Intrinsic stability of ferroelectric and piezoelectric properties of epitaxial PbZr$_{0.45}$Ti$_{0.55}$O$_3$ thin films on silicon in relation to grain tilt

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Abstract
Piezoelectric thin films of PbZr$_{0.45}$Ti$_{0.55}$O$_3$ were grown on Si substrates in four different ways, resulting in different crystalline structures, as determined by x-ray analysis. The crystalline structures were different in the spread in tilt angle and the in-plane alignment of the crystal planes between different grains. It is found that the deviations of the ferroelectric polarization loop from that of the ideal rectangular loop (reduction of the remanent polarization with respect to the saturation polarization, dielectric constant of the film, slanting of the loop, coercive field value) all scale with the average tilt angle. A model is derived based on the assumption that the tilted grain boundaries between grains affect the film properties locally. This model describes the observed trends. The effective piezoelectric coefficient $d_{33,\text{eff}}$ shows also a weak dependence on the average tilt angle for films grown in a single layer, whereas it is strongly reduced for the films deposited in multiple layers. The least affected properties are obtained for the most epitaxial films, i.e. grown on a SrTiO$_3$ epitaxial seed layer, by pulsed laser deposition. These films are intrinsically stable and do not require poling to acquire these stable properties.

Keywords: ferroelectric, piezoelectric, thin film, grain boundary, PZT, stability, epitaxial

1. Introduction
Ferroelectric and piezoelectric thin films are of enormous importance for many technological applications, specifically in micro-electromechanical systems (MEMS) [1–8]. The improvement and understanding of their properties is the topic of much fundamental research as well as technological development. In particular, the family of PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) ferroelectrics, notably the morphotropic phase boundary (MPB) composition or the various tetragonal compositions, have been widely investigated for applications [9]. A major step forward is the deposition of PZT ferroelectric thin films on Si substrates, opening the route toward the integration of piezo- and ferroelectric (we will use the shorthand notation PFE) devices in Si-technology [10–12, 15], for example in MEMS-devices as cantilevers or membranes for sensing, actuation or energy scavenging.
Table 1. Fabrication processes of PZT thin film capacitors.

| No.  | Piezoelectric stack | Top electrode | PZT Film | Bottom electrode | Buffer layer | Substrate           |
|------|---------------------|--------------|----------|------------------|-------------|---------------------|
| SG(001) | PZT on (111)  | 100 nm Pt, sputtering | 500 nm, SG | Pt(100 nm)/Ti(15 nm) | 500 nm SiO₂ | (001)Si             |
| Text(001) | PZT/LaNiO₃ on (111)  | 100 nm Pt, sputtering | 500 nm, (10 nm LaNiO₃) | Pt(100 nm)/Ti(15 nm) | 500 nm SiO₂ | (001)Si             |
| Epi(110) | PZT on (110) SrRuO₃/YSZ/Si | 100 nm SrTiO₃, PLD | 500 nm PLD | 100 nm SrTiO₃, PLD | 50 nm YSZ, PLD | (001)Si             |
| Epi(001) | PZT on (001) SrRuO₃/SrTiO₃/Si | 100 nm SrTiO₃, PLD | 500 nm PLD | 100 nm SrTiO₃, PLD | 30 nm SrTiO₃, MBE | (001)Si             |

Basicall any PFE-device consists of a capacitor structure, in which the active PFE-layer is sandwiched between two electrodes. Alternatively an in-plane (ip) interdigitated electrode design is used, but this configuration will not be considered further here. Several techniques exist to deposit the PFE-layer, such as sol-gel (SG), sputtering and pulsed laser deposition (PLD). This results in layers with varying crystallographic properties, which one expects to be reflected in their PFE properties. The role of the base electrode layer (eventually in combination with an additional thin seed layer, for example TiO₂, LaNiO₃ or PbTiO₃), which functions as the seed layer for the PFE-layer, is of great importance, especially if one strives to obtain a crystallographically well oriented layer [11, 12]. It is by now well established that also the electrode layers may have a significant effect on the device characteristics. In particular, the presence of thin passive layers at the electrode–ferroelectric interfaces may affect the polarization (P–E) loops drastically: reduction of the remanent polarization (P₀), rapidly decreasing slope of the P–E loop at the coercive field (Eₙ) and change of the capacitor (effective) dielectric constant (εₑff) [13, 14].

We have investigated the effect of the fabrication method and the capacitor structure on the ferroelectric and piezoelectric device properties. We compare SG based devices with three families of PLD-based devices, with different crystallographic properties depending on the seed layer design. It is well known that in many cases the PFE-capacitor has to be subjected to a poling procedure to attain its best properties. We have found that these properties saturate to a given level depending on the fabrication method. Surprisingly, the variation in the ferroelectric properties between the different devices can all be related to a single crystallographic parameter, namely the width of the x-ray rocking curve. This suggests that the crystallinity of the film is the dominant parameter determining the ferroelectric properties. This aspect has hardly been investigated in literature, probably since it requires the capability to vary the crystalline properties of the films on Si. We have developed some simple models that relate crystallinity to the ferroelectric properties.

2. Experimental

2.1. Device fabrication

We fabricated four sets of PFE capacitor structures on Si substrates. The composition PbZr₀.₄₅Ti₀.₅₅O₃ (PZT45/55) was used, which is at the tetragonal side of, but close to, the bulk MPB in the phase diagram. This implies that one may expect for (001)-oriented films a mixture of c-domains with the long c-axis in the out-of-plane (oop) direction and a-domains with the c-axis in the plane (ip) of the film. Note that the a and c lattice parameters are not very different for this composition.

In three cases PLD was used to produce the 500 nm thick PFE-layer, varying the properties of the base electrode (sputtered Pt versus SrRuO₃ deposited by PLD). Also the crystallographic orientation of the SrRuO₃ base electrode was changed from (001) to (110). By varying the deposition conditions of the SrRuO₃ layer we are able to tune the crystallographic orientation of this layer to either (110) or (001) [15]. Because of the cube-on-cube growth of PZT on SrRuO₃ we can in this way also control the orientation of the PFE layer. The devices with Pt base electrode also had a Pt counter electrode, whereas the other devices have a SrRuO₃ counter electrode. The fourth set comprises SG devices with Pt base and counter electrodes. These variations were made to manufacture PFE capacitors on Si of different structural and crystallographic quality.

The fabrication steps of the PZT thin film capacitors are given in table 1. The PLD was done with a fluence of 2–3 J cm⁻², at 5–10 Hz repetition rate, using a 248 nm KrF excimer laser, in an oxygen atmosphere of 75 mTorr at a substrate temperature of 600 °C and a target–substrate distance of 60 nm. Details on the PLD deposition parameters of SrRuO₃, LaNiO₃ electrodes and yttria-stabilized zirconia (YSZ) buffer layers grown on Si substrates are given in [10]. The 30 nm SrTiO₃ buffer layer was deposited on the Si substrate by molecular beam evaporation. The textured PZT thin films were prepared by a SG technique, where a PZT precursor solution was prepared from lead acetate (Pb[OAc]₂), 3H₂O, titanium iso-propoxide (Ti[i-OPr]₄) and zirconium n-propoxide (Zr[n-OPr]₄) in 2-methoxyethanol solvent. The 0.4 M PZT precursor with 10 mol% excess lead content in solutions was prepared and spin coated on Pt/Ti/SiO₂/Si wafers at 4000 rpm for 30 s, followed by pyrolysis at 400 °C for 10 min. The process was repeated until the PZT thin films with required coating layers were obtained. Finally, the thermal annealing process at 650 °C for 60 min was carried out to obtain the ferroelectric phase PZT thin films.

To improve the properties of ferroelectric capacitors generally a poling procedure is applied, which involves

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4 Samples kindly provided by Professor D G Schlom, Cornell University, USA.
subjecting the device to a high dc bias voltage, preferably at an elevated temperature. Here, we show the effect of a procedure in which the devices are subjected to a (unipolar) static electrical field of 400 kV cm$^{-1}$ (well above the coercive field of about 50 kV cm$^{-1}$), during 30 min, while the device is maintained at 200°C. With this procedure the properties have largely saturated and are stable for at least 10$^5$ cycles. All properties discussed in this paper are determined at room temperature.

### 2.2. Structural characterization

Structural characterization of the PFE layers was performed by x-ray diffraction (XRD) and scanning electron microscopy (SEM).

The $\theta - 2\theta$ scans (figure 1(a)) show that the films have a well-defined oop orientation. As is well known, PZT grows predominantly in the (001) direction on Pt(111)/Ti/Si(001) [16]. On SrTiO$_3$-buffered Si(001) substrates the SrRuO$_3$ electrode layer and the PZT copy the orientation of the (001)-oriented STO. On YSZ buffered Si(001) the PZT growth orientation is (110). This was changed to (001) growth by depositing the first few monolayers of the SrRuO$_3$ electrode in a reducing O$_2$ environment [10, 15]. Note that for the crystallographic description of the orientation of the films (and the identification of the reflections in figure 1) we use the pseudocubic indices (001), (110) and (111). However, the (001) films consist of $c$ and $a$ domains of tetragonal unit cells with different oop lattice parameters. For the composition considered here the $\theta - 2\theta$ reflections of the $a$ and $c$ domain lattice parameters overlap. The SG(001) film shows an admixture of domains with (111) crystallographic orientation.

From the omega-scan ($\omega$-scans) of the (002) reflections one obtains the spread in the tilt angle $\alpha = |\alpha - \alpha_0|$ ($\alpha_0$ is the angle at which the rocking curve peak reaches its maximum and corresponds to the Bragg angle of the $\theta - 2\theta$ scan) of the (001), respectively (110), surface planes of the individual grains with respect to the film normal (figure 1(b)). The effect of other mechanisms that can lead to peak broadening, such as grain size, stress and instrumental broadening are relatively small. From our experience PZT films of the thickness used here are nearly fully relaxed, hence stress broadening can be neglected. The instrumental broadening is much less than the smallest peak width. The grain size estimated from Scherrer’s formula using the observed peak widths in the $\theta - 2\theta$ scans, indicate grain sizes of at least 100 nm for all films. Hence the maximum broadening of the rocking curve reflection can at the most be that of the Epi(001) film. We conclude that grain boundaries can therefore not explain the large rocking curve widths observed. Although all films show a well-defined (001), respectively (110) growth direction, their crystallographic quality varies, as is evident in the different full width half maximum (FWHM) of the rocking curves. The average tilt angle of the grains is estimated from the FWHM value of the Gaussian distribution as $\alpha_{av} = \sqrt{2/\pi} \text{FWHM}$. In table 2 the values of $\alpha_{av}$ are given. The average tilt increases slightly from 0.3$^\circ$ for the Epi(001) film to 1.3$^\circ$ for the Epi(110) film, but jumps to a few degrees when the buffer layer is Pt-based. $\alpha_{av}$ is a measure of the angle (in a plane perpendicular to the substrate) between the (oop oriented) crystal planes at both sides of a grain boundary. We assume that this tilt angle is also a measure for the tilt angle of the grain boundary planes between grains. Further on we will explore the consequences of this assumption for the properties.

Phi-scans ($\phi$-scans) (not shown here, but given in [15] for similar films) give information about the ip registry of the lattice with the substrate. For the Epi(001) film there is full registry with the substrate, i.e. the $\phi$-scan shows four-fold symmetry, with the ip (100) axes of the PZT film parallel to the ip Si (110) directions. The finite rocking curve width indicates that there are areas with slightly different oop orientation, thus these films are considered to be epitaxial films (with very little texture), with nearly perfect alignment across the boundaries between the domains. For the Epi(110) film there is twinning of the four-fold symmetry, with the ip PZT(001) oriented approximately $+10^\circ$ and $-10^\circ$ away from

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**Figure 1.** XRD (a) $\theta - 2\theta$ patterns and (b) rocking curves of (A) (100)-oriented textured SG film (SG(001)); (B) (100)-oriented textured PLD film on Pt electrode (Text(001)); (C) (110)-oriented, epitaxial PLD film (Epi(110)), and (D)(001)-oriented, epitaxial PLD (Epi(001)) PZT thin films. The peak labels refer to the growth direction in the pseudocubic lattice system.
the *ip* Si(110), thus increased texture of the epitaxial film. The Text(001) and SG(001) films show no *ip* orientation, and may be labeled as textured polycrystalline films.

In conclusion, one can describe the films as being composed of grains separated by grain boundary planes that make an average angle $\alpha_{av}$ with the film normal. The *ip* alignment of the crystalllographic orientation of the grains is nearly perfectly aligned for the Epi(001) films. In the Epi(110) film the grain boundary planes separate grains in which the *ip* crystal axes make an angle of approximately 20°. We suppose that this structure exists in larger regions of the film, whereas in other regions this structure is rotated 90°, due to the twinning. In the case of the Text(001) and SG(001) films the grain boundaries separate grains with random orientation of the *ip* crystal axes.

Figure 2 shows high resolution scanning microscope photographs of cross sections of the films. The columnar growth is clearly visible in all films, with a typical diameter of the grains of about 100 nm. For the Epi(001) and Epi(110) films the majority of the grains appear to grow without interruption from the bottom to the top electrode. The grain boundaries are in essence perpendicular to the surface. The surface of the Epi(001) film is extremely smooth, reflecting the (001) surface of the SrTiO$_3$(001)/Sr(001) substrate. In the case of the Epi(110) film the surface reflects the granular structure of the underlying layers. The rounding of the tops of the grains is ascribed to the (110) growth orientation. In the Text(001) film the surface shows more differences between each other, also resulting in a rougher surface. The grains have a less regular shape and differing dimensions and many grains appear to be interrupted during growth, or end or start within the film thickness. The SG(001) film is clearly different from the PLD films: several layers can be distinguished, due to the repeated deposition and pyrolysis process steps. Further many approximately spherical voids with diameter up to tens of nanometers are visible.

Table 2 summarizes the crystallographic characterization of the different films, and gives characteristic ferroelectric parameters as well as values derived from descriptive models.

### 2.3. Ferroelectric and piezoelectric characterization

The polarization hysteresis loop measurements were performed using the ferroelectric mode of the aixACCT TF-2000 Analyzer. The $P$–$E$ loop was measured at room temperature using a (bipolar) triangular excitation field with amplitude $E_T = 200$–300 kV cm$^{-1}$ at 1 kHz cycling frequency. The maximum *oop* piezoelectric displacement ($\delta$) of the thin-film capacitors was measured using a Polytech MSA-400 scanning laser Doppler vibrometer. The effective piezoelectric coefficient was determined as $d_{33,\text{eff}} = \delta/V_{ac}$, where $V_{ac}$ is the 8 kHz sinusoidal ac driving voltage amplitude of 3 V ($6V_{pp}$).

Figure 3 shows the $P$–$E$ loops for the different capacitors before (this is the second $P$–$E$ cycle), after the unipolar, elevated temperature, high field poling procedure, and after 10$^6$ switching cycles. It is obvious that the quality of the film has a large effect on the change of the loops with poling and aging. The loop of the Epi(001) sample is most square and is hardly affected by poling and cycling. The other devices produced by PLD show some improvement (larger remanent polarization and less slanting) of the loops on poling, but no degradation on aging. In contrast the SG(001) device improves significantly on poling, but deteriorates even more on cycling. In Table 2 the saturation polarization $P_s$ (obtained from the $P$-axis cutoff of the tangent to the $P$–$E$ loop at high fields); the effective dielectric constant $\varepsilon_{\text{eff}}$ of the capacitor (obtained from the slope of the tangent); the remanent polarization $P_r$; the coercive field $E_c$ and the slope $S = |(\partial P/\partial E)|_{E_c}$ of the loop at $E_c$, are given. These characteristic parameters were shown to be more or less

| Crystallinity | SG(001) | Text(001) | Epi(110) | Epi(001) |
|--------------|---------|-----------|----------|----------|
| *Oop* crystal orientation | (001) | (001) | (110) | (001) |
| *ip* crystal orientation | Arbitrary | Arbitrary | $\pm 10^3$ from Si(001) | $\pm 10^3$ from Si(110) |
| Polarization domain | Arbitrary *ip*; Arbitrary *ip*; | Arbitrary *ip*; Arbitrary *ip*; | $45^\circ$ from film normal *oop* | $45^\circ$ from film normal *oop* |
| Orientation | $\| [001]_{oop}$ | $\| [001]_{oop}$ | $\| [001]_{oop}$ | $\| [001]_{oop}$ |
| Average domain tilt $\alpha_{av}$ (deg) | 4.9 | 3.6 | 1.3 | 0.3 |

| Polarization | $P_{\text{mean}}^s (\mu \text{C cm}^{-2})$ | $\phi = \phi_s = P_s/P_0^c$ | $\phi_c = P_{\text{mean}}^s/\phi_s P_0$ | $P_{\text{mean}}^c (\mu \text{C cm}^{-2})$ | $P_s/P_0$ | $P_{\text{mean}}/P_s$ | $\varepsilon_{\text{eff}}$ | $E_c$ (MV m$^{-1}$) |
|--------------|-------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\phi_{\text{av}} = \phi_{s}$ | 33 | 0.62 | 92 | 19 | 0.35 | 0.58 | 294 | 5.03 |
| $\phi_{\text{c}} = P_0^c/\phi_{\text{av}}$ | 30 | 0.55 | 0.82 | 22 | 0.41 | 0.76 | 272 | 4.68 |
| $P_{\text{mean}}^s (\mu \text{C cm}^{-2})$ | 38 | 0.67$^d$ | na | 29 | 0.54 | 0.80 | 378 | 3.54 |
| $P_{\text{mean}}^c (\mu \text{C cm}^{-2})$ | 36 | 0.67$^d$ | na | 31 | 0.57 | 0.86 | 481 | 2.86 |
| $P_s/P_0$ | na | 0.67 | 1 | na |
| $P_{\text{mean}}/P_s$ | na | $\phi_{\text{c}}$, Epi(001) | $\phi_{\text{av}} = \phi_{s}$, Epi(001) | $\phi_{\text{c}}$, Epi(001) | $\phi_{\text{av}} = \phi_{s}$, Epi(001) |

| $\phi_{\text{av}} = \phi_{s}$ | $\phi_{\text{c}}$, Epi(001) | $\phi_{\text{av}} = \phi_{s}$, Epi(001) |
| $\phi_{\text{c}}$, Epi(001) | $\phi_{\text{av}} = \phi_{s}$, Epi(001) |

$^a$ *oop* = out-of-plane; *ip* = in-plane.

$^b$ After poling procedure.

$^c$ $P_0 = 54 \mu \text{C cm}^{-2}$ [20].

$^d$ Equal to $\phi_c$, Epi(001).
Figure 2. Cross-sectional SEM images: (a) SG(001), (b) Text(001), (c) Epi(110) and (d) Epi(001) PZT thin films (the 45° inclined structure visible in the SrRuO₃ electrode layers of the Epi(001) device is due to the preparation of the sample).

Figure 3. Polarization hysteresis loops of (a) SG(001), (b) Text(001), (c) Epi(110) and (d) Epi(001) PZT thin films, measured at the initial stage, after poling and after 10⁸ switching cycles.

sensitive to the presence of a passive layer in ferroelectric thin films [13, 14]. In section 3 we show that these ferroelectric parameters can be related to the crystalline parameter $\alpha_{av}$. Figure 4(a) shows the remanent polarization before and after poling and after prolonged cycling. This clearly visualizes the difference between the films prepared by
different processes. The Epi(001) film does not require any poling to achieve maximum $P_r$, whereas the other PLD and the SG films do. Moreover, the PLD films do not show any degradation of the polarization on cycling, whereas the SG(100) film clearly degrades. In this paper we concentrate on the plateau values of the remanent polarization, obtained after poling and before aging sets in. In figure 4(b) the $P_r$ values in different stages are plotted as a function of the average grain boundary tilt angle $\alpha_{av}$. Also shown is the change in polarization, $\Delta P_r = P_r(\text{after poling}) - P_r(\text{before poling})$, before and after (thermal) poling. No significant improvement in $P_r$ (Epi(001)) is achieved, whereas for the other devices the absolute improvement is approximately the same, on average 5.6 $\mu$C cm$^{-2}$, and does not depend on either the initial or final $P_r$ value. The relative change $\Delta P_r / P_r(\text{before poling})$ varies from 2 to 50%. The figure suggests that there is a strong effect of the grain boundary tilt angle on the maximum achievable $P_r$ value, decreasing linearly with increasing $\alpha_{av}$. Figure 4(c) gives the same data for the $d_{33,eff}$ values before and after poling. Here, we see a relatively small increase in $d_{33,eff}$ values on poling. Also the absolute values are only slightly different for the PLD films, decreasing slightly with increasing $\alpha_{av}$. For the SG(100) a strongly decreased $d_{33,eff}$ is found, much more than follows from a linear dependence on $\alpha_{av}$. However, the absolute increase of $d_{33,eff}$ due to the poling procedure scales approximately linearly with $\alpha_{av}$.

3. Discussion

In the following we propose a simple model that relates measurable quantities, obtained from the $P-E$ loops of the various devices to a characteristic crystalline parameter $\alpha_{av}$, which we relate to the grain boundaries. We will systematically analyze several measured parameters within this model. A consistent description arises, which is taken as a strong indication that the grain boundary parameter $\alpha_{av}$ is a significant parameter, determining the properties of ferroelectric films. The model is based on the assumption that the effect of dielectric grain boundaries can be described by an effective dielectric layer parallel to the electrodes. The effect of the latter on the $P-E$ loop characteristic parameters has been investigated in detail by Tagantsev et al [13] and Tagantsev and Gerra [14].
3.1. Crystal structure

Structurally, the distinguishing difference between the PFE-films in the different devices is the ip and oop crystallographic orientation of the grains. In the body of the grains the structure is expected to be single crystalline, except for isolated defects, as is reflected in the sharpness of the XRD reflections. Therefore one may expect that the deviations of the P–E loops from the ideal square loop (partly) can be associated with the orientation distribution of the grains, and the properties and orientation distribution of the grain boundaries. The ip orientation distribution of the grains is likely to have no large effect on measured properties like \( P_\text{t} \) and \( d_{33} = (\partial S_1/\partial E_3) \) (indices 1 and 2 correspond to ip coordinate axes, 3 to the oop coordinate axis), that depend on parameters directed in the oop direction only. The grains are approximately cylindrical in cross section, thus any ip directed property of the grain boundaries is expected to be averaged out.\(^5\) We conclude that the P–E and \( d_{33}–E \) loops are expected to depend predominantly on the oop orientation of the grains and GBs, characterized by the parameter \( \alpha_{\text{av}} \).

A second distinguishing factor between the different devices is the electrode materials: conducting oxide (SrRuO\(_3\)) electrodes at both sides of the ferroelectric layer in the case of the Epi(001) and Epi(110) capacitors; metal (Pt) electrodes for the SG(100) device and a Pt top and a combined conducting oxide/metal (LaNiO\(_3\)/Pt) bottom electrode for the Text(100) device. There is extensive literature on the effect of possible passive dielectric layers at the ferroelectric–electrode interface [13, 18, 19] on the P–E loops of PFE capacitors. Therefore the structural differences between the various devices is considered in the following, since we need to separate the consequences of possible ip passive layers from the effects of the grain boundaries.

3.2. Saturation and remanent polarization

3.2.1. Scaling. PZT45/55 is at the tetragonal side of the phase diagram of the PZT-mixture. According to the characterization of PZT by Haun et al [20]\(^6\) the intrinsic polarization \( P_\text{i} \) is directed along the long crystal axis and is equal to 54 \( \mu \text{C/cm}^2 \). For a single crystal the intrinsic piezoelectric coefficient is given by \( d_{33} \approx 245 \text{ pm V}^{-1} \) at room temperature. We have observed in thick (1 \( \mu \text{m} \)) clamped films, that all stress is relaxed and that the films have bulk lattice parameters, irrespective of both the substrate used and growth orientation ((001) or (110)) [17, 21]. Therefore we assume that one can use \( P_\text{i} \) as the value of the intrinsic polarization within a polarization domain.

In a stress/strain-free (001)-oriented film the domain fraction \( \phi_\text{S} \) of ferroelectric and crystallographic domains, with the long c-axis (and the polarization vector) perpendicular to the substrate, is then solely determined by the composition (determining the bulk lattice parameters) and the substrate (determining the thermal strain). At large enough applied field the effect of any (local) depolarizing field in the film is compensated for and all oop domains are polarized in the field direction. The effect of switching ip polarized domains into oop domains is neglected here. Because of the large elastic energy cost required to switch an a domain into c domains in a clamped film, we expect that the amount of switching is small and that therefore also the change in the overall polarization is relatively small. The maximum switchable polarization, equal to the measured saturation polarization \( P_\text{s} \), in a poled (001)-film of tetragonal composition is then related to the fraction of c-domains by

\[
P_s(001) = \phi_c P_0.
\]  

Any value lower than according to this formula can be ascribed to other effects (voids, screened polarization, domain wall-pinning), which we describe by an additional multiplicative factor \( \phi_s \) [21]. \( P_\text{i} \) is determined from the polarization axis cutoff of the tangent to the P–E loop at high applied fields. It was shown that a relatively thin dielectric layer (thickness \( d \)) in a ferroelectric film (thickness \( L \)) does, within a factor \( d/L \), not reduce the switching part of the polarization, \( P_\text{s} \) [13]. We assume that the film with the best crystallinity, Epi(001) film, has a value of \( \phi_s \) close to 1. Then one has \( \phi_s = 0.67 \) for the bulk of the grains of the (001) films. Using this value one can calculate \( \phi_c \) for the SG(001) and Text(001) films, as given in table 1. The measured remanent polarization should be equal to \( P_\text{s} \) unless there are factors present that change the shape of the P–E loop, such as passive layers and grain boundaries.

In a (110) oriented film there are domains with the polarization direction directed 45\(^\circ\) and 90\(^\circ\) away from the surface normal. Only the first domains contribute to the oop polarization. The fraction of such domains is defined here as \( \phi_{\text{DS}} \). Recent works have shown that (110) films of the considered composition on Si can be considered to be in the rhombohedral phase in which the net polarization vector rotates in the (101) plane of the tilted pseudocube (which is perpendicular to the film plane). This phase arises from nano-sized a and c polarization domains, which arise in (110) films on Si, but not on SrTiO\(_3\)/(110) [22].\(^7\) Assuming easy rotation of the polarization vector under influence of the applied \( E_s \) field, maintaining its absolute value, the saturation polarization is given by (see appendix A)

\[
P_s(110) = P_0/\sqrt{2} \approx 0.71 P_0.
\]

In this case the polarization vector rotates toward the body diagonal of the 45\(^\circ\) rotated pseudocube when the field is removed, and the remanent polarization is (see appendix A)

\[
P_r(110) \approx 0.58 P_0.
\]

\(^5\) Note that this does not hold for the body of the grains, where for the Epi-films there are preferential directions, thus one may expect orientation dependence of any film property that depends on the in-plane direction. The in-plane orientation distribution may affect parameters as \( e_3 = (\partial D_3/\partial S_3) \), which depends on the in-plane strain \( S_1 \) and therefore on the in-plane crystallographic structure.

\(^6\) Here, we used the average values of the compositions \( x_{\text{Sr}} = 0.5 \) and 0.4 of the piezoelectric coefficients from [20] and elastic parameters from [30].

\(^7\) Note that the tilt of the grains has only a marginal effect. Assuming that within a grain \( P_\text{i} \) is oriented in the (001) direction of the grain the effect of the grain tilt on the overall saturation polarization can be estimated by a multiplying factor \( \phi_{\text{DS}} = \cos \alpha_{\text{av}} \approx 1 \) for the tilt angles considered.
For the Epi(110) film we measure \( P_L / P_0 = 0.69 \) and \( P_S / P_0 = 0.54 \). Both values are very close to the values expected for the (110) nanodomain phase, for polarization directed maximally oop and along the body diagonal respectively. In Figure 5(b) the measured saturation and remanent polarizations are plotted versus the average tilt angle \( \alpha_{av} \). The polarizations are normalized to the theoretically expected value, equation (1), with \( \phi = \phi_\circ \) for the (001) films (in that case \( P_{exp}^{P_E} / P_0^{P_E} \) corresponds to the factor \( \phi_\circ \)) and normalized to equation (2), respectively equation (3) for the (110) films. It is observed that the films with larger \( \alpha_{av} \) values have a somewhat reduced saturation polarization. The largest deviation is found for the remanent polarization of the (001) films, which show an approximately linear decrease of \( P_{exp}^{P_E} / P_0^{P_E} \) with increasing \( \alpha_{av} \). Even for the Epi(001) film \( P_0^{P_E} / P_0^{P_E} \) is reduced from the theoretical value 1 applicable to a film without degrading effects of, for example, passive layers and grain boundaries.

### 3.2.2. Reduced remanent polarization due to grain boundaries

During the poling process the (leakage) current of the films, presumed to be along defective grain boundaries, is strongly reduced down to the level of the Epi(001) film, in which the poling does not decrease the current [15]. It is assumed that by the poling process the mobile charges in the grain boundaries are removed and the grain boundaries become insulating and uncharged, passive layers.

In [13] it was shown that \( P_L \) is strongly affected by the presence of a passive (insulating dielectric) layer parallel to electrode(s), whereas \( P_S \) is not affected. Above we have shown that the main distinguishing difference between the different films is the crystallinity, specifically the average grain tilt. In a simplified picture we decompose the ensemble of tilted grain boundaries into an array of vertical dielectric grain boundaries and a thin dielectric layer with fractional area \( \alpha_{av} \), adjacent to one of the electrodes. It was shown that the depolarizing field due to such a layer with thickness \( d \) and dielectric constant \( \varepsilon_d \) is given by \( E_d = -P_d / \varepsilon_0 \varepsilon_d L \), where \( L \) is the thickness of the PFE layer and \( P \) its polarization in the \( z \)-direction [13]. The total field across the PFE is then \( E_t = E + E_d = -P_d / \varepsilon_0 \varepsilon_d L \), where \( E \) is the externally applied field. The film with grain boundaries can then be modeled as two PFE parallel capacitors, one with area \( \alpha_1 \) and additional dielectric layer, which has reduced bulk (remanent) polarization \( P_{br} \), and one with area \( \alpha_2 \), without such a layer, and bulk (remanent) polarization \( P_{br} \). Considerig average lateral grain dimensions \( D \times D \) and length \( L \) (film thickness) the relative surface areas are then given by \( \alpha_1 = (D - W) / D \) and \( \alpha_2 = (D^2 - (D - W)^2) / D^2 \), where \( W = L \tan \alpha_{av} \) is the width of the area in which a grain boundary is present (see figure 5(a)). Note that \( W \) can be a considerable fraction of the grain diameter for thick films. For example for \( L = 500 \) nm and \( \alpha = 1^\circ \), one has \( W = 8.7 \) nm. Writing the ratio \( W / D \equiv l \tan \alpha_{av} \) with \( l = L / D \) the aspect ratio of the average grain, one can express the areas as \( \alpha_1 = (1 - l \tan \alpha_{av})^2 \) and \( \alpha_2 = (1 - \alpha_1) \). Thus for an average grain diameter of \( D = 100 \) nm, the fractional affected area \( \alpha_2 \) is 17% of the total film area for the above numbers. Taking the area weighted average of the \( P-E \) loops of, respectively, the unaffected and affected areas of the

---

**Figure 5.** (a) Left: schematic cross section of film with tilted dielectric grain boundaries, with average tilt angle \( \alpha_{av} \). \( D \) (L) is average grain diameter (length or film thickness), \( W \) is average width of grain boundary area; right: simplified representation. (b) Saturation and remanent polarization normalized to the theoretically expected value for film without grain boundaries. The full curve is a fit with equation (4). (c) Effective dielectric layer thickness obtained from measured remanent polarization and from the slope of the \( P-E \) loop at \( E = E_c \). The lines are linear fits.
device, specifically of the $P_t$ values, one obtains the effective remanent polarization

$$P_{t_{\text{eff}}} = P_{t1} \left[ a_1 + p \left( 1 - a_1 \right) \right] \approx P_{t1} \left[ 1 - 2 \left( 1 - p \right) \alpha_{av} \right]. \quad (4)$$

Here, we will use $p = P_{t2}/P_{t1}$ as a fitting parameter. The right-hand approximation is for small $\alpha_{av}$. Fitting the experimental (001) films’ $P_t$ data with equation (4) results in the fit parameters $P_{t1}/\phi P_0 = 0.87$ and $p \ell = 2.7$. Estimating $l \approx 5$ one has $p = 0.6$ and $P_{t2}/\phi P_0 = 0.53$. Thus it follows from this simple model that the remanent polarization in the grain boundary affected regions $\alpha_2$ is significantly reduced by the factor $p$ from the expected value. But the fitting shows that also in the non-affected regions $\alpha_1 P_{t1}$ is reduced to 87% of the theoretical value. The latter reduction might be ascribed to an additional thin dielectric layer in areas $\alpha_1$ and $\alpha_2$. The (110)-film data point deviates from the model. The large (normalized) effective remanent polarization value indicates that $P_{t1}$ is not or only slightly reduced from the theoretical value and that the effect of the grain boundaries is small. We think that this is due to the different nature of lattice mismatch at the grain boundaries in the (110) as compared to the (001) films. Secondly, the (110) film shows the characteristics of the nanodomain phase, whereas the other films still have macroscopic tetragonal domains [21, 22].

In deriving equation (4) the only assumption was that in the areas $\alpha_1$ and $\alpha_2$ the remanent polarizations are different, without the need to specify the cause of this reduction. It was already suggested that the cause of this reduction is the dielectric character of the grain boundaries. As stated above even for very thin dielectric layers a significant reduction of $P_t$ is possible [13]. An upper bound for the remanent polarization of a PFE-capacitor with a thin dielectric layer was derived as

$$P_t = K \frac{\varepsilon_0 \varepsilon_{eq} L}{d} E_c. \quad (5)$$

Here $E_c$ is the coercive field, $d$ the thickness of the thin dielectric layer and $K \leq 1$ a constant. The upper bound is for a capacitor with a rectangular $P$-$E$ loop, affected by a dielectric layer. For small $d/\varepsilon_{eq}$ values the equal sign is a good approximation, so that one can obtain an effective value $\bar{d} \equiv \left( d/\varepsilon_{eq} \right)_{\text{eff}} = L E_c / P_t$ from the measured values for $E_c$ and $P_t$. (Here effective refers to the effect of both nearly vertical dielectric grain boundaries and an in plane dielectric layer, that might be present.) In figure 5(c) the values for the various films are shown as function of the angle $\alpha_{av}$. A linear relation between $\bar{d}$ and the tilt angle is found, $\bar{d} \approx \left( \bar{d}/\alpha_{av} \right)_{\text{eff}} \alpha_{av} + \left( \bar{d}/\alpha_{av} \right)_{0} = p_1 \alpha_{av} + p_2$. The term linear in $\alpha_{av}$ (with coefficient $p_1 = 1.9 \left( \text{V m}^2 \text{C}^{-1} \right)$ per degree) is attributed to the change of the effective dielectric constant of the system with grain boundary tilt, whereas the constant term $\left( \bar{d}/\alpha_{av} \right)_{0} = p_2 = 3.8 \left( \text{V m}^2 \text{C}^{-1} \right)$ can be ascribed to the effect of vertical grain boundaries plus any additional dielectric layer present in the capacitor. The latter could be dielectric layers present at the electrode interfaces (as already suggested by the fitting of $P_{t_{\text{eff}}}$), but also in plane oriented grain boundaries.

Assuming that the dielectric layer thickness is of the order of 1 nm, one estimates from the value $p_2$ that $\varepsilon_{eq} \approx 30 d_\parallel$ (nm) over the whole capacitor area. This seems a reasonable value for a non-ferroelectric dielectric. Assuming that the dielectric constant of the grain boundary is the same for the devices implies that the increase of $\bar{d}$ with tilt angle is due to an increase of the grain boundary thickness. This is plausible since with increasing tilt the angular lattice mismatch at the grain boundary increases and the thickness over which the lattices are connected (by probably largely amorphous material) is likely also increased.

It seems rather fortuitous that the $\bar{d}$ data point of the Epi(110) sample lies on the line through the data points of the (001) oriented samples, whereas $P_t$ does not follow the modeled dependence for the (001) samples. This may be due to the very different nature of the grain boundaries in the Epi(110) film as compared to the (001) samples.

3.3. Coercive field due to surface and grain boundary pinning

In figure 6 the coercive field (determined as $E_c = (E_c^- - E_c^+)/2$) is plotted as a function of the angle $\alpha_{av}$. The coercive field increases approximately linearly with a factor 2 over the range of tilt angles considered. Polarization switching arises from the nucleation and movement of 180° domain walls. As discussed in [23] the experimental data for thin films in literature indicate that $E_c$ is determined by surface pinning of the domain walls and the nucleation of the walls. The surface pinning arises from surface inhomogeneities. In the films considered here there are two types of surfaces: the interfaces with the electrodes and the grain boundaries. The domain walls separating ferroelectric domains with opposite polarization directions are perpendicular to the film. These domain walls can therefore pin at the film surfaces and cross the grain boundaries for tilted grain boundaries (figure 6(a)). When the 180° domain walls move through the film they can be pinned everywhere at the film surface, but in addition also in the grain boundaries, for a fraction $\alpha_2$ of the surface area. Therefore we conjecture that the domain wall pinning scales with the area $\alpha_2$ that is affected by the grain boundaries, thus that the coercivity increases as $E_c = E_c(0(1 + \alpha_2))$. Here, we have assumed a priori that the pinning strength of the grain boundaries is equal to that of the electrode interfaces. After substitution of the expression for $\alpha_2$, we find in lowest order in $\alpha_{av}$

$$E_c \approx E_c(0) \left( 1 + 2l \alpha_{av} \right). \quad (6)$$

From fitting the experimental values one obtains $E_c(0) = 2.80 \times 10^6 \text{V m}^{-1}$ and $l = L/D = 4.9$. The latter is the same value as found from fitting the independent dielectric constant and remanent polarization data. This model indicates that the coercive field strength can be increased strongly by increased tilting of the grains, but also by increasing the film thickness–grain size ratio $l$. On the other hand, it was found experimentally [23] and theoretically [24] that $E_c$ decreases with $1/L$. Assuming that in the experiments the tilt angle remained constant when $L$ was varied one has $E_c(0) = C/L$, with $C$ a constant. Using this in equation (6), one finds that $E_c = C \left( \frac{1}{l} + \frac{\alpha_{av}}{D} \right)$, saturating at $2\alpha_{av}/D$ for large thicknesses, where the pinning is dominated by the grain boundaries.
while for thin layers the pinning is dominated by the $1/L$ dependence. This predicted saturation in thicker films might provide an additional experimental check on the thickness dependence of the coercive field.

Since $I$ is found to have the same value as determined from independent measurements, we find that the prefactor $E_{c0}$ is the same for the contribution of the electrode interfaces and the grain boundaries to $E_c$. This means that the energy landscape for the intersection between the domain wall and the grain boundary in the different films due to inhomogeneities is the same as for the intersection between the domain wall and the electrode interface. The differences between the grain boundaries of different films, in terms of pinning, are negligible, despite the fact that in Epi(001) films these are composed of only slightly mismatched (in tilt and lateral and vertical position) lattice planes, whereas in the SG(100) these are largely mismatched (especially with respect to the angles in the ip directions). Thus one has to conclude that the pinning is mainly due to the discontinuity of the PFE crystal lattice at the grain boundaries, respectively due to the transition from the PFE to the electrode material, be it a pure metal or metallic oxide. A common parameter between all these interfaces is the roughness of these planes. Lebedev and Sigov derived a model \[24\] that attributes the pinning to the surface roughness. In this model the coercive field scales as $E_c = (\alpha/L) \exp\left[-(V_0/V)^2\right]$, with $\alpha$ and $V_0$ constants and $V$ the amplitude of the potential landscape of the inhomogeneities. $V$ is proportional to the roughness. It was estimated that $V_0 \approx V$ for a few unit cell roughness. Thus with decreasing roughness the coercivity also decreases exponentially. Further the data indicate that the coercive field does not depend on the dielectric properties of the grain boundary (i.e. the parameter $d/\varepsilon_d$), but only on its fractional area $a_2$, thus on the grain boundary tilt and density. This again indicates that the roughness of the electrode and grain boundary surfaces is the main cause of the domain wall pinning. For $a_2 = 0$ the approximately unit-cell thick 180° domain walls do not cross the grain boundaries and $E_{c0}$ is only due to the electrode interfaces. The domain wall is pinned at the bottom and the top electrode, thus $E_{c0}$ corresponds to the combined pinning effect of both interfaces. The fact that the same coefficient is found for the grain boundary, suggests that the domain wall is pinned at both sides of the domain wall separately, as depicted in figure 6(a). If the grain boundary would act as a single pinning point it would be rather coincidental that the pinning force of the grain boundary is twice that of a single film–electrode interface.

3.4. Slope at coercive field

Another characteristic of the effect of a dielectric layer in a PFE capacitor is the change of the slope of the $P$–$E$ loop (slanting of the loop), specifically at $E_c$. In the dielectric layer model \[13\] this is found from the expression for $E_f$ as

$$L \left[ \frac{\partial E}{\partial P} \right]_{E_c,\alpha_\nu} - \left( \frac{\partial E_f}{\partial P} \right)_{E_c} = \left( \frac{d}{\varepsilon_0 \varepsilon_d} \right)_{\alpha_\nu} \equiv \tilde{d}. \quad (7)$$
Here we have introduced explicitly a dependence of the slope on the angle $\alpha_{\text{GW}}$. For a perfectly square loop the second derivative equals 0 ($\partial^2 P/\partial E)_{E_c} \rightarrow \infty$). However, for the films considered here, even for the films with $\alpha_{\text{GW}} = 0$, this is not the case, since we have seen that $P_c(\alpha_{\text{GW}} = 0)$ is reduced from the theoretical value, thus one also expects that $L(\partial E_l/\partial P)_{E_c} = S_0$ is a finite, non-zero positive constant. Decomposing the right-hand side of equation (7) in an $\alpha_{\text{GW}}$ dependent term and a constant term, we fit the measured slope in figure 5(c), with $S = L(\partial E_l/\partial P)_{E_c} = (\partial d/\partial a_{\text{GW}})_{E_c} + [\partial d]_{a_{\text{GW}} = 0} + S_0 = q_1 a_{\text{GW}} + q_2$, giving $q_1 = 2.2$(Vm$^2$/C$^1$ per degree) and $q_2 = 1.3$(V/m$^2$/C$^{-1}$). These independent methods predict equal slopes $\partial d/\partial a_{\text{GW}} = q_1 = p_1$, which in good approximation is indeed found experimentally. The offset between both curves is attributed to the assumption of a rectangular intrinsic loop (i.e. $K = 1$) in using equation (5) to obtain values for $(\partial d)_{\text{eff}} = p_1 a_{\text{GW}} + p_2$. For $K < 1$ the data points shift down toward the line $S = q_1 a_{\text{GW}} + q_2$. It was already discussed that the intrinsic loop is not expected to be rectangular, explaining the shift.

3.5. Dielectric constant

The effective (high field) dielectric constant of the films, $\varepsilon_{\text{eff}}$, is determined from the slope of the saturated $P$-$E$ loop. The obtained values are given in table 2 and shown in figure 7 as a function of $a_{\text{GW}}$. Again there appears a clear relation between the effective dielectric constant and the grain boundary tilt angle. One can establish this relation assuming that the capacitor is composed of a fractional area $a_1$ where the electrical field lines perpendicular to the electrodes do not cross a grain boundary and the area $a_2$, where this is the case. In area $a_1$ the capacitor is buildup of the PFE layer with a dielectric constant equal to a bulk film value $\varepsilon_{l}$, whereas in area $a_2$ it is built up of two layers, due to the PFE and the grain boundary respectively, with a different effective dielectric constant $\varepsilon_2$. $\varepsilon_2$ is strongly dependent on the grain boundary tilt angle (see appendix B) and the dielectric constant of the grain boundary, $\varepsilon_{GB}$. The complete device is then a parallel circuit of these two capacitors and one obtains for the effective dielectric constant

$$\varepsilon_{\text{eff}} = \varepsilon_l \frac{1}{1 + \varepsilon_2 / a_1} \left( 1 + \frac{a_2}{a_1} \left( \frac{\varepsilon_{GB}}{\varepsilon_l} \right) \right). \tag{8}$$

In this model the angle dependence of $\varepsilon_{\text{eff}}$ enters predominantly through the volume ratio $a_2/a_1$ and is therefore dominated by the right-hand prefactor in equation (8), given by the dashed, black line in figure 6(c), obtained for $\varepsilon_l = 520$ and $\varepsilon_2 = 0$, whereas the red line is according to equation (8), with $\varepsilon_{GB} = 30$. The simple model describes surprisingly well the experimentally found change of the dielectric constant for the various films. This indicates that the underlying assumptions: (i) the dependence on the ratio of areas that are affected and not affected by the grain boundaries and (ii) the dielectric constant $\varepsilon_2$ does not depend strongly on the different fabrication processes and the grain boundary tilt angle are plausible. The reason for the increased value of the dielectric constant of the SG(100) film, despite the larger average tilt angle, may be that the crystallographic structure not only consists of near vertical grain boundaries but also of more or less horizontal grain boundaries in the film, due to the production process. The granular structure is thus more like stacked boxes separated by dielectric layers. In contrast, the PLD films are predominantly made up of bottom-to-top continuous grains, without horizontal grain boundaries.

3.6. Piezoelectric coefficient

In literature several mechanisms that can influence the piezoelectric coefficient, $d_{33}$, have been investigated [25–29]. A significant effect of grain size in BaTiO$_3$ polycrystalline films on $d_{33}$ as function of pressure amplitude was found by Damjanovic and Demartin [29]. However, there is little known about the effect of grain boundaries.

In figure 4(c) it is seen that the effective $d_{33,\text{eff}}$ coefficient decreases approximately linearly with increasing $a_{\text{GW}}$, both before and after poling for the PLD films. The data points for the SG film drop far below this linear trend. The linear dependence is found straightforwardly if one assumes that in the grain boundary area $a_2$, the displacement $\Delta z_2$ is a fraction $f$ from the displacement $\Delta z_1$ in area $a_1$. The measured area average $d_{33}$ is then

$$d_{33} = \frac{\Delta z_1}{\Delta V}a_1 + f a_2 \Delta z_1 \frac{\Delta V}{\Delta V} = d_{33}^{\text{pol}} a_1 f (a_{\text{GW}}) (1 - f) + f, \tag{9}$$

where $d_{33}^{\text{pol}}$ is the piezoelectric coefficient of the area of the device that is not affected by the grain boundaries, but which may be affected by, for example, domain walls and domain wall pinning. In figure 4(c) the curves are fitted to the PLD data points with $l = 5$, $d_{33}^{\text{pol}}$(polled) = 125 pm V$^{-1}$ and $f = 0.85$, respectively $d_{33}^{\text{pol}}$(unpoled) = 123 pm V$^{-1}$ and $f = 0.75$. First consider the piezoelectric coefficient of the bulk of the grains, $d_{33}^{\text{pol}}$. The theoretical value $d_{33}^{\text{pol}}$ for an unclamped film is reduced to that of a film clamped to the substrate, $d_{33}^{\text{clamped}} = d_{33} - 2d_{33} \frac{a_1}{a_1 + a_2}$ (see footnote 6). This value compares very well with the fitted parameter $d_{33}^{\text{pol}}$, indicating that the bulk of the grains can be considered as being clamped by the substrate. The effect of the grain boundaries enters through the factor $f$ and the area fraction $a_1 (f, a_{\text{GW}})$. Following the model the grain boundaries reduce $d_{33}^{\text{clamped}}$ by 15–25%. This reduction should be ascribed to field screening. The large decrease in $d_{33}$ for the SG film is ascribed to the additional, large effect of ip grain boundaries, arising from the multiple depositions.

4. Conclusions

We have fabricated epitaxial thin film capacitor structures of PbZr$_{0.45}$Ti$_{0.55}$O$_3$ on Si substrates, in four different ways, using PLD and SG techniques, resulting in different crystalline structures. The crystalline structures were analyzed by XRD and SEM. The devices were poled and their piezoelectric and ferroelectric properties were measured before and after poling. We have found a systematic correlation between the
rocking curve width (characterized by an average angle $\alpha_{av}$) and these properties.

Assuming that the bulk of the grains in the films have the same crystal structure and properties, we attribute all differences in the properties of the films to the differences in grain boundaries. We have established simple relations between the observed spread in the average tilt angle $\alpha_{av}$ of the lattice plains of the grains in the PFE thin film capacitors and their (large signal) properties, specifically the high field dielectric constant $\varepsilon$, the coercive field $E_c$, and the slope $S$ of the $P$-$E$ loop at $E_c$. We have assumed that the average tilt angle $\alpha_{av}$ is a measure for the tilt of the grain boundaries between the grains. The tilted grain boundaries are considered as a thin dielectric layer, and their average effect is modeled as a thin dielectric layer adjacent to the electrode in the area made up of the projection of the grain boundaries on the electrode. The PFE properties are calculated as being due to two parallel PFE capacitors, one with and one without this additional effective dielectric layer. With respect to the coercivity, the 180° domain walls are assumed to be pinned at both sides of the grain boundary and the electrode interfaces. The small-signal, effective piezoelectric parameter $d_{33,eff}$ is only slightly influenced by the grain boundaries.

It is somewhat surprising that the models, in essence based on simple geometric scaling of the properties with the areas affected and not affected by the grain boundaries, work so well. However the systematic change of all parameters with grain boundary tilt angle, is a strong indication of the importance of control over the crystalline growth. The least affected properties are obtained for the most epitaxial films, with grain boundary tilt angle, is a strong indication of the importance of control over the crystalline growth. The least affected properties are obtained for the most epitaxial films, and these properties.

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Appendix A. Polarization in the (110) nanodomain phase

The net polarization of the rhombohedral phase of a (110) oriented film, made up of $c45$ (with polarization vector under 45° with the film plane) and $a$ (with polarization in plane) nanodomains, can be described by

$$
\vec{P} = P(\phi_{45}) \begin{bmatrix}
\phi_{45}/2 & 1/\sqrt{2} \\
0 & 1/\sqrt{2}
\end{bmatrix} + P(\phi_{45}) \begin{bmatrix}
\phi_{45}/2 & -1/\sqrt{2} \\
0 & 1/\sqrt{2}
\end{bmatrix} + (1-\phi_{45}) \begin{bmatrix}
0 & 1 \\
0 & 0
\end{bmatrix}
$$

(A.1)

$$
P(\phi_{45}) = \frac{1}{\sqrt{1 - 2\phi_{45}^2 + 2\phi_{45}}}.
$$

(A.2)

The right-hand vectors of A.1 are respectively the polarization vectors of the $c45$ domain, aligned oop in the positive $x$-direction, oop in the negative $x$-direction and ip in the $y$-direction. The prefactor $P(\phi_{45})$ depends on the domain fraction $\phi_{45}$ of $c45$ domains, such that $|\vec{P}|$ is constant. Here we have assumed that there are equal fractions of $c45$ domains aligned in positive and negative $x$-direction. This implies that on changing $\phi_{45}$ the net polarization rotates in the $yz$-plane, as can be seen from equation (A.2). The definition of $|\vec{P}|$ follows from the assumption that the polarization vector only changes direction, but does not change strength. In this paper we identify $|\vec{P}|$ with the bulk polarization vector of the underlying tetragonal composition. The polarization vector described by equations (A.1) and (A.2) applies to the case of PZT growth on SrTiO$_3$(110) substrates. (110) films on Si show multiple ip twinning. That case can be described by a superposition of polarization vectors in which the ip vector components are rotated over fixed angles. However, the oop components, in which we are interested here, are not affected by the twinning. Therefore, we can restrict ourselves to a description by equations (A.1) and (A.2).

It is straightforward to show that

$$
P(\phi_{45}) = \frac{|\vec{P}|}{\sqrt{1 - 2\phi_{45}^2 + 2\phi_{45}^2}}.
$$

(A.3)

The oop component of the polarization, $P_3(\phi_{45})$, and the angle $\theta_p$ of $\vec{P}$ with the $z$-axis are

$$
P_3 = -\sqrt{\frac{\phi_{45}}{1 - 2\phi_{45}^2 + 2\phi_{45}^2}}, \quad \theta_p = \alpha \cos \left(\frac{\phi_{45}/\sqrt{2}}{\sqrt{1 - 2\phi_{45}^2 + 2\phi_{45}^2}}\right).
$$

(A.4)

Assuming that the polarization can easily rotate in the $zy$-plane because of easy shift of the domain walls between the nanodomains, polarization rotation corresponds to a change of $\phi_{45}$. In saturation the polarization vector is oriented oop as much as possible, i.e. $\phi_{45} = 1$, hence $P_3 = |\vec{P}|/\sqrt{2} \approx 0.71|\vec{P}|$. In zero field, in the rhombohedral phase the polarization is in the body diagonal direction, here that is for $\theta_p \approx 35^\circ$, i.e. for $\phi_{45} \approx 0.59$ and thus $P_3 \approx 0.58|\vec{P}|$. Note that if the polarization vector cannot rotate, the value of $\phi_{45}$ is fixed, e.g., by substrate induced thermal strain, and one finds that $P_3 = P_z \leq |\vec{P}|/\sqrt{2}$. Therefore finding saturation and remanent polarization values as given above, are a strong indication for the presence of nanodomains. Further, only when the unit cell is perfectly rhombohedrally distorted one expects the polarization to be along the body diagonal. Any deviation may rotate the polarization vector away from this direction, giving a smaller or larger $P_z$ value.

As discussed elsewhere, the nanodomain phase also shows deviating XRD patterns, most notably the single reflection of the oop lattice parameter, where one would expect two slightly different parameters for respectively the $c45$ and the $a$ domains.
Appendix B. Effective dielectric constant of cross section with tilted grain boundary

The electrical field line perpendicular to the electrodes traverses both the grain boundary over a length $d_{\text{eff}} = d / \sin \alpha$ and the ferroelectric film over a length $L - d_{\text{eff}}$ (here we assume for simplicity that the field lines are not ‘broken’ when passing through the grain boundary). Considering this as a stack of two dielectrics, with dielectric constants $\varepsilon_{\text{DW}}$ and $\varepsilon_f$ respectively, one obtains for the inverse of the capacitance per unit area of the resulting capacitor in area $a_2$

$$\frac{a_2}{C_{a_2}} = \frac{L}{\varepsilon_2} = \frac{d_{\text{eff}}}{\varepsilon_{\text{DW}}} + \frac{L - d_{\text{eff}}}{\varepsilon_f}.$$  \hfill (B.1)

From this follows the effective dielectric constant in area $a_2$

$$\varepsilon_2 = \frac{\varepsilon_{\text{DW}} \left( \frac{d_{\text{eff}}}{L} + \left( 1 - \frac{d_{\text{eff}}}{L} \right) \frac{\varepsilon_{\text{DW}}}{\varepsilon_f} \right)^{-1}}. \hfill (B.2)$$

In the small $\alpha_{\text{av}}$ approximation one has $\varepsilon_2 \approx \varepsilon_{\text{DW}} \frac{a_{\text{av}} L}{d}$. $\varepsilon_2$ is a rapidly increasing function of $\alpha_{\text{av}}$, showing the large effect of a tilted grain boundary.

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