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ORIGINAL ARTICLE

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Influence of PbO content on the dielectric failure of Nb-doped {100}-oriented lead zirconate titanate films

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Abstract

A series of niobium-doped, {100} textured, "gradient free," lead zirconate titanate (PNZT) films with different PbO contents were fabricated by the chemical solution deposition method. The films' PbO content was controlled by changing the average PbO content in the solution from 114.7 to 117 at.%. During the dielectric breakdown process of 1.5 μm thick PNZT films with Pt top and bottom electrodes, two phenomena were observed: cracking and thermal breakdown of the piezoelectric film. At 150°C, with an applied 400 kV/cm electric field, the crack density of PNZT films induced by electromechanical failure increased from 0.060/μm to 0.090/μm as the solution's PbO content increased from 114.7% to 117%. In addition, the films showed higher crack densities and more frequent thermal breakdown events when the electric field was oriented downward (from top to bottom electrode) compared with an upward oriented electric field (from bottom to top electrode). The films with higher PbO content had a lower breakdown strength. Also, all films showed lower breakdown strength when measured in the field down direction. The Schottky barrier height (SBH) decreased from 0.82 ± 0.06 to 0.68 ± 0.04 eV in the field up direction measurement as the PbO content increased. The SBH value did not show significant change in the field down direction measurement. This suggests that the asymmetry in the film/electrode interfaces is a function of the PbO content in the original solution.

KEYWORDS

ferroelectric materials, lead oxide, lead zirconate titanate, thin films

1 | INTRODUCTION

Highly {100} oriented lead zirconate titanate ($Pb(Zr_{0.52}Ti_{0.48})O_3$, PZT) films are applied as the piezoelectric element in microelectromechanical systems (MEMS) including ultrasonic transducer arrays, sensors, and actuators for inkjet print heads.[1,2] Niobium donor doping is sometimes employed to optimize the piezoresponse of PZT films and ceramics.[3,4] It has been reported that Nb doping increases the dielectric, ferroelectric, and piezoelectric properties of PZT by increasing the domain wall mobility.[5–7] The dielectric reliability of the PNZT films is critical for these piezoelectric MEMS systems and is influenced greatly by the film defect population, charge carrier migration, interface asymmetry, and donor and acceptor dopant.[8]

PZT films are frequently nonstoichiometric. Introduction of excess PbO is normally used in preparation of lead-based ceramics and films to compensate for Pb volatilization in the heat-treatment steps.[9,10] Excess PbO can also enhance nucleation of the perovskite phase in PZT films, and promote {100} preferred orientation.[9,11] However, the PbO content also influences the electrical properties.

Marincel et al sought to elucidate the effects of PbO content on the dielectric and ferroelectric properties of PZT films by thermodynamically controlling PbO content with a controlled Pb oxide atmosphere, and found that $e_{31,f}$ showed a peak value in PZT 52/48 films with medium PbO content.[10] Moreover, defects such as Pb vacancies, and either PbO or pyrochlore second phases[12,13] influence the leakage current density.[3,14] For example, Stolichnov et al reported that the leakage current density of PLZT films increased as the PbO content increased.[15]

In bulk dielectric ceramics, failure under dc degradation is normally caused by either thermal breakdown events; electromechanical breakdown; internal discharge due to local defects (voids, cracks, and pores), charge accumulation and partial discharge.[16] As described before, in PZT films, the PbO content has a strong influence on both the defect population and electrical conductivity of the films. Investigation of the relationship between PbO content and dielectric breakdown phenomenon of PZT films is a critical part of understanding the influence of defects in breakdown behavior of piezoelectric devices.[17]

This paper focuses on the dielectric breakdown behavior of Nb-doped PZT films prepared from solutions with different PbO contents. The relationship between solution PbO content, film/electrode interface status and dielectric breakdown behavior is also discussed.

2 | EXPERIMENTAL METHODS

{100}-oriented lead zirconate titanate films (with a Zr/Ti ratio of 52/48) with 2 mol% Nb doping on the B site (PNZT) were deposited on platinized Si substrates by chemical solution deposition. Commercial solutions (PZT-E1; Mitsubishi Materials Corporation, Tokyo, Japan) were employed to create PNZT films with reduced Zr/Ti gradients through the thickness (so called "gradient free"). A 2 mol% Nb-doped PZT (44/56) precursor solution was spun on the platinum-electroded Si wafer and crystallized at 700°C; it was previously demonstrated that when the layer thickness of the first layer was in the range from 30 to 70 nm, it served as a seed layer for {100} preferred orientation of PNZT films deposited on top. A schematic of the deposition of the PNZT films from solutions with different PbO contents (114.7 at.% [PNZT film with low PbO content, PNZT-L], 116 at.% [PNZT film with medium PbO content, PNZT-M], and 117 at.% [PNZT film with high PbO content, PNZT-H]), along with details of the deposition condition can be found in a previous publication.[18] All films were 1.5 μm in thickness.

Platinum top electrodes with ~100 nm thickness were deposited by sputtering and patterned by a lift-off process. A Hewlett Packard 4284A LCR meter was employed to measure the relative permittivity and dielectric loss of the films, from 1 kHz to 1 MHz with a 30 mV small AC signal. The polarization-electrical field loops of all films were measured using a Radiant Technologies Multiferroics Analyzer.

Samples with 500 μm circular top electrodes were poled (150 kV/cm, 150°C for 20 minutes) before piezoelectric measurement. A double beam laser interferometer (DBLI; aixACCT Systems, Aachen, Germany) was employed to measure the remanent piezoelectric $d_{33,f}$ coefficient. The DC bias was increased using a staircase function up to 100 kV/cm; the piezoelectric response was measured using a 500 mV AC signal. Alternatively, the large signal $d_{33,f}$ coefficient was measured using a 100 Hz 100 kV/cm triangular waveform.

Videos were taken of the dielectric breakdown process using an AmScope MU853B microscope digital camera. For all films, the data were taken for an applied electric field of 400 kV/cm DC (the Hewlett Packard 4140B pA meter used as a DC voltage source). This voltage was applied for 20 minutes while the sample was maintained at 150°C, to investigate the dielectric failure process under accelerated conditions. The electrical field was applied in one of two polarities: field up—where the electric field is directed toward the top electrode, and field down—where the electric field is directed toward the bottom electrode. The DC electric field dependence of the leakage current density was measured using the Hewlett Packard 4140B pA meter. The DC breakdown strength was determined at room temperature. High-temperature data (100-200°C) were used to calculate the Schottky Barrier Height.

3 | RESULTS AND DISCUSSION

The relative permittivity at 1 kHz of the PNZT-L, PNZT-M, and PNZT-H films was 1610 ± 18, 1590 ± 11, and 1600 ± 10, respectively, the dielectric loss tangents were all around 0.024. No obvious difference in the dielectric properties was found as the PbO content changed in the solutions, as shown in Figure 1A; Figure 1B shows the saturated polarization-electric field hysteresis loops of the films. The remanent polarization was 25 ± 0.2, 29 ± 1.2, and 27 ± 0.3 μC/cm^2 for the films from low (114.7%), medium (116%) to high (117%) PbO content solutions, respectively. In spite of the comparable permittivity and remanent polarization values, there was a significant decrease in dielectric breakdown strength with increasing PbO content in the films (see Figure 1C).

Figure 2 presents the piezoelectric properties of the three PNZT films. The films from solutions with medium PbO content showed slightly higher remanent $d_{33,f}$ (Figure 2A), while no obvious trend was found in large signal

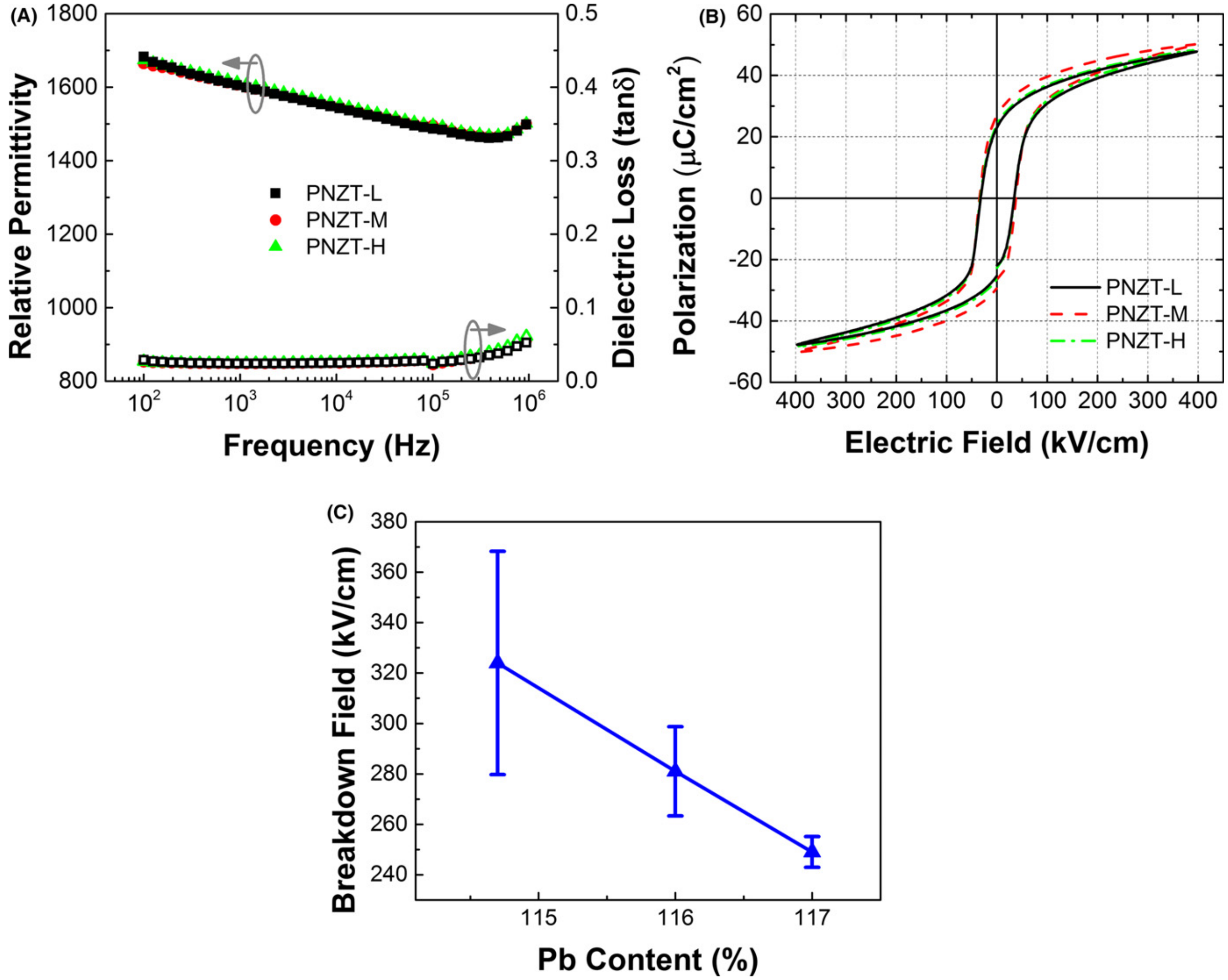

FIGURE 1 (A) Dielectric properties, (B) hysteresis loops, and (C) dielectric breakdown strength of PNZT films with low (PNZT-L), medium (PNZT-M), and high (PNZT-H) PbO content [Color figure can be viewed at wileyonlinelibrary.com]

$d_{33,f}$ data (Figure 2B) with solution PbO content. In all cases, the piezoelectric response was polarity dependent, possibly because of the pre-existing imprint in the films as deposited; samples poled in the field down direction had higher piezoelectric coefficients than the samples poled in the field up direction.

Videos were acquired of the dielectric breakdown process of these PNZT films for an electric field of 400 kV/cm in either field up or field down directions at 150°C. Images were clipped from the video at fixed times after the electric field was applied. Figure 3 shows captured images of the dielectric failure process of PNZT films with low PbO content, measured in the field up direction.

Two dielectric failure steps were detected. In the first step (Figure 3A), the film cracked 1 minute after the electric field was applied; the cracks propagated rapidly across the film, and achieved the final crack density in a short period of time. The cracked films were still good electrical insulators. In the dielectric breakdown process investigation, all original images (videos) are in color; to improve contrast so that cracks are readily imaged, black and white renderings were also used. The mechanical failure was followed by a second step (Figure 3B), characterized by thermal breakdown events and localized delamination. This implies that the clamped {100} oriented PNZT films tend to crack due to the stress caused by the piezoelectric deformation at these field levels.[9,19] Most thermal breakdown events happened along the cracks. All three films showed a similar two steps failure process: cracking followed by thermal breakdown.

The observed crack density depended on the PbO content of the film and the electric field polarity, as shown in Figure 4. The surface crack density value was calculated by: (a) counting the total number of intersections of cracks and 4 diameter lines (the angle between two adjacent lines is 45°) on a top electrode; (b) the value of the total number

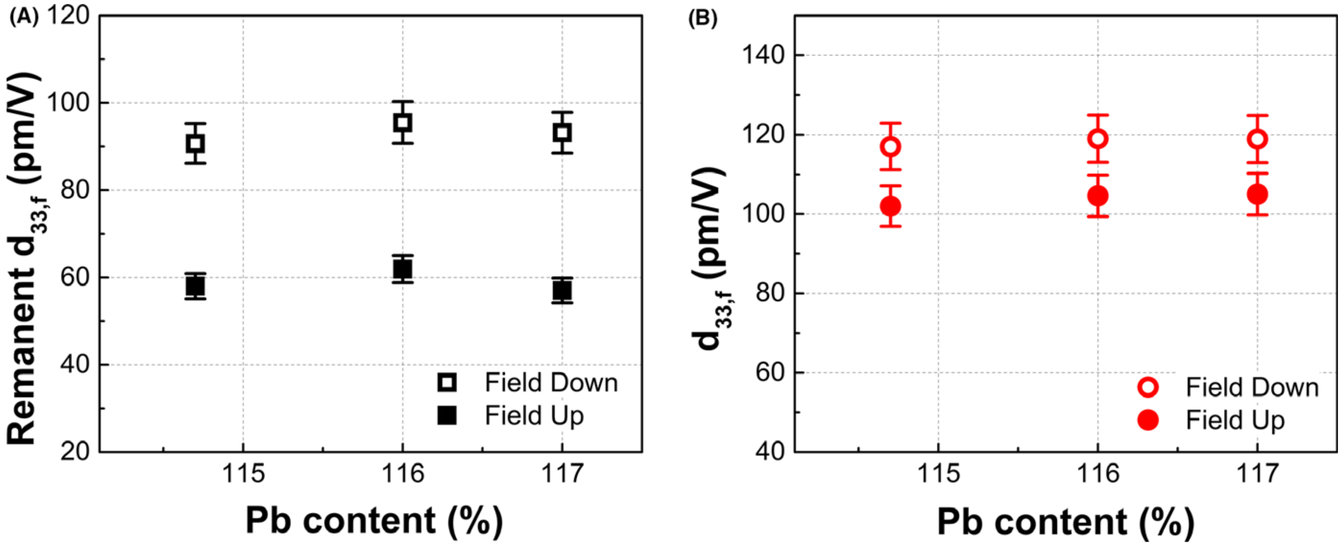

FIGURE 2 (A) Remanent $d_{33,f}$, (B) large signal $d_{33,f}$ of PNZT films with different PbO content [Color figure can be viewed at wileyonlinelibrary.com]

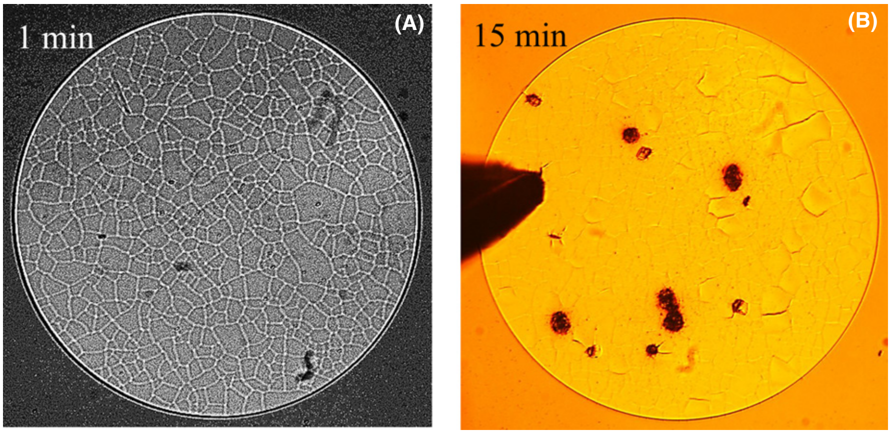

FIGURE 3 The two-step dielectric failure behavior in PNZT with low PbO content: (A) cracking after 1 minute of measurement; (B) thermal breakdown events with localized delamination after 15 minutes of measurement [Color figure can be viewed at wileyonlinelibrary.com]

of intersections divided by the total length of the four lines was defined as the surface crack density. For the field up direction, the surface crack density increased from 0.059/µm to 0.074/µm to 0.090/µm as the PbO content increased. As reported elsewhere,[18] excess PbO segregates to the grain boundaries, especially in films with high PbO content. It is believed that the higher crack density in the films prepared from more lead-rich solutions is thus a function of a lower mechanical toughness[20] due to weaker grain boundaries. This may also be exacerbated by localized Joule heating associated with the lower electrical resistivity of the PbO-rich boundaries compared with the PNZT films.[14]

In all cases, the films showed higher crack densities for the downward electric field. This is attributed to the higher piezoelectric coefficient in the field down direction which induced higher stress in the films.

A comparison of the second breakdown stage between films from solutions with different PbO contents and measurement electric field polarities can be found in Figure 5. The number of thermal breakdown events increased significantly with increasing solution PbO content. Again, the frequency of thermal breakdown events also increased in the field down direction measurement.

Because the thermal breakdown events require local conduction, the mechanism governing electrical conduction in the films was studied. As reported elsewhere,[21] the best fits were found for the Schottky mechanism. The Schottky barrier height (SBH) of these films was calculated based on the current density curves measured at different temperatures.[22] As shown in Table 1, the SBH showed a very clear trend with PbO content and measurement polarity. The electric field used for the Richardson constant calculation is ~145 kV/cm. It can be seen that the SBH decreased as the PbO content increased in the PNZT films, and was polarity dependent. The films had lower SBH in the field down measurement direction, compared with the field up direction. In the field down direction, the SBH showed no

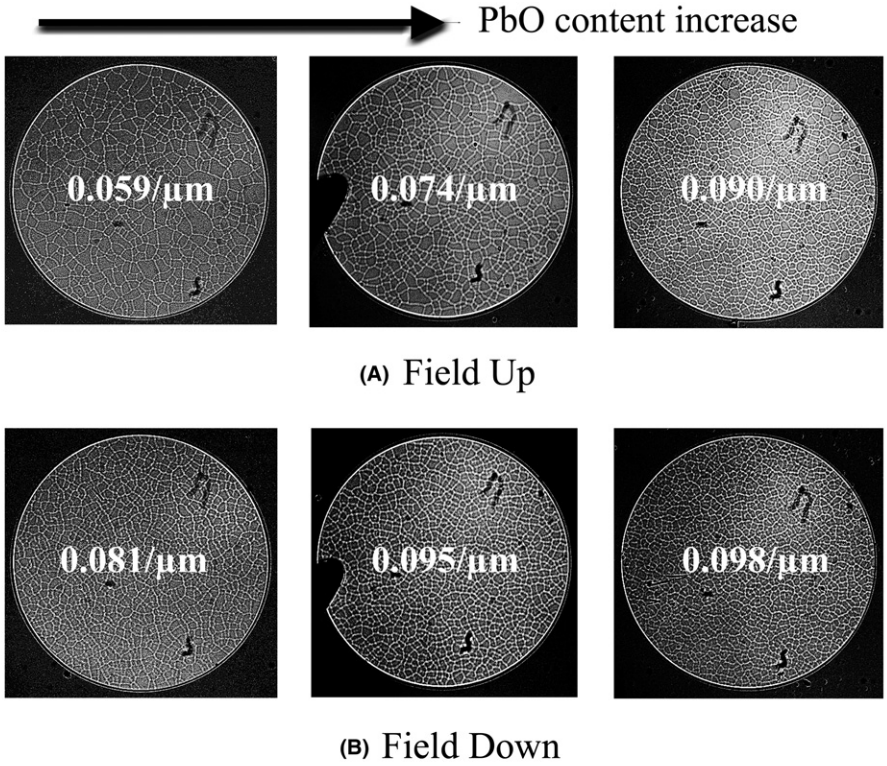

FIGURE 4 The crack density of PNZT films with different PbO content investigated for different dielectric breakdown measurement polarities: (A) field up, (B) field down

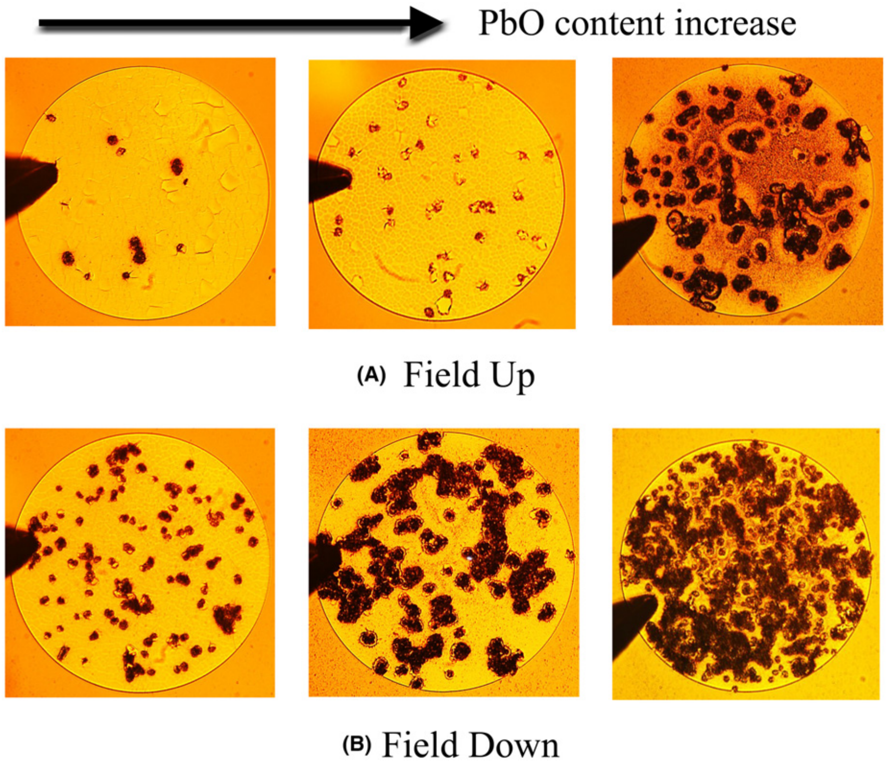

FIGURE 5 The thermal breakdown events of PNZT films with different PbO contents investigated for different dielectric breakdown measurement polarities: (A) field up, (B) field down [Color figure can be viewed at wileyonlinelibrary.com]

obvious dependence on the solution PbO content. It is possible that Pb dissolved into the bottom Pt electrode during the thermal processing.[23] According to the mixing law for the work function,[24,25] Pt_x-Pb alloys should have a lower work function compared with pure Pt.[26] This would account for the low SBH in the field down direction.

4 | CONCLUSIONS

In summary, the effect of PbO content on the dielectric failure behavior of PNZT films was studied. 2 mol% niobium-doped, {100} textured, “gradient free,” lead zirconate titanate (PNZT) films were prepared by chemical solution

TABLE 1 Schottky barrier height calculation results of PNZT films prepared from solutions with different PbO content

		Schottky barrier height (eV)	
Film	E-field (kV/cm)[a]	Field up	Field down
PNZT-L	146	0.82 ± 0.06	0.64 ± 0.06
PNZT-M	147	0.78 ± 0.06	0.63 ± 0.04
PNZT-H	144	0.68 ± 0.04	0.64 ± 0.06

[a]The Richardson constant calculation was done using this electric field.

deposition from solutions with PbO content levels of 114.7 at.%, 116 at.% or 117 at.%. All films were found to crack due to electromechanical strain induced by 400 kV/cm; films were still good electrical insulators at this point. Subsequent to this, thermal breakdown events, largely decorating the pre-existing crack structure, ultimately caused dielectric breakdown. The observed crack density of PNZT films increased with PbO content. This was attributed to the combined effect of lower mechanical toughness and electrical resistivity of films with a high PbO content. Moreover, the films showed higher crack densities when measured in the field down direction, suggesting an asymmetry in the top and bottom interfaces. The thermal breakdown events showed exactly the same trend as the crack density. The PbO content of the film and the measurement polarity, dependent of the Schottky barrier height of the top and bottom interface, dominated the thermal breakdown events.

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