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Thermal stress accommodation in dip cast lead zirconate-titanate ferroelectric films on flexible substrates

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Abstract

Piezoelectric thin films were dip coat deposited onto flexible metal substrates to investigate the dependence of dielectric and ferroelectric properties on the coefficient of thermal expansion mismatch and substrate thickness. The bending stiffness was controlled by the thickness of the substrate. Grazing incidence X-ray diffraction displayed distinct peak splitting for $[Pb_{0.98} \bullet_{0.01} (Zr_{0.52} Ti_{0.48})Nb_{0.02}O_3]$ on flexible Pt, Ni, Ag, and stiff Ni substrates, where the out-of-plane d-spacing and integrated peak area for *c*-domains were highest with the largest film compressive stress. As expected, lead zirconate titanate (PZT) films on stiff Si were under tensile stress and contained more in-plane domains. The dielectric permittivity was highest in PZT on stiff Si and lowest for PZT on thick Ni, while remanent polarization displayed the opposite trend, commensurate with the residual stress state as well as the resistance to bending in thick substrates as a strainrelief mechanism. The irreversible Rayleigh coefficient decreased dramatically upon poling for PZT on flexible substrates compared to PZT on stiff substrates; the $\alpha_{\varepsilon}/\varepsilon_{initial}$ ratio was 56% higher in PZT on a flexible Ni substrate relative to a stiff Ni substrate at 100 Hz prior to electrical poling. This investigation distinguishes the impact of substrate flexibility from thermal expansion on ferroelectric domain mobility and provides dip-coating conditions for high-quality piezoelectric films on any substrate.

KEYWORDS

ferroelectricity/ferroelectric materials, lead zirconate titanate, stress, thermal expansion, thin films

INTRODUCTION 1

Piezoelectric microelectromechanical systems on flexible metal foils enable an array of applications not possible with stiff substrates, such as robust energy harvesters exposed to high strains,1-5 ambulatory sensing,6-9 and biomedical monitoring.^{5,10,11} Lead zirconate titanate (PZT) films on metal foils provide an alternative to polyvinylidene difluoride when higher piezoelectric coefficients are needed. In particular, niobium-doped lead zirconate titanate [Pb_{0.99}=_{0.01}(Zr_{0.52}Ti_{0.48})Nb_{0.02}O₃] has considerable commercial relevance due to its high piezoelectric coefficient, dielectric constant, and remanent polarization values (where - denotes a vacancy on the Pb site).

Chemical solution deposition (CSD) is often used to deposit high-quality piezoelectric thin films on flexible substrates, via spin coating, dip coating, microcontact printing,¹² or inkjet printing.^{13,14} The spin coating enables

excellent uniformity of film thickness on flat, circular substrates.¹⁵ Complications arise in the spin coating process; however, when substrates are non-circular, flexible, and/or have non-planar surface topography. In the case of flexible foils susceptible to plastic deformation, the vacuum hold during spin coating can produce a permanent dimple in the substrate, rendering the center unusable. Additionally, a large fraction of excess precursor had spun off the wafer and wasted during mass production via spin coating.¹⁵ In dip coat CSD, a substrate is withdrawn vertically from a solution reservoir at a constant speed. The moving substrate entraps the liquid in a fluid mechanical boundary layer that splits into two layers above the liquid bath and returns the outer layer to the bath.¹⁵ Depositions can be conducted simultaneously on both foil surfaces, avoiding unbalanced stress that induces bending of the foils associated with single side deposition.¹⁶ Dip coating also simplifies the production of bimorphs and conserves precursor solution. Takahashi et al. reported on the dip coating of piezoelectric thin films onto stiff substrates such as glass, platinum, and single-crystal plates.^{17,18} He et al. investigated the effects of solution ionic concentration, substrate roughness, and withdrawal speed on the resulting films' crystalline structure, single-layer thickness, and electrical properties.¹⁹ Hida et al. investigated the dielectric and piezoelectric properties of bimorphs with high flexibility produced by dip-coating PZT films onto flexible stainless steel metal foils.²⁰ Dip coating of a humidity insensitive chemical solution was selected for this work, as it will allow for mass manufacture of high-quality piezoelectric films on flexible or oddly shaped substrates that are not amenable to spin coating, for example, cylinders, rods, pyramids, or flexible foils.

It is well-established that the substrate coefficient of thermal expansion (CTE) has a strong influence on the domain state of thick PZT films.²¹⁻²⁵ Upon cooling PZT films from the crystallization temperature, domains form to minimize elastic or electrical energy and release stress buildup between the film and substrate. The volume fraction of the domains depends on the magnitude of the substrate CTE, specifically at and above the Curie temperature (T_c) ²¹ If the substrate CTE is smaller than that of the piezoelectric film, the film will be placed in tensile stress upon cooling and preferentially align domains in-plane, since the unit cell of many of the ferroelectric perovskites elongates parallel to the polarization direction.^{21,22} Conversely if the substrate CTE exceeds that of the ferroelectric film, domains align out-of-plane. Assuming that the film is strain-free at the crystallization temperature, the resulting thin film in-plane biaxial stress is a function of the film (f) and substrate (s) CTE (α_{CTE}), elastic modulus (Y), thickness (t), and Poisson's ratio (ν). The residual stress is approximated with Equation (1).²⁶ As described

by the Funakubo group,^{24,25} in cases where the substrate CTE exceeds the film CTE, the out-of-plane domain volume fraction increases, where PZT at the morphotropic phase boundary has a lower dielectric relative permittivity with a higher remanent polarization along the polar direction.²⁷ Specifically, the dielectric relative permittivity for a single domain oriented parallel to the film surface is approximately 1721 at room temperature; for a domain-oriented perpendicular to the surface it is 382.²⁷

$$\sigma_{t} = \frac{f_{T_{c}}^{T_{max}} \left(\alpha_{CTE,f} - \alpha_{CTE,s}\right) dT}{\left(\frac{1-\nu_{f}}{Y_{f}}\right) + \left(\frac{1-\nu_{s}}{Y_{s}}\right) * \left(4\frac{t_{f}}{t_{s}}\right)}$$
(1)

In addition to the substrate CTE, the substrate thickness is hypothesized to influence stress relief during PZT film cooling. Thick, rigid substrates both apply stresses to the ferroelectric film and resist the electromechanical deformation associated with the application of electric fields. This acts to clamp both the intrinsic and the extrinsic contributions to the piezoelectric properties. Griggio et al. showed that the most significant factors reducing the irreversible motion of domain walls in PZT films on Si are a combination of residual stress and substrate rigidity.²⁸ They attributed a large increase in irreversible domain wall motion of a released PZT film to the partial release of the residual in-plane tensile stress developed from CTE mismatch, compared to the clamped film.²⁸ Residual stresses are known to mechanically suppress domain mobility or domain wall motion, and the release of a film from a rigid substrate will enhance domain mobility during the poling process.28

Rayleigh analysis is utilized to investigate the contributions of reversible and irreversible domain responses to electrical properties. Equation (2) describes the linear dependence of relative dielectric permittivity on the electric field, where ε_r is relative dielectric permittivity, $\varepsilon_{initial}$ is the reversible dielectric Rayleigh coefficient, α_{ε} is the irreversible Rayleigh coefficient, and E_0 is the electric driving field. Reversible extrinsic contributions and intrinsic contributions are characterized by $\varepsilon_{initial}$, whereas α_{ε} describes irreversible motion of interfaces such as domain walls or phase boundaries.²⁸ If a large enough field is applied to a piezoelectric film, domain wall motion can switch from pinned reversible oscillation to depinning.

$$\varepsilon_r = \varepsilon_{initial} + \alpha_{\varepsilon} E_0 \tag{2}$$

One factor that has not been widely discussed in the literature is the interplay between substrate clamping and residual stresses in controlling the dielectric and ferroelectric thin film properties. Of particular interest is whether



FIGURE 1 Coefficient of thermal expansion (CTE) for lead zirconate titanate (PZT), silicon, platinum, nickel, and silver from room temperature to PZT crystallization temperature. Data extracted from²⁹ for Si,³⁰ for Pt, Ni, and Ag, and³¹ for PZT

stresses can be relieved through substrate bending in a way that influences the resulting behavior. Here, the adopted approach is to hold the substrate CTE constant while varying the substrate thickness, and hence its bending rigidity. Several metal foils with different thermal expansion coefficients but constant thicknesses were also explored. Rayleigh analysis was then used in conjunction with other electrical characterization techniques to assess the dependence of domain clamping and motion on film residual stress. For this purpose, a humidity-insensitive acetic acidbased PZT solution was developed and deposited onto substrates of various thicknesses and CTE via dip coating. A thickness of $2 \mu m$ PZT was deposited on all substrates. It is demonstrated that the flexibility of the substrate can have a higher effect on the film domain structure than the thermal expansion coefficient mismatch with the substrate.

2 | EXPERIMENTAL PROCEDURE

Figure 1 displays the CTE of PZT and the substrate materials selected in this study, which are silicon, platinum, nickel, and silver, from room temperature to the PZT crystallization temperature of 923 K. Table 1 illustrates the calculated stresses from Equation (1) for PZT on five different substrates, where the CTE integration was from the PZT T_c to the T_{max} used in this study, which was 650°C. To explore the effect of substrate thickness, 25 μ m thick Ni foil was compared to a Ni plate of 500 μ m in thickness. Throughout the balance of the paper, the substrates will be referred to by the composition and thickness, such that Ni-500 denotes a 500 μ m thick Ni substrate.

2.1 | Sample preparation

Three thin metal foils, one thick metal plate, and a platinized silicon wafer (all 25×25 mm) were selected as substrates according to their CTE, resistance to oxidation, and thickness. Table 2 displays the five substrates with their thickness, purity, Young's modulus (E), CTE, and manufacturer selected for this study. The calculated thermal stress values displayed in Table 1 used a PZT Young's modulus of 90 GPa³² and a Poisson's ratio of 0.38, extracted from the work of Cook et al.³¹ The three 25 μ m foils and 500 µm Ni plate were polished on both surfaces with an ALLIED High Tech Products MetPrep automatic polishing tool, as shown in Table S1. To remove the ambient surface oxide formed on the Ni substrates, they were annealed in an H₂/N₂ reducing gas atmosphere at 900°C for 1 h. An insignificant amount of surface oxide was verified on all four metal substrates using a Woolam M2000X spectroscopic ellipsometer. The four metal substrates were blanket coated with 50 nm amorphous HfO₂ via atomic layer deposition (Lesker ALD System 150LE) at 200°C (515 cycles). The chemical precursor for Hf was Tetrakis(dimethylamido)hafnium (Hf(NMe₂)₄) and the oxidant used was H₂O. To provide a consistent bottom electrode for each substrate, 30 nm Ti was sputtered at room temperature as an adhesion layer followed by 100 nm platinum sputter deposited at 550°C onto both sides of the substrates. The substrate mounting plate is shown in Figure S1. The silicon wafer used in this study was doubleside polished 500 μ m thick P-type Si <100> oriented with 300 nm SiO₂ wet thermal oxide, 10 nm sputtered Ti, and 150 nm sputtered Pt oriented (111). A PZT (20% excess Pb, 44/56 Zr/Ti ratio, 2% Nb) sol-gel Mitsubishi seed solution was spin-coated at 3500 rpm for 45 s, pyrolyzed at 200°C for 2.5 min on a hotplate, and annealed at 700°C for 1 min in a rapid thermal annealer (RTA) with 2 standard liters per minute (SLPM) O2 gas flow. This seed layer was deposited to attempt to preferentially orient the dip coat PZT layers along the {100} axis.

2.2 | Solution chemistry

An inverted mixing order solution preparation procedure was adapted from Olding et al. to reduce the humidity sensitivity of the solution relative to 2-methoxyethanolbased routes.³³ Acetic acid-based PZT (52/48) with 2% niobium dopant was prepared following the procedure outlined in Table S2. Precursors for zirconium (zirconium(IV)butoxide solution [80 wt.% in 1-butanol]), titanium (titanium(IV)butoxide [>97% gravimetric]), niobium (Niobium *n*-butoxide), lead (lead(II) acetate trihydrate), and glacial acetic acid were purchased from **TABLE 1** Thermal stress calculated for $2-\mu$ m lead zirconate titanate (PZT) deposited on substrates of varying CTE and thickness following Equation (1)

	PZT on Si-500	PZT on Pt-25	PZT on Ni-25	PZT on Ni-500	PZT on Ag-25
Thermal Stress	158 MPa	-102 MPa	-342 MPa	-368 MPa	-529 MPa

TABLE 2 Substrate properties. The coefficients of thermal expansion are given at 624 K, the Curie temperature of the lead zirconate titanate (PZT) films used in the study

Substrate	Thickness (μm)	Purity	E (GPa)	Poisson's ratio	CTE at 624 K (ppm/K)	Supplier
Silver (Ag)	25	99.9%	80.0 (annealed) ³³	0.37 33	21.0	Sigma-Aldrich
Nickel (Ni)	25	99.98%	196 (annealed) ³³	0.32 33	17.5	Hpulcas
	500	99.98%	196 (annealed) 33	0.32 33	17.5	Sigma-Aldrich
Platinum (Pt)	25	99.99%	170 (annealed) ³³	0.44 33	9.8	Alfa Aesar Premion
Silicon (Si)	500	$110\ \Omega\ \text{cm}$		0.278 33	3.9	KO Tech

Abbreviation: CTE, coefficient of thermal expansion.

Sigma-Aldrich. An excess of 14 mol% Pb was added to minimize non-ferroelectric pyrochlore (or fluorite) formation during crystallization. Molarity of 0.6 was found to enable a uniform film thickness during dip coat deposition.

2.3 | Sol-gel dip coat deposition

Dip coating was conducted using a home-built apparatus pictured in Figure S2. The dip and withdrawal rates were controlled with an automated user interface panel. The system was installed in a low-humidity (20% relative humidity) class 1000 cleanroom. Each substrate was dipped and withdrawn at either 30 or 40 mm/min rate and held in the solution bath for 1 s. The film was dried at 250°C for 30 s, pyrolyzed on a hotplate at 400°C for 1 min, then heated in an RTA at a rate of 6.25° C/s- 650° C and held for 2 min using a flow of 2 SLPM O₂ gas to crystallize the film. The RTA script is displayed in Table S3. The procedure was repeated 18–20 times to reach a film thickness of 2 μ m on both surfaces of all five substrates.

2.4 | Crystallographic and microstructure characterization

A Zeiss Merlin field emission scanning electron microscope (FESEM) equipped with a Gemini II column was utilized to image the surface of all five PZT films and the cross-section of PZT on Si-500. An operating voltage of 5 kV was used with a working distance of 5 mm and an in-lens secondary electron detector. The analysis included verifying film density, pyrochlore content, cracking, and relative grain size. X-ray diffraction was performed with a Malvern Panalytical Empyrean III with a generator voltage of 45 V and a tube current of 40 A in two modes: Bragg-Brentano with a scan range of $10-70^{\circ}$ and a scanning rate of 0.0673° /s, and grazing incidence with a scan range of $42-48^{\circ}$, a scanning rate of 0.0026° /s, and an incident angle of 1° . Bragg-Brentano allowed for overall film orientation and minor substrate peak analysis while the grazing incidence mode probed near the surface of the film in the 2θ range of the (002)/(200) peaks.

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2.5 | Electrical characterization

Circular electrodes ranging from 200 to 1000 μ m in diameter were patterned via a standard photolithographic spin, expose, develop process, followed by 100 nm platinum sputter deposition and a photoresist lift-off process. A postanneal was performed at 600°C for 1 min in 2 SLPM O₂ gas flow in an RTA to improve adhesion between the PZT and Pt electrodes. Prior to dielectric frequency sweeps and ferroelectric measurements, the capacitance and loss of 15-20 electrode structures on each sample were measured at 1 kHz with 30 mV AC voltage. The capacitance varied between electrodes on each sample due to thickness variation of the film, with the edge having larger PZT thicknesses than the center (<300 nm difference). Loss values ranged from 0.02 to 0.10. A Nanometrics Nanospec Thin Film Thickness System was utilized to search for capacitor structures that had a thickness closest to $2 \,\mu m$ (±0.05 μ m). Capacitors with this thickness range and electrode diameter between 400 and 1000 μ m varied in dielectric permittivity less than 1.5%. Additionally, capacitors with the same shape and size displayed a variation of 8.1% in remanent polarization, 3.3% in the coercive field, and 1.0% in maximum polarization. For dielectric and ferroelectric 4062 JOURNAL _

data published in this report, a single representative electrode was measured for each sample.

Dielectric permittivity and loss tangent were measured 30 min after the post-anneal with an HP 4284A Precision LCR Meter in the range of 100 Hz-100 kHz with 30 mV applied AC voltage. Rayleigh coefficients were established by applying an electric field in the range of 0-12.5 kV/cm and measuring the dielectric permittivity with the same instrument. Linear least-square fitting was performed on Rayleigh data at 100, 200, 500, and 1000 Hz for each sample in the electric field range of 2.5-7.5 kV/cm. The reversible and irreversible domain wall motion contributions were extracted from the linear fit with Equation (2). Polarization-electric field (P-E) hysteresis loops were measured with a Radiant Technologies Precision Multiferroic tester from -600 to +600 kV/cm. Poling was performed on the electrodes at 5x the measured coercive field (\sim 35 V) at 150°C for 30 min in the poled-up direction (where the voltage was applied to the bottom electrode), then allowed to cool to room temperature for 1 h. Dielectric permittivity/loss tangents and Rayleigh coefficients were measured after the poling procedure.

3 | RESULTS AND DISCUSSION

3.1 | Structural analysis

Bragg-Brentano X-ray diffraction data are plotted in Figure 2 for PZT films deposited on all five substrates. Clearly seen are the (100)/(001) peaks, whose relative intensity depends on the orientation of the hot sputtered platinum and PZT Mitsubishi seed layer. XRD scans for PZT on Ni display NiO peaks from residual oxidation of the substrate, while all substrates except Si show small HfO₂ passivation layer peaks. All five PZT films show partial (100)/(001) orientation, while PZT on Si displays a high intensity (111) peak. Displayed in Figure S3 is a Bragg-Brentano XRD plot showing the variation in platinum (111) intensity between the platinum-coated Si wafer (100% volume fraction) and the hot sputtered platinum on Ni-25 substrate (85.17% volume fraction). Brennecka et al. showed a similar occurrence, where a Pt₃Ti intermetallic layer may have formed below the PZT film and promoted (111) PZT growth.³⁴ Figure 3 displays grazing incidence X-ray diffraction data near the PZT 200/002 peak.

Background intensity was subtracted from the observed data and LIPRAS³⁵ was used to fit each peak with an asymmetric pseudo-Voigt function, holding peak breadth as the constraint. LIPRAS provided each peak's constrained fullwidth half maximum (FWHM, *f*), 2θ at maximum peak intensity (x#), asymmetry (a#), and intensity of each peak (N#), where # indicates the peak number in each fit. The



FIGURE 2 Bragg-Brentano X-ray diffraction (XRD) analysis of 2- μ m lead zirconate titanate (PZT) on all five substrates. Labeled in the figure is S for substrate, O for NiO, and * for HfO₂. The ICDD inorganics database pdf file for PZT (52/48) [01-070-4060] was utilized as the reference

peak profile coefficients and their errors are given in Table S4, as well as the overall R^2 value and root-mean-square deviation. A Matlab script was written to calculate the integrated intensity from peak fitting parameters, which is given at the end of Supporting Information. A single discernable peak was found for PZT on Si, and the calculated FWHM was $0.8634 \pm 0.0126^{\circ}$. This FWHM value was significantly larger than all other peaks in PZT on metal substrates, for which the FWHM was all $0.4858 \pm 0.0128^{\circ}$. Due to the tensile stress in the PZT film on cooling through T_c , it is inferred that the film on Si has a higher volume fraction of in-plane domains rather than out of the plane. Peak splitting is observed for PZT on the other four substrates, as illustrated in Figure 3B-E. In each figure, the black data points are the observed data, the blue curve fits the tetragonal (002) peak, the red curve fits the (024) rhombohedral peak, the orange curve fits the tetragonal (200) peak, and the grey curve shows an overall fit through all peaks. The (002) peak intensity is significantly larger than the other two peaks for all four PZT films on metal substrates. Figure 3F displays the fit results for the tetragonal (002) peaks (peak 1) in PZT on Pt, PZT on Ni-25, and PZT on Ni-500; the volume fraction of (002) domains was calculated with Equation (3) and is labeled next to each peak. I_{002} is the integrated intensity of peak 1, I₀₂₄ is the integrated intensity of peak 2, I_{200} is the integrated intensity of peak 3, and I'_{hkl} is the reference intensity of the powder diffraction file ($I'_{002,tet.} = 107$, $I'_{024, rhomb.} = 435$, $I'_{200, tet.} = 260$).³⁶



FIGURE 3 Grazing incidence X-ray diffraction (XRD) near the 200/002 lead zirconate titanate (PZT) peaks on all five substrates: (A) PZT-Si-500, (B) PZT-Pt-25, (C) PZT-Ni-25, (D) PZT-Ni-500, (E) PZT-Ag-25, and (F) LIPRAS (002) peak (peak 1) fit for PZT-Pt-25, PZT-Ni-25, and PZT-Ni-500. The labels show the volume fraction of tetragonal (002) domains to the total integrated intensity, calculated with Equation (3)

The (002) peak area is representative of the c-domain volume fraction and is expected to be directly dependent on the magnitude of film compressive stress, which is largest for the PZT film on the 500 μ m thick nickel plate. Shown in Figure 3F is PZT on Ni-500 displaying the highest (002)domain volume fraction of 87.6%, whereas PZT on Pt-25 is 81.6% and 76.4% for PZT on Ni-25. Aruchamy et al. reported a ratio of 0.79:0.21 for out-of-plane to in-plane (002):(200) peak area for 52/48 PZT on a stiff sapphire substrate for which the PZT film had compressive stress of 100 MPa.³⁷ This is comparable to the data shown here for PZT on the flexible Pt-25 substrate, which had calculated compressive stress of 102 MPa and a (002):(200) ratio of 0.816:0.184.

$$\nu_{002} = \frac{\frac{I_{002}}{I_{002}'}}{\frac{I_{002}}{I_{002}'} + 2\frac{I_{200}}{I_{200}'} + 2\frac{I_{024}}{I_{024}'}}$$
(3)

As the compressive stress of the PZT film increases in magnitude, the out-of-plane spacing of c-oriented domains increases as well. The lattice parameters were computed from the 2θ at maximum intensity generated from LIPRAS and are plotted in Figure 4 at the 52/48 PZT composition. The black data points are the lattice parameters vs PZT composition extracted from the study by Shirane and Suzuki.³⁸ The three lattice parameters calculated from

the (002) peak for PZT on Pt-25, Ni-25, and Ni-500 in Figure 3F fall on the tetragonal c-axis lattice parameter line in Figure 4, increasing with film compressive stress magnitude. The lattice parameters calculated from the 200 peaks for the same three samples fall slightly higher than the predicted tetragonal a-axis lattice parameter. Extracted lattice parameters from the (024) rhombohedral peaks appear to lay along with extrapolation from the low Ti concentration rhombohedral region in Figure 4. This data suggests that the (200) tetragonal peak and the (024)rhombohedral peak may not be fully deconvoluted such that both peaks have contributions arising from a mixture of tetragonal and rhombohedral phases. All three lattice parameters increase as film compressive stress increases in magnitude.

Some of the variations from the expected in-plane tetragonal lattice parameter may be explained with energydispersive X-ray spectroscopy (EDS) via high-angle annular dark-field transmission electron microscopy (TEM). An analysis of the Zr/Ti composition gradient was performed on a $\sim 2 \ \mu m$ thick 52/48 PZT with 2% Nb film that was spun coat on a platinized Si wafer. The PZT solution was fabricated identically to the solution used for dip coating experiments. Prior to film growth, a 44/56 Zr/Ti ratio PZT with 20% excess Pb Mitsubishi seed layer was spun coat and crystallized. Figure 5 displays the EDS results overlain

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FIGURE 4 Lead zirconate titanate (PZT) lattice parameter versus composition. Black data points extracted from Shirane et al.³⁸ Data points placed at 48% PbTiO₃ composition show rhombohedral, tetragonal a, and tetragonal c lattice parameters extracted from Figure 3B–D



FIGURE 5 Transmission electron microscopy image overlain with energy dispersive X-ray spectroscopy results for zirconium, titanium, and lead content in a 2 μ m PZT 52/48 thin film

on the TEM image with all 26 layers shown with orange tick marks signifying each layer boundary.

As described earlier, the PZT film is characterized by strong Zr/Ti gradients through the film thickness. The Tirich seed layer provides a higher concentration of Ti near the electrode/film interface and reduces lead loss to the bottom electrode. As the second PZT layer nucleates from the first seed layer (right side of Figure 5), the Ti-rich tetragonal phase nucleates preferentially and is shown by a high Ti fraction near the start of the layer. Zr is excluded towards the top of each crystallized layer, such that the Zr concentration exceeds 0.52, resulting in a larger volume fraction of the rhombohedral phase.³⁹ It is also noted that the lead concentration is lower at the surface of each crystallized layer, as lead oxide is volatile at the crystallization temperature. This process repeats for each layer, resulting in composition gradients throughout the thickness of each PZT layer, as reported by Calame and Muralt.³⁹ It is likely that these gradients help stabilize the rhombohedral distortion in these films.

Coleman et al. deposited thin film PZT onto a 50 μ m nickel foil to investigate the effect of applied stresses on dielectric, piezoelectric, and ferroelectric properties.²⁶ Subsequent grazing incidence XRD measurements performed near the (200)/(002) peaks on those samples yielded lattice parameters of 4.111 Angstroms and 4.066 Angstroms. These values match the lattice parameters calculated for PZT on Ni-25 in this work (4.116, 4.080, and 4.054 Angstroms for (002), (024), and (200), respectively), indicating that both PZT films on Ni foils contained mixed tetragonal and rhombohedral phases. The large gap from that study in remanent polarization versus total stress state between tensile and compressive stresses may be a function of the higher volume fraction of the rhombohedral phase than anticipated.

FESEM was utilized to visualize the surface microstructure of the 2 μ m thick PZT films. Figure 6 displays the PZT grain structure on platinized silicon (a), platinum foil (b), nickel foil (c), thick nickel plate (d), and silver foil (e). A cross-section image of PZT on Si is displayed in Figure 6F. Each PZT film contained limited amounts of nonferroelectric pyrochlore (or fluorite) decorated near the grain boundaries; the films displayed high density with little to no porosity. It is notable that the grain sizes shown in the bottom right of each SEM scan tended to be smaller for the thicker substrates. This effect may be linked to the processing conditions; where the thick nickel plate and thick silicon plate rested directly on a silicon carrier wafer during pyrolysis and crystallization steps, the three thin metal foils were propped up by their four corners (See Figure S4). For all samples, the same side was facing up for each anneal step; this was the side onto which the electrodes were deposited. Thermal transfer to the thick plates was expected to be different than that of the foils, where a difference in surface temperature could affect the nucleation density of PZT on foils and hence the grain sizes. Figure 6E displays PZT film blistering on the silver foil substrate, presumably due to the high compressive stresses experienced by the film. Coupeau reported that above a critical equibiaxial compressive stress, buckling above a circular separation near the film/substrate interface is likely.⁴⁰ The buckled area may have occurred as a straight-sided wrinkle, a circular blister, or as a dendritic, brain-like, or telephone cord-like shape and may result in full delamination of the



FIGURE 6 Field emission scanning electron microscopy images of thin-film lead zirconate titanate (PZT) on 500 μ m Si (A), 25 μ m Pt (B), 25 μ m Ni (C), 500 μ m Ni (D), low magnification 25 μ m Ag (E) and cross-section PZT on 500 μ m Si (F)

film in some areas.⁴⁰ This is especially the case when a stiff film such as PZT is placed under large compressive stress on a soft substrate, such as a flexible Ag foil. 41

3.2 | Characterization of dielectric and ferroelectric properties

Dielectric permittivity and loss tangent were measured as a function of frequency before and after poling. Due to the buckling and subsequent cracking of the PZT film on Ag foil, electrical measurements were unattainable. Figure 7 displays the dielectric properties of PZT films on silicon, platinum, and both nickel substrates at 30 mV AC from 100 Hz to 100 kHz, where each PZT film displays loss tangents below 0.06. The dielectric permittivity was highest for PZT on silicon and lowest for PZT on the thick nickel plate. This effect was expected due to the thermal stress in the films, where a large volume fraction of in-plane polarization developed in the PZT on Si-500 due to tensile stress. PZT on Pt-25 displayed the next largest dielectric permittivity followed by PZT on Ni-25 and Ni-500, respectively. Increasing film compressive stress forced a larger volume fraction of domains out of the plane, which reduced the dielectric permittivity.27

On poling, it was found that the dielectric permittivity of films on flexible foils dropped considerably more than the



FIGURE 7 Dielectric permittivity and loss tangent versus frequency for lead zirconate titanate (PZT) films on four substrates. Loss tangent for as-grown capacitors displayed with closed symbols (
for Si-500) and open symbols for poled capacitors (
for Si-500)

films on thicker, more rigid substrates, and the loss tangent decreased for all four films. After poling, the permittivity was hardly affected for PZT on silicon, consistent with prior reports of limited ferroelastic switching.42,43 In contrast, poled PZT on Pt-25 almost overlaps the permittivity of the as-processed PZT on Ni-25, indicating that domain reorientation on poling is less dependent on the CTE of the substrate when the substrate is flexible.

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FIGURE 8 Dielectric permittivity at 1 kHz versus calculated film stress for lead zirconate titanate (PZT) on four substrates prior to and after poling

This effect is exemplified in Figure 8, which displays dielectric permittivity at 1 kHz versus film stress for PZT calculated with Equation (1) prior to and after poling. As compressive film stress increased, the dielectric permittivity decreased due to the higher volume fraction of outof-plane domains. The trend is not linear and appears to depend on whether the substrate is stiff or flexible, as seen in comparing the permittivity between the two nickel substrates. There is a rapid drop in permittivity for the stiff nickel substrate, indicating there are a significantly higher volume fraction of c-domains compared to the flexible nickel substrate. Prior to poling, the difference between the permittivity of the PZT on Ni-25 and Ni-500 is larger than that between PZT on Ni-25 and Pt-25. This result shows that although the CTE of the substrate is critical in domain configuration after processing, substrate clamping of domain re-alignment may exceed the effect of the CTE difference.

Ferroelectric properties of the films were measured via P-E hysteresis loops for PZT on silicon, platinum, and both nickel substrates, as shown in Figure 9. The inset shows a magnified view of the positive remanent polarization values, where PZT on the thick nickel plate is highest and PZT on silicon is lowest. PZT on flexible platinum and nickel are essentially equivalent. Coercive fields for the PZT on all four substrates are comparable, as stress does not control the field required to switch domain polarization.⁴⁴ Figure 10 displays both positive and negative remanent polarization values for PZT on silicon, platinum, and both nickel substrates. An inverse relationship is displayed between P_r and dielectric permittivity; as film compressive stress increases, Pr increases; this is attributed to the domain population variation for PZT on the four substrates. The sharp difference in Pr for PZT on Ni-25 and Ni-500 follows the



FIGURE 9 Polarization versus Electric Field hysteresis loops at 600 kV/cm field for lead zirconate titanate (PZT) films on four substrates



FIGURE 10 Positive and negative remanent polarization for lead zirconate titanate (PZT) versus film stress for four substrates

same rapid, but an inverse trend to dielectric permittivity, where a higher volume fraction of out-of-plane domains in PZT on Ni-500 forces P_r significantly higher. PZT on silicon displays the lowest P_r while PZT on platinum shows an intermediate value, consistent with mixed in and out-of-plane domain populations. None of the films show significant imprints. An unexpected result is a very small variation in P_r between PZT on Ni-25 and PZT on Pt-25 based on their calculated stress values. It is proposed that this is a result of the improved ferroelastic domain reorientation in films on flexible substrates, relative to more rigid substrates.

Rayleigh analysis was used to probe reversible and irreversible contributions to the dielectric response to further investigate the effect of substrate clamping on domain mobility. Figure 11 shows the irreversible contributions as a function of frequency for PZT on silicon, platinum foil, nickel foil, and on a nickel plate. Prior to poling, PZT on



FIGURE 11 Irreversible Rayleigh coefficient at 100, 200, 500, and 1000 Hz for lead zirconate titanate (PZT) on four substrates prior to and after poling

platinum shows the highest irreversible contributions at all frequencies followed by PZT on nickel foil, PZT on silicon, and PZT on a thick nickel plate. The drop-in α_{ε} after poling suggests either a lower population of domain walls or reduced wall mobility.

The decreases in α_{ε} for PZT on thick silicon and nickel after poling are significantly smaller than the decreases for PZT on flexible platinum and nickel, which would be consistent with the reduced ferroelastic domain reorientation on more rigid substrates. It is speculated that the flexibility of a metal foil may relieve residual film stress developed during cooling from the crystallization temperature by bending, such that the resulting PZT films possess more in-plane domains than estimated from the calculated residual stress from Equation (1). This is clearly seen in the dielectric permittivity and Pr plots versus film stress, where the permittivity is significantly smaller and P_r is much higher for PZT on the thick nickel plate compared to the flexible nickel foil. Thus, a second contribution to the lower permittivity change on poling for the PZT on the thick nickel plate would be the larger extent of preexisting out-of-plane oriented domains in the as-prepared films. That is, the substrate flexibility enhances irreversible domain wall motion upon PZT poling while the CTE of the substrate determines the initial post-fabrication domain structure.

Figure 12 displays Rayleigh coefficients for PZT on flexible and stiff Ni substrates in the as a grown condition. The irreversible and reversible coefficients are significantly higher for PZT on flexible foils, consistent with the clamping effect of thick substrates, as well as a higher population of in-plane domains in the PZT on thinner Ni. The bottom plot in Figure 12 shows the ratio of irreversible to reversible



FIGURE 12 Rayleigh coefficients of lead zirconate titanate (PZT) on Ni-25 and Ni-500 substrates in the as-grown condition. Irreversible Rayleigh coefficient (top), reversible Rayleigh coefficient (middle), and the ratio of irreversible to reversible Rayleigh coefficients (bottom)

Rayleigh coefficients. Presuming that the Ni foil allows PZT to behave more like an unclamped film than the one on thick nickel, then the trend shown here is opposite of the results displayed by Griggio et al., where after PZT release the $\alpha_{\varepsilon}/\varepsilon_{initial}$ ratio was higher in the clamped PZT film.²⁸ However, the released PZT film in their study was under a significant amount of tensile stress and domains remained predominantly in their as-grown condition.

To summarize, nickel has a higher CTE than platinum at the PZT crystallization temperature, both of which are higher than the CTE for PZT; silicon has a lower CTE than PZT. The two flexible substrates relieve stress developed in the PZT film upon cooling by bending, but PZT on stiff Si is placed in tension upon cooling, arranging the majority of domains parallel (or nearly so) to the film surface. The film on the Ni plate is in compression, and domains are arranged predominantly perpendicular to the film surface upon cooling. The stress in the film on platinum is partially relieved by bending, but the film contains fewer out-of-plane domains than the film on flexible Ni due to Pt's lower CTE than Ni. Ferroelastic domain wall and/or phase boundary motion is reduced in films on stiff substrates; therefore, poling provides only modest changes in the as-grown ferroelastic domain configuration. In contrast, on flexible substrates, domain reorientation (including ferroelastic domains), is easier. As a result, the



FIGURE 13 Plastic deformation observed for lead zirconate titanate (PZT) on Ni-500

irreversible Rayleigh coefficient decreases significantly after poling PZT films on foils.

One consideration excluded from this investigation is the yield strength of each metal substrate. The yield stress of metals depends on their purity, defect concentration, grain size, grain boundary concentration, and thermal history. Without direct measurement of yield strength for each metal substrate, it is unknown whether the calculated compressive thermal stresses for PZT in Table 1 on the metal exceed the tensile yield strength. Evidence that this can occur, however, is shown in Figure 13, where the thick nickel plate is bent after 20 heating and cooling PZT crystallization cycles. Thus, for the 25 μ m flexible metal foils, it is possible that local permanent substrate plastic deformation or recrystallization of the foils can occur during the PZT heat treatment steps. Substrate plastic deformation may, in principle, affect the domain orientation, domain wall density, and domain wall motion activation energy.

4 | CONCLUSIONS

Thin-film (2 μ m) PZT was deposited via dip coat deposition onto five substrates with varying thickness and CTE to investigate the dependence of thermal stress on the dielectric and ferroelectric properties of the films. It was found through grazing incidence XRD that with higher thermal compressive stresses, the films displayed larger volume fractions of out-of-plane domains. The lattice parameter determined from the position of the (002) peak matched well with existing literature for the c-domain of the tetragonal phase; however, the positions of the rhombohedral (024) and tetragonal (200) peaks matched poorly with the expected lattice parameters, indicating mixture of the two phases. Dielectric permittivity and P-E hysteresis loops showed a large dependence on substrate thickness, where with the same substrate material and CTE, PZT on 500 μ m Ni had 35% lower permittivity and 12% higher remanent polarization than PZT on 25 μ m Ni. Rayleigh coefficients displayed a similar trend, where the $\alpha_{\varepsilon}/\varepsilon_{initial}$ ratio was 56% higher in PZT on a flexible Ni substrate relative to a stiff Ni substrate at 100 Hz prior to electrical poling. It is concluded that substrate flexibility enhances irreversible domain wall and/or phase boundary motion upon PZT poling while the CTE of the substrate determines the initial post-fabrication domain structure.

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