Effect of Top Electrode Material on Radiation-Induced Degradation of Ferroelectric Thin Films

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Abstract: The effects of gamma radiation on the dielectric and piezoelectric response of Pb[Zr₀.₅₂Ti₀.₄₈]O₃ (PZT) thin films was investigated as a function of metallic (Pt) or conductive oxide (IrO₂) top electrode. All samples showed a general degradation of dielectric, polarization, and electromechanical response when exposed to 2.5 Mrad (Si) ⁶⁰Co gamma radiation. At low-fields, the relative permittivity, ɛr, remained largely unaffected by irradiation: -0.8% and -1.2% in samples with IrO₂ and Pt electrodes, respectively. At high fields, samples with IrO₂ electrodes showed substantially less degradation of remanent polarization, P_r (<5%) compared to those with Pt electrodes (-32%). Samples with IrO₂ electrode compositions showed resistance to degradation of electromechanical response, d₃₃, after irradiation, while samples with Pt electrodes experienced a significant loss of piezoelectric response (-10%). Our findings illustrate a radiation-induced damage at the PZT-electrode interface that is dependent on the top electrode material. These results suggest promising avenues to radiation-hard devices and material stacks.

Introduction

Ferroelectric thin films enable numerous applications in science and industry such as precision positioners and optics, microelectromechanical systems (MEMS) sensors and actuators, non-volatile memories, and energy harvesting systems. The multifunctional properties of ferroelectric materials - i.e. large dielectric, piezoelectric, and pyroelectric coefficients - make these ideal candidates for enabling a "More-than-Moore" paradigm in microelectronic devices. Of specific interest are autonomous, millimeter-scale robotics for performing tasks at locations that are either difficult to reach or otherwise dangerous for humans in energy and security applications, such as nuclear power plants and aerospace [1]. It is necessary to characterize the multifunctional properties as a function of radiation exposure in radiation-hostile environments in order to evaluate device performance and functionality in the same conditions.

Large dielectric and piezoelectric response in ferroelectric thin films, such as lead zirconate titanate (PZT), are largely due to the presence of hysteretically and nonlinearly mobile internal interfaces, e.g. domain walls and eventual phase boundaries [2]. The mobility of these interfaces is determined by the internal energy landscape of the material, affected largely by presence of defects, including vacancy and dopant point defects, grain boundaries and heterointerfaces [3, 4].

Radiation exposure is expected to affect such defect-defect interactions (e.g. pinning/unpinning of domain walls on point defects, grain boundaries, etc.) through both displacement and ionization events. Prior research has dealt primarily with polarization degradation in PZT thin films for applications in memory devices [5, 6]. Here we discuss the role of top electrode material on the radiation-induced degradation of ferroelectric properties of PZT thin films. Pt is currently the industry standard for the majority of piezoelectric thin film applications, mostly due to its very high conductivity, maintained through the high processing temperatures (~700°C) required for processing of these functional materials. However, previous studies for ferroelectric random access memory (FRAM) devices have reported the positive effects of oxide electrodes on reducing ferroelectric cycling fatigue by enabling oxygen vacancy to traverse the ferroelectric-electrode interface [7].

Experimental Procedure

Pb[Zr₀.₅₂Ti₀.₄₈]O₃ (PZT) thin films and device structure were fabricated at Army Research Laboratory using 150mm platinized (100) silicon wafers. The substrates, in addition to 500µm-thick Si, included 500 nm thermal SiO₂, 35 nm sputtered Ti (thermally oxidized to form TiO₂), and 100 nm Pt to act as the bottom electrode. Textured PZT thin films using a PbTiO₃ seed layer were prepared via a 2-methoxyethanol (2MOE) route and sequentially deposited to achieve a thickness of approximately 500 nm [8, 9]. After the final PZT crystallization anneal, a 100 nm-thick top electrode, IrO₂ or Pt was sputter-deposited onto the wafer at 500°C. The IrO₂ electrodes are also processed with a post-
deposition furnace anneal at 650°C in flowing O₂. The electrode and piezoelectric actuator materials are patterned through a series of argon ion-milling procedures followed by a series of additional metallization procedures for creating proper interconnects to device structures. This general process flow is generically discussed in Ref [9].

Various dielectric and electromechanical characterization experiments were conducted on the samples prior to and following irradiation at Georgia Institute of Technology. Low-field dielectric measurements were performed at 1 kHz and 100 mV using an Agilent 4284 A precision LCR meter. Polarization-electric field (P-E) hysteresis experiments were carried out at 1 kHz at fields up to 400 kV/cm using a P-PM2 Radiant ferroelectric test system. Measurements to probe the converse, effective longitudinal piezoelectric response (d₃₃,f) were performed on an aixACCT double-beam laser interferometer (DBLI) system at 1 kHz and Vₑₛ = 0.25Vₑ (coercive voltage) with DC electric field up to 200 kV/cm, or approximately equal to twice the coercive voltage of all samples. All reported measurements are subject to ~3-5% error, due to instrumental resolutions.

All samples were irradiated with 2.5 Mrad (Si), using a ⁶⁰Co gamma radiation source at a dose rate of approximately 602 rad (Si)/sec at the Naval Research Laboratory (NRL). The ferroelectric and piezoelectric response of the material stack and devices were characterized after irradiation and compared to measurements taken beforehand. Sample electrodes were left floating during radiation exposure.

Results
Low-field relative dielectric permittivity of virgin PZT films with IrO₂ and Pt electrodes was approximately 998 and 953, respectively. Distribution of various samplings of low-field relative permittivity of samples with both Pt and IrO₂ electrodes are show in Figure 1, both before and after irradiation. Exposure to irradiation resulted in a degradation of relative permittivity by 0.8% and 1.2% for films with IrO₂ and Pt electrodes, respectively. We note that while these changes are statistically relevant, they were within the range of instrumental error. However, the reduction of dissipation factor (tan δ) was more substantial: 0.017 to 0.016 (~6%) for samples with IrO₂ electrodes and 0.030 to 0.024 (~20%) for samples with Pt electrodes.

Table 1. Extracted Rayleigh parameters from nonlinear dielectric AC field measurements performed at 1 kHz.

<table>
<thead>
<tr>
<th>IrO₂</th>
<th>Pt</th>
<th>α (cm/V)</th>
<th>εₑₛ</th>
<th>αₑₛ × 10⁵ (cm/V)</th>
<th>α (cm/V)</th>
<th>εₑₛ</th>
<th>αₑₛ × 10⁵ (cm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>52.3 ± 9</td>
<td>1103 ± 258</td>
<td>48.7 ± 26</td>
<td>34.8 ± 14</td>
<td>918.5 ± 132</td>
<td>40.0 ± 29</td>
<td></td>
</tr>
<tr>
<td>Irradiated</td>
<td>48.8 ± 6.5</td>
<td>1128 ± 66</td>
<td>42.7 ± 7</td>
<td>22.5 ± 4</td>
<td>1024 ± 103</td>
<td>22.1 ± 6</td>
<td></td>
</tr>
<tr>
<td>% Change</td>
<td>-8%</td>
<td>+2%</td>
<td>-12%</td>
<td>-36%</td>
<td>+12%</td>
<td>-44%</td>
<td></td>
</tr>
</tbody>
</table>

Rayleigh analysis involves probing the sample with a 1 kHz AC waveform of increasing voltage amplitude allows for extraction of parameters describing the reversible (εₑₛ) and irreversible (α) contributions to dielectric response of the material; reversible contributions describe mostly lattice deformation and reversible motion of internal interfaces, while irreversible contributions relate to larger-scale irreversible domain wall motion and are therefore considered a quantitative measure of extrinsic contributions to the functional response [10].

Irradiation of films with both electrode compositions resulted in degradation of α, but films with Pt electrodes showed degradation in excess of 4 times (36% vs 8% degradation) the degradation of samples with IrO₂ electrodes (Table 1). This implies that irreversible effects contributing to the response in the films are inhibited by irradiation, resulting in greater degradation for samples with Pt electrodes.

Table 2. Remanent and saturated polarization (Pᵣ, Pₛₐₜ) and percent difference before/after irradiation for films with IrO₂ and Pt electrodes.

<table>
<thead>
<tr>
<th></th>
<th>IrO₂</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pᵣ (μC/cm²)</td>
<td>Pₛₐₜ (μC/cm²)</td>
<td>Eₛ (V/cm)</td>
</tr>
<tr>
<td>Virgin</td>
<td>20.4 ± 1.1</td>
<td>48.1 ± 0.7</td>
</tr>
<tr>
<td>Irradiated</td>
<td>19.6 ± 1.6</td>
<td>48.1 ± 0.9</td>
</tr>
<tr>
<td>% Change</td>
<td>-4.2%</td>
<td>-0.2%</td>
</tr>
</tbody>
</table>

Polarization-electric field (P-E) hysteresis curves are reported in Figure 2. The remanent polarization is reduced in all samples after irradiation (Table 2), however, films with Pt electrodes showed a substantially larger degradation when compared to samples with IrO₂ electrodes (Table 2). Saturated polarization remained largely unaffected for samples.
with IrO₂ electrodes, while those with Pt electrodes resulted in a modest 4% reduction, yet again, comparable to the instrumental error.

Figure 2. Polarization-field (P-E) loops performed at 1 kHz

Figure 3. Capacitance-voltage (CV) curves for samples with IrO₂ (left) and Pt electrodes (right), with 1 kHz, 500 mV overlapping small signal amplitude.

Capacitance-voltage (C-V) curves, allow for analysis of the electrical behavior of oxide heterostructures as a function of DC bias [11]. Figure 3 shows CV curves for films with both electrode compositions. Samples with Pt show slight horizontal peak shift, indicating changes in the defect landscape and creation of an internal bias field upon irradiation. Additionally, the irradiated platinized samples' curves show the presence of an additional peak at positive voltages, which is indicative of creation of a new family of defects with an increased pinning energy. Such new family of defects can originate both through ionization events (and charge trapping in existing defects) or displacement events, as discussed below.

**Table 3. Electromechanical response before/after irradiation for films with IrO₂ and Pt top electrodes.**

<table>
<thead>
<tr>
<th></th>
<th>IrO₂</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d_{33,\text{saturation}}) (nm/V)</td>
<td>(d_{33,\text{saturation}}) (nm/V)</td>
</tr>
<tr>
<td>Virgin</td>
<td>0.045 ± 0.005</td>
<td>0.068 ± 0.024</td>
</tr>
<tr>
<td>Irradiated</td>
<td>0.046 ± 0.005</td>
<td>0.064 ± 0.004</td>
</tr>
<tr>
<td>% Change</td>
<td>+1%</td>
<td>-10%</td>
</tr>
</tbody>
</table>

Discussion
For both types of electroded material stacks, minimal changes in low-field relative permittivity (~1%), saturated polarization (<5%), and electromechanical response (≤10%, see Table 3) is promising for use of ferroelectric material stacks in radiation-hard required applications. However, irradiated samples with IrO₂ electrodes substantially smaller changes of dielectric and electromechanical response than those with Pt electrodes, suggesting that the heterointerface between the PZT thin film and electrode plays a critical role in either the radiation-material interaction or in the subsequent stages for reaching a new equilibrium.

Various features of P-E and CV plots shed some light on the defect-defect interactions in the ferroelectric material: the P-E field hysteresis loops showed pinching in samples with Pt electrodes, exacerbated after irradiation, and a horizontal shift of peaks in the CV curves for samples with Pt electrodes was also accompanied by presence of additional peaks after irradiation. These features are indicative of changes in the population and/or energy of defects pinning domain wall motion in the ferroelectric material.

A radiation-induced reduction in motion of the internal interfaces is also highlighted by the reduction of the irreversible Rayleigh parameter (\(\alpha\)), counterpointed by the increasing reversible Rayleigh component (\(\epsilon_{\text{init}}\)). Indeed the above are consistent with radiation-induced “higher energy” pinning sites (defects) for the motion of the internal interfaces, resulting in increased vibration (reversible motion) and decreased overall mobility (irreversibly contribution) of these interfaces to the overall dielectric response. We note that such higher-energy defects are consistent with both creation of trapped charges as a consequence of ionization events, as well as with new vacancies and interstitials created through displacement events.

Lastly, we note that the observed differences in the radiation effects on the functional response of the material stack points at the “healing” quality of the oxide electrode material. Previous studies, for ferroelectric capacitor and memory applications, have reported a more closely matching work-function of PZT with oxide electrodes as compared to metallic ones, resulting in improved conductivity at the interface and potential for oxygen vacancy migration [7, 12-14]. Additionally, theoretical studies of ferroelectric dead layers and metallization of the dielectric material suggest that metallic electrodes induce creation of dead layers, resulting in decreased ionic motion and thereby exacerbating defect accumulation and domain wall pinning [15, 16].

Conclusions
This work reports on degradation of dielectric and electromechanical response of PZT thin films, after gamma ray irradiation, as a function of the top electrode material. PZT thin films with both metallic Pt and metal-oxide IrO₂ top electrodes were exposed to 2.5 Mrad (Si) \(^{60}\)Co gamma radiation, and results of dielectric,
electromechanical, and polarization response were compared before and after irradiation. Samples with IrO$_2$ top electrode showed a higher tolerance to radiation within the radiation dosage range studied compared to those with Pt top electrodes. Formation of an ion-blocking oxide layer, a ferroelectric dead layer, or a metallic layer at the interface between the ferroelectric PZT and metallic Pt top electrode have been previously reported for capacitor and memory devices. Formation of said layers is substantially more limited in material stacks with metal-oxide IrO$_2$ top electrodes, due to the oxide’s amenability to the motion of ionic species. Changes in the defect landscape are thus less damaging to the dielectric, electromechanical, and polarization response of ferroelectric films and material stacks incorporating a metal-oxide top electrode, and provide a promising avenue to radiation-hard materials and devices based on ferroelectric materials.

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References