It is important to note that for nuclear materials as well as some devices in space, they can be bombarded by nuclear particles and electromagnetic radiation from both internal and external sources [78, 86, 87].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Alpha</th>
<th>Proton</th>
<th>Beta</th>
<th>Photon</th>
<th>Neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>( \frac{2}{3} \alpha ) or He(^{2+})</td>
<td>( \frac{1}{2} p ) or H(^{1+})</td>
<td>( \frac{1}{2} e ) or β</td>
<td>( \frac{1}{2} \gamma )</td>
<td>( \frac{1}{2} \eta )</td>
</tr>
<tr>
<td>Charge</td>
<td>+2</td>
<td>+1</td>
<td>-1</td>
<td>neutral</td>
<td>neutral</td>
</tr>
<tr>
<td>Mass (amu)</td>
<td>4.001506</td>
<td>1.007276</td>
<td>0.00054858</td>
<td>---</td>
<td>1.008665</td>
</tr>
<tr>
<td>Speed of Light</td>
<td>2.3%</td>
<td>4.6%</td>
<td>94.1%</td>
<td>100%</td>
<td>4.6%</td>
</tr>
<tr>
<td>Range in Air (cm)</td>
<td>0.56</td>
<td>1.81</td>
<td>319</td>
<td>82,000*</td>
<td>39,250*</td>
</tr>
</tbody>
</table>

*Table 2: Ionizing radiation [adapted from 89] Radiation of 1 MeV *range based on 99.9% reduction.*

### 1.7.2 Radiation Sources

Nuclear materials, space devices and spacecraft are subject to bombardment by nuclear particles and electromagnetic radiation from both internal and external sources [78, 86, 87]. In space, sources of radiation come from the geo-magnetically trapped radiation belts known as the Van Allen belts, solar flares, solar wind, solar electromagnetic radiation, cosmic and auroral radiation. These produce an array of energetic electrons, alpha particles, protons, photons, and heavy ions. Onboard a space craft, sources or radiation can come from nuclear reactors for
propulsion and electrical power, emitting neutrons, gamma rays, and beta particles. [86] Only the trapped radiation of protons and electrons in the inner Van Allen belt, between 1.2 and 3.2 earth radii, can be considered constant. The intensity and spectral characteristics of the remaining external sources are functions of the solar activity and the location in the solar system.

In nuclear reactors, the energy released in the core by fission appears in various forms, mainly as kinetic energy of fission fragments, beta particles from radioactive decay of fission products, and fission neutrons. Fission fragments with penetration depth of 0.01 mm, high energy beta particles penetrating up to 2 mm, and fission neutrons which can travel distances between a few cm to a few feet make up about 90% or more of the total energy created. The remaining 10% or less of the energy produced in fission appears as gamma rays. Gamma rays and the radioactive decay of fission fragment generate heat that continues after reaction shutdown. [88]

1.7.3 Radiation Effects

In general, there are four types of radiation effects on materials [89] as summarized in Table 3, are impurity production, the transmutation of nuclei into another nuclei; atomic displacement, a disruption of the atomic arrangement or crystalline structure; ionization, the formation of ions; and energy release, resulting from thermal heating.
Table 3: Radiation Effects and Damage [adapted from 89].

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Impurity Production</th>
<th>Atom Displacement</th>
<th>Ionization</th>
<th>Energy Release</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal (eV) neutron</td>
<td>Directly by absorption</td>
<td>Yes, indirectly</td>
<td>Indirectly</td>
<td>Indirectly</td>
</tr>
<tr>
<td>Fast (MeV) neutron</td>
<td>Directly by absorption</td>
<td>Multiple via scattering reactions; “knock-on” atoms</td>
<td>Indirectly</td>
<td>Indirectly</td>
</tr>
<tr>
<td>Alpha</td>
<td>He buildup</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes (very short range)</td>
</tr>
<tr>
<td>Proton</td>
<td>H buildup</td>
<td>Yes</td>
<td>Directly</td>
<td>Yes (short range)</td>
</tr>
<tr>
<td>Beta</td>
<td>n/a</td>
<td>Some</td>
<td>Directly</td>
<td>Localized</td>
</tr>
<tr>
<td>Photon</td>
<td>n/a</td>
<td>Rare (Compton effect)</td>
<td>Indirectly</td>
<td>Over large distance (gamma)</td>
</tr>
</tbody>
</table>

The magnitude and balance of effects and damage summarized in response to ionizing radiation can furthermore be very sensitive to the specific materials. This primarily couples with bonding types. Materials such as polymers based largely on covalent bonds can experience the most damage due to a chemical change. Specifically, the ionizing radiation strips electrons, breaking atomic bonds, and hence alters or forms new molecules. On the other hand, materials comprising ionic bonds do not receive as much damage.

Electron migration may also occur due to the possibility that a collision between ionizing radiation and an atom overcome that atom’s electron affinity. The resulting electron deficient site may of course be refilled by a different displaced electron, restoring charge neutrality. But this process generally increases conductivity during irradiation due to the increased proportion of free
carriers, creating problems especially for dielectrics or ionic conductors. A displaced electron may also become localized to a crystal lattice defect, resulting in a Farbe-centre, so known because this is often accompanied by a change in color. These color-centers can last for days, weeks, or years, and are most commonly observed with glass and other transparent or colored ceramics. In fact consumer gems are routinely ‘brightened’ via irradiation. Unsurprisingly, ionizing radiation typically has only transient effects for metals, since any electrons stripped from an atom are promptly replaced from by the sea of electrons available from the lattice [87]. In any case, none of these electron mechanisms tend to have a significant effect on mechanical properties as long as the defect density resulting from irradiation is relatively small.

Mechanical properties are directly related to the microstructural characteristics of a given material. Nuclear radiation tends to destroy the lattice structure, altering the basic material properties i.e. ductility due to point defects created by the radiation. This microstructural change then affects the macroscopic properties due to various mechanical properties are affected by the way in which one plane of atoms slips over the adjacent plane. Dislocations caused by the radiation can inhibit the slip process, requiring more energy to initiate the slipping. As a consequence, the hardness and strength of the material increase, but the toughness and ductility properties decrease as less energy is needed for failure by fracture and permanent strain.

Radiation can change the electrical properties of a material such as conductivity, by creating lattice defects from atomic displacement, reducing the mean free path for electron movement. Ionizing radiation can excite large numbers of valence electrons to the conduction band in both semiconductors and insulators. This leaves a hole in the valence band, creating an electron-hole pair. This event is called photoconduction, and it increases intrinsic carrier concentration, both electrons and holes, the resistivity of semiconductors decreases according to
\[ \sigma = \frac{1}{\rho} = q \left( n_n \mu_n + n_p \mu_p \right) \]  

*Equation 5*

where conductivity (\( \sigma \)) and resistivity (\( \rho \)) are related to the fundamental charge unit (q), the number of charge carriers (n), and the carrier mobility (\( \mu \)). The subscript n denotes negative electron carriers and p signifies positive hole carriers. This can significantly increase the electrical conductivity of both a semiconductor and an insulator, also known as radiation-induced conductivity.

### 1.7.4 Radiation Units

In the field of ionizing radiation, there are three SI units which are given special names because of their importance to human health [90]. The becquerel (Bq) is the activity referred to a radionuclide and has units of s\(^{-1}\). The gray (Gy) is the unit for absorbed dose and is expressed in J/kg (m\(^2\)s\(^{-2}\)). The Sievert (Sv), also expressed in J/kg (m\(^2\)s\(^{-2}\)), is the equivalent dose of a Gy multiplied by the relative biological effectiveness (Q). This last term, Table 4 takes into account the different effects on humans caused by various radiation sources, i.e. essentially how strongly the radiation is absorbed by specific tissue (materials).

<table>
<thead>
<tr>
<th>Q</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-Rays, gamma, beta particles</td>
</tr>
<tr>
<td>3</td>
<td>Slow neutrons</td>
</tr>
<tr>
<td>10</td>
<td>Protons and fast neutrons</td>
</tr>
<tr>
<td>20</td>
<td>Alpha particles</td>
</tr>
</tbody>
</table>

*Table 4: Biological Effectiveness, Q, for the different types of radiation sources.*
More broadly, and separate from questions of human health and medicine, the most commonly used units of radiation are the Radiation Absorbed Dose (rad) and the Radiation Equivalent for Man (rem). One rad corresponds to the absorption of 0.01 Joules of energy per kilogram of matter (1 rad = 0.01 Gy). Rem is the rad multiplied by the relative biological effectiveness as follows. 1 rem = 1 rad*Q. [91]

1.8 Tools

Ferroelectric materials and top electrode materials are typically characterized by several methods and tools: X-ray diffraction, Atomic Force Microscopy, Scanning Electron Microscopy, ferroelectric tester, impedance analyzer, laser doppler vibrometry, and four-point probe testing.

1.8.1 X-ray Diffraction

X-ray diffraction (XRD) is a rapid analytical technique primarily used for identifying material phases and composition. When a material is subjected to X-rays of a fixed wavelength, they interact with the lattice and scatter to cause either absorption or diffraction. Diffraction occurs specifically when there is constructive interference of the scattered x-rays. The general relationship between the incident X-ray wavelength, spacing between the lattice planes of atoms, and angle of incidence is known as Bragg’s law, expressed as:

\[ n\lambda = 2d \sin \theta \]

Equation 6

Where \( n \) is an order of reflection, the wavelength of the incident X-ray (\( \lambda \)) is known, the interplanar spacing (\( d \)) is typically sought, and the angle of incidence for constructive interference occurs (\( \Theta \)) is measured. As a result, for each unique separation between atomic planes, distinct diffraction peaks are possible. XRD peaks thereby yields the atomic spacings and hence unit cell dimensions, while the relative positions of a multiple peaks reveals atomic arrangements and
specifically symmetries within a unit cell (or, by extension, the presence of additional phases in
the sampled volume). Analysis of the relative intensities of coupled peaks furthermore reveals the
composition, and the peak breadth can identify strain gradients or nanoscale feature dimensions.
For this work, XRD is primarily used to confirm crystal phases present in various specimens, and
also to determine or confirm grain orientation and/or texture. More sophisticated ‘rocking curve’
analysis is also sometimes employed to assess dislocation densities and generally film quality.

1.8.2 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a branch of Scanning Probe Microscopy (SPM) that
utilizes a sharp tip and integrated cantilever to mechanically interact with a material. As seen in
Figure 6, forces between the probe apex and an underlying specimen are measured via optical
reflection of a laser spot from the spring-like cantilever which essentially obeys Hooke’s law
(F=k_cz). In particular, a 4-quadrant segmented photodiode constantly reports the position of the
laser spot, which is displaced anytime the tip-sample force changes and hence the cantilever
deflects. Via piezoelectric scanners the tip rasters a sample surface with nanoscale control.
Simultaneously a feedback loop typically maintain a constant tip-sample interaction by pushing or
pulling the lever towards or away from the specimen as necessary. This change in z-position as a
function of the xy location is recorded to generate images of the topography. Additional imaging
modes can achieve maps of mechanical properties, piezoactuation, current pathways, detect forces
from PiezoMEMS switch contacts [92], etc.
**Figure 6:** Basic schematic for AFM. Any interactions between the tip and sample cause the attached cantilever to deflect, resulting in displacement of the reflected laser on a segmented photodiode. Cantilever deflections as small as 10 pm can be resolved above the instrumental noise floor.

In this work, AFM is used to map topography in order to quantify surface roughness. An advanced variation of AFM is also implemented to measure the much needed Young’s Modulus (E) of IrO$_2$ thin films, section 1.6.2. This method is based on force-indentation measurements at one or more locations on a sample that itself is fabricated as another cantilever. From the geometry of this structure, and pre-calibration of the spring constant of the AFM probe, the sample Young’s Modulus can be evaluated based on Euler-Bernoulli beam theory [93]:

\[ k_{IrOx} = \frac{Ewt^3}{4L^3} \]  
*Equation 7*

### 1.8.3 Scanning Electron Microscopy

Scanning Electron Microscopy, SEM, produces high resolution images with a very large depth of field (tens to hundreds of micrometers), making it highly effective for evaluating surface
structure even for high aspect ratio structures like MEMS [47]. It uses a focused beam of high energy electrons, which interact with the surface creating a variety of possible signals connected to interactions between these impinging electrons and the atoms at and near the focal point. Secondary electrons are the most widely employed, providing the highest resolution images of the surface morphology. Backscattered electrons are also sometimes employed as a quick way to distinguish distinct compositions based on the different atomic numbers (and hence scattering efficiencies) in a field of view.

1.8.4 Ferroelectric Tester

The ferroelectric properties, section 1.3.1, are most often measured with a ferroelectric tester, in this case the Precision Premier II (Radiant Technologies Inc.). Upon application of a positive or negative field, however, any change in charge magnitude or polarity as expected for a ferroelectric specimen will cause an electromotive force that can only be neutralized with current flow. The ferroelectric tester monitors these fine currents as a function of time and/or field. A variety of voltage sequences (ramps, pulses, PUND pulse sequences, and cycles of these possibilities) are especially employed to distinguish ferroelectric polarization from other charge mechanisms or artifacts. In this manner, hysteresis loops can be generated to identify ferroelectric properties.

1.8.5 Impedance Analyzer

An impedance analyzer measures the dielectric properties, capacitance (C), permittivity (\(\varepsilon\)), and loss tangent (\(\tan \delta\)) of a specimen. It does this by measuring AC impedance, i.e. the resistance to flow of an AC current. Most commonly this is monitored during a voltage sweep, a normalized
Capacitance vs Voltage (CV) graph is created. Modifying the capacitance equation, we can obtain the relative permittivity of the material.

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad \text{Equation 8.}
\]

where the unit-less relative permittivity, \( \varepsilon_r \), is related to C, the capacitance (F), d, the thickness of the ferroelectric material (m), \( \varepsilon_0 \) is the permittivity of free space \( (8.854187 \times 10^{-12} \text{ F/m}) \), and A, the area of the top electrode (m²). The loss tangent (\( \tan \delta \)) is also obtained with an impedance analyzer through a direct measurement. It measures the angle (\( \delta \)) of the ratio of real/imaginary permittivity reaction to the electric field.

1.8.6 Laser Doppler Vibrometry

The mechanical property strain (S) and the piezoelectric constant can be derived for a piezoelectric device using Laser Doppler Vibrometry (LDV) [95]. The LDV is an interferometer, comprising a laser beam that is split into an internal reference beam and a measurement beam reflected from the sample. This target beam strikes the moving or vibrating target, imparting a Doppler shift that is detected in the LDV when compared to the reference beam. By performing such measurements as a function of DC or AC biases, in this case typically simple displacement vs voltage loops, one can determine and even map piezoelectric coefficients, actuation efficiencies, frequency dependencies, etc.

The piezoelectric properties specifically correlate to displacement through strain according to Equation 9

\[
S = \frac{2\beta}{L^2} \quad \text{Equation 9.}
\]
where $z$ is the cantilever displacement, $\beta$ is the material stack constant, and $L$ is the distance of the LDV laser spot on the cantilever from the base. The material stack constant is obtained according to Equation 10

$$
\beta = \frac{2EI_{\text{comp}}}{wt_pEp\delta_p}
$$

using the effective composite Young’s modulus and area moment of inertia, $EI_{\text{comp}}$ [96], the beam width, the thickness and Young’s modulus of the piezoelectric film, $t_p$ and $E_p$ respectively, and the distance between the neutral axis of the beam and midpoint of the piezoelectric film, $\delta_p$.

1.8.7 Four Point Probe

A four-point probe measurement tool provides the sheet resistance ($R_s$) of a thin film. Most appropriate for uniform films, this is a convenient and non-destructive method to quickly assess film quality. It employs two pairs of probes, one pair applying or measuring the voltage between them, while the other pair measures or sources a simultaneous current. This separation of voltage and current functions eliminates from the measurement any challenges associated with contact resistance and impedance matching, improving precision in a very simple to use tool.

1.9 Summary

This chapter summarizes piezoelectric, pyroelectric, and ferroelectric properties. PZT is one of the leading such material in commercial thin film MEMS and employed throughout the work of this thesis. The importance of the top electrode on thin film ferroelectrics is also introduced, especially with respect to the still-relatively-unreported properties and performance of the
promising conducting oxide IrO$_2$. Background on radiation types and effects are also covered. Lastly, the principal experimental tools and techniques used for this thesis work are described.

The aim of this body of work is to further our understanding and improve our knowledge and modeling capabilities for MEMS employing IrO$_2$ as a top electrode. This dissertation describes optimization of the fabrication parameters to achieve the desired application (piezoelectric or pyroelectric), experimentally obtaining the Young’s modulus of thin film IrO$_2$ which is especially crucial for future device modeling, analyzing and minimizing performance issues assumed to be caused by fabrication induced defects, and understanding ionizing radiation effects for devices with IrO$_2$ electrodes via pre-post and during in-situ piezoactuation.
Chapter 2

Optimization of IrO$_2$

A different top electrode is needed to improve performance in thin-film piezoelectric and pyroelectric PZT devices. Pyroelectric applications require an electrode that increases the absorption of the radiated energy to maximize the temperature change in the system. For piezoelectric applications, the material properties of the electrode (e.g. mechanical properties, resistivity, and fatigue) play important roles in material selection. The Young’s Modulus can change the strain produced by the device, and the mechanical quality factor has a strong influence in resonant device performance [63]. Resistivity of the material is important, as the electrical loss can be a dominant loss mechanism for some applications [62]. Reducing mechanical fatigue at the electrode interface is of great importance for improving device reliability.

This requires a material that can function a dual purpose with little change in the fabrication process to not disrupt production. The following chapter discusses how IrO$_2$ is optimized for PiezoMEMS and PyroMEMS devices.

2.1 IrO$_2$ for PiezoMEMS

The oxygen flow rate, and deposition temperature of IrO$_2$, was first optimized for ferroelectric and piezoelectric properties by depositing on a TiO$_2$ substrate prior to working with PZT devices. Material orientation, sheet resistance, and microstructure were used to determine the optimal parameters for deposition on wafers selected for device fabrication.

Using a 300 mm diameter and 99.9% purity Iridium target, IrO$_2$ was deposited as the top electrode using a Clusterline 200 Sputter System (Unaxis), with 1 kW DC cathode power, Ar flow rate of 100 sccm, and a deposition time of 33 seconds for an approximate thickness of 100 nm. For
the optimization process, the deposition temperature was varied from 40°C and 500°C, which is the highest deposition temperature the sputter system can achieve and it also approaches the crystallization temperature of the PZT. The O₂ flow rate was varied from 0 sccm to 80 sccm to obtain pure Ir or IrO₂ with a range of thickness and film properties. Sheet resistance (Rₛ), XRD, and surface roughness with an AFM were obtained for the thin film before and after a supplementary O₂ anneal.

2.1.1 Characterization

The sheet resistance, as seen in Figure 7, is essentially constant when depositing pure Ir, i.e. at 0 sccm O₂. For higher flow rates Rₛ increases by only a factor of approximately 10 even though it becomes IrO₂. As anticipated, deposition at 40°C is clearly suboptimal due to the high absolute sheet resistance compared to the higher temperature or oxygen annealed cases.

![Figure 7: Sheet resistance at different deposition temperatures before and after O₂ anneal (a) and a representative data set from the 4 point probe (b).](image-url)
Annealing the film caused a reduction in $R_s$ of 71% when the deposition temperature was low. For the deposition temperature of 500°C, a 650°C O$_2$ anneal caused a 16-25% decrease in resistivity. This is due to the O$_2$ anneal filling in possible O$_2$ vacancies, reducing the number of defects in the material making it more conductive. Additionally, electrical uniformity increased for all wafers after O$_2$ anneal, Figure 8. Additional properties for films grown throughout this range of processing conditions are considered further.

![Figure 8: Sheet resistance uniformity as deposited (top row, a-e) and post O$_2$ anneal (bottom row, f-j) for various O$_2$ flow rates (in sccm); 15 (a, f), 30 (b, g), 45 (c, h), 60 (d, i), and 70 (e, j). Uniformity increases post anneal.](image)

XRD measurements were performed on a Rigaku Ultima III Θ-2Θ X-ray diffractometer (Cu Kα x-ray tube) in the range $10^\circ < 2\Theta < 50^\circ$, for the samples in Figure 7. The results for the samples deposited with an O$_2$ flow rate of 60 sccm are shown in Figure 9. For the 40°C as deposited sample, the 101 peak is not present, but appears after the 650°C O$_2$ anneal. The anneal causes a
broadening and a slight shift of the peaks, suggesting the lattice constant increasing in size, in particular residual stress at the 40°C deposited sample.

Figure 9: XRD for IrO2 samples deposited at O2 flow rate of 60 sccm, at 40°C (blue), 40°C with a post anneal (gray), 500°C (orange), and 50°C with a post anneal (yellow).

XRD measurements were performed at a variety of O2 flow rates, Figure 10. For the 15 sccm case, there are no visible (110) or (101) IrO2 peaks, respectively at 27° and 35° of 2Θ. Instead there are prominent Ir (111) and (200) peaks. But for higher oxygen flow rates the Ir peaks diminish and the IrO2 peaks grow, confirming there is a clear transition from Ir to IrO2 around an O2 flow rate of 30 sccm as evidenced previously by [68]. No significant difference in the crystal structure was observed for even higher O2 flow rates above 45 sccm as seen in Figure 11.
Figure 10: X-ray Diffraction of IrO$_2$ at different oxygen flow rates during deposition 15 sccm (blue), 30 sccm (orange), and 45 sccm (gray). IrO$_2$ transitions from a metal, Ir, to an oxide, IrO$_2$, at oxygen flow rates beginning at 30 sccm.

Figure 11: X-ray Diffraction of IrO$_2$ at higher oxygen flow rates during 33 s deposition; 60 sccm (blue), 70 sccm (orange), and 80 sccm (gray). No significant change in crystal structure was found.
Surface roughness at the nanoscale is crucial in determining the functional performance of many devices. Characterizing and understanding the surface roughness is important to further our ability to continue building better devices of a small scale. To obtain the surface roughness, tapping mode was used with an OTESPA-R3 tip on a Veeco Nanoman 5 AFM, to obtain 2 μm × 2 μm topographical images. Based on calibration both vertically and laterally on an AFM XYZ Calibration Nanogrid, the AFM measurements had an uncertainty of <2%. Samples as deposited and post O₂ anneal of different O₂ flow rates were measured. Figure 12 shows a representation of the raw data from the AFM for the O₂ flow rate of 60 sccm sample.

Figure 12: AFM topographical map of IrO₂ with O₂ flow rate of 60 sccm as deposited (a) with a 3-D image (b), and after a 650°C O₂ anneal (c) with its corresponding 3-D image (d).
There are various parameters reported to describe surface roughness, three of the most common and used in this work are average surface height ($z_{avg}$), average roughness ($R_{avg}$) and root mean squared (RMS) roughness ($R_{rms}$). $R_{avg}$ is the mean value of the surface height ($z$) relative to the center plane given by Equation 9, where $N$ is the number of points in the sample area.

$$R_{avg} = \sum_{n=1}^{N} \frac{|z_n - z|}{N} \quad Equation\ 11$$

$R_{rms}$ is given by the standard deviation of the $z$-values for the sample area

$$R_{rms} = \sqrt{\sum_{n=1}^{N} \frac{(z_n - z)^2}{N}} \quad Equation\ 12$$

Plotting the values for average surface height (a) and root mean square roughness (b) versus O$_2$ flow allow us to gather information of the material and deposition conditions.

![Figure 13: Average surface roughness (a) and Root mean square roughness (b) of IrO$_2$ deposited at various O$_2$ flow rates](image-url)
Annealing results in an increase in surface roughness, particularly for the 45 sccm samples where a two fold increase is displayed for $z_{\text{avg}}$ and $R_{\text{rms}}$ respectively. The change in surface roughness result from growth of crystalline structures due to temperature. With increasing annealing temperatures, the grain size and thus the surface roughness increase [97]. A comparison of the surface roughness at different deposition temperature, $R_{\text{avg}}$ of 500°C at different O$_2$ flow rates is shown in Figure 14, with 40°C for comparison. With the average surface roughness being similar at the various oxygen flow rates, temperature is the main mechanism for surface roughness.

![Figure 14: Average surface roughness of IrO$_2$ at different O$_2$ flow rates deposited at 500°C (blue) and 40°C (orange) as reference with no O$_2$ anneal.](image)

Surface roughness helps determine how the material will interact with the environment, although it is not vital as a top electrode for piezoMEMS, it allows for the potential of the material to be considered as a bottom electrode [98].
An additional set of IrO₂ films were deposited with a thickness of 1 μm with an oxygen flow rate of 60 sccm at different temperatures. The film stress was tested using a Toho FLX-2320S thin film stress measurement tool and sheet resistance was retested.

Figure 15 shows the trend, with increasing temperature, the IrO₂ film is deposited more compressive and sheet resistance decreases, making the film more conductive.

![Figure 15: Stress (green) and sheet resistance (orange) of 1μm thick IrO₂ films deposited at varying temperatures.](image)

Based on the combined results of the XRD, Rₛ, stress, and AFM analyses, the IrO₂ sputter deposition process on TiO₂ with post-anneal was found to be optimized at a deposition temperature of 500°C and an O₂ flow rate of 60 sccm with Rₛ = 9.2 ± 0.2 Ω/sq. (7.5 ± 0.2 Ω/sq. post anneal) and Rₘᵋ = 2.3 ± 0.1 nm (4.0 ± 0.1 nm post anneal). Therefore, these deposition parameters were used for subsequent deposition on PZT substrate, where the XRD data is shown in Figure 16.
Figure 16: XRD of optimized IrO$_2$ on PZT with a Pt bottom electrode.

2.1.2 Young’s Modulus

The top electrode material significantly affects the piezoelectric performance of a PZT device by manipulating the composite mechanical properties of the free-moving structures including changing the overall stress of the structure. Of particular importance is the composite modulus of a released device, dictated in part by the Young’s Modulus ($E$) of the top electrode material. Despite its use in commercially available FRAM, experimental mechanical properties for IrO$_2$ thin films are not present in the literature, especially when compared to copious reports for Pt and other industrially important electrode materials. To the author’s knowledge, the only published Young’s modulus of IrO$_2$ is a first-principles calculation, computed with density functional theory (DFT) within a generalized gradient density approximation [77].
To determine the Young’s Modulus (E) of IrO$_2$, a thin film was reactively sputtered on a 150 mm diameter Si wafer at 500°C for 35 seconds using the same 100:60 sccm Ar:O$_2$ flow rate and power as described above in 2.1. Photolithography, Ar ion milling, and a XeF$_2$ etch were performed to create fully released, rectangular cantilever beams, 116 nm thick, ~20 μm wide and ranging from 50 to 200 μm in length seen in Figure 17.

**Figure 17: SEM image of rectangular cantilever beams for Young's modulus test.**

Single Point Force measurements were then completed using AFM at the Aberdeen Proving Grounds Army Research Laboratory facility in Maryland. The free ends of these IrO$_2$ beams are probed, specifically by applying a range of calibrated loads and measuring the corresponding beam deflections [99, 100]. This results in generation of linear force-distance curves, where the measured slope of the force-distance curve, $k_{\text{measured}}$, is related to the unknown spring constant of the sample iridium oxide beam, $k_{\text{IrO}_x}$, and the known AFM cantilever spring constant, $k_{\text{AFM}}$, through the following equation:
Based on the widely employed thermal calibration method [101], the spring constant of the silicon AFM probe (Asylum Research AC240) was 1.8 N/m, well within the manufacturer’s nominal range of 0.6-3.5 N/m. Figure 18 shows an optical image of an AFM probe aligned at the free end of an IrO2 cantilever beam among an array of beams fixed at the left edge of the micrograph. SEM imaging was used to confirm the width and thickness of the IrO2 material.

\[
\frac{1}{k_{\text{measured}}} = \frac{1}{k_{\text{IrOx}}} + \frac{1}{k_{\text{AFM}}} \quad \text{Equation 13}
\]

The Young’s modulus for IrO2 is then determined according to Euler–Bernoulli beam theory [93]:

\[
k_{\text{IrOx}} = \frac{Ewt^3}{4L^3} \quad \text{Equation 7}
\]

where \(w\) is the patterned width, \(t\) the thickness, \(L\) the length of the IrO2 cantilever where the force is being applied, and \(k_{\text{IrO2}}\) the outcome of the AFM indentation study. This relationship assumes that the material is isotropic and is applicable for these planar, monolithic IrO2 beams.
Accordingly, the AFM was initially used to image the cantilever beam and identify the location of fixed end of the cantilever, then force-indentation curves were acquired at known positions from the fixed base (in this case L=23 μm).

\[
\begin{align*}
\text{Force [N]} & \quad \text{IrO}_2 \text{ Cantilever displacement [nm]} \\
& \quad \gamma = 0.1428x + 1.5203 \\
& \quad R^2 = 0.9984
\end{align*}
\]

*Figure 19: Linear force displacement curve from AFM on IrO\textsubscript{2} thin film cantilever beam.*

The linear force displacement curve from the AFM, Figure 19, shows a \( k_{\text{measured}} \) of 0.143 N/m. There are several abrupt decreases in force, attributed to tip slip but also possibly to a change in boundary conditions with the tip of the cantilever reaching the bottom of the pit. The influence of these slips in the highlighted region in Figure 19 is negligible. Incorporating these values in Equations 11 and 12, the experimentally measured elastic modulus of iridium oxide is 262 GPa. This is in reasonable agreement with the theoretical value of 290 GPa calculated by DFT, but the nearly 10% difference is significant for practical device design and modeling.
2.2 IrO$_2$ for PyroMEMS

For both IR and energy applications, it is advantageous to have a dual-purpose top electrode/absorber that benefits the polar properties of the material, optimizes IR absorption, yet minimizes the overall thermal mass. To also maximize infrared absorption for pyroelectric applications, high oxygen flow deposition conditions are proposed because they develop plate-like IrO$_2$ morphologies which dramatically increase the surface area and thereby increase photon absorption efficiencies without adding a substantial thermal mass. While such plate-like structures have previously been observed [70-72], this work thoroughly investigates their processing, microstructure, and performance.

2.2.1 Nanostructured Platelet Growth

A high surface area film of iridium oxide for pyroelectric structures, will be referred to as platelets or nanostructured IrO$_x$ with an x subscript from here on. To obtain platelets, IrO$_x$ was reactively sputtered, with 1 kW DC cathode power and Ar flow rate of 100 sccm with the only difference from planar IrO$_2$ (for PiezoMEMS), is that the O$_2$ flow rate is 100 sccm instead of 60 sccm. Deposition times from 5 seconds to 99 seconds and substrate temperatures from 40-500 °C are explored.

The Ar:O flow rate dictates the morphology of the film. Figure 20 shows the difference in morphology between the O$_2$ 60 sccm and O$_2$ 100 sccm reactively sputtered IrO$_x$ films (both with 100 sccm Ar) after 33 s of deposition.
Figure 20: SEM images of the surface morphology of IrO₂ deposited for 33 s with different O₂ flow rates; (a) 60 sccm and (b) 100 sccm.

The film sputtered with an O₂ flow rate of 60 sccm is grey in appearance and shows a rough surface with visible grains. Films sputtered at 100 sccm exhibited a different growth mode where 2 dimensional structures, grow normal to the film surface, giving the sample a black appearance.

Platelet growth is observed in as little as 5 seconds. By 15 seconds (Figure 21a), primary platelets become more abundant. For still longer depositions, Figure 21b through e, primary platelets become more abundant and continue to grow. From these primary platelets, smaller or secondary platelets begin to form and continue to grow with deposition time.
The platelet structure appears to be primarily oriented normal to the z direction and without any particular in-plane texture. For longer deposition times the lack of texture remains, but secondary platelets begin to branch out as in Figure 21b. Larger and continuous primary platelets form over time with smaller but clear secondary platelets, becoming more abundant as in Figure 21c-e.

Cross sections of these specimens reveal multiple morphologies, where the platelet geometry actually extends from a dense IrO$_x$ film beneath. The underlying continuous film exhibits
columnar grain growth normal to the substrate surface. Figure 22 shows the cross section images of the 25 s, 33 s, and 45 s depositions. The platelet density and height clearly increases with deposition time.

![Cross section SEM images of plate-like IrO$_2$ deposited at 500°C at (a) 25 s, (b) 33 s, and (c) 45 s. The platelets, labeled P, grow from a dense columnar film, labeled d.](image)

Analyzing the mean thickness of these distinct film morphologies reveals a self-limiting dense columnar film as the base of the plate-like structures. While the plate-like region continues to grow with increased deposition, at a rate of ~6 nm/s, the dense film appears to reach a critical thickness of approximately 60 ± 10 nm, Figure 23. This self-limiting characteristic is assumed to result initially from preferential growth at nucleated platelet edges, and ultimately from shadowing by
the ever-increasing platelets [102]; regardless, the platelets effectively consume the sputtered material and dense film growth terminates.

![Figure 23: Height of platelet and dense film vs deposition time. The dense film appears to reach a self-limiting thickness of ~60 nm, beyond which the platelet height grows at a rate of ~6 nm/s. Standard deviation error bars are within the displayed markers.](image)

To assess processing versatility and robustness of the nanostructured IrO$_2$, films deposited for 70 seconds at 50°C were subjected to a range of cleanroom processes. First, the films were deposited on photoresist-patterned substrates. Platelet growth occurred on both the exposed and photoresist-covered surfaces. Upon dissolving the photoresist in acetone solvent, the IrO$_2$ on resist was completely removed via liftoff (Figure 24), with clear delineation at the photoresist boundary, limited by the morphology of the platelets.
The patterned IrO$_x$ was also subjected to ultrasonication for 30 minutes in isopropyl alcohol (IPA). The platelets are suitably mechanically robust that there was no observable platelet damage. Platelet IrO$_x$ was sputtered on deep-reactive-ion-etched structures, based on 2, 10, and 100 etch cycles which created patterned trenches of 0.87 µm, 5.70 µm, and 62.34 µm. Figure 25 shows an SEM image of the platelet deposition on patterned surfaces.

**Figure 24: SEM image of patterned IrO$_2$ after lift-off process.**

**Figure 25: SEM image of platelet growth on 62.34 µm deep etched trench.**
For each of these trenches, platelet structures are still observed, although the growth rate is diminished in the deep structures, observed by a reduced density of platelets. This test shows that this IrO\(_2\) platelet morphology can feasibly be integrated into functional devices.

### 2.2.2 Characterization

Sheet resistance is a critical parameter for electronic device performance and changes in sheet resistance can indicate changes in film morphology. For the platelet IrO\(_x\), the sheet resistance increases until a critical deposition time of 33 seconds, beyond which it decreases Figure 26.

![Sheet resistance vs deposition time for IrO\(_2\) with platelet structures (IrO\(_x\) -100) and planar (IrO\(_x\) -60) as a referent point, deposited at 500°C.](image)

**Figure 26: Sheet resistance vs deposition time for IrO\(_2\) with platelet structures (IrO\(_x\) -100) and planar (IrO\(_x\) -60) as a referent point, deposited at 500°C.**

This may indicate a crossover from electrically isolated IrO\(_x\) platelets to increasingly interconnected features via the increasing density especially of secondary platelets. For reference, the sheet resistance of planar IrO\(_2\) at 33s is 8-9 \(\Omega/\text{sq}\), showing that the dense film growth contributes to lower resistance, but the platelets introduce a new resistive element that dominates the response.
The optical properties of the IrO$_x$ film are critical to realizing the dual function of electrode and absorber intended for pyroelectric applications. The nanostructured IrO$_x$ film was assessed via spectral reflectance, implementing a Fourier Transform Infrared (FTIR) spectrometer sampling the percent reflectance versus deposition time, as seen in Figure 27. The decrease in reflection after the 25 second deposition time is attributed to the increase in volume of primary platelets and their shape allowing for the reflection of the photons to be in-plane.

![Figure 27: % reflectance at a wavelength of 1.5 um vs deposition time for IrO$_2$ with platelet structures deposited at 500C. Decrease in reflection is attributed to the increase in primary platelet size and shape able to reflect in-plane.](image)

Further characterization using XRD, shows platelet IrO$_x$ to decrease peak intensity in the 110 direction while increasing in the 101. It was believed that the platelets were growing in the 101 direction but due to their volume, XRD was not optimized for such information. To obtain better understanding, grazing X-Ray diffraction was needed and corroborated that the platelets grow in the 101 orientation.
Figure 28: XRD of platelet IrO$_x$ (orange) and planar IrO$_2$ (blue). 110 peak decreases with higher O$_2$ flow rate, but the 101 peak increases in magnitude.

Figure 29: AFM topographical image of nanostructured IrO$_x$ deposited at 500C for 44 seconds.
2.3 Chapter Summary

This chapter presents the deposition optimization of iridium oxide thin films for piezoelectric and pyroelectric applications. Iridium oxide films of different morphologies are produced by manipulating the reactive gas flow rate in a sputtering process. Planar IrO$_2$ for piezoelectric applications was optimized at 60 sccm O$_2$ flow rate at a deposition temperature of 500°C. Nanostructured, 2D platelets are observed for high oxygen flow rates (100 sccm) producing a self-limiting dense columnar film as the base of the plate-like structures. While the plate-like region continues to grow with increased deposition, at a rate of ~6 nm/s, the dense film appears to reach a critical thickness of approximately 60 ± 10 nm. The dense film growth contributes to lower resistance, but the nanostructured platelets introduce a new resistive element that dominates the response. The compatibility with various cleanroom processes, such as lift-off, ultrasonic cleaning, and the deposition on etched surfaces is confirmed for the IrO$_x$ nanostructures, adding to the possibility for inclusion to the production line without major changes to the fabrication process.

For the first time, the Young’s modulus of planar IrO$_2$ was directly measured at 262 GPa ± 3, approximately 10% lower than the DFT calculation, this measurement allows for precise stress engineering and control of the neutral axis in released devices. Stress engineering and control of neutral axis location is essential for many device applications such as switches, mechanical digital logic, and micro-robotics [44, 45, 92]
Chapter 3

IrO\textsubscript{2} versus Pt

The ferroelectric and piezoelectric performance is affected by processing conditions, device design \cite{103}, PZT composition, electrode materials, and the presence of substrate clamping effects. The most common electrode material for thin film PZT devices is platinum. Pt is used as a top and bottom electrode and has advantages and disadvantages as discussed in section 1.6.1. The purpose of this chapter is to gain an understanding of what fabrication steps induce defects and determine if it is possible to undo any defects caused by the fabrication process for both platinum and iridium oxide top electrode devices, as well as to directly compare through characterization the performance of devices with Pt and IrO\textsubscript{2} top electrodes.

3.1 Fabrication Process

Full device fabrication commenced once optimal IrO\textsubscript{2} deposition parameters were identified for piezoelectric applications, described in section 2.1. PZT based devices are built with a combination of steps, the first few creating a multilayer structure. The fabrication process starts with a commercially available single sided polish Si wafer. A stress compensating thermal SiO\textsubscript{2} created by annealing at the Si substrate at 700°C. The elastic layer is polished to 3μm using chemical mechanical polishing from Axus Technology (Chandler, AZ). A 30 nm film of titanium (Ti) is sputtered in a DC magnetron sputter system (Evatec Clusterline 200) with DC power of 500 W, 30 sccm of Ar at a substrate temperature of 40°C followed by a 30 minute O\textsubscript{2} anneal at 750°C. The Ti is oxidized to create TiO\textsubscript{2} producing a template for a \{111\}-textured platinum bottom electrode which is sputtered using 0.5 kW DC cathode power on a 200 mm diameter and 99.9% purity Pt target with an Ar flow rate of 50 sccm and a substrate temperature of 500°C, and sputtered
for 67 seconds for a nominal thickness of 100 nm. The oriented Pt bottom electrode forms a template for a 500 nm thick chemical solution deposited (001)-textured Zr/Ti ratio of 52/48 PZT film. A seed layer for the PZT of PbTiO$_3$ is deposited to induce nucleation of the 001 orientation [104]. A PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) precursor solution is prepared via a 2-methoxyethanol (2-MOE). A PZT film thickness of 500 ± 15 nm results by spin coating the 2-MOE PZT solution on the wafer with intermediate pyrolysis and crystallization steps. The [111] textured Pt bottom electrode is necessary to obtain a preferential 001 oriented PZT film due to lattice matching [105].

In order to determine the difference in material selection for top electrode, on one wafer, a 100 nm Pt top electrode is sputtered with the same parameters as the bottom electrode. On a second wafer, a 100 nm top electrode of iridium oxide is sputtered for 33 seconds at a substrate temperature of 500°C with an Ar flow rate of 100 sccm and a O$_2$ flow rate of 60 sccm and furnace anneal in an oxygen environment at 650°C for 30 minutes. The material composite stack is now complete as seen in Figure 30.

![Figure 30: Profile view of material composite stack. Not to scale.](image)
For this dissertation, two specific device architectures are characterized, a capacitor and an actuator. With the material composite stack deposited, the devices are then patterned. AZ5214 photoresist is spin coated at 2000 rpm for 30 seconds. The top electrode pattern is UV-cured unto the wafer before an argon (Ar) ion mill is used to etch the top electrode, Figure 31a. To be able to take the first measurement, access to the bottom electrode is achieved by a HF:H₂O wet etch in an unused bottom right corner of the wafer. After the first set of measurements are taken, the photoresist process is repeated for the PZT and the bottom electrode, Figure 31b. Followed by a PZT wet-etch using a combination of HCl:HF:H₂O (120:1:240). The wafer is rapidly thermally annealed at 500°C in an oxygen rich environment to mitigate hydrogen damage from the ion mill [95].

Figure 31: Diagram of profile and top view of overall architecture of key device fabrication process. Top electrode mill with an Ion Mill, measurement taken (a), PZT and bottom electrode mill with an Ion Mill (b), contact deposition through evaporation, measurement taken (c), oxide etch, measurement taken (d), and XeF2 etch to release the actuators, measurement taken. Not all steps are shown and figures are not to scale.
A tri-layer of Au/Pt/Cr (730nm/20nm/20nm) is deposited via electron beam evaporation and patterned via liftoff, Figure 31c. Chromium (Cr) and Pt are used for proper adhesion while the gold (Au) is used as contact pads for probing or wire bonding. A fourth etch, Figure 31d, is used to pattern the SiO$_2$ elastic layer by reactive ion etching providing access to the Si substrate for release. Another measurement was taken at this step. A sacrificial photoresist layer is deposited before 2000 nm thick Au layer is deposited via electron beam evaporation. This allows a bridge structure from the contact pads to the top electrode to prevent an electrical short. The Au bridge layer is patterned via lift off and the sacrificial photoresist layer is removed using oxygen plasma. The wafer is finally exposed to XeF$_2$ gas, Figure 31e, which isotropically etches the Si substrate, fully releasing the actuator beam structures where the last measurement is then taken. The devices are collocated and separated by 100 m as seen in the SEM image of the devices shown in Figure 32, where the released actuators are in the dark red square and the capacitor in the dark blue.

Figure 32: SEM image of final device structures; Actuators inside the red box and capacitor inside the dark blue box.
3.1.1 Fabrication Process Results

Ferroelectric and dielectric data was obtained at certain steps throughout the fabrication process to analyze any fabrication-induced effects on the material and its performance. Data was collected after the top electrode mill, Figure 31a, after the O\textsubscript{2} anneal Figure 31c, and before, Figure 31d, and after the XeF\textsubscript{2} etch, Figure 31e.

Figure 34 shows representative ferroelectric hysteresis curves of the fabrication process on the Pt top electrode circular capacitor (a) and rectangular actuator (b) devices. For both devices, a ‘pinched’ loop is observed after the first step, the top electrode mill (blue) but more pronounced in the capacitor. A pinched loop is a hysteresis loop with a decrease in polarization at zero electric field, Figure 33 believed to be caused by inhomogeneity and structural defects pinning domain walls [106,107] or intrinsic to the material at MPB [108]. The O\textsubscript{2} anneal (orange), produces several changes to the ferroelectric hysteresis. In both devices, it undoes the pinching, increases $P_{\text{max}}$ by 7\%, the $P_{\text{rem}}$ by 294\%, and increases the slope of the tilt.

Figure 33: Pinched hysteresis loop. Red dashed line for visual aid.
Figure 34: Ferroelectric hysteresis loops during fabrication process for Pt top electrode capacitor (a) and actuator (b). Top electrode mill, Figure 28a (blue), post anneal Figure 28c (orange), pre-release Figure 28d (green), and post release Figure 28e (violet).
The following fabrication steps appear to produce defects within the material, producing again a pronounced pinched hysteresis loop for the capacitor device and less so but still present for the actuator. $P_{\text{max}}$ decreases by 8% and $P_{\text{rem}}$ decreases by 47% for the capacitor and relatively unchanged for the actuator with less than 1% for $P_{\text{max}}$ and 8% for $P_{\text{rem}}$. Once released, the capacitor has no change, and the fully released actuator has an increase in $P_{\text{max}}$ of 9% and 31% for $P_{\text{rem}}$. From the initial values of the top electrode mill, for the capacitor device, $P_{\text{max}}$ degradation of only 2% was measured and $P_{r}$ improved by 107% from the initial values. For the actuator, an improvement of 4.6% and 117% was measured for $P_{\text{max}}$ and $P_{r}$ respectively.

Figure 35 shows equivalent ferroelectric hysteresis loops during the fabrication process on the IrO$_2$ top electrode capacitor (a) and actuator (b). No ‘pinching’ or other statistically significant changes to $P_{\text{max}}$ ($\leq 3.1\%$), $P_{\text{rem}}$ ($\leq 4.1\%$) or hysteresis tilt are visible. The only significant change is the coercive field in the actuator device increases ~60%. A 4.2% degradation is seen in the final value for $P_{\text{max}}$ from the top electrode value for capacitor while < 5% degradation is detected with the actuator. For $P_{\text{rem}}$, the capacitor has a decrease of 17% while the actuator increases 18%.
Comparing Figure 34 and Figure 35, devices with an IrO$_2$ top electrode are less affected ferroelectrically throughout the fabrication process compared to those with Pt top electrode. Figure 36 shows the quantitative data throughout the process for Pt and IrO$_2$ capacitors (clamped) and actuators (unclamped). For IrO$_2$ capped devices, the $P_{\text{max}}$ of the completed device is approximately
5% of the initial value taken after the top electrode mill. There are statistically significant
differences between capacitors and actuators throughout the process. Not until the final step do the
actuators become released, corroborating that device geometry changes the electrical properties of
the device. IrO₂ is believed to be less effected due to the ability of IrO₂ to prevent hydrogen
diffusion and the ability to allow oxygen vacancies to migrate across the electrode interface.

![Figure 36: P max (a) and P rem (b) of the clamped (circular markers) and unclamped (square
markers) devices with Pt (blue) and IrO₂ (gray) throughout the major fabrication steps; Top
electrode mill (step 1), post O₂ anneal (step 2), pre-release (step 3), and post release (step 4).]

Dielectric data was also taken, during these steps. Pinching of a ferroelectric hysteresis loop is
corroborated with the presence of a triple peak in permittivity. Figure 32 shows the relative
permittivity throughout the fabrication process. Triple peaks are clearly present during the top
electrode mill for both circular (a) and rectangular (e) shaped devices. As expected from the
ferroelectric data from Figure 34, the O₂ anneal creates a standard double peak but decreases the
permittivity by 26% for circular and 22% for rectangular devices. This is believed to be caused by
the etching of the material in the steps leading to the O₂ anneal.
The following steps leading up to the pre-release measurement decreased the relative permittivity by 24% for the circular and 18% in the rectangular devices. For the XeF₂ etch step, there is a decrease of 6% in the now fully released (unclamped) rectangular actuator, and as expected, no change in the capacitor device. Comparing the final value to the value obtained from the first measurement, the relative permittivity decreased in all devices: 77% for Pt capacitors, 41% for Pt actuators, 42% for IrO₂ capacitors, and 30% for IrO₂ actuators. From the original value to the final, the loss tangent (tan δ) improved in all cases. A 75% improvement for Pt capacitors, 65% for Pt actuators, 84% for IrO₂ capacitors, and 77% for IrO₂ actuators. The quantitative data can be seen in Figure 38.
Figure 38: Relative permittivity (a) and tan δ (b) of the clamped (circular markers) and unclamped (square markers) devices with Pt (blue) and IrO₂ (gray) throughout the major fabrication steps; Top electrode mill (step 1), post O₂ anneal (step 2), pre-release (step 3), and post release (step 4).

3.1.2 Hydrogen diffusion

Due to the results in the previous section where only Pt capped devices demonstrate pinching, and literature stating IrO₂ prevents hydrogen diffusion, I hypothesized that the pinching was caused due to hydrogen diffusion. Hydrogen is known to affect the functionality and properties of PZT [109]. There are two different scenarios that can cause hydrogen interaction, incorporation and diffusion. One mechanism found in bare PZT possibly including sidewalls is hydrogen molecules can dissociate at PZT surface making hydrogen atoms to diffuse into the structure, seen in Figure 39a in dark red. The other possible mechanism is incorporation of hydrogen through the metallic electrode, diffusing into the electrode/PZT interface, seen in Figure 39a in dark blue.
Figure 39: Hydrogen diffusion mechanism (a) through bare PZT or sidewall (dark red) or through the metallic electrode (dark blue); effects of H diffusion (b) O and Pb vacancies at the interface and grain boundaries and degraded layer due to hydroxyl group formation. [adapted from Shafiei]

Hydrogen atoms diffusing along the grain boundaries may undergo the following reaction

$$2H + O^{2-} \rightarrow H_2O + V_{O}^x$$  

Equation 14

where $V_{O}^x$ is the oxygen vacancy with two captured electrons. The oxygen vacancy can be ionized and the freed electrons can decrease the resistivity of PZT. This reaction can only occur on the surface and grain boundaries because H$_2$O cannot exist inside the PZT atomic lattice. For the interface, the oxygen must diffuse from the bulk of the grains to the interface and the water should diffuse along the grain boundaries. Therefore H damage is limited to surfaces and to grain boundaries as seen in Figure 39b. Another mechanism proposed for the changes of the electrical properties of PZT is hydrogen atoms being ionized inside the PZT crystal lattice. The electron released decreases PZT resistivity while the proton may interact with oxygen ion to form a polar hydroxyl bond (OH$^-$) seen in the following reaction

$$H^+ + O^{2-} \rightarrow [OH]^-$$  

Equation 15
The polar hydroxyl group, seen in Figure 39b, acts as a fixed dipole, may cause a change in the atomic bonding of oxygen with Pb, Zr, and Ti, and not allowing the switching of ferroelectric domains.

3.1.2.1 Hydrogen anneal

To confirm that hydrogen diffusion was causing the pinching, a modified hydrogen annealing test was performed. Since no pure H$_2$ was able to be used, H$_2$N$_2$ forming gas (3% H$_2$) and N$_2$ gas were used with the idea that the N$_2$ results would act as a baseline for H$_2$ damage expected in the H$_2$N$_2$ samples. Using rapid thermal annealing, a set of samples with both different top electrodes (IrO$_2$ or Pt) were exposed to N$_2$ gas and a second set was exposed to H$_2$N$_2$ forming gas for 1, 3, and 5 minutes at a temperature of 300°C. It is important to note that only 1/3 of the Pt samples survived the H$_2$N$_2$ annealing process, as seen in Figure 40. H$_2$N$_2$ created what appear to be bubbles on the surface of the top electrode and changed the optical properties by turning it black, known to happen to ceramics exposed to H$_2$ [110], seen in Figure 40b. The formation of bubble and what appear to be delamination is attributed to the formation of fissures in the PZT [111] at the electrode interface.
Figure 40: Optical image of Pt top electrode capacitors after $N_2$ anneal (a) and $H_2N_2$ (b) anneal.
**Figure 41**: P-E hysteresis loops of IrO$_2$ (blue, a and c) and Pt (red, b and d) devices before (solid) and after (dashed) annealing at 300 C for 5 minutes in N$_2$ (a and b) and H$_2$N$_2$ (c and d).

Figure 41a and b, as expected show no significant change for the devices undergoing a N$_2$ anneal. Figure 41c and d, show a significant decrease in $P_{\text{max}}$, $P_r$, and tilt, but no pinching. $P_{\text{max}}$ can be seen in more detail in Figure 42.
Figure 42: Maximum polarization of IrO$_2$ (a) and Pt (b) capped capacitors before (solid) and after (ring) 300°C anneal of N$_2$ gas (dark) and H$_2$N$_2$ forming gas (light). Note: there is no 3 min Pt H$_2$N$_2$ anneal.

where the N$_2$ gas anneal decreased the $P_{\text{max}}$ of both IrO$_2$ and Pt capped devices around 1%, not statistically significant, whereas the H$_2$N$_2$ forming gas anneal decreased the $P_{\text{max}}$ of IrO$_2$ capped devices between 11% to 23% while decreasing up to 32% for the Pt capped devices. For $P_r$, Figure 43, we again see N$_2$ gas anneal doing statistically insignificant damage but the H$_2$N$_2$ forming gas
anneal decreasing the remnant polarization of IrO$_2$ capped devices from 43% to 79%, and the Pt capped devices seeing a decrease from 26% up to 88%.

Figure 43: Remnant polarization of IrO$_2$ (a) and Pt (b) capped capacitors before (solid) and after (ring) 300°C anneal of N$_2$ gas (dark) and H$_2$N$_2$ forming gas (light).
The coercive field for both the IrO₂ and Pt capped devices change similarly, with devices with an IrO₂ top electrode showing a more negative polarization preference. In the H₂N₂ gas annealing samples, for both IrO₂ and Pt capped devices, the coercive field improved for the 1 and 3 minute anneals, and worsened for the 5 minute anneal 13% for IrO₂ capped devices and up to 37% for its metallic counterpart.
Although hydrogen has been shown to cause significant damage to the devices, it was not the cause of pinching seen in the ferroelectric hysteresis loops as originally hypothesized. This finding allows us to narrow down the probable cause of the pinching, now believed to be due to the injection of charged particles during the fabrication steps of ion milling and etching.

3.2 IrO₂ vs Pt for Piezoelectric Applications

This section explores the benefits of using planar IrO₂ top electrodes, described in section 2.1, for PZT devices employed in piezoelectric applications compared to conventional platinum electrodes. A laser confocal microscope was used to determine the free end height of released 0 biased actuator cantilevers for devices with either IrO₂ or Pt top electrodes. The ferroelectric properties of the completed PZT devices, with either Pt or IrO₂ top electrodes, were characterized by polarization hysteresis loops operating at testing frequencies of 10 kHz, with triangular wave from -19 to 19 volts (Radiant Precision Premier II). The capacitances and leakage currents for the films were also acquired using the same system. Actuator displacement was measured with a laser Doppler vibrometry (Polytech OFV5000) and converted to piezoelectric strain.
Figure 45: Free end height vs cantilever length for IrO₂ (blue) and Pt (orange).

The deposition and annealing of top electrode has a significant influence on the stress of the PZT film as well as on the electrical properties [112]. Figure 45 shows less curvature for the IrO₂ samples when compared to that of Pt, due to the higher compressive stress of IrO₂ versus Pt. In house measurements using Toho FLX-2320S thin film stress measurement tool, a thin film stress value of -913.3 MPa was obtained for 100 nm thick IrO₂. Pt becomes largely tensile after an anneal [112]. IrO₂ thin film as a top electrode allows for the fabrication of flatter structures, helping released devices. MEMS require their components in devices to be planar, if the structures are curled, it increases the difficulty to create a good contact point in switches for example. Changing any layer in the device can result in significant changes. For example, changing the elastic layer to a 500 nm thermal SiO₂ and capping the PZT with IrO₂ produced flat devices, seen in the SEM image of Figure 46.
Figure 46: SEM image of flat released actuator structures with IrO$_2$ top electrode.

For the following ferroelectric and dielectric data, capacitors were created using a single PZT wafer. Before top electrode deposition, the wafer was cleaved into several pieces and IrO$_2$ and Pt were then deposited. These samples were again cleaved and some were annealed in an O$_2$ environment at 650°C for 30 minutes. This was done to compare the top electrodes directly, using the same PZT to negate any PZT variability that occurs from wafer to wafer.
Figure 47: Ferroelectric hysteresis loops IrO$_2$ (blue) and Pt (orange) capped PZT capacitor devices before (a) and after (b) annealing in O$_2$ environment at 650°C for 30 minutes.

The as deposited samples show a minor reduction in maximum polarization for the Pt capped devices, Figure 47a, with a slight imprint but with the same $P_{\text{rem}}$ as IrO$_2$. Once annealed, Figure 47b, the increase in $P_{\text{max}}$ of Pt ($<5\%$) and the decrease of $P_{\text{max}}$ of IrO$_2$ ($<2\%$) are statistically not significant, but a shift of the Pt capped structure occurs, aligning itself with that of the IrO$_2$. The dielectric data, Figure 48, shows an increase in permittivity from before the anneal (a) to after the anneal (b) of 8\% for IrO$_2$ and 13\% for Pt.
Figure 48: Relative permittivity of PZT capacitors with IrO\(_2\) (blue) and Pt (orange) top electrodes before (a) and after (b) anneal in O\(_2\) environment at 650\(^\circ\)C for 30 minutes.

Figure 49: Relative strain for devices capped with IrO\(_2\) and Pt.
Displacement data was obtained from laser Doppler vibrometry, for the cantilever structures with the different top electrode types from section 3.1.1. No applied bias was introduced to the samples prior to the measurement. The LDV measurement are averages of 20 scans in which each scan is operating the device with a bipolar triangular waveform. The sample with Pt top electrode displays lower displacement magnitude and symmetry. Devices with IrO₂ top electrode display an asymmetric bias towards the positive side as seen in Figure 49. Calculating the strain using Equation 8 results in a strain of IrO₂ devices to be 4.49 x 10⁻³ in the negative bias, 5.34 x 10⁻³ in the positive bias, compared to 3.88 x 10⁻³ for Pt.

3.3 IrO₂ vs Pt for Pyroelectric Applications

This section explores the benefits of using the nanostructured IrO₂ top electrodes, described in section 2.2, for PZT devices employed in pyroelectric applications compared to conventional platinum electrodes. Nanostructured IrO₂ samples were created from the same PZT wafer that was used for planar IrO₂ and Pt and the same ferroelectric and dielectric tests performed, as described in section 3.2. No LDV tests were performed due to the lack of reflectivity of the nanostructured IrO₂. The pyroelectric properties in PZT arise from the interaction between polarization and thermal energies, \( \Pi = \frac{dP}{dT} \) coupling coefficients where \( \Pi \) is the pyroelectric coefficient. The polarization dependence on voltage of PZT capacitor devices with both nanostructured IrO₂ is shown in Figure 50.
We see similar data in the before annealing samples as we did in the Piezo section. Once annealed, the nanostructured IrO$_2$ sample displays characteristics of an extra dielectric in series due to the 17% reduction in $P_{\text{max}}$ and a 4X increase in coercive voltage, seen in Figure 50b. Cross section SEM of the nanostructured IrO$_2$ show a distinct change at the interface after the anneal, highlighted by the white dotted rectangle in Figure 51.
Figure 51: A cross section SEM of before (left) and after (right) annealing of nanostructured IrO$_2$. Inside the dotted rectangle, the interface between the top electrode and PZT is visibly different.

Dielectrically, the changes in the annealed sample indicate the presence of two dielectric layers in series. The 44% reduction in relative permittivity of the annealed sample highlights this effect, seen in Figure 52.

Figure 52: Relative permittivity of nanostructured IrO$_2$ (black) and Pt (orange) capped PZT capacitor devices before (a) and after (b) an O$_2$ anneal at 650°C for 30 minutes.
The optical properties of the IrO\textsubscript{x} film are critical to realizing the dual function of electrode and absorber intended for pyroelectric applications. Figure 53 compares the specular reflectance across the infrared spectrum. The low specular reflection for IrO\textsubscript{x} is believed to be of high absorption, although it could also possibly be due to the possible scattering of the photons and the equipment cannot collect the scattered fraction. Since reduce reflectivity can result from both absorption and scattering, we cannot assume that the full reduction in Figure 53 is due to absorption only.

![Figure 53: Percentage of specular reflectance of Pt (blue) and nanostructured IrO\textsubscript{x} (red) across the infrared spectrum taken with Fourier Transform Infrared Spectroscopy (FTIR).](image)

The pyroelectric performance of PZT devices with Pt and nanostructured IrO\textsubscript{x} top electrodes are compared. To measure the pyroelectric coefficient, an oscillating temperature was provided by the periodic heating of the samples while simultaneously measuring current and temperature.
Temperature was measured on the surface of a calibrated platinum resistive thermal device, co-located on the surface of the hotplate, in a manner similar to ref [24].

\[ I_p = \Pi A \frac{dT}{dt} \]

From Figure 54, the pyroelectric coefficient can be calculated from the synchronous waveforms using Equation 4, with a given electrode area of 0.00181 cm², the pyroelectric coefficients \( \Pi \), of 70 µC/m²K and 63 µC/m²K are obtained for the nanostructured IrOₓ and Pt samples, respectively. While there may be a modest difference in pyroelectric coefficients, the benefits of IrOₓ are apparent when comparing the energy harvesting figure of merit [113],

\[ FOM_{EH} = \frac{\Pi^2}{\varepsilon_r} \]

where the significant difference in the dielectric constant between the annealed samples leads to >2X improvement in expected pyroelectric energy harvesting performance. Figures of merit for
pyroelectric bolometer applications typically have the dielectric constant in the denominator \[114\], so similar benefits are expected.

### 3.4 Chapter Summary

By taking measurements throughout the fabrication process, key pieces of information where able to be obtained. For difference in top electrode, devices with Pt experience pinching and devices with IrO₂ do not. IrO₂ is less effected throughout the fabrication process compared to Pt, probably due to its ability to allow O₂ vacancies to migrate across the electrode interface allowing it to prevent an increase in oxygen vacancy density at the electrode interface. It was found that hydrogen diffusion is not the source for the pinching effect of the ferroelectric hysteresis loop and could possibly be charge injection. Each fabrication step can have a significant effect, lithography and etching introduce defects while annealing can alleviate the damage and increase max polarization by approximately 2-4%. Testing after the first step, top electrode mill, can be a good indicator of the final \( P_{\text{max}} \) (<5% change) saving time and money.

This chapter also explores the benefits of using planar and nanostructured IrOₓ top electrodes for PZT devices considering piezoelectric and pyroelectric applications, compared to conventional platinum. Planar IrO₂ thin film was found to be compressive with -913.3 MPa when deposited at 100 nm thick, which contributes to the reduction in curvature of cantilever devices which is an added benefit to actuating structures increasing the point of contact as well as allowing for thinner structures that are capable of larger deflection. IrO₂ devices showed 16% to 20% more strain compared to those capped with Pt. The nanostructured IrOₓ thin films are shown to have low reflectivity while retaining good film polarization (>30 \( \mu \text{C/cm}^2 \)) and reducing the dielectric
constant, which improves the pyroelectric energy harvesting figure of merit by over 2X compared to Pt films on the same PZT, enabling better performing pyroelectric applications.
Chapter 4
Radiation Effects in PiezoMEMS

With the decreasing size in satellite technology [115,116], and the functionality of piezoelectric, pyroelectric, and ferroelectric devices, the Department of Defense can utilize these components for satellite communications, intelligence surveillance and reconnaissance, space control, space environmental monitoring, satellite operations, as well as safety monitoring and security applications in other radiation rich environments, such as nuclear reactors. Understanding the effects of radiation on the electromechanical properties of materials and devices is of the utmost importance for the advancement of this technology in extreme hazardous environments.

The large dielectric and piezoelectric response in PZT thin films, are largely due to the presence of hysteretically and non-linearly mobile internal interfaces, e.g. domain walls and eventual phase boundaries. Radiation exposure is expected to largely affect such defect-defect interactions (e.g. pinning/unpinning of domain walls on point defects, grain boundaries, etc.) through both displacement and ionization events. However, prior research has primarily concentrated only on the effects of irradiation as polarization degradation in ferroelectric memory devices, while a more complete and complex picture of interaction of radiation with the functional material stacks in MEMS device configuration has been missing.

The goal of this chapter is to address the effects and mechanisms of radiation interaction with PZT based thin film PiezoMEMS with IrO$_2$ or Pt top electrodes, described and used in Chapter 3, by performing a dose study of ionizing radiation with a $^{60}$Co source, displacing radiation with a Fe$^{3+}$ ion source, as well as an in situ study of ionizing radiation with $^{60}$Co.
4.1 Ionizing ($^{60}$Co) dose study

Devices from Chapter 3, were irradiated with 0.2, 0.5, 1, 2, 5, and 10 Mrad (Si), using a $^{60}$Co gamma radiation source at a dose rate of approximately 600 rad (Si)/sec at the Naval Research Laboratory (NRL) in Washington, D.C. The electrodes were left floating during irradiation. The ferroelectric, dielectric, and piezoelectric response for actuator devices were characterized as function of top electrode material (IrO$_2$ or Pt).

![Figure 55: Comparison of P-E Hysteresis loops of actuator devices with IrO$_2$ (a) and Pt (b) top electrode before (dark) and after (light) 10 Mrad $^{60}$Co exposure.](image)

As an extreme example, Figure 55 shows a comparison of polarization hysteresis loops before and after exposure of the maximum dose of this study. The pinching characteristic at low voltages is observed in both irradiated samples, with the Pt electrode devices (b) displaying a higher level of pinching while in the IrO$_2$ electrode capped structure (a), a significant imprint of the hysteresis occurs but the predominant effect is a decrease in the hysteresis tilt, associated with heterogeneities in local coercive fields [111]. The trend of $P_{max}$ and $P_r$ at the different radiation doses is plotted in Figure 56. Although the polarization values of IrO$_2$ capped devices for $P_{max}$ (a) and $P_r$ (b) are less
than those of Pt, IrO$_2$ devices are less affected throughout the varying doses. For $P_{\text{max}}$, IrO$_2$ capped devices have a 2% decrease compared to the 8% decrease of Pt capped devices, while for $P_r$, IrO$_2$ capped devices decrease 16% compared to Pt capped devices which suffer a significant decrease of 55%. IrO$_2$ capped devices are more predictable and have a more radiation resistant $P_{\text{max}}$ and $P_r$ based on Figure 56.

![Figure 56: Trend of $P_{\text{max}}$ (a) and $P_r$ (b) vs radiation dose of actuator devices with IrO$_2$ (blue) and Pt (green) top electrode. IrO$_2$ samples show less variation.](image)

A comparison of the relative permittivity ($\varepsilon$) as a function of electric field before (dark) and after (light) 10 Mrad (Si) $^{60}$Co exposure of actuator devices with IrO$_2$ and Pt top electrode is shown in Figure 57. The presence of a third peak corroborate the ‘pinching’ characteristic seen in Figure 55.
Figure 57: Comparison of relative permittivity as a function of electric field before (dark) and after (light) 10 Mrad $^{60}$Co exposure of actuator devices with IrO$_2$ (a) and Pt (b) top electrodes. Presence of a third peak corroborate pinching mechanism.

Figure 58: Trend of maximum permittivity values (a) and percent change of the relative permittivity (b) in reference to the baseline (virgin) versus dose for devices with a IrO$_2$ (blue) and Pt (green) top electrode actuator devices.

Figure 58a shows the trend of the maximum relative permittivity values of IrO$_2$ (blue) and Pt (green) top electrode actuating devices. IrO$_2$ has a higher relative permittivity compared to Pt and is less effected through the varying doses with a 4% decrease compared to the 12% decrease of Pt capped devices. Since the PZT film performance varies between wafers, a percentage change from...
the baseline measurement was used to evaluate the radiation effects, seen in Figure 58b. The percent change follows a similar trend, IrO$_2$ deteriorated between 2% - 5% while Pt electrode devices show an improvement of 2% at low doses and significantly deteriorates up to 7% at higher doses. With a higher and more constant permittivity, IrO$_2$ capped devices are preferred for applications such as capacitors. As a figure of merit for tunability of capacitance, the tuning ratio ($\eta$) was calculated by Equation 16

$$\eta = \frac{C_{\text{max}}}{C_{\text{min}}} = \frac{\varepsilon_{\text{max}}}{\varepsilon_{\text{min}}}$$  

*Equation 17*

and the values across the doses are plotted in Figure 59. Although the tuning ratio for Pt capped devices is larger, it experiences a 13% decrease, more than double of the 6% decrease for IrO$_2$ capped devices.

*Figure 59: Tuning ratio ($\eta$) of IrO$_2$ (blue) and Pt (green) top electrode devices with varying dose.*
In addition to examining the ferroelectric and dielectric response, the piezoelectric response of the released cantilever actuators was tested for each of the dose levels of the study. A comparison of the relative strain for the devices exposed to 10 Mrad (Si), as seen in Figure 60. The asymmetry of the IrO$_2$ is due to the top and bottom electrodes being different, IrO$_2$ and Pt respectively, compared to the symmetrical Pt top and bottom electrode sample.

![Graph showing relative strain vs. electric field](image)

*Figure 60: Relative strain obtained from LDV data for IrO$_2$ (blue) and Pt (green) top electrode actuators after exposure to 10 Mrad (Si) of $^{60}$Co.*

Due to the asymmetry of IrO$_2$ capped devices, plotting both the maximum positive and maximum negative values of the relative strain compared to the maximum relative strain of Pt devices for each dose is seen in Figure 61.
Both top electrode materials exhibit a similar decrease in strain at the lower doses, with IrO$_2$ capped devices stabilizing at the 2 Mrad (Si) dose and above.

4.2 Displacing (Fe$^{3+}$ ion) dose study

Electronic devices can be disturbed by passing high energy electrons, protons, or heavy ions that can alter the state of the circuit producing the single event effects stated previously [118]. The National Aeronautics and Space Administration (NASA) conducts heavy ion testing on candidate spacecraft electronic devices, i.e. Static Random Access Memory (SRAM), Analog to Digital Convertors (ADCs), Input-Output (I/O) devices, microprocessors, etc. NASA utilizes the guidelines in [119] to determine the minimum Linear Energy Transfer (LET), the amount of energy transferred from the ion to the target material per unit distance, value to cause a temporary damage called Single Event Upset (SEU) or permanent damage known as a Single Event Latchup (SEL).
Devices described in Chapter 3, were irradiated at Auburn University under a 4 MeV Fe$^{3+}$ ion source with fluences of $2.21 \times 10^{10}$, $8.84 \times 10^{10}$, $2.21 \times 10^{11}$, and $2.21 \times 10^{13}$ ions/cm$^2$, equivalent to total ionizing doses of 1, 4, 10 and 1000 Mrad (Si) seen in section 4.1. The electrodes were left floating during irradiation. The ferroelectric, dielectric, and piezoelectric properties were measured before and after irradiation.

![Ferroelectric hysteresis loops of IrO$_2$ (a) and Pt (b) before and after 1000 Mrad (Si) exposure with Fe$^{3+}$ ions.](image)

*Figure 62: Ferroelectric hysteresis loops of IrO$_2$ (a) and Pt (b) before and after 1000 Mrad (Si) exposure with Fe$^{3+}$ ions.*
Figure 62 shows a comparison of polarization hysteresis loops before and after exposure of the maximum dose of 1000 Mrad (Si), showing similar ferroelectric results as in section 4.1. The pinching characteristic at low voltages is observed in both irradiated samples, with the Pt electrode devices (b) displaying a higher level of pinching while in the IrO$_2$ electrode capped structure (a), the predominant effect is a decrease in the hysteresis tilt without the shift seen in Figure 55. With increasing radiation fluence, the concentration of radiation-induced defects, i.e. vacancy production, is expected to increase. As the concentrations of cation and anion vacancies increase, the concentration of defect dipoles increase and can provide a strong restoring force for domain wall motion, explaining the pinching of the hysteresis loop [120]. It is also generally observed that in samples irradiated without an applied field electron trap buildup is produced by the displacement damage [121]. The trend of $P_{\text{max}}$ and $P_r$ at the different radiation doses is plotted in Figure 63. There is no clear trend other than the IrO$_2$ capped actuator devices appear to be more constant with a 5% decrease up to 10 Mrad(Si) for $P_{\text{max}}$.

![Figure 63: % change for maximum polarization (a) and remnant polarization (b) of IrO$_2$ (orange) and Pt (gold) top electrode actuator devices irradiated with Fe$^{3+}$ heavy ions at varying doses.](image)
The dielectric measurements are shown in Figure 64, with the % change in relative permittivity (a) and the tan δ (b). No clear trend can be made from the permittivity data set while tan δ worsens as the dose increases.

Figure 64: % change for relative permittivity (a) and tan δ (b) of IrO₂ (orange) and Pt (gold) top electrode actuator devices irradiated with Fe³⁺ heavy ions at varying doses.
Figure 65: Strain plots for IrO$_2$ (a) and Pt (b) capped actuators before (blue/dark red) and after (orange/gold) 1000 Mrad(Si) dose of Fe$^{3+}$ ions.
Figure 66: Relative strain versus dose of virgin (blue) and irradiated (orange) IrO$_2$ and virgin (dark red) and irradiated (gold) Pt capped actuators.

The strain before and after the extreme dose of 1000 Mrad (Si) for both different top electrode devices are plotted in Figure 65. While being subjected to the same environment, both exhibit different behavior. IrO$_2$ (a) capped device has a negative shift in strain overall, with an area that goes into negative strain spanning approximately 70 kV/cm. Pt (b) capped decreased at the max electric field but not only shifted to the positive side of the electric field, the strain remained on the positive end. It also demonstrates a pinching effect at negative low electric field. This drastic change in hysteretic strain loop suggests displacement of atoms or Fe$^{3+}$ atoms coming to a stop within the lattice, which would in turn create interstitial defects changing the strain of the lattice. Looking at the strain of the devices with all the doses in Figure 66, both different capped devices show a similar trend in max strain.
4.3 Ionizing ($^{60}$Co) in situ

In situ tests are important to have a better understanding of the effects of radiation on the devices in addition to providing more precise information about the device and material properties while they are irradiated. For example, CMOS devices can operate after being irradiated but not during. Studies have shown that large irreversible changes in the electrical conductivity may develop in oxide ceramics if an electric field is applied during irradiation [122-125].

Previous in-situ radiation effects studies have uncovered the existence of operational conditions in which degradation of the physical properties of ceramics may occur at extremely low doses $\ll 10^{-3}$ displacements per atom (dpa), due to a synergistic relation between ionization, displacement damage, and applied electric field. For physical properties, post-irradiation data are often not indicative of the property values during irradiation, and should not be used for design purposes in general [121]. The following radiation test was performed at the Naval Research Laboratory (NRL) in Washington, D.C. with the $^{60}$Co source now producing approximately 397.1 rad(Si)/s.

4.3.1 Set up

To be able to test the devices in situ, a new set up had to be designed and built. The devices from Chapter 3 were wirebonded with a wedge wirebonder on a 24 pin dip. Two different printed circuit boards (PCBs) were designed, referred to as testing PCB and relay PCB from here on, and were fabricated by Advanced Circuits in Aurora, CO. The testing PCB is 19 cm x 7.3 cm to be able to fit inside the cylindrical canister used to expose the samples to the $^{60}$Co source. The testing PCB included a zero insertion force (ZIF) socket 8 cm from the bottom to align the samples with the $^{60}$Co source. The ZIF socket is connected to two Ethernet sockets and four SMA female connectors. 25 foot long Ethernet and SMA cables connect the testing PCB to the relay PCB. The
$^{60}$Co source lies at the bottom of an approximately 20 foot deep pool so the cables had to be inserted through a 20 foot clear PVC plastic tube. The relay PCB measures 8 cm x 31 cm, with two Ethernet ports on one end connected to 16 BNC 90 degree connectors (8 per Ethernet port). The relay PCB was then connected to the various instruments: Ferroelectric tester (Radiant) to ferroelectric data, Impedance analyzer (HP) to obtain dielectric data, and two multimeters (Keithley) for switch closure tests.

The switch closure test is ran by performing a voltage sweep to determine the contact voltage, what voltage a piezoelectric switch requires to closes the circuit, as well as the voltage required to re-open the circuit again. For this test, two multimeters were used, one to do the voltage sweep, and the second to read the input/output signal.

4.3.2 Test procedure

To be able to run the 7+ hour test effectively and efficiently, a MATLAB code was written to run the entire test without human input past the first set of commands. These commands are the dose rate of the $^{60}$Co source, the maximum dose, sample number, and execute. Using a relay switch, two different tests are able to be performed simultaneously to be more effective. Iridium oxide and platinum capped actuators and capacitors, as well as IrO$_2$ switches were tested. The test procedure is as follows:

1) P-E of Actuator / C-V of Capacitor
2) P-E of Capacitor / C-V of Actuator
3) Switch Closure test

The P-E tests were performed by running a positive bipolar loop from, from 0 V to 19 V back to -19 V and ending at 0 V. A negative unipolar loop was taken, from 0 V to -19 V, to not produce
switching. A negative bipolar loop followed, from 0 V to -19 V sweeping up to 19 V and returning to 0 V. A positive unipolar loop, from 0 V to 19 V, finished the P-E set of tests. The C-V test was performed from -10 V to 10 V and returned to -10 V with steps of 0.25 V. The switch closure test alternated the bias voltage between 0 V and 15 V.

The test procedure ran every 300 seconds, once the set of tests were complete, the program would wait until the remainder of the time before starting at step one again, until the maximum dose was met.

4.3.3 Test results

\[\text{Figure 67: P-E hysteresis during }^{60}\text{Co irradiation for actuators with IrO}_2 \text{ (a) and Pt (b) top electrodes, and capacitors with IrO}_2 \text{ (c) and Pt (d) top electrodes.}\]
Comparing the ferroelectric hysteresis loops of this data set with the dose study, section 4.1, the first thing that is noticed is none of the P-E loops are ‘pinched’. The in situ hysteresis loops, Figure 67, general shape do not change, for both actuator and capacitor devices for both top electrodes. Believed to be due to the cycling of the biasing not allowing the radiation induced defects to be embedded into the grain boundaries or vacancy sites. In Proire, et al., cycling the irradiated devices showed signs of repair. The actuator device with IrO$_2$ top electrode appears to be less effected throughout the process, and confirmed by the polarization trend graphs in Figure 68.

Figure 68: Trend of maximum polarization ($P_{\text{max}}$), positive remnant polarization ($+P_{\text{rem}}$), and the absolute value of the negative remnant polarization ($-P_{\text{rem}}$) of actuators capped with IrO$_2$ (a) and Pt (b), and capacitors capped with IrO$_2$ (c) and Pt (d) during irradiation from 0 to 10 Mrad(Si) with a $^{60}$Co source.
IrO$_2$ continues to assist PZT in resiliency when exposed to irradiation. The maximum polarization for IrO$_2$ capped actuator and capacitor devices decreased approximately 2% and under 3% respectively while the Pt capped actuator decreased over 6% and the capacitor decreased 5%. The negative remnant polarization is significantly less affected than its positive counterpart. This finding, plus the shift in the positive end of the electric field of the P-E hysteresis loops in Figure 67 suggest the PZT domains have a negative preference. Negative $P_{\text{rem}}$ change less than 2% for actuator devices and around 10% for capacitors, while the positive $P_{\text{rem}}$ changes 150%, 50%, 58% and 69% for IrO$_2$ actuator, Pt actuator, IrO$_2$ capacitor, and Pt capacitor respectively. It is important to note that the starting $P_{\text{rem}}$ values already had a negative preference.
Figure 69: Trend of internal electric field (E_i), negative coercive field (-E_c), and positive coercive field (+E_c) of actuators capped with IrO_2 (a) and Pt (b), and capacitors capped with IrO_2 (c) and Pt (d) irradiated from 0 to 10 Mrad(Si) with ^{60}Co.

The coercive fields shown in Figure 69, show with more clarity that the domains have a negative preference, requiring a larger positive electric field to induce switching of 50% of the domains. The trend for all for different devices show an increase in electric field needed to switch the domains as dose increases. This suggests that the radiation induced defects are creating negatively charged defects or preferentially pinning domains in the negative orientation.
In Figure 70, the minimum permittivity for all 4 different devices remains unchanged, while the maximum permittivity has a sudden increase at doses in the low krad(Si) range before reaching an apparent equilibrium for both actuator devices and decrease for both capacitor devices. Both actuator and capacitor devices with IrO$_2$ top electrodes show higher permittivity than Pt capped devices. Permittivity is the only material property that matches the magnitude with the first $^{60}$Co test from section 4.1.

*Figure 70: Trend of maximum permittivity (blue) and minimum permittivity (orange) during exposure to $^{60}$Co for actuators with IrO$_2$ (a) and Pt (b) top electrodes, and capacitors with IrO$_2$ (c) and Pt (d) top electrodes.*
Actuator devices experienced an increase in tunability similar to a natural log (ln(x)) as dose increased with the IrO$_2$ capped actuator having the highest tunability, Figure 71a and b. While both capacitors experienced a linear decrease in tunability with IrO$_2$ top electrode capacitor having an average of 8% higher tunability than Pt capped capacitor device, both devices decreased < 4%.

![Figure 71: Trend of tunability ($\varepsilon_{max}/\varepsilon_{min}$) during exposure to $^{60}$Co for actuators with IrO$_2$ (a) and Pt (b) top electrodes, and capacitors with IrO$_2$ (c) and Pt (d) top electrodes.](image)

### 4.4 Chapter Summary

PiezoMEMS devices have been reported to function, with slight decreased electromechanical properties, to total ionizing doses of 10 Mrad (Si) with gamma rays and up to 1000 Mrad (Si) with
Fe$^{3+}$ ions. Although IrO$_2$ capped devices displayed certain smaller ferroelectric properties such as $P_{\text{max}}$ when compared to Pt capped devices, IrO$_2$ devices were less impacted through the varying doses of radiation in all three radiation experiments, with Pt showing stochastic ferroelectric and dielectric results when irradiated with the Fe$^{3+}$ ion source but with a negative trend with increasing total ionization dose in both gamma ray experiments. Devices exposed to radiation without an applied electric field exhibit pinching, while the in situ measurements showed no signs of the pinching effect. Both actuator and capacitor devices with IrO$_2$ top electrodes show higher permittivity than Pt capped devices. Permittivity was the only parameter that matched in both $^{60}$Co radiation exposure. Tuning ratio (tunability) decreased for actuating devices in the in situ test compared to the first radiation test starting at 39% to 32% for devices with IrO$_2$ and 50% to 42% for devices with Pt top electrodes. In situ irradiated actuator devices experienced an increase in tunability similar to a natural log ($\ln(x)$) as dose increased with the IrO$_2$ capped actuator having the highest tunability. In the first radiation test, Pt capped actuators had a more than 2X decrease in tunability than the IrO$_2$ devices, while both capacitors experienced a linear decrease in tunability during in situ irradiation. The remnant polarization and coercive field for in situ, show a clear negative preference. The shape of the strain loop for the Pt top electrode actuator was significantly altered only during Fe$^{3+}$ exposure, suggesting displacement damage occurred since no similar evidence is present for gamma ray only irradiation. Overall, the data for both $^{60}$Co irradiation, one being in situ, show completely different results, suggesting that the radiation induced defects are also affected by the presence of an electric field.
Chapter 5

Conclusions and Future Work

The primary objective of this work was to develop a standard deposition process for iridium oxide as a top electrode to enhance thin film PZT based piezoelectric, pyroelectric, and ferroelectric MEMS devices. Developing this material has required interaction between materials, proficiency in over 15 fabrication and characterization tools, and structures design. This secondary objective of this work was to investigate the influence of iridium oxide top electrodes on the properties of PZT films and MEMS devices subjected to gamma and heavy ion radiation for applications in radiation rich environments. This secondary objective required the learning of writing computer programming language for testing and analysis as well as design and fabrication of testing equipment. This chapter highlights the results of this work, provides the work output of this journey, and supplies recommendations for future research projects.

5.1 Conclusions

The first chapter summarizes and describes the piezoelectric, pyroelectric, and ferroelectric effects and properties that are exploited that make PZT one of the leading materials in thin film MEMS. The importance of the effects of top electrodes on thin film ferroelectrics such as the manipulation of the composite mechanical properties and electrical properties is described along with details on conventional Pt top electrode and IrO$_2$. Background information on radiation, the types and effects on materials are covered. Lastly, a description of the function of the tools and techniques used throughout this work is presented.

The second chapter presents the deposition optimization of iridium oxide thin films for piezoelectric and pyroelectric applications by the manipulation of the O$_2$ gas flow rate during
sputter deposition producing films of different morphologies. Planar IrO$_2$ for piezoelectric applications was optimized at 60 sccm O$_2$ flow rate and a deposition temperature of 500$^\circ$C. Nanostructured, 2D platelets are observed for high oxygen flow rates (100 sccm) regardless of temperature, producing a self-limiting dense columnar film as the base of the plate-like structures. While the plate-like region continues to grow with increased deposition, at a rate of $\sim$6 nm/s, the dense film at the base appears to reach a critical thickness of approximately $60 \pm 10$ nm. The dense film growth contributes to lower resistance, but the nanostructured platelets introduce a new resistive element that dominates the response. The IrO$_x$ nanostructures are proven to be compatible with various cleanroom processes, such as lift-off, and ultrasonic cleaning. The deposition on etched surfaces is confirmed for the IrO$_x$ nanostructures, adding to the possibility for inclusion to the production line with the only change to the fabrication process being the selection of a higher O$_2$ flow rate. For the first time, the Young’s modulus of planar IrO$_2$, which is crucial to improving device modeling was directly measured at 262 GPa $\pm$ 3, allowing for improvements for future device design.

The third chapter explores the fabrication process, where key pieces of information on how the process itself affects the ferroelectric and dielectric properties of the devices. IrO$_2$ is compared to Pt, and it was found that devices with Pt experience pinching and devices with IrO$_2$ do not. IrO$_2$ is less effected throughout the fabrication process compared to Pt probably due to its ability to allow O$_2$ vacancies to migrate across the electrode interface and preventing an increase in oxygen vacancy density at the electrode interface. It was found that hydrogen diffusion is not the source for the pinching effect of the ferroelectric hysteresis loop. Each fabrication step can have a significant effect, lithography and etching introduce defects while annealing can alleviate the damage and increase max polarization. Testing after the first step, top electrode mill, can be a good
indicator of the final $P_{\text{max}}$ ($<5\%$ change) saving time and money. This chapter also explores the benefits of using planar and nanostructured IrO$_x$ top electrodes for PZT devices considering piezoelectric and pyroelectric applications, compared to conventional platinum. Planar IrO$_2$ thin film was found to contribute to the reduction in curvature of cantilever devices which is an added benefit to actuating structures increasing the point of contact. The nanostructured IrO$_x$ thin films are shown to improve the pyroelectric energy harvesting figure of merit by over 2X compared to Pt films on the same PZT, enabling better performing pyroelectric applications.

The fourth chapter reports on the effects of different types of radiation on PiezoMEMS actuator and capacitor devices. They are reported to function, with mostly decreased electromechanical properties, to doses of 10 Mrad (Si) with gamma rays and up to 1000 Mrad (Si) with Fe$^{3+}$ ions. Although IrO$_2$ capped devices usually displayed smaller properties compared to Pt capped devices, devices with IrO$_2$ top electrode were less impacted through the increasing doses in all three radiation experiments. The remnant polarization and coercive field for in situ, showed a clear negative preference of the PZT. Devices exposed to radiation without an applied electric field exhibit pinching, while the in situ measurements showed no signs of the pinching effect. The strain loop for the Pt top electrode actuator during Fe$^{3+}$ exposure, was the only one suggesting displacement damage occurred. Overall, the data for both $^{60}$Co irradiation, one being in situ, show completely different results, suggesting that the radiation induced defects are also affected by the presence of an electric field.

5.2 Recommended Future Work

Recently, the U.S. Army Research Laboratory has an objective to improve Positioning Navigation and Timing (PNT). Positioning is the ability to accurately and precisely determine one’s location. Navigation is the ability to determine current or desired position both relative and absolute [131].

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Relative, as the name implies signifies in relation to a point of reference. Absolute refers with reference to latitude and longitude. Timing is the ability to acquire and maintain precise time form a coordinated universal time anywhere in the world. When PNT is used in combination with map data and other information, the result is the modern navigation system known as the Global Positioning System (GPS). For decades, GPS technology has been incorporated into vehicles and munitions to meet Department of Defense requirements (DoD) for precision guidance and navigation [132]. The DoD has changed with the use of GPS-based PNT, from reactive to real-time mode of situational awareness in both command and control [133]. The dependence on GPS creates vulnerabilities when the GPS signal is degraded or unavailable. Currently, the Defense Advanced Research Projects Agency (DARPA), has a program called Micro-PNT, which is developing high-performance, low cost, size, weight and power, solutions for improved PNT in harsh environments relevant to DoD needs [132]. With more research and development, the devices presented in this work have the potential to complete the tasks in harsh environments.

5.2.1 Neutron irradiation

Neutron radiation is considered indirectly ionizing. The neutron can interact with a nucleus in two distinct ways. The first, a neutron can cause nucleus recoil, ionizing the nucleus and subsequently ionizing other atoms. The second, the neutron can get absorbed into a nucleus and this causes a gamma ray emission, which can remove an electron from the atom causing ionization. Neutron radiation is found in radiation rich environments such as space and within nuclear reactors. Neutrons produced in space are called high-energy neutrons. In space there are three principal sources of high-energy neutrons near the Earth: 1) the atmosphere of Earth; 2) the sun; and 3) other sources outside the Earth-Sun region [134] with the exact sources still trying to be discovered [135]. In nuclear reactors, depending on the energy of the neutron, they are categorized as slow
(thermal) neutrons (0.025-10 eV) or fast neutrons (1-20 MeV). Due to a higher cross section, the likelihood of interaction between incident neutron and target nuclei, thermal neutrons are usually absorbed more easily by nuclei [136].

Several material properties of ceramics are substantially affected by neutron irradiation, i.e. density, elastic modulus, compressive strength, mechanical integrity, and thermal conductivity. Fast-neutron, with energy greater than 1 keV effects are significant at levels near 5 x 10^{11} n/cm^2. In general, the mechanical properties of ceramics are not appreciably changed by exposure to ionizing radiation doses of less than 10^9 rad (ceramic) or by neutron fluences less than 10^{19} n/cm^2. Large changes in thermal conductivity have been observed at neutron fluences of 10^{18} n/cm^2 to 10^{19} n/cm^2 [89]. Mechanical property and substantial volumetric changes, which can cause formation of microcracks and reduce strength in bulk ceramics, has been found with fast neutron fluences up to about 10^{22} n/cm^2 [137-147].

By the end of calendar year 2018, a new particle accelerator at the U.S. Army Research Laboratory Adelphi Lab will be available. This new accelerator can reach fluences of fast neutrons equivalent to 10 Mrad (Si) in hours, compared to the previous accelerator which would take 28 days of constant exposure. The location of this new accelerator will allow for ease of access and contribute to obtaining a more complete picture of how different types of radiation effect PZT based PiezoMEMS, both for RF and PNT applications. This test would also be effective in helping to determine if the devices are suitable for sensors in nuclear facilities. For testing procedure, the standard test method TM 1017: Neutron irradiation, updated in 2014 for both military standards MIL-STD-750-1 Environmental Test Methods for Semiconductor Devices and MIL-STD-883 Microcircuits should be followed with the caveat that because radiation hardness assurance (RHA)
is dynamic, test standards and guidelines will always be “behind the times” because they are a compromise between technical rigor and economic realities [148].

5.2.2 PiezoMEMS Device Reliability

The acceptance of MEMS devices for critical and space applications depend largely on their reliability. MEMS reliability is one of the most challenging areas in MEMS development for space applications [Miller]. MEMS devices qualification for reliable and robust operation in the harsh environment of space has been a focus for NASA for some time now [149, 150]. Aside from the damaging radiation exposure, space MEMS devices can encounter extreme environmental and operational conditions such as acoustic noise greater than 150 dB from launch vehicles, temperatures ranging from 3K to almost 2000°Cat atmospheric entry, and acceleration forces, from 3g for NASA Space Shuttle launch [150] to equivalent to thousands of g’s on planetary surface impact [152]. A space environmental verification and testing program should be designed and implemented. Typical space environmental verification and testing programs involve a series of dynamic and thermal tests, including pyroshock, acoustic noise, acceleration, random and sinusoidal vibrations, and thermal cycling. The order in which the different tests are conducted should simulate the flight sequence as close as possible. It has been shown that testing order has an effect on the effectiveness of screening for potential failures [148].

Determining device reliability and integrity of PiezoMEMS when subjected to shock, vibrations, temperature extremes, and radiation of the space environment is necessary to facilitate the integration into critical and space applications. A couple of device reliability issues that have been found in piezoelectric devices are fracture and heat production [150] By inducing stress in the material, they should be treated as structural devices and stress distribution should be analyzed to prevent fracture. Due to the mechanical stress and electrical loss, heat transfer across a device will
occur. Therefore heat generation must also be considered in determining the reliability characteristics [149]. Stiction, wear, fatigue, and delamination are other modes of failure that should be understood [153]. Many of these can be understood through materials properties. Packaging is another factor to consider due to thermomechanical mismatch during die attachment and packaging steps [151], as well as trapped gases in metal packaging which can pressurize the package and degrade device performance due to damping effects [150].

At the U.S. Army Research Laboratory, there are several tools that can help determine the device environmental reliability of the PiezoMEMS structures. In the PiezoMEMS laboratory, the V408 shaker table (LDS) with a PA100L amplifier and forced air cooling, we can subject the devices to a force up to 196 N using a square wave function, acoustic noise up to 105 dBA at a distance of 1 m, accelerations up to 100 g, random and sinusoidal vibrations through a frequency range from 5 Hz to 9 kHz. In the Power Electronics laboratory, a centrifuge currently with the capability of going up to 20 g with the possibility of more with the purchase of different bolts, has been designed to allow electronic in situ g-force testing. In the same laboratory, on the PyroMEMS side, a probing station with a special set up that can reach temperatures as low as 70 K up to 675 K can be utilized for thermal cycling. In situ and floating electrodes tests are recommended in the g force tests and thermal cycling to give us more information similar to that in Chapter 4.

Non environmental mechanisms of failure should be investigated as well. To determine mechanical fracture, the device must be stressed beyond its fracture strength (ultimate strength/final cross-sectional area) [152]. This can be done with a tensile test and plotting a stress-strain curve. Allowing us to also obtain, the device strength from the yield stress, the yield strength, and the elastic limit. Heat production, or change in temperature, \( \Delta T \), can be calculated for a rectangular piezoelectric actuator driven at a frequency \( f \), using the following equation [149]:

\[
\Delta T = \frac{1}{C_{\text{actuator}}} \left( \frac{1}{2} \rho V^2 + \frac{1}{2} m \ddot{V} \right)
\]
$$\Delta T = \frac{ufv_e}{k(T)A} \quad \text{Equation 18}$$

where $u$ is the loss of the material per cycle, $v_e$ is the effective volume of the piezoelectric actuator (volume of the material not at equilibrium), $A$ is the surface area of the piezoelectric actuator, and $k(T)$ is defined as the overall heat transfer coefficient, obtained through

$$k(T) = \sigma \varepsilon (T^2 + T_0^2)(T + T_0) + \overline{h_c} \quad \text{Equation 19}$$

where $\sigma$ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W/(m}^2\text{K}^4)$), $\varepsilon$ is the emissivity of the sample, and $\overline{h_c}$ is the average convective heat transfer coefficient ($6-30 \text{ W/m}^2\text{K}$ in air).

Stiction and fatigue can simultaneously be done by performing a switch closure test and actuating released non-switch devices in the same die. All of these tests should be repeated once the devices have been packaged and a comparison should be made. Obtaining all of this information is vital for improving design, since it has been shown that operation stability during packaging and thermal cycling is highly depending on the geometrical design of a switch and should be taken into account at the design stage [151]. This will also provide a better understanding for integration into PNT devices.
5.3 Ph.D. Research Output

5.3.1 Poster Presentations

• *Optimization of IrO$_2$ Deposition on TiO$_2*
  
  2015 U.S. Army Research Laboratory, Adelphi, MD

• Comparison of PbZr$_x$Ti$_{1-x}$O$_3$ Devices with Either IrO$_2$ or Pt Top Electrodes
  
  2016 U.S. Army Research Laboratory, Adelphi, MD

• *Ferroelectric Behavior Comparison of Gamma Irradiated PbZr$_x$Ti$_{1-x}$O$_3$ Devices with Either IrO$_2$ or Pt Top Electrodes*
  
  2016 Defense Threat Reduction Agency Review, Fort Belvoir, VA

• *Evaluating PZT Thin Films Exposed to both Ionizing and Displacement Radiation*
  
  2017 U.S. Army Research Laboratory, Adelphi, MD

• *Growth Behavior for Sputtered IrO$_2$ Thin Film Plate-like Structures*
  
  2017 U.S. – Japan Seminar on Dielectric and Piezoelectric Ceramics, Santa Fe, NM

• *Effects on Ferroelectric Thin-Film Stacks and Devices for piezoelectric MEMS Applications at Varied Total Ionizing Dose (TID)*
  
  2017 Government Microcircuit Applications & Critical Technology Conference, Reno, NV

• *Determination of Elastic Modulus of IrO$_2$ Thin Films for PiezoMEMS Applications*
  
  2017 International Symposium of Applied Ferroelectrics, Atlanta, GA

• *Varied Total Ionization Dose (TID) study on PZT based Thin-Film Stacks and Actuator Devices for Piezoelectric MEMS applications*
  
  2017 Nuclear and Space Radiation Effects Conference, New Orleans, LA
5.3.2 Oral Presentations

- *Optimization of IrO$_2$ as a Top Electrode for PZT Thin Film Devices*
  2016 Electronics and Materials Applications, Orlando, FL

- *Comparison of PbZr$_x$Ti$_{1-x}$O$_3$ Devices with Either IrO$_2$ or Pt Top Electrodes*
  2016 International Workshop on Acoustic Transduction Materials and Devices, Penn St. University, State College, PA

- *Evaluation of Fabrication Induced Damage on the Ferroelectric & Piezoelectric PZT Thin Films for Clamped and Unclamped Final Devices*
  2017 Electronics and Materials Applications, Orlando, FL

- Fabrication-Induced Defects in PZT-based devices
  2018 ISAF-FMA-AMF-AMEC-PFM Joint Conference, Hiroshima, Japan
5.3.3 Publications


• D.M. Potrepka, M. Rivas, H. Yu, R.G. Polcawich, M. Aindow, and G.R. Fox “Effect of IrO2/Pt bottom electrodes on the structure and electrical properties of PZT PiezoMEMS devices” Submitted 2017


Chapter 6 Bibliography


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