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ABSTRACT
The role of interfacial defect chemistry in time dependent breakdown and associated charge transport mechanisms was investigated for Pb0.99(Zr0.52Ti0.48)0.98Nb0.02O3 (PNZT) films. Electrical degradation was strongly dependent on the sign of the electric field; a significant increase in the median time to failure from 4.8 ± 0.7 to 7.6 ± 0.4 h was observed when the top electrode was biased negatively compared to the bottom electrode. The improvement in the electrical reliability of Pt/PNZT/Pt films is attributed to (1) a V̂O4+ distribution across the film due to PbO nonstoichiometry and (2) Ti/Zr segregation in PNZT films. Compositional mapping indicates that PbO loss is more severe near the bottom electrode, leading to a V̂O4+ gradient across the film thickness. Upon degradation, V̂O4+ migration toward the bottom Pt electrode is enhanced. The concentration of V̂O4+ accumulated near the bottom Pt interface (6.2 ± 1.8/cm3) after degradation under an electric field of 350 kV/cm for 12 h was two times higher than that near the top Pt/PNZT interface (3.8 × 1018/cm3). The V̂O4+ accumulation near the bottom Pt/PNZT interface causes severe band bending and a decrease in potential barrier height, which in turn accelerates the electron injection, followed by electron trapping by Ti4+. This causes a dramatic increase in the leakage current upon degradation. In contrast to the bottom Pt/PNZT interface, only a small decrease in potential barrier height for electron injection was observed at the top Pt/PNZT interface following degradation. It is also possible that a Zr-rich layer near the top interface reduces electron trapping by Ti4+.

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I. INTRODUCTION
Lead zirconate titanate (PZT) films are used extensively in MEMS devices such as energy harvesters,5 inkjet printers,6 actuators,7 medical transducers,8 and resonators9 due to their high piezoelectric properties. However, for MEMS actuators, the magnitude of the electric fields utilized often exceeds 100 kV/cm. As a result, DC resistance degradation, one of the limiting factors for the lifetime of PZT films, is of great concern. Therefore, it is crucial to understand the causes of the leakage current increase to control electrical breakdown and device failure.

For PZT films with metal electrodes, electrons, holes, and ions can all contribute to conduction and DC resistance degradation. Various conduction models have been proposed for PZT films: from bulk-controlled mechanisms, such as Poole–Frenkel emission,6,7 space charge-limited,8 and ionic conduction,9 to interface-controlled conduction mechanisms, such as Schottky emission10,11 and Fowler–Nordheim tunneling.11,12 It is probable that the wide range of models is a function of the fact that the electrical behavior depends explicitly on the stoichiometry and the defect chemistry, as well as the interface characteristics of PZT thin films and electrodes. One consequence of this is that films prepared under different conditions are likely to behave differently.
PZT is typically a p-type wide gap semiconductor due to unintentionally introduced acceptor ions and/or lead loss during processing.13 There is debate in the literature as to whether holes or electrons are the majority carriers in PZT films; the fact that donor doping tends to reduce the leakage currents suggests p-type conductivity,14,15 while experimental observations of Schottky barriers at the Pt/PZT films necessitate n-type surfaces since the
work function of Pt is higher than that of PZT.\textsuperscript{16,17} Such n-type interfaces can develop due to accumulation of oxygen vacancies during electrode deposition or on annealing in a reducing atmosphere.\textsuperscript{18,19} The oxygen vacancies act as a donor with an energy level 0.22–0.28 eV below the edge of the conduction band. Each oxygen vacancy is compensated by two electrons that are thermally excited at room temperature to form an n-type layer near the PZT surface,\textsuperscript{20} as verified by the presence of Ti\textsuperscript{4+} at the Pt/PZT interface.\textsuperscript{21} In previous work, it was demonstrated by electron energy loss spectroscopy (EELS) that the concentration of Ti\textsuperscript{3+} ions gradually increases toward the cathode in degraded Nb doped PZT films.\textsuperscript{22}

In the p-type bulk of PZT films,\textsuperscript{23} a variety of different electronic conduction mechanisms can occur simultaneously: (1) hole hopping between Pb\textsuperscript{2+} and Pb\textsuperscript{3+} (0.24–0.38 eV),\textsuperscript{20,21} (2) hole migration between lead vacancies (1.4 eV),\textsuperscript{22,23} and (3) small polaron hopping between acceptor ion sites (0.7–1 eV for hole hopping between Mn sites).\textsuperscript{24} Because films often show Poole-Frenkel-dominated conduction in the bulk and a Schottky barrier at the interface, films behave as a pair of nonlinear resistors in series.

As reported elsewhere,\textsuperscript{20,21,26} the lifetime of PZT films under DC electrical fields is a function of the doping type and dopant concentration. It was found that the lifetime is governed by the migration of oxygen vacancies through the PZT films. As V\textsubscript{O}\textsuperscript{−} build up at the interface, they modulate the local charge distribution near the PZT/electrode interface and then modify the interface characteristics; the local accumulation of V\textsubscript{O}\textsuperscript{−} can reduce both the Schottky barrier height and the width of the depletion layer, which accelerates electron injection and charge trapping on the Ti\textsuperscript{4+} sites in the PZT films.\textsuperscript{20,27–29} In this work, films with PZT films with 2% Nb doping were chosen to further probe the impact of this field-induced oxygen vacancy migration on the asymmetry of the leakage currents. This Nb concentration was found to allow the thermally stimulated depolarization current (TSDC) signatures to be high enough to allow ready probing of the phenomena.

DC resistance degradation in PZT films could, in principle, be strongly influenced by interfacial defect chemistry. The interfacial defect chemistry can differ at the top and the bottom PZT/electrode interfaces due to (1) an inhomogeneous distribution of defects across the PZT film (e.g., a variation in PbO stoichiometry), (2) Ti/Zr segregation during film preparation, and/or (3) variation in the oxidation state of ions across the film that can act as charge trap sites. PZT films are prone to varying trap state densities near the top and bottom electrodes, with a potential for large gradients due to a higher possibility of defect percolation in a single layer due to a higher possibility of defect percolation in a single layer across the entire thin film.\textsuperscript{24,25} The coating and drying process, as well as rapid thermal treatments, was repeated until a desired thickness of 350–400 nm was reached. Finally, a PbO layer was spun onto the surface of the PZT films and annealed at 700 °C in air, to eliminate surface pyrochlore. Residual PbO was then removed by immersing the sample in a 4M acetic acid solution for 60 s.

To grow the film, PZT solution was dispensed on platinized silicon substrates and spun at 1500 rpm for 30 s. Then, each layer was exposed to two sequential pyrolysis treatments for 3 min at 250 and 450 °C, respectively. Following pyrolysis, each PZT layer was crystallized at 700 °C for 60 s by rapid thermal annealing (RTA) using a ramp rate of 50 °C/s in an O\textsubscript{2} flow to reduce PbO loss at temperatures higher than 450 °C. The use of multiple crystallization steps leads to (1) phase pure films and (2) avoids low yield due to a higher possibility of defect percolation in a single layer across the entire thin film.\textsuperscript{24,25} The coating and drying process, as well as rapid thermal treatments, was repeated until a desired thickness of 350–400 nm was reached. Finally, a PbO layer was spun onto the surface of the PZT films and annealed at 700 °C in air, to eliminate surface pyrochlore. Residual PbO was then removed by immersing the sample in a 4M acetic acid solution for 60 s.

More details on the film orientation and grain size are available elsewhere.\textsuperscript{24,25}

II. EXPERIMENTAL PROCEDURE

Lead zirconate titanate thin films with 2% Nb (PNZT) were grown on commercial Pt/Ti/SiO\textsubscript{2}/Si substrates (Novel Electronic Materials, Flower Mound, TX) via chemical solution deposition. PZT (52/48) solutions with 10 mol. % Pb excess were prepared to compensate for lead loss during heat treatment. The details of solution preparation are explained elsewhere.\textsuperscript{24,25} The Nb doping concentration in solution was calculated presuming B site occupancy to reach final film compositions of Pb\textsubscript{1−x}Zr\textsubscript{x}O\textsubscript{2−y}Ti\textsubscript{y}O\textsubscript{3}, where x = 0.02.

To grow the film, PZT solution was dispersed on platinized silicon substrates and spun at 1500 rpm for 30 s. Then, each layer was exposed to two sequential pyrolysis treatments for 3 min at 250 and 450 °C, respectively. Following pyrolysis, each PZT layer was crystallized at 700 °C for 60 s by rapid thermal annealing (RTA) using a ramp rate of 50 °C/s in an O\textsubscript{2} flow to reduce PbO loss at temperatures higher than 450 °C. The use of multiple crystallization steps leads to (1) phase pure films and (2) avoids low yield due to a higher possibility of defect percolation in a single layer across the entire thin film.\textsuperscript{24,25} The coating and drying process, as well as rapid thermal treatments, was repeated until a desired thickness of 350–400 nm was reached. Finally, a PbO layer was spun onto the surface of the PZT films and annealed at 700 °C in air, to eliminate surface pyrochlore. Residual PbO was then removed by immersing the sample in a 4M acetic acid solution for 60 s. More details on the film orientation and grain size are available elsewhere.\textsuperscript{24,25}
For electrical characterization, Pt top electrodes with diameters ranging from 200 μm to 1 mm were prepared by double layer photolithography and liftoff processing. For this purpose, a ~100 nm Pt film was sputter deposited on the PZT surface (CMS-18 Sputter System, Kurt J. Lesker Company, Pittsburgh, PA) over a resist stack with a re-entrant profile. After liftoff, the samples were postannealed at 650 °C for 1 min by RTA using a ramp rate of 50 °C/s in an O2 flow.

The microstructure and local composition were studied using an FEI TITAN transmission electron microscope (TEM, FEI, G2 60–300 kV) with an operating voltage of 300 kV. Electron energy-loss spectroscopy (EELS) was performed using an FEI TITAN in DualEELS mode equipped with a Gatan Imaging Filter (GIF) quantum spectrometer and operated at 80 kV. A 2.5 mm aperture and an energy dispersion of 0.01 eV/pixel were utilized to acquire EELS spectra.

Leakage current measurements were performed using a 4140 pA m/DC Voltage Source (Hewlett Packard) in order to understand the steady state condition before current-voltage measurements. Measurements of current were made 60 s after any change in voltage to allow the current to stabilize. The field range utilized was up to 500 kV/cm for both voltage polarities.

TSDC measurements were performed using a HP 4140b PA meter at temperatures ranging from 25 to 300 °C. The noise level measured under open-circuit conditions was on the order of picoamps from 50 to 600 °C. First, the sample was heated to a poling temperature (Tp), and then it was poled under a DC field to orient or move defects. After poling the sample at Tp for 12 h, the sample was field-cooled to Tc to freeze the defect dipoles, space charges, and/or trapped charges into the poled state. Finally, the sample was heated at a constant heating rate and the relaxation current was recorded with a picoammeter. No bias voltage was applied during measurements.

Highly accelerated lifetime testing, HALT, was used to estimate the lifetime of Nb doped PZT films and probe the degradation mechanisms. The films were diced into 1 × 1 cm square samples, which were mounted into DIP packages with silver paste. The top Pt electrodes were connected to the contact pads of the package with gold wire bonding. Eight equivalent 400 μm diameter top platinum electrodes were used to monitor the current across the PZT films vs time for each HALT condition. The HALT measurements were conducted at temperatures from 150 to 200 °C with dc electric fields of 300–450 kV/cm. Both polarities of the applied electric field were investigated. The bottom electrode was always grounded. The resulting data were treated using the empirical relationship suggested by Prokopowicz and Vaskas,

\[
\frac{t_1}{t_2} = \left( \frac{V_2}{V_1} \right)^{\eta} \exp \left[ \frac{E_0}{kT_1} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right],
\]

where t is the median time to failure (MTTF), V is voltage, k is Boltzmann’s constant, E0 is the activation energy, and T is temperature. For this study, device failure was defined as the time at which the leakage current increased by two orders of magnitude with respect to the steady state leakage current. The MTTF was calculated from the reliability function R(t) described using a Weibull distribution as follows:

\[
\ln \left[ \ln \{ R(t) \} \right] = \ln \left( \frac{1}{1 - F(t)} \right) = \beta \ln t - \beta \ln \eta,
\]

where F(t) is the cumulative failure distribution function, the slope β is the dimensionless shape parameter, t is the time, R(t) is the reliability function (i.e., cumulative survival probability), and η is the characteristic lifetime at which 63% of the devices have failed. The MTTF was then estimated based on the following equation:

\[
\text{MTTF}(t_{50}) = \eta x \exp \left( \frac{1}{\beta} \right) x \ln(-\ln(1 - F(t_{50}))),
\]

where F(t50) = 0.5, which can be defined as the time at which 50% of the devices have failed.

Details on the associated changes in imprint caused by degradation are shown in the supplementary material.

III. RESULTS AND DISCUSSION

Figure 1 shows the voltage polarity dependence of the current density-time (J-t) response and the resistance degradation behavior of 2% Nb doped PZT films (PNZT) with Pt top and bottom electrodes. A noticeable difference in DC resistance degradation behavior and time dependent electrical breakdown was observed for opposite bias polarities. As can be seen in Fig. 1, the steady-state current rises upon resistance degradation. Failure occurred abruptly when the bottom electrode was negatively biased with respect to the top electrode. On the other hand, a more gradual current increase was observed when the top electrode was biased negatively, accompanied by a remarkable increase in the median time to failure (MTF).
from 4.8 ± 0.7 to 7.6 ± 0.4 h. These results clearly indicate that the electrical reliability characteristics of Nb doped PZT films are superior when the top Pt electrode is biased negatively, for the PZT and Pt deposition conditions utilized.

To explore the variation in the charge transport mechanism with voltage polarity, I–V measurements were conducted on 2 mol. % Nb doped PZT films before and after degradation at 180 °C under an electric field of ∼350 kV/cm (called field-down since the direction of the electric field is from the top to the bottom Pt electrode, and the bottom electrode is negatively biased) and 350 kV/cm (called field-up since the direction of the electric field is from the bottom to the top Pt electrode, and the top electrode is negatively biased) for 12 h (Fig. 2). The leakage current of undegraded PNZT films exhibits negligible voltage polarity dependence; the current-voltage characteristics are nearly symmetric for negative and positive bias. However, the I–V characteristics become remarkably asymmetric after degrading the PNZT films. The absolute value of current after degradation was found to increase in the direction in which the PNZT films had been degraded; the leakage current increase upon DC resistance degradation was governed by the Pt/PNZT interface that was negatively biased (the cathode). To distinguish which Pt/PNZT interface dominated the leakage current, equivalent PZT samples with asymmetric top IrO₂ and bottom Pt electrodes were used. Since IrO₂ has a lower work function than Pt, large differences were observed between I–V characteristics of top IrO₂ and bottom Pt contacts.

For degradation at ∼350 kV/cm, where the bottom Pt/PNZT interface was biased negatively, the leakage current increased at the bottom Pt/PNZT (cathode) interface, accompanied by a subtle change in the leakage current at the top Pt/PNZT interface (anode). In contrast, after degrading PNZT films at 350 kV/cm, a strong increase in the leakage current at the negatively biased top Pt/PNZT interface (cathode) was detected with a trivial change in the leakage current for the positively biased bottom Pt/PNZT interface. Thus, the reverse biased cathode determines the leakage current behavior of PZT films.

The I–V response of PNZT films before and after degradation was fit to the equations for various conduction mechanisms. The strongly asymmetric leakage currents observed for the same family of PZT/Pt films but with IrO₂ top electrodes [see especially the data in Fig. S1(a) at electric fields higher than 150 kV/cm] imply that the leakage current is controlled by an interface-related conduction mechanism. The possibility of Fowler-Nordheim tunneling has also been ruled out due to the temperature dependence of leakage current [Fig. S1(b)]. Thus, Schottky emission is believed to be the dominant conduction mechanism in Nb doped PZT films at the fields utilized for degradation. Figure 3(a) shows the disparity in the conduction mechanism near the bottom Pt/PNZT interface in the pristine state and after degradation under an electric field of ∼350 and 350 kV/cm for 12 h. Current density-electric field (J–E) characteristics in the pristine state exhibited good linearity for both Poole-Frenkel [ln (J/T²) vs E¹/₂] and Schottky emission [ln (J/E) vs E²] conduction mechanisms.

While the Schottky-Simmons model would be preferable in these partially depleted films, neither the Richardson constant nor the Schottky barrier height can be directly estimated from the data without information on the interfacial dielectric permittivity, the concentration of donors in the depletion region, and the built-in potential. Given that the permittivity of PZT films is both highly nonlinear and thickness dependent due to changes in domain wall motion,30 it is not possible to extract the relevant parameters from C–V data on films of different thickness, for example. As a result, a simplified approach using the standard Schottky model was utilized to estimate the relative dielectric constant. The appropriate dielectric permittivity is limited by the optical permittivity when the carriers move through the insulating layer faster than the relaxation time and by the static dielectric permittivity when the carriers are slow. Assuming that the electron movement across the film is faster than the relaxation time, the optical dielectric permittivity, ε₁, was extracted from the slope of the linear fits and the refractive index, n = √ε₁. At low electric fields (<122.5 kV/cm), n calculated from Poole-Frenkel plots ranged from 2.2 to 2.6, in good agreement with the refractive index of PZT (n ~ 2.25).40 This suggests that Poole-Frenkel emission controls the conduction at low electric fields. It has been previously reported that (1) electron trapping by Ti⁴⁺ and hole hopping between Pb⁺⁺ and Pb⁺⁺⁺ sites are the main mechanisms that contribute to Poole-Frenkel conduction in PZT films.48 With increasing electric fields (>122.5 kV/cm), a refractive index of about 2.2 was obtained from the slopes of Schottky plots,49 indicating that Schottky emission dominates the leakage current.

In contrast to the bottom Pt/PNZT interface, the switch from Poole-Frenkel to Schottky emission occurs at higher electric fields (>360 kV/cm) for the top Pt/PNZT interface, accompanied by a larger potential barrier height (1.2 ± 0.07 eV) for electron injection from the Pt electrode into the PNZT. Typically, the Schottky barrier height depends not only on the PZT work function and electron affinity but also on the density and distribution of impurity sites at the interface due to Fermi-level pinning.31,32 The role of V_D** on Schottky formation is critical in PZT films. Oxygen vacancies in PZT create electronic states that are 0.22–0.28 eV below the conduction band; these are reported to cause Fermi level pinning at the interface, reducing the Schottky barrier.32,49 Two important sources for V_D** formation in Nb doped PZT films are (1) unintentionally introduced acceptor ions and (2) loss of PbO upon annealing.

Although the incorporation of donor ions (Nb) into PZT decreases the V_D** concentration, it cannot entirely prevent V_D**
formation. Given that the pristine films are close to intrinsic, electroneutrality can be expressed as

\[ 2[V_{\text{Pb}}^{\bullet\bullet}] + [\text{Nb}_{\text{n}}^\bullet] + [h^\bullet] = 2[V_{\text{Pb}}'] + [e'] \]  

(5)

PbO loss during the deposition of the film can occur at the surface of each layer of PZT films during annealing, as well as to the bottom electrode.\(^\text{14}\) Figure 4(a) exhibits energy dispersive X-ray (EDX) mapping of Pb. The Pb/(Zr + Ti) ratio was found to be low in the PZT layers close to the bottom Pt electrode. Similar PbO loss was not observed in the PZT close to the top Pt electrode; any lead loss at this surface should have been compensated by the PbO overcoat. It is noted that in this work, PbO stoichiometry was attained by a kinetically controlled process. The variation in PbO stoichiometry
through the PNZT films creates disparities in the interfacial defect chemistry near the top and bottom electrodes. Higher PbO loss near the bottom Pt/PZT interface leads to formation of oxygen and lead vacancies. It is believed that the higher concentration of vacancies near the bottom Pt interface is one factor responsible for the low potential barrier height for electron injection and the low transition electric field from Poole-Frenkel to Schottky emission.

A second possibility is an asymmetry in the B-site stoichiometry at the top and bottom Pt/PNZT interfaces. Figure 4(b) illustrates EDX mapping of the Ti/Zr ratio across the PNZT film. As shown in Fig. 4(b), there are strong Ti/Zr gradients through the thickness of each crystallized PNZT layer. The growth of PNZT thin films is strongly nucleation controlled. Since the crystallization temperature of PbTiO$_3$ is lower than PbZrO$_3$, a Ti-rich composition initially nucleates at the bottom of each layer and the composition gradually becomes enriched in Zr near the top surface. The Ti/Zr gradients lead to formation of Ti- and Zr-rich layers at the bottom and top Pt electrode interfaces, respectively. Moreover, Zr is less reducible than Ti and could result in a lower $V_{th}^{\ast\ast}$ concentration at the film top surface.

The I-V characteristic of the Pt/PNZT/Pt can be described via an equivalent circuit model composed of two back-to-back Schottky diodes connected in series with the bulk (Poole-Frenkel dominated). As the resulting films are columnar [Fig. S4(b)], the potential influence of grain boundaries parallel to the electrodes can be neglected. Both forward and reverse biased interfaces were modeled using the Schottky equation, taking into consideration the potential barrier height for electron injection and the low transition electric field from Poole-Frenkel to Schottky emission.

\[ J_r = A^{\ast\ast} T^2 \exp \left( \frac{-\phi_0}{kT} \right) \left[ \exp \left( \frac{qV_F}{nkT} \right) - 1 \right] \]  \hspace{1cm} (6)

\[ J_r = A^{\ast\ast} T^2 \exp \left[ \frac{q\theta_0 - \sqrt{q\phi_0}}{kT} \right] \]  \hspace{1cm} (7)

where $A^{\ast\ast}$, $V_F$, $\phi_0$, $\theta_0$, and $N_D$ are the Richardson constant, built-in potential, maximum electric field at the interface, dielectric permittivity, potential barrier height, and donor density at the interface, respectively. It should be noted that because the carrier concentration is quite low, only a small number of carriers can tip the balance from $n$-type to $p$-type. This will result in the appearance of a $p$-$n$ junction. The explicit influence of this junction is difficult to quantify and was neglected in this work.

The potential barrier height at the bottom Pt/PNZT interface was calculated from the Schottky plot and found to be $1.1 \pm 0.05$ eV in the pristine state. Following electrical degradation at 350 kV/cm, no significant change was observed in potential barrier height for the positively biased bottom Pt/PNZT interface (anode), and the leakage current was suppressed. When the bottom Pt/PNZT interface was negatively biased upon degradation ($\sim$350 kV/cm), on the other hand, a significant reduction in Schottky barrier height from $1.1 \pm 0.06$ to $0.85 \pm 0.05$ eV was observed. This was coupled with an expansion in the electric field range over which Schottky emission is dominant. This suggests that electron injection from the negatively biased Pt into PNZT films is the rate-limiting mechanism in electrical degradation of PNZT films (see Fig. 3). If the leakage current was controlled by injection of holes and/or electron extraction at the anode, a significant increase in leakage currents should have been observed from the positively biased Pt/PNZT interface region upon degradation.

These findings are consistent with a well-known degradation mechanism in perovskite systems, as described by Baiatu et al. According to this model, field-driven ionic migration and subsequent accumulation of $V_{th}^{\ast\ast}$ near the cathode, with concurrent depletion of $V_{th}^{\ast\ast}$ near the anode, are responsible for electrical degradation. The redistribution of $V_{th}^{\ast\ast}$ leads to increases in the electron and hole concentrations near the cathode and anode regions, respectively. The leakage current in Pt/PNZT/PT thin films upon degradation is determined by the change in the height and the width of all of the potential barriers. As electrons accumulate in the space charge...
region near the cathode, mirror charges with the same magnitude and opposite polarity appear on the metal side of the interface. This causes formation of an image force that opposes the potential in the space charge region, which significantly decreases the Schottky barrier height,

\[ \Delta \theta_b = \left( \frac{eE_m}{4\pi} \right)^{1/2}, \]  

\[ E_m = \sqrt{\frac{2qN_{\text{eff}}}{\varepsilon} \left( V_b + V_i - \frac{kT}{q} \right)}, \]

where \( V_b \) is the maximum electric field at the interface. The Schottky barrier lowering is primarily determined by the maximum electric field at the interface. The large electric field in the depletion layer can both drive the diffusion of \( V_{O^\bullet} \) and increase the likelihood of charge injection.

Another mechanism that contributes to the leakage current increase upon degradation is the change in the depletion width, which is given by

\[ W = \sqrt{2e(V_b - \frac{kT}{q})/(qN_d)}, \]

where \( \varepsilon, V_b, q, \) and \( N_d \) are the dielectric permittivity, the built-in potential, the magnitude of an electron charge, and the donor concentration at the interface, respectively. The accumulation of \( V_{O^\bullet} \) at the cathode interface upon electrical degradation is expected to cause severe band bending, which reduces the depletion width of the potential barrier. This makes it easier for electrons to overcome the barrier at the interface.

As was the case for the bottom Pt/PNZT interface, enhanced leakage current together with a decrease in potential barrier height from 1.20 \( \pm \) 0.07 to 1.04 \( \pm \) 0.08 was only observed when the top Pt/PNZT interface was negatively biased upon electrical degradation under an electric field of \(-350 \) kV/cm [Fig. 3(b)]. No significant change in either the leakage current or the potential barrier height were found when a positive voltage was applied to the top Pt/PNZT interface, suggesting that \( V_{O^\bullet} \) accumulation and subsequent electron injection controls the leakage current enhancement during electrical degradation.

However, there are some discrepancies between the leakage current behavior arising from the top and bottom Pt/PNZT interfaces in the degraded states. The decrease in potential barrier height and the resultant enhancement in leakage current upon electrical degradation are more severe when the bottom Pt/PNZT interface is negatively biased upon degradation. This is consistent with the possibility that the increase in leakage current upon degradation is influenced by the local chemistry near the Pt electrodes. In particular, the Schottky barrier lowering is related to the density of donor states, mainly \( V_{O^\bullet} \), near the interface [Eqs. (4) and (5)]; this, in turn, induces additional injection of electrons. Furthermore, the electron depletion width may decrease due to the high density of \( V_{O^\bullet} \).

To investigate the migration of \( V_{O^\bullet} \) and resultant change in local interfacial defect chemistry near the top and the bottom Pt electrodes, TSDC analysis was performed on electrically degraded PNZT films. Figure 5(a) shows the TSDC results of PNZT films after degradation under an electric field of 350 (top electrode is negatively biased) or \(-350 \) kV/cm (bottom electrode is negatively biased) for 12 h. The temperature of the current maximum for the TSDC peak around 200 \(^\circ\)C shifts higher with increasing poling electric field, suggesting that the TSDC peak corresponds to depolarization of space charges. An activation energy of 0.68 \( \pm \) 0.04 eV was found, which is associated with migration of oxygen vacancies. However, the concentration of migrated \( V_{O^\bullet} \), which is represented by the area under the TSDC peak, depends strongly on the electrical field polarity during degradation. The concentration of \( V_{O^\bullet} \) accumulated near the bottom and the top interfaces after degradation at \(-350 \) and \(350 \) kV/cm for 12 h at 180 \(^\circ\)C was found to be \(6.2 \times 10^{19}/\text{cm}^2 \) and \(3.8 \times 10^{18}/\text{cm}^2 \), respectively. The difference in the concentration of accumulated \( V_{O^\bullet} \) most likely arises from inhomogeneous distribution of \( V_{O^\bullet} \) across the PNZT film in the pristine state. It is suggested that additional PbO loss upon annealing in the layers close to the bottom Pt/PNZT electrode causes a lead vacancy gradient through the film. Given that some of the lead vacancies are ionically compensated with oxygen vacancies, a gradient in \( V_{O^\bullet} \) concentration through the thickness of the PNZT films is probable. This will increase the number of mobile \( V_{O^\bullet} \) near the bottom interface,
which accentuates accumulation of those vacancies when degraded at $\sim 350$ kV/cm. This could be augmented by the existence of Ti-rich layers near the bottom surface that increase the propensity for reduction.

In either case, near the cathode, the high concentration of $V_{\text{O}}^{\bullet\bullet}$ is charge compensated by electrons via $n \sim 2[V_{\text{O}}^{\bullet\bullet}]$. Figure 5(b) presents the EELS spectra for the Ti-L edges acquired near the bottom and top Pt electrodes after electrical degradation. When the bottom electrode was biased negatively upon electrical degradation ($\sim 350$ kV/cm), the Ti-L$_{2,3}$ edges shifted to lower energy near the bottom interface. This is consistent with some reduction of Ti$^{4+}$ to Ti$^{3+}$. As no comparable reduction was observed in the pristine films, the lower Ti valence is likely to be due to the compensating electrons for the migrated $V_{\text{O}}^{\bullet\bullet}$. Moreover, no chemical shift is observed near the top Pt/PNZT electrode interface (cathode) after degradation under an electric field of 350 kV/cm, as shown in Fig. 5. The result is a higher concentration of trapped charges near the bottom Pt/PNZT interface in the degraded state, accounting for the observed asymmetry in conductivity and lifetime.

IV. CONCLUSIONS

The electrical reliability characteristics and associated charge transport mechanisms in PZT films with identical Pt top and bottom electrodes vary depending on voltage polarity; the HALT lifetime is significantly improved when the top electrode was biased negatively compared to the bottom Pt electrode. The underlying mechanism responsible for the improved electrical degradation behavior is correlated with a variation in interfacial defect chemistry. In the pristine state, the presence of higher concentration of $V_{\text{O}}^{\bullet\bullet}$ near the bottom Pt interface results in (1) a lower potential barrier height for electron injection and (2) a decrease in transition electric field from Poole-Frenkel to Schottky emission. Upon degradation, the increase in the absolute value of current was always observed in the direction in which the PZT films had been degraded. This was accompanied by an increase in the electrical field range over which Schottky emission is dominant. This indicates that electron injection from the cathode into PZT governs the leakage current rise upon electrical degradation. TSDB and EELS results confirmed that field driven electromigration of $V_{\text{O}}^{\bullet\bullet}$ and subsequent electron trapping by Ti$^{4+}$ are primarily responsible for electrical degradation in PZNT films. A higher concentration of $V_{\text{O}}^{\bullet\bullet}$ was found near the bottom Pt/PNZT interface relative to the top interface. This causes more severe Schottky barrier lowering at the bottom Pt/PNZT interface, which in turn accelerates injection of electrons and a subsequent charge trapping process. This may be coupled with the fact that a Zr-rich layer near the top interface reduces the propensity for trapping electrons near the top Pt/PNZT interface.

Because most deposition techniques for PZT films rely on the kinetic control of the PbO content, the interfacial defect chemistry is expected to vary as a function of the doping and the processing parameters. The defect chemistry determines the dominant conductive and associated charge transport mechanisms; these, in turn, are responsible for DC degradation in PZT films. It is very likely that the contradictory reports on activation energies and transport mechanisms proposed in the literature arise from the variation in the defect chemistry of the PZT films studied.

SUPPLEMENTARY MATERIAL

See the supplementary material for current-voltage data showing the differences between Pt/PZT/Pt and IrO$_2$/PZT/Pt film stacks, as well as microstructural information and compositional profiling of the samples. Polarization—electric field hysteresis loops on degraded samples are also provided.

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