Enhancing the Energy-Storage Density and Breakdown Strength in PbZrO$_3$/Pb$_{0.9}$La$_{0.1}$Zr$_{0.52}$Ti$_{0.48}$O$_3$-Derived Antiferroelectric/Relaxor-Ferroelectric Multilayers

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Multilayer thin-film dielectric capacitors with high energy-storage performance and fast charge/discharge speed have significantly affected the development of miniaturized pulsed-power devices. Here, the interfacial strain in epitaxial multilayers of antiferroelectric PbZrO$_3$ and relaxor-ferroelectric Pb$_{0.9}$La$_{0.1}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ is shown to significantly enhance the maximum polarization of the multilayer thin-film capacitors, beyond that of the composing individual layers. Insights obtained from atomically resolved energy-dispersive X-ray spectroscopy and high-resolution X-ray diffraction analysis of the interface and domain structure are used to develop phenomenological models that explain the observed trends in breakdown strength and energy-storage density as a function of multilayer period number. The underlying mechanism is the mechanical coupling between the layers that depends on the individual layer thicknesses. These factors result in a strongly enhanced recoverable energy-storage density (increased by a factor of 4 to $\approx 128.4$ J cm$^{-3}$) with high efficiency ($\approx 81.2\%$). Moreover, the multilayer films show almost fatigue-free energy-storage performance after $10^{10}$ switching cycles, even at elevated temperatures up to 220 °C, demonstrating their robustness. The outstanding properties show the great potential of epitaxial multilayers for energy-storage applications, due to the well-defined separate layers and coupling of properties across the interfaces, not present in ceramic composites.

1. Introduction

Nowadays, dielectric thin-film capacitors, which can store and release ultralarge energy densities in an extremely short time, are extensively investigated for applications in pulsed-power electronic systems. Such systems are used in many application fields, ranging from medical devices (such as pacemakers and defibrillators), consumer or industrial systems (camera flash, oil and gas exploration), transportation (hybrid electric vehicles), and in military applications (radar and high-power microwave devices). Recent studies focused on the enhancement of the energy-storage density of dielectric thin-film capacitors by using advanced materials and novel device architectures, employing also ferroelectric (FE), antiferroelectric (AFE), or relaxor-ferroelectric (RFE) materials. In general, it is found that a large difference between maximum polarization ($P_{\text{m}}$) and remanent polarization ($P_{r}$), and a high electric breakdown field/breakdown strength ($E_{\text{BD}}$) are beneficial for high energy-storage densities. Using a simple parametric model (see Section S10, Supporting Information), it is shown that an enhanced $E_{\text{BD}}$ can improve the energy-storage density and the energy efficiency very effectively. (The energy-storage density scales approximately quadratically with $E_{\text{BD}}$. Also the energy efficiency strongly increases with increasing $E_{\text{BD}}$ and becomes much less dependent on the value of $P_{\text{m}}$ at high field, because $P_{\text{m}}$ increases approximately linearly with $E_{\text{BD}}$, whereas $P_{r}$ is largely independent of $E_{\text{BD}}$). The contribution of the high field dielectric properties (which determine the value of $P_{\text{m}}$ to the storage properties of the device) can be significant, especially for large maximum applied fields. Optimizing the breakdown field alone may therefore not lead to maximum stored energy, since the high field dielectric constant may not remain constant while optimizing the breakdown strength. In fact, enhancing the high field dielectric properties may be an alternative route toward enhancing the storage density and efficiency, next to increasing the value of $E_{\text{BD}}$. In this paper it is shown for the discussed multilayer structures that both the breakdown field and the high field dielectric constant of the multilayer change with thickness of the individual layers. Both parameters determine the maximum stored energy that can be achieved in this series of multilayers. The changing dielectric constant can be correlated to the changing strain states of the individual layers.
Many strategies have been explored to improve the $E_{\text{BD}}$ values in order to enhance the energy-storage performance of dielectric film capacitors, such as microstructure control, domain engineering, and interface engineering, as well as the development of new materials. Previous studies have shown that there is a strong relationship between the microstructure and the breakdown strength of dielectric capacitors, in which the grain size plays a major role in the enhancement of breakdown strength. In general, it was found that a smaller average grain diameter ($D$) results in a higher $E_{\text{BD}}$ ($\sim 1/\sqrt{D}$), which was attributed to the enhanced density of grain boundaries and thus higher density of barriers for leakage current flow. Chemical modification and process engineering have been demonstrated to refine the grain size in dielectric film capacitors. Pan et al. indicated that the incorporation of SrTiO$_3$ (STO) into FE BiFeO$_3$ (BFO) films could promote the formation of polar nanoregions, resulting in a sizable recoverable energy-storage density ($U_r$) of 51 J cm$^{-3}$ with an energy efficiency ($\eta$) of 64% at an applied field of 3.6 MV cm$^{-1}$. Diao et al. evaluated the energy-storage properties of Mn-doped Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) films, in which the Mn doping resulted in a reduced grain size. The largest $U_r$ of 9.4 J cm$^{-3}$ (at 1.63 MV cm$^{-3}$) was achieved in the 3 mol% Mn-doped BST films. By controlling the deposition temperature, superfine columnar nanograins with a diameter of about 10–15 nm were obtained in 200-nm-thick BaTiO$_3$ thin films, sputter deposited at 350°C. As a result, an ultrahigh $U_r$ of 130 J cm$^{-3}$ and a large $\eta$ of 76% were achieved at a very high breakdown field of 6.5 MV cm$^{-3}$. Another strategy that has been used to enhance the energy-storage performance is domain engineering. Pan et al. reported a fairly large energy density ($U_r$ = 70.3 J cm$^{-3}$ at 3.85 MV cm$^{-3}$) and high efficiency ($\eta$ = 70%) in mixed (BiFeO$_{0.4}$SrTiO$_{3.6}$) films. It was suggested that the incorporation of STO transforms the micrometer-scale FE domains of the FE BFO films into highly dynamic, polar nanoregions in the mixed-film systems. Using PLD to synthesize the PL/PZ multilayers with a slim polarization loop (Figure S1c, Supporting Information) multilayer thin films with different period numbers ($N = 1$–12) were deposited on SrRuO$_3$/SrTiO$_3$/Si substrates (Figure 1). The aim is to combine the complementary advantages of the RFE PL layer with a slim polarization loop (Figure 1c, Supporting Information) and the AFE PZ layer with a double polarization loop (Figure S1d, Supporting Information) to achieve polarization loops with low hysteresis and very wide loops, that is, with large volumetric energy-storage density ($U_r$). We used pulsed laser deposition (PLD) to synthesize the PL/PZ multilayers and the SrRuO$_3$ electrodes, since PLD allows for the deposition of single and multilayer Pb-based oxide thin films because of the possibility of stoichiometric transfer of the composition from target to film. Using a fixed total film thickness of 500 nm, a giant $U_r$ = 128.4 J cm$^{-3}$ with a large $\eta$ = 81.2% at a high $E_{BD}$ = 4.4 MV cm$^{-3}$, along with a superior temperature stability in a wide range (20–220°C) and excellent fatigue endurance (up to 10$^{10}$ bipolar switching cycles), have been achieved in the PL/PZ multilayer thin films with $N = 8$. The microscopic structure of the multilayers was analyzed with X-ray diffraction (XRD) and scanning transmission electron microscopy [11–16].
techniques. We determined the changes in the ferroelectric loops as function of the number of layers $N$ (i.e., the thickness of the individual layers) and correlate these changes with the change in lattice parameters (i.e., the strain state) of the individual layers. To do this we developed parametric models to describe the observed period number dependence of the ferroelectric and dielectric properties. Further, this material system allows us to also study the effect of the presence of interfaces on the breakdown strength. A Weibull analysis of the breakdown data was used to describe the breakdown strength of the multilayer in terms of the thicknesses and breakdown strengths of the composing materials. These models may guide further research into understanding the performance of multilayer devices.

2. Results

In this section the experimental results of our study into the structural, ferroelectric, and energy-storage properties of the fabricated series of PL/PZ multilayer devices are presented. In Section 3, we correlate the experimental results with each other, connecting structural data to electrical properties of the multilayers. To that end we use several tentative and phenomenological models (developed and presented in Sections S6, S7, and S10, Supporting Information) to describe a) the dependence of the energy-storage properties on the relation between polarization properties and the stacking of the multilayers, mainly described by the period number $N$ of the multilayers, b) the dependence of the leakage current on the number of interfaces in the multilayers, and c) the dependence of the breakdown strength on the layer thickness.

2.1. SEM, AFM, STEM-HAADF, and EDX Analysis

Schematic cross-sections of PL and PZ single-layer, and PL/PZ multilayer films are shown in Figure S2a–f, Supporting Information, together with the cross-sectional scanning electron microscopy (SEM) images (Figure S2g–l, Supporting Information). The microstructure of the multilayer films strongly depends on the period number $N$ of the multilayer. The PL layer (Figure S2a, Supporting Information) has a dense structure, whereas the PZ single layer shows a columnar grain structure (Figure S2h, Supporting Information). The root-mean-square surface roughness ($R_q$), determined from atomic force microscopy (AFM), increases from 0.91 to 5.40 nm with a change in microstructure from densely packed columnar grains in the PL layer (Figure S2n, Supporting Information) to more loosely packed grains in the PZ layer (Figure S2o, Supporting Information). The microstructure of the $N = 1$ multilayer film (Figure S2i, Supporting Information) shows the dense PL layer deposited on the SRO electrode and the columnar grain PZ layer on top of the PL layer. If the PL were deposited on top of the PZ layer, the PL layer would also be columnar,[36] as can be seen for the $N = 3$ multilayer film, for which the microstructure starts with the dense PL layer, but exhibits columnar grains in the next PZ and subsequent PL layers. Interestingly, the films obtain a smoother top surface with increasing period number (see Figure S2k,l, Supporting Information). The cross-sectional image of the $N = 8$ multilayer is featureless and has a dense morphology. The development of microstructure in multilayer films is also exhibited in the AFM images and corresponding $R_q$ values (Figure S2p–s, Supporting Information). The surface of the multilayer films becomes smoother as the $N$ value increases from 3 to 8, which can be attributed to the decreasing surface roughness and grain size with the reduction of PZ layer thickness (see Figure S2t,u, Supporting Information).

As it is difficult to observe the interfaces between the different PL and PZ layers by SEM, scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) and energy-dispersive X-ray (EDX) spectroscopy mappings were performed, as presented in Figures 2 and 3.

The cross-sectional morphology and elemental composition of the multilayer film ($N = 8$) were analyzed by STEM and
EDX techniques (Figure 2). The high-angle annular dark-field (HAADF) image in Figure 2a shows the multilayer structure composed of alternating PL and PZ layers. Pb ions cause most of the contrast in the HAADF, thus the faint contrast between the PL and PZ layers is mainly due to the small difference in Pb concentrations in these layers. In this case the nominal thickness of each PL and PZ layer is close to 31 nm. The distribution of the constituent ions in the multilayered films are shown in the corresponding EDX maps (Figure 2b–i). EDX line profiles across this multilayer (Figure S3, Supporting Information) show the distribution of the five elements (Pb, O, Ti, Zr, and La), and exhibit the expected

![Figure 2. Analytical transmission electron microscopy study of a cross-section of N = 8 multilayer thin film: a) High-angle annular dark-field (STEM-HAADF) image; b–i) EDX spectroscopy mapping of each element distribution; j) overlapping image of the EDX maps of all elements.](image)

**Figure 2.** Analytical transmission electron microscopy study of a cross-section of $N = 8$ multilayer thin film: a) High-angle annular dark-field (STEM-HAADF) image; b–i) EDX spectroscopy mapping of each element distribution; j) overlapping image of the EDX maps of all elements.

![Figure 3. a,b) Integrated EDX line profiles across the 1st PL/PZ interface (near the bottom electrode) and the 15th (PL/PZ) interface (near the top electrode) of a $N = 8$ multilayer (the order of the interfaces is shown in Figure S2v, Supporting Information), c,d) along the yellow arrows in the HAADF images. The lines in (a,b) show the intensities of Pb, La, Zr, Ti, and O. Ti and La interdiffusion is observed over a distance $\approx 3$ nm into the PZ layer at the 1st PL/PZ interface, and to $\approx 7$ nm at the 15th interface (i.e., 8th/top PL/PZ interface).](image)

**Figure 3.** a,b) Integrated EDX line profiles across the 1st PL/PZ interface (near the bottom electrode) and the 15th (PL/PZ) interface (near the top electrode) of a $N = 8$ multilayer (the order of the interfaces is shown in Figure S2v, Supporting Information), c,d) along the yellow arrows in the HAADF images. The lines in (a,b) show the intensities of Pb, La, Zr, Ti, and O. Ti and La interdiffusion is observed over a distance $\approx 3$ nm into the PZ layer at the 1st PL/PZ interface, and to $\approx 7$ nm at the 15th interface (i.e., 8th/top PL/PZ interface).
periodic changes with chemical composition in the PL/PZ multilayers.

To gain a better understanding of the formation of the interfacial layers, the chemical composition of the first and last PL/PZ interface in the \( N = 8 \) multilayer were studied by atomic resolution cross-section STEM with integrated EDX analysis (Figure 3a,b). There is a nearly linear change in the Ti, La (and somewhat less clearly in the Zr) concentrations over a distance of about 3 and 7 nm at the first and last PL/PZ interfacial layers, respectively, suggesting Zr/Ti and Pb/La interdiffusions. The interdiffusion layer, which we term PLZ, is attributed to the reaction of the PL and PZ layers at the high temperature (525 °C for PZ layer and 600 °C for PL layer) during the deposition process. The change in the thickness of the PLZ interdiffusion layers may be attributed to the difference in the interface roughness: a smoother first PL/PZ interface and rougher last interface. The interdiffusion layer is characterized using XRD analysis, as discussed in the next section.

### 2.2. Crystal Structure

XRD analysis in Figure S4, Supporting Information shows the full range of all XRD \( 2\theta-\omega \) scans, encompassing the (001)–(004) Bragg reflections of the single-layer and multilayer films, and the Si-substrate peaks. All Miller indices refer to the commonly used pseudocubic perovskite structure. It shows that predominantly (00l) reflection peaks of the films and oxide electrodes are present, demonstrating that all films are grown with a single out-of-plane orientation. Figure 4a shows a section of the high-angle region of the XRD scans capturing all essential features of the films. We observe, in addition to the (004) reflections of PL, PZ, SRO, and STO, the development of an additional peak (labelled “*”) which grows in intensity with increasing period number \( N \). The lines indicate the positions of the PL and PZ single-layer reflections and the PLZ reflection of the \( N = 12 \) device.

![Figure 4](image-url)

Figure 4. a) \( 2\theta-\omega \) scans of the (004) reflections of single-layer and multilayer structures on SRO-buffered Si/STO substrates. The bottom two scans, labeled PZ and PL, correspond to the single PbZrO\(_3\) and Pb\(_{0.9}La_{0.1}(Zr_{0.52}Ti_{0.48})O_3\) layers, respectively, while the upper five scans belong to the [PL/PZ]\(_N\) multilayers with \( N = 1, 3, 5, 8, \) and 12. b–h) Reciprocal space maps of the (103) features of the same samples, confirming the emergence of an additional peak (labeled “*”) in all panels, which grows in intensity with increasing period number \( N \). The lines indicate the positions of the PL and PZ single-layer reflections and the PLZ reflection of the \( N = 12 \) device.

Reciprocal space maps (RSMs) around the perovskite (103) feature were collected to confirm the epitaxial nature of all grown films and multilayers and to obtain a better understanding of the emergent PLZ phase. The well-defined Bragg spots in out-of-plane (Figure 4b–h) and in-plane (not shown) RSMs attest to the high crystalline order of all phases in these samples. Figure 5 summarizes all pseudocubic lattice parameters extracted from the XRD analysis and the resulting unit-cell volumes. The (average) in-plane lattice parameter of the PZ layers is larger than that of the PL layers (the lattice mismatch between PZ and PL single layers is about 1.8%, but is decreasing for increasing \( N \), as will be shown below and can be seen from Figure 5a), therefore all PL layers in the [PL/PZ]\(_N\) stacks are under tensile in-plane stress and the PZ layers under compressive stress due to the adjacent layers (see ref. [37] for...
the orthorhombic-like bulk unit-cell parameters. The PZ unit-cell volume decreases with increasing $N$ and stabilizes at the bulk value of about $V_{\text{PZ}}^{\text{bulk}} = 70.9 \text{ Å}^3$ for $N \geq 5$ (Figure 5b). It is also seen from Figure 5a that in this $N$ range the PZ lattice parameters are in good approximation equal to the relaxed bulk values. It is known that in general for ABO$_3$ perovskites (such as SrTiO$_3$ and BaTiO$_3$), the unit-cell volume increases if O vacancies (and associated charge compensating metal vacancies and/or valence changed metal ions) are present, which for the titanates is attributed to the elongation of the Ti–O vacancy distance compared to the Ti–O distance.$^{[38–42]}$ Therefore, we propose that the observed increased PZ unit-cell volume for $N < 5$ is likely to be due to such defects. Some additional XRD data on the PZ crystal structure is given in Figure S5, Supporting Information. The PL layer shows a decreasing $c/a$ ratio from about 0.999 for the single PL layer to 0.985 for $N = 12$, while simultaneously the unit-cell volume increases significantly. To our knowledge there are no single crystal lattice parameter data of PL available, only thin-film data for which it is not well known how defective and/or strained the material is. However one may expect the PL material to be comparable in structural properties with PZT(52/48, PbZr$_{0.52}$Ti$_{0.48}$O$_3$), which has a tetragonal unit cell, but with a slightly smaller unit-cell volume than the PL layer. Therefore, we expect that the PL layer is in all cases tensile strained in the film plane and, considering the rapidly increasing unit-cell volume, that it also becomes increasingly defective with increasing $N$.

The reflection peaks of the emergent PLZ layer (Figure 4) are very clear and have similar widths as those of the PZ and PL layers. The PLZ layer has approximately constant average lattice parameters and unit-cell volume for all multilayers in which this layer is observable ($N \geq 5$). The PLZ crystal symmetry is tetragonal, with the long axis in the out-of-plane direction. Based on the thickness of the constituent layers in these multilayers (at least 20 nm), it can be excluded that the emergent peak is caused by superlattice interference effects (which typically only occur for coherently grown multilayers with atomically sharp interfaces, consisting of ultrathin individual layers with small lattice mismatch, and for high period numbers). Figure S5, Supporting Information shows the superstructure reflections of the PLZ layers of the $N = 12$ device, indicating antiferroelectrically aligned polarization vectors in the (101) and (100) side faces of the PLZ pseudocube, directed along the face diagonals, thus with an out-of-plane polarization component.

In summary, the XRD analysis indicates that with increasing period number, the PZ grows increasingly coherently strained to the PL and vice versa. An additional out-of-plane reflection peak is attributed to a layer with a tetragonally deformed pseudocubic unit cell with the long axis out-of-plane with average pseudocubic lattice parameters $a_{\text{PLZ}} = 4.134 \text{ Å}$ and $c_{\text{PLZ}} = 4.152 \text{ Å}$. This contrasts with the PL and PZ phases, for which the out-of-plane axes are the shortest, and the AFE PZ polarization is exclusively in-plane. Figure 6 gives the PL, PLZ, and PZ intensities, normalized to the total intensity in the three (103) reflections determined from integrated peak intensities in Figure 4. The green data points clearly show that the intensity of the emergent (PLZ) increases with the period number. The purple diamond data point is obtained from STEM-EDX on the $N = 12$ multilayer, from which $d_{\text{PLZ}} = 5 \text{ nm}$ is calculated, while the shaded green band indicate the same trend for a diffusion width of 3–7 nm (lower and upper bounds).

### 2.3. Polarization Properties

#### 2.3.1. Single Layers

The $P$–$E$ loops and switching current ($I_{SW}$–$E$) curves of all thin films, measured up to 1 MV cm$^{-1}$ at 1 kHz and room temperature, are presented in Figure 7. (An enlarged view of the first quadrant of the $P$–$E$ loops is also shown in Figure S6, Supporting Information.) The PL thin film has a slim $P$–$E$ loop and...
exhibits typical RFE behavior with low $P_r$ (1.8 μC cm$^{-2}$), whereas the $P$–$E$ loop of the PZ film shows the double, square-shaped hysteresis behavior of an AFE. Note also that the finite slope below and beyond the switching fields indicate a strong dielectric response of the AFE films. The RFE and AFE behaviors can also be seen in the $I_{SW}$–$E$ curves: The four sharp current switching peaks of the PZ film, associated with the phase transformation from AFE to FE states (AF) and vice versa (FA), occur at high electric fields ($E_{AF} = 0.83$ MV cm$^{-1}$ and $E_{FA} = 0.51$ MV cm$^{-1}$, see also Figure S7a, Supporting Information). The switching curve of the RFE PL film suggests some FE-like switching, although at two closely spaced coercive fields in the low electric-field region ($\pm 120$ kV cm$^{-1}$) (Figure 7b–PL). Note that the latter coercive fields are relatively large as compared to those of typical high quality normal-FE PZT(52/48) films, with coercive fields of the order of 50 kV cm$^{-1}$,[43] indicating that polarization reversal in the PL layer is impeded significantly.

2.3.2. Multilayers

The $N=1$ bilayer film has a double, square-shaped $P$–$E$ loop but with lower $E_{AF}$ (0.52 MV cm$^{-1}$) and $E_{FA}$ (0.33 MV cm$^{-1}$) values

Figure 6. Ratio of PL, PLZ, and PZ peak intensities, normalized to the total peak intensity, based on the (103) RSMs. The purple diamond data point is obtained from STEM-EDX on the $N=8$ multilayer, indicating that $d_{PLZ} = 5$ nm. The green shaded area indicates the case for constant $d_{PLZ}$ in the range 3 to 7 nm.

Figure 7. a) Polarization hysteresis ($P$–$E$) loops and b) corresponding switching current ($I_{SW}$–$E$) curves, of single layers (PL, PZ) and multilayers ($N=1$ to $N=12$). The measurements were performed up to a maximum field of 1 MV cm$^{-1}$, at 1 kHz scan frequency and at room temperature.
and smaller hysteresis \(E_{\text{AF}}-E_{\text{FA}}\) than the PZ single layer. With increasing \(N\) the \(P-E\) loops undergo a transition from the double AFE loop to the RFE-like loop. Further the double loops become increasingly more slanted and slimmer. However, for all samples the \(I_E\) curves still exhibit four widely spaced switching current peaks, which become broader and decrease in amplitude (see also Figure S7, Supporting Information, where the curves are plotted in the same graph). Another observation is that the switching fields strongly decrease when the PZ device is combined with a single PL layer \((N=1\) device), but that for the multilayers with \(N > 1\), the switching fields (switching peak positions) only decrease slightly more.

The maximum polarization \(P_m\) at \(E_m = 1\) MV cm\(^{-1}\) of the \(N=1\) device is approximately equal to the average of the values in the single-layer PZ and PL films, and \(P_m\) (PL) > \(P_m\) (PZ) (Figure S8a, Supporting Information). With increasing period number \(P_m\) (N) increases up to \(N = 5\) to a value \(P_m(5) = 48.4\) μC cm\(^{-2}\), that is larger than \(P_m\) (PL), indicating some enhancing effect arising from a positive coupling mechanism between the polarizations of the individual PL and PZ layers. In the following, we will propose that there is a relation with the strain in the layers that varies with \(N\). For \(N = 8\) and \(N = 12\), the \(P_m\) value decreases again, suggesting the increasing strength of another mechanism that weakens this coupling. Finally, we note that the \(P_m\) remains small for all \(N\) values (Figure S8a, Supporting Information).

### 2.4. Energy Storage @ 1 MV cm\(^{-1}\)

Figure S8b, Supporting Information, shows the energy-storage properties at \(E_m = 1\) MV cm\(^{-1}\), calculated from the corresponding \(P-E\) loops. The \(U_r\) values are similar in both single PL and PZ thin films, but a higher efficiency \(\eta\) is achieved in the PL film due to the slimmer \(P-E\) loop. With increasing period number \(N\), the \(U_r\) values first increase and reach a maximum value of \(19.5\) J cm\(^{-3}\) for \(N = 5\), and then slightly decrease with further increase of \(N\). Meanwhile, the \(U_r\) value follows a similar trend. The initially relatively large loss \(U_l\), arises from the AFE character of the \(P-E\) loops for \(N = 1-5\), but drops significantly for \(N = 8\) and \(N = 12\), with the more RFE-like \(P-E\) loops, with efficiencies close to that of the PL layer.

### 2.5. Breakdown Strength

Since pulsed-power energy-storage systems are normally operated with a high applied voltage (electric field) to achieve maximum energy storage, it is important to investigate the electric-field breakdown strength (the applied electric field before dielectric breakdown occurs in the capacitors), of the dielectric capacitors. Figure 8a shows the measured breakdown fields for a series of the different devices, analyzed with a two parameter Weibull distribution. The steep, and for all types of devices nearly equal, slope of the fitted lines indicates a narrow distribution of breakdown strengths around the central value \(E_{\text{BD}}\), that can be obtained for the \(y\)-axis value equal to 0. These values are shown in Figure 8b as function of \(N\). Compared to the single-layer films, the multilayer films exhibit an enhanced \(E_{\text{BD}}\) value that strongly increases with increasing \(N\) up to \(N = 8\) and then appears to saturate. The \(E_{\text{BD}}\) of the \(N = 1\) multilayer film (2.7 MV cm\(^{-1}\)) is approximately equal to the average value (2.65 MV cm\(^{-1}\), dotted line in Figure 8b) of the \(E_{\text{BD}}\) values of the PL (2.8 MV cm\(^{-1}\)) and PZ (2.5 MV cm\(^{-1}\)) single-layer films.
2.6. Leakage Current

The leakage current of a dielectric capacitor may be a possible indicator for the breakdown strength, since a (leakage) conduction path that dominates the low bias electrical conduction is expected to be a likely location where electrical breakdown may occur. Thus, if a strong correlation between the leakage current and the breakdown strength is found one has an easy and nondestructive test for the breakdown properties of the device. Figure 8c shows the electric-field dependence of the leakage currents of representative multilayer films as function of the period number, demonstrating that an increasing \( N \) suppresses the leakage current. (Figure 8d). In the literature, the decrease in leakage current is attributed to the restriction of the movement of charge carriers across the interfaces of different layers.[3,28,44–46] Following this idea we can infer that the remarkable enhancement in breakdown strengths in the multilayer films is related to the number of layers and it suggests that the interfaces, by some interface related effect, block the conductive paths and in this way decrease the chance of the growth of an electrical breakdown path in the multilayer structure.

In Section S7, Supporting Information, we give a parametric, descriptive model that provides an analytical description of these ideas. It connects the period number with the leakage current and breakdown field of the devices (Figures S12–S14, Supporting Information). The conclusions from this model will be further discussed in Section 3.4. This model needs additional experimental support but may give hints toward further device improvement.

2.7. Polarization and Energy Storage at High Fields

Figure 9a–e shows the \( P–E \) loops of multilayer films measured at 1 kHz and room temperature, up to the \( E_{BD} \) value of the device. The variation of \( P_m \) (at \( E_{BD} \)) and \( P_r \) values is summarized in Figure 9f. The largest \( U_r \) value (≈128.4 J cm\(^{-3}\)) is achieved for the \( N = 8 \) multilayer film. The \( P_m \) and \( E_{BD} \) values are similar for both \( N = 5 \) and 8 multilayer films, but the loss of the \( N = 8 \) multilayer is smaller due to the slimmer loop (Figure S15, Supporting Information). This is the main reason why the \( N = 8 \) device has the largest \( U_r \). Although the \( E_{BD} \) is even larger for the \( N = 12 \) multilayer, it has a lower \( U_r \) which is associated with a lower \( P_m \), demonstrating that the change in high field polarization properties of the film stack for large \( N \) degrade the energy-storage properties, despite the larger breakdown fields.

From the application point of view, it is concluded that for the present material system, in which the period number is changed, keeping the total stack thickness constant, the multilayer film with \( N = 8 \) is the optimal design with respect to maximum recoverable energy and efficiency. For this reason, this stack was chosen for further investigation into the thermal stability and fatigue endurance, discussed in the next sections of this Results section.
2.8. Thermal Stability and Fatigue Endurance

Good temperature stability and high fatigue endurance are crucial factors for the practical application of energy-storage dielectric capacitors. Figure S16a, Supporting Information, shows the first quadrant $P$-$E$ loops of $N=8$ multilayer films, measured at temperatures between 20 and 220 °C up to a maximum field of 3 MV cm$^{-1}$. From this figure it is seen that there is no significant change in the shape of the $P$-$E$ loops (as can also be seen in Figure S17a, Supporting Information) in the 20–100 °C range. Above 100 °C the loop opening slightly increases and becomes more slanted. This figure further shows that the $P_m$ value slightly decreases, and $P$ increases with increasing temperature in the range 100–220 °C (Figure S17b, Supporting Information). However, the $U_p$ values remain almost unchanged in the whole 20–220 °C temperature range, 770 J cm$^{-3}$ ± 3.3% (Figure S16b, Supporting Information). The $U_p$ and $\eta$ values are almost constant between 20 and 180 °C (94.8 J cm$^{-3}$ ± 1.6%, and 81.2% ± 1.8%, respectively) but do exhibit a small up, respectively, downturn for higher temperatures. The slightly increased $U_p$ values above 180 °C are due to the broadening of the $P$-$E$ loops. The opening of the $P$-$E$ loops and the increase of the leakage current at higher temperatures (Figure S17c, Supporting Information), is associated with increasing mobility of the oxygen vacancies. These results show the excellent temperature stability of the energy-storage properties of this device up to a temperature of at least 180 °C.

The cycling fatigue endurance of the $P$-$E$ loop and the energy-storage properties of the $N=8$ multilayer were investigated using bipolar fatigue cycling up to 1 MV cm$^{-1}$ at 100 kHz, at room temperature and at 220 °C, respectively. The pulse height of 1 MV cm$^{-1}$ used in the fatigue measurements is much larger than the coercive field of the devices to ensure that all domains will switch during electric-field cycling. The $P$-$E$ loops were measured up to 3 MV cm$^{-1}$ (Figure S18, Supporting Information). The high stability against cycling is reflected in the largely unchanged $P$-$E$ loops (Figure S18a–c, Supporting Information), not only at room temperature (20 °C) but also at high temperature (220 °C), resulting in the largely fatigue-free energy-storage density and efficiency behavior (Figure S18b–d, Supporting Information). The slight decrease in energy efficiency during cycling at 220 °C is due to the reduction in $U_p$ and increase in $U_{\text{arc}}$, which can be seen from the lower $P_m$ and broader $P$-$E$ loop (see Figure S19, Supporting Information).

3. Discussion

Above we have described the experimental observations on the various devices. One expects a relation between, on the one side the variation in the crystal structure as function of the period number $N$, and on the other side the (high field) polarization, breakdown strength and leakage current properties and consequently the energy-storage properties of the multilayers. Below we give a qualitative description of this connection, which is made more quantitative in Section S7, Supporting Information, by phenomenological modeling.

3.1. Crystal Structure

From the structural analysis it was concluded that the PZ layer is orthorhombic, with the long $a_{\text{PZ}}$ and $b_{\text{PZ}}$ axes in the film plane. Compared to the bulk values, the PZ layers (for $N < 5$) appear to be under tensile in-plane strain, both in the case of the single PZ layer and of the low-$N$ multilayers (see Figure 5a). The large in-plane strain $S_{\text{ap}} = (a_{\text{PZ}} - a_{\text{bulk}})/a_{\text{bulk}} = 0.35\%$ of the PZ layer decreases to a fully relaxed state for $N \geq 5$. Further it is observed that the out-of-plane $c_{\text{PZ}}$ parameter is for all layers approximately equal to the bulk value. The increased unit-cell volume for $N < 5$ is assumed to be indicative for a significant vacancy density in the PZ films in these multilayers (Figure 5b). Together this leads to the somewhat surprising conclusion that the tensile in-plane strain for low $N$ values is not accompanied by a Poisson-ratio-driven out-of-plane contraction, but that the dominant mechanism determining the in-plane strain is the incorporation of defects, causing the unit-cell volume change.

In the case of the PL layer, one observes the opposite trend in the strain. The initially nearly cubic unit cell becomes increasingly tetragonally distorted by the increasing in-plane strain. The in-plane lattice parameter approaches that of the PZ layer with increasing $N$ (thus decreasing thickness of the individual PL and PZ layers). Simultaneously the unit-cell volume increases with increasing distortion from the cubic unit cell, indicating an increasing defect density (presumably oxygen and associated metal vacancies).

Thus, with increasing number of interfaces the in-plane lattice parameters of the PL and PZ layers approach each other. The STEM analysis (Figure 3) indicates that this happens by cube-on-cube growth of the layers by interfacial diffusion of both the A- and B-site atoms over a distance of the order of 5 nm. The average composition of this interfacial interdiffusion layer appears to form a new distinct phase, with an average in-plane lattice parameter in between that of the PL and PZ layer and approaching that of the strained PL layer for larger $N$ and an average unit-cell volume close to that of the relaxed PZ phase (Figure 5). The average composition of this so-called PLZ layer is expected to be close to $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.75}\text{Ti}_{0.25}\text{O}_3$, that is, the average composition of the PL and PZ layers. From the La doping, we expect relaxor-like behavior in this strained interfacial layer. Because of the cube-on-cube commensurate epitaxial growth the layer adopts a tetragonal symmetry, with the long axis out-of-plane. In the following it is seen that the PLZ phase, which appears to have a strong dielectric response, contributes significantly to the total energy-storage properties of the multilayers for large $N$.

3.2. Polarization Loops—Maximum Polarization

For the energy-storage application, one is interested in the total out-of-plane polarization $P_m$ that is measured at the maximum applied field ($E_m$), here at $E_m = 1$ MV cm$^{-1}$ (Figure 7 and Figures S6 and S8, Supporting Information) or $E_m = E_{\text{BD}}$ (Figure 9) (here we discuss the first case). This polarization is determined by the volume-fraction average of the $P_m$ values of the PL, PZ, and PLZ layers. To discuss the change of the $P_m$ with changing $N$, we describe the high field sections of the $P$-$E$ loops of the constituting layers by the tangents, $P(E) = P_0 + \varepsilon_{\text{HF}} E$, from which one obtains the value of $P_m = P(E_m)$. 
The unit cell of the PL layer becomes increasingly orthorhombic with increasing $N$, thus one may expect that the extrapolated zero field (out-of-plane component) of the polarization vector $P_{PL,0}$ rotates toward the film plane and decreases with increasing $N$ (The $c/a$ ratio changes from $\approx 0.999$ for the PL single layer to $\approx 0.985$ for $N = 12$, see Figure 5b). One may also expect that with decreasing $c/a$, it becomes increasingly difficult to rotate the polarization in the out-of-plane direction under applied out-of-plane field, hence that the high-field dielectric constant ($\varepsilon_{PL,HF}$) decreases with increasing $N$. The total effect is that $P_{PL,m}(N,E_m) = P_{PL,0}(N) + \varepsilon_{PL,HF}(N)E_m$ decreases with increasing tensile in-plane strain, hence increasing $N$. This can be due to decreasing values of $P_{PL,0}(N)$ and/or of $\varepsilon_{PL,HF}(N)$.

From the $P$–$E$ loop of the PZ layer (Figure S6a, Supporting Information) it is estimated that $P_{PZ,m}(E_m)$ is for about equal parts due to the AFE–FE transition around 0.8 MV cm$^{-1}$ and the dielectric response below and above this transition. This dielectric response means that the AFE (below switching field, $E_{SW}$) or FE (above $E_{SW}$) aligned polarization vectors rotate increasingly out of the film plane with increasing applied field. Because the $c/a$ ratio of the PZ layer slightly increases with increasing $N$ (Figure 5b), one may also expect that the dielectric response, $\varepsilon_{PZ,HF}$, increases. The same argument holds for the out-of-plane contribution, $P_{PZ,0}$, due to the AFE–FE transition. The total effect is that $P_{PZ,m}$ increases with $N$. The unit cell of the PLZ layer does not appear to change, hence one anticipates that $P_{PZ,m}$ remains approximately constant.

In this model, the total polarization $P_m(N)$ as function of $N$ is then due to the competing trends of the polarizations in the PL and PZ layers and the changing volume fractions (see Section S6, Supporting Information, for the mathematical formulation, based on a) a linearized polarization-field relation at high field, thus a $P_m$ that depends linearly on the $E_m$ or the $E_{BD}$, and b) a linear relation between the high-field dielectric constant and the period number $N$. It also follows that $P_m(N = 1)$ is in good approximation equal to the average of the $P_m$ values of the PZ and PL single layers, as is also observed experimentally (Figure S8, Supporting Information). Figures S9 and S11, Supporting Information show the results of fitting the model based on linear dependencies of $P_0$ and $E_{BD}$ on the number of layers $N$. The found trends with $N$ of the changes of $P_0$ and $E_{BD}$ of the different layers are in line with those predicted above from the changes of the unit-cell parameters. In Figure S10, Supporting Information, the polarization states of the single layers and the layers in the multilayer stack are depicted schematically for the zero field and applied field case, as deduced from the XRD analysis and the $P$–$E$ loop measurements.

A similar qualitative description can be given for $P_m$ at $E_m = E_{BD}$ with the complicating effect that also $E_{BD}$ is a monotonously increasing function of $N$. Experimentally it is found that $P_m$ peaks at somewhat larger $N$ than for $E_m = 1$ MV cm$^{-1}$.

3.3. Polarization Loops—Hysteresis

The energy loss scales with the area of the hysteresis in the $P$–$E$ loop, therefore it is important to study the mechanisms that cause hysteresis.

The unit-cell volume in the PL layer varies considerably with changing $N$. As discussed above, this indicates the presence of a large and varying number of oxygen vacancies. Polarization pinning by fixed charges and dipoles is a likely cause for the finite hysteresis and $P_1$ in all samples containing PL layer(s) (Figures 7 and 9 and Figure S8, Supporting Information).

In general, the large switching fields in AFEs arise from the large structural energy barrier between the AFE and FE states. It is observed that with increasing $N$ the switching field decreases. The change (decrease) in switching field is particularly large between the PZ and the $N = 1$ layer. We think that this cannot be attributed to the change in the crystal structure, since the change in $(c/a)_{PZ}$ is only small, but attribute the large $E_{SW}(N = 0 \rightarrow 1)$ to the additional PL/PZ interface. The PL layer is already strongly polarized at non-zero applied fields and the associated field will facilitate the switching in the PZ layer and thus reduce $E_{SW}$. For the multilayers with $N > 1$, the further decrease in switching field is only small, since the effect of the adjacent PL layer is already considered. Any further decrease in $E_{SW}$ may then be attributed to the further change in $(c/a)_{PZ}$.

Further it is speculated that the increased tilting of the AFE $\rightarrow$ FE hysteresis in the $P$–$E$ loops (reflected in the smearing of the switching peaks in the $I_{SW}$–$E$ loops; Figure 7b) is due to an increasing width of the distribution of local switching fields at the PL/PZ interfaces, with increasing $N$. For $N = 12$ the peak width is so large that it becomes hardly distinguishable from the relaxor-like hysteresis of the PL layers.

There is a considerable difference in hysteresis in the loops for $E_m = 1$ MV cm$^{-1}$ and $E_m = E_{BD}$, as can be seen from comparison of Figure 7a with Figure 9a–e and from comparison of the energy losses in Figure S8b, Supporting Information with Figure 9g, which are of the order of 1–6 and 20–40 J cm$^{-1}$, respectively. From the comparison of the shapes of the loops for both cases it appears that this large hysteresis increase with increasing $E_m$ is largely due to an increase in the hysteresis of the RFE-like part of the loop. This is plausible if one assumes that with increasing applied maximum field the defect dipoles become more and more aligned (one expects that oxygen vacancies can be moved easily in a strong field), causing increasingly strong local pinning fields, and thus larger hysteresis. Finally, it is observed that for large $N$ the hysteresis area is smaller than for smaller $N$. This might be an indication that in the thinnest PL layers the pinning becomes less effective, possibly because in absolute terms fewer defects contribute to the polarization pinning, even when the defect density is the same.

3.4. Leakage Current and Breakdown Field

The general argument in the literature is that with increasing density of grain boundaries and interfaces the breakdown field increases, because the chance that the branches of a breakdown path are interrupted increases by these defects. We therefore speculate that the number of leakage paths, that determine the leakage current in a capacitor device, are a measure of the chance of electrical breakdown. In Section S7, Supporting Information, a phenomenological model is developed and applied to the leakage current dependence on the period number $N$. It is assumed that each PL/PZ and PZ/PL interface decreases the
chance that a potential leakage path connects the outer electrodes by an equal probability factor $p < 1$. The leakage current is found to decrease rapidly with increasing $N$. This decrease can be described very well with a power law dependence on $N_i = p^{2N - 1}$, following from the model (Figure S12, Supporting Information).

One may expect that breakdown starts in the layer in which the local field surpasses the local breakdown field. Secondly, we expect that the breakdown field depends on the defect density (a bulk property) in that layer. With these assumptions and employing Weibull statistics (see Section S7, Supporting Information), that also takes into account the changing volume of the layers with changing $N$, we can describe accurately the layer thickness dependence, $d_i = d_i/2N$, of the measured breakdown field from Equation (S19), Supporting Information (see Figure S13, Supporting Information). The model further suggests that breakdown starts in the layer with the lowest breakdown field, that is, in the present case the PZ layer.

The observed exponential relation (Figure S14, Supporting Information) between the number of layers in the stack and the breakdown field may therefore be coincidental and arises from the inversely linear relation between $d_i$ and $N$. Considering the describing models, the underlying physics is however unrelated, the leakage current being determined by the interfaces and the breakdown field by the bulk defect density.

### 3.5. Energy-Storage Properties

Equations (S26) and (S27), Supporting Information, give parametrizations of the maximum stored energy density and energy-storage efficiency in terms of the parameters that describe the high field behavior of the $P–E$ loop ($E_{HF}$) and the breakdown field ($E_{BD}$), which in turn depend on the number of bilayers $N$. Above we explained qualitatively the period number dependence of the $P_m(E_{HF}, E_{BD})$ in terms of the response of the individual PZ and PL layers, and PLZ interfacial layer on the changing strain and defect densities in these layers with changing $N$.

Figure S20, Supporting Information shows that the storage energy, modeled by Equations (S23) and (S26), Supporting Information, gives an accurate estimate of the measured values. The increasing trends in storage and recoverable energy up to a maximum value for $N = 5$ (respectively $N = 8$) for $E_{m} = 1$ MV cm$^{-1}$ (respectively for $E_{m} = E_{BD}$) and the decrease for larger $N$ can therefore largely be attributed to the dependence of the total $P_m$ of the layer stack on the period number.

The observed energy-storage efficiencies (Figures S8b and S9h, Supporting Information) are a monotonously increasing function of $N$, despite the decreasing trends in storage and recoverable energies for large $N$. This is because the latter trend is more than 100% compensated by the decrease in hysteresis, hence energy loss, for large $N$.

In conclusion, the above scenarios, that give possible explanations for the various changes in ferroelectric and breakdown properties, show that the net energy properties of a multilayer device are a complicated function of opposing trends in the dependence of the layer properties on the number of layers. We observe an increasing breakdown field with increasing number of layers $N$ (with decreasing thickness of individual layer thicknesses for equal total thickness, $d_i = d_i/2N$) and a maximum in the $P_m$ of the multilayer at $E_{m} = 1$ MV cm$^{-1}$ and $E_{m} = E_{BD}$ for $N = 5$ and $N = 8$, respectively. The $P_m$ value of the multilayer appears in turn to be due to the different response of the $P_m$ and volume fractions of the PL, PZ, and PLZ layers on changing layer thicknesses.

### 3.6. Fatigue

Despite the fact that these devices have a Pt top electrode, which generally causes rapid switching fatigue in PZT devices,[47] this is not observed for the devices here. We attribute this difference to the fact that the PZT(52/48) devices with Pt electrode, discussed by Do et al.,[47] show abrupt switching events in each cycle. The nucleation of a reversal domain in their devices is accompanied by an extremely large screening field in a thin dielectric layer that is generally present at the FE/Pt interface.[47] This field causes electron injection into the dielectric layer and in this way builds up fatigue upon continued cycling. One might expect a similar process to happen in an AFE capacitor, because these also show abrupt switching. However, in a RFE capacitor the polarization changes only gradually and the amount of polarization switching is very small. The $N = 8$ multilayer device, investigated for fatigue properties, shows predominantly RFE behavior and little and gradual switching as can be inferred from the $P–E$ and $I_{SW–E}$ loops of this device (Figure S18, Supporting Information, shows polarization and maximum stored energy fatigue, that were determined using a bipolar square pulse of 100 kHz and 1 MV cm$^{-1}$ pulse height at room temperature and at 220 °C operating temperature, respectively). We think that this explains the excellent switching fatigue performance of our device.

### 4. Conclusions

In summary, by varying the number of interfaces between the RFE PL and AFE PZ layers, a recoverable energy-storage density of 128.4 J cm$^{-3}$ (to our knowledge the highest reported so far for a multilayer structure) together with an energy efficiency of 81.2% have been achieved in the PL/PZ multilayer film with an optimal period number of $N = 8$ for a fixed film thickness of 500 nm. This optimum value arises from the combined effect of the period number dependence of the $P_m$ (showing a maximum around $N = 8$), increasing breakdown strength (saturating above $N = 8$), and the amount of hysteresis in the $P–E$ loop (that increases up to $N = 5$ and then decreases significantly for larger $N$).

The dependence of the $P_m$ is attributed to the increasing number of layers, which changes the in-plane strain in the individual layers, but above all by the polarization contribution from the increasing volume fraction of the arising interfacial PLZ layer. It is argued that by the changing in-plane strain, the polarization behavior of the individual layer’s also changes. Further it is argued that there is polarization coupling between the PL and PZ layers, that changes the switching in the PZ layer. This coupling is thought to smear out the switching peak and to decrease the total hysteresis for large $N$. 

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The PLZ interfacial layer hinders the development of electrical conduction paths, resulting in a lower leakage current and results in a greatly enhanced breakdown strength in multilayer thin films. Moreover, the multilayer thin films exhibit an excellent stability over a wide range of temperatures (20–220 °C) and long-term cycling performance (up to \(10^{10}\) cycles) at room as well as at elevated temperatures. These properties give these multilayer devices significant potential for energy-storage applications under harsh operating conditions.

5. Experimental Section

Thin-Film Depositions: RFE PL and AFE PZ single layers, and [PL/PZ]_N (N = 1–12) multilayers were grown on 100-nm-thick SrRuO_3 (SRO) electrode-buffered SrTiO_3/Si (STO/Si) substrates using PLD method, employing a KrF excimer laser source (Lambda Physik, 248 nm wavelength). The total thickness of the single layers and multilayers was close to 500 nm. For the STO/Si substrates, a 20-nm-thick epitaxial STO buffer layer was grown by reactive molecular beam epitaxy on the Si substrates. This layer acted as a seed layer for highly (001)-oriented epitaxial growth of the subsequent perovskite layers. The deposition conditions of the PL and PZ layers, as well as SRO electrodes were given in previous reports.

Fabrication of Top Electrodes: In each sample, there are about 80 capacitors (with 100-nm-thick Pt top electrodes and with dimensions of 100 × 100 μm^2) fabricated by a lift-off photolithography technique.

Analysis and Characterization: The crystallographic properties of the thin films were analyzed by X-ray theta–2theta (XRD, θ–2θ) scans and reciprocal space mapping (RSM) using a high-resolution Bruker D8 Discover X-ray diffractometer with Cu-Kα radiation (wavelength: 1.5406 Å) and an Eiger2 R 500K area detector. On the incident beam side, this unique system used a rotating anode generator (TXS-HE), a hybrid (parallel-focusing) Montel multilayer mirror optic, an asymmetric Ge (022) channel-cut monochromator, and a circular 1 mm diameter pinhole collimator to shape and condition the intense X-ray beam. The specular θ–2θ scans were performed with a step size of 0.02° and a counting time of 1 s per step. For those measurements, the detector was operated in 2D mode with a small region of interest (13 × 61 pixels, pixel size 75 × 75 μm²). A multilevel rotary absorber was used to automatically adjust the intensity of the incident beam to optimize the effective dynamic range of each measurement and to avoid detector saturation. The RSMs were constructed from sets of omega rocking curves collected with a step size of 0.015° while the detector remained stationary and operated in 2D snapshot mode. This was possible thanks to the large field of view, especially at small sample to detector distances, here 160 mm. Grazing-exit configuration was chosen to geometrically compress the beam, resulting in narrow reflections.

The film thickness, microstructure, and the interface characterizations were investigated by means of cross-sectional high-resolution scanning electron microscopy (HRSEM: Zeiss MERLIN) and high-resolution scanning transmission electron microscopy (Spectra 300 S/TEM, Thermo Fisher Scientific), operated at 200 kV with a Super-X four-quadrant EDX detector. The surface morphology of the films was characterized by contact-mode AFM (Bruker Dimension ICON).

The polarization-electric field (P–E) hysteresis loop and switching current (I_{SW–E}) measurements were performed with a triangular voltage waveform (at a frequency of 1 kHz) in the dynamic hysteresis measurement mode (DHM) of the aixACCT TF-2000 Analyzer (aixACCT Systems GmbH, Aachen, Germany). In this study, the P–E loops were measured from a relatively low electric field (such as 1 MV cm\(^{-1}\)) up to (close to) a high electric field at which the capacitors become damaged, with a ramp rate of 50 kV cm\(^{-1}\).

The electric breakdown field (breakdown strength) was the maximum electric field that the dielectric capacitor can withstand before it broke down. From each sample, 9 of the 80 capacitors were randomly selected for Weibull statistics, to determine the breakdown field of the sample. In those 9 capacitors, 4 capacitors were used to determine average energy-storage properties from P–E measurements. In addition, the reproducibility of the results was investigated by repeating the Weibull tests for three samples of the N = 8 multilayer films fabricated in three different deposition runs. It was found that the breakdown strength and energy-storage properties were reproducible. Additional information can be found in Section S11 “Repeatability” and Figure S21, Supporting Information.

The fatigue measurements were performed by applying a bipolar rectangular pulse train of 100 kHz (or 5 μs pulse width) and 1 MV cm\(^{-1}\) (pulse height). The pulse height used in the fatigue measurements was much larger than the coercive field of the devices to ensure that all domains will switch during electric-field cycling. After a certain number of switching cycles, the ferroelectric properties were evaluated with a P–E hysteresis loop at a frequency of 1 kHz. The leakage current measurements were carried out with a Keithley 4200A-SCS Parameter Analyzer (Tektronix, Beaverton-Oregon, United States), using a 2 s delay time and a dc-voltage sweep with a ramp rate of 1 kV cm\(^{-1}\ s^{-1}\) (or 0.05 V s\(^{-1}\)).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
antiferroelectrics, breakdown strength, energy storage, multilayers, relaxors

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In our films the PZO unit cell is tetragonal, hence the in-plane lattice unit cell, \(a_{pc} = (V_{pc})^{1/3} = 4.139 \text{ Å}\). For the bulk orthorhombic unit cell \(V_{O} = a_{O}b_{O}c_{O} = 2V_{pc} = 2V_{pc}^{2}\), since \(a_{O} = b_{O} = a_{pc} = a_{pc}\). In our films the PZO unit cell is tetragonal, hence the in-plane lattice parameters are equal, \(a_{pc} = a_{pc}\). Further assuming that the out-of-plane lattice parameter is equal to the bulk value, \(c_{O} = 4.113 \text{ Å}\), we find \(a_{pc} = a_{pc} = \sqrt{V_{O}/(2c_{O})} = 4.151 \text{ Å}\). The used orthorhombic lattice parameters are from https://doi.org/10.1002/adma.201907208.