Role of texture on the antiferroelectric switching of PbZrO$_3$ films

Cosme Milesi-Brault,$^{1,2}$ Nicolas Godard,$^{1,2}$ Stéphanie Girod,$^1$ Yves Fleming,$^1$ Sebastjan Glinšek,$^1$ Emmanuel Defay,$^{1,2}$ Mael Guennou$^{2,*}$

$^1$Materials Research and Technology Department, Luxembourg Institute of Science and Technology, 41 rue du Bril, L-4422 Belvaux, Luxembourg
$^2$Department of Physics and Materials Science, University of Luxembourg, 41 rue du Bril, L-4422 Belvaux, Luxembourg

Antiferroelectrics have been recently sparking interest due to their potential use in energy storage and electrocaloric cooling. Their main distinctive feature is antiferroelectric switching, i.e., the possibility to induce a phase transition to a polar phase by an electric field. Here we investigate the switching behavior of the model antiferroelectric perovskite PbZrO$_3$ using thin films processed by chemical solution deposition in different geometries and orientations. Both out-of-plane and in-plane switching configurations are investigated. We discuss the different characteristics of the switching loops and the switching fields in relation with the texture of the films, and show that those are consistent with a switching to a rhombohedral polar phase. We finally estimate the importance of crystallite orientation and film texturation in the variations observed in the literature.

Antiferroelectric (AFE) materials are recognized by a set of experimental signatures: a phase transition between two non-polar phases exhibiting an anomaly of the dielectric constant, antiparallel atomic displacements identified as sublattices of electric dipoles, and finally, in their low-symmetry phase, a characteristic double hysteresis loop of the polarization as a function of electric field $P(E)$, which reflects the presence of a polar polymorph close in energy to the non-polar ground state $^{[1,2]}$. This double loop is probably the most remarkable signature of AFE materials, and this "antiferroelectric switching" the property that is most promising for a practical use of antiferroelectric materials, as exemplified by capacitors for energy storage $^{[3]}$ or antiferroelectric tunnel junctions $^{[4]}$. Yet, it has been studied in details in a very limited number of cases.

The model antiferroelectric perovskite, PbZrO$_3$, is in that respect particularly complex. Its AFE transition involves complex couplings and several order parameters, including oxygen octahedra tilts $^{[5,7]}$. In the AFE phase, lead displacements are considered to be along the orthorhombic $\alpha$ axis (i.e., along a [110]-pseudo cubic direction). The transition to the polar phase, however, probably does not proceed through a simple flipping of a sublattice but by a transition to a totally different phase with a different pattern of octahedra tilts. It is usually admitted that the polar phase of PbZrO$_3$ is rhombohedral with polarization along a [111]$_{pc}$ direction; as inferred from the presence of a rhombohedral phase in the phase diagram of PZT at low Ti concentrations $^{[8]}$. First-principle calculations have confirmed that the energy of the polar rhombohedral phase is indeed very close to the antiferroelectric polymorph $^{[9,10]}$, but other structures have been proposed $^{[11,12]}$. Experimentally, early diffraction, optical and dielectric studies seemed to confirm the rhombohedral hypothesis $^{[13,10]}$, but there is in general little direct experimental evidence for the symmetry and crystal structure of this polar phase.

This relative lack of knowledge, even on materials considered as models, hinders the optimization of antiferroelectric switching. The difficulty largely finds its origin in the very high electric fields needed to switch bulk samples at ambient conditions. Thin films or multilayer capacitors, in contrast, can usually sustain much higher fields before breakdown $^{[17]}$. In this work, we use this approach and investigate the importance of film texture, i.e., the crystallographic orientation of the grains, on the switching properties of antiferroelectric PbZrO$_3$ films. We demonstrate both out-of-plane and in-plane switching, using two different sample geometries. We compare their characteristics within a simple switching model, and estimate the importance of this parameter based on a review from literature data.

Lead zirconate (PbZrO$_3$) films were deposited by chemical solution deposition (CSD) on two different substrates: platinized silicon (Si $675\ \mu$m/SiO$_2$ $500\ \text{nm}/\text{TiO}_x$ $20\ \text{nm}/\text{Pt} \ 100\ \text{nm}$) and fused silica covered with a $23\ \text{nm}$-thick ALD-deposited HfO$_2$ buffer layer. In both cases, seeds of lead titanate (PbTiO$_3$) were deposited prior to PbZrO$_3$. Lead zirconate solutions were processed following a standard process commonly used for PZT $^{[15]}$ (details in the supplementary information). Films with thicknesses of $85\ \text{nm}, 170\ \text{nm}$ and $255\ \text{nm}$ were obtained. On platinized silicon, Pt electrodes were sputtered to obtain a Metal-Insulator-Metal (MIM) geometry, as sketched in Fig. 1(a). On fused silica, Pt interdigitated electrodes (IDE) with a gap of $5\ \mu$m were sputtered and patterned with lift-off photolithography (Fig. 1(b)). Surface and cross-section imaging of the films was done by a Helios NanoLab scanning electron microscope from FEI; the surface appears to be non-porous and defect-free (Fig. 1(c)), and the cross-sections show dense films of homogeneous thickness with a columnar structure (Fig. 1(d)).

X-ray diffraction measurements were performed on a Bruker D8 Discover diffractometer equipped with a Goebel mirror and a 5-axis cradle in the Bragg-Brentano geometry ($\lambda_{Cu(K\alpha)} = 1.541\ 84\ \text{Å}$) and confirmed that the films crystallized in the perovskite phase, without any indication of parasitic phase (Fig. 1(a)). Besides, all films show a pronounced preferred orientation along a [001]$_{pc}$ direction as shown in Fig. 1(e). Comparing with a refer-
Interdigitated electrodes (IDE)

The electric field is simply defined as the applied voltage, we followed the procedure described in Ref. [21] and calculated the electric field as $E = V/(\Delta a)$ where $a$ is the gap between IDE fingers and $\Delta a$ depends only on the film thickness $t_f$ as $\Delta a \approx 1.324 t_f$. Qualitatively, the double loops for the different sample thickness show a similar trend: the samples show some variations, the loop at zero field is significantly more opened. Finally, we compare in Fig. 2c. the double hysteresis loops in both MIM and IDE geometries for 255 nm-thick samples: the switching in the IDE sample occurs at a lower electric field, and the current peak is significantly broader. We also include in this comparison the sample with a lower preferred orientation. It is markedly different from the other MIM samples, with broader current peaks at lower electric fields. The difference clearly exceeds the variations seen with sample thickness, so that we attribute the difference primarily to the different texture of the films. Overall, the sample with the best orientation in the MIM geometry is the one displaying the sharpest switching behaviour, with thin current peaks and a correspondingly sharp hysteresis.

In addition to the main antiferroelectric switching signal, we observe in the $I(V)$ curves a smaller but significant current peak at lower electric fields, typically below 100 kV cm$^{-1}$. This peak is particularly noticeable in the IDE geometry (Fig. 2b.), but is also present in the MIM geometry for the thinner films (inset in Fig. 2a.). The presence of additional ferroelectric displacements of lead ions is not unheard of in PbZrO$_3$ in the context of structural studies [22,23], and similar features have even been reported in the switching loops of PbZrO$_3$ thin films [24]. However, in our case, this contribution could also originate from the presence of the additional PbTiO$_3$ seeds and we cannot make a conclusive statement about its origin. This is therefore left for future work.

We now discuss the characteristics of the AFE switching loops in relation to the film textures determined by XRD. We will assume that the polar phase of PbZrO$_3$ is rhombohedral with a polarization along a (111)$_{pc}$-direction, and that the switching occurs when the energy...
of the polar phase under field reaches some threshold. For a given crystallite, the switching field is expected to be lowest if the field is applied along a (111)pc-direction, highest for a field applied along (001)pc-direction, and to otherwise scale with $1/\cos \theta$ where $\theta$ is the angle between the applied electric field and the closest (111)pc-direction. For a polycrystalline film, switching will occur according to a distribution of switching events and fields determined by the texture of the film.

This crude toy model is qualitatively consistent with the observations. With a perfect texture, i.e. all grains oriented along a (001)pc direction, the switching field in the MIM geometry is the same for all grains, therefore the sharp current peak, and with the highest possible value (Fig 3b). In contrast, the switching peaks for the film with a lower degree of preferred orientation are found to be broader and at lower field values. Similarly, when the field is applied in-plane, we expect a distribution of switching fields. The grain orientations for minimum and maximum switching fields are shown schematically in Fig. 3c, whereby the field is constrained by texture to lie into a (001)pc plane. The lowest and highest switching fields will be obtained when the electric field is aligned along a (110)pc direction and a (100)pc direction, respectively, of the crystallites. The former happens to be equal to the field in the MIM geometry; the latter is expected to be lower by a factor of 1.41. These field values are qualitatively coherent with Fig. 2c. Indeed, in the MIM geometry, the switching current peaks are much sharper (FWHM $\approx 30$ kV cm$^{-1}$) than in the IDE case (FWHM $\approx 100$ kV cm$^{-1}$) and also shifted towards lower electric field values.

The agreement is only qualitative and the ratios between switching fields do not match the estimations based on geometry only. This may find its origin in the other parameters affecting the values of the switching fields. This might include slightly different strain states, as a result of the different thermal expansion coefficients of silicon vs. fused silica. Note that in both cases, this mismatch is expected to drive the PbZrO$_3$ films in a tensile strain state. Another effect might come from grain boundaries, which are mostly aligned out-of-plane because of the columnar grain shape, and might affect differently the building-up of the electric field depending on the geometry. However, the general picture remains that grain orientation is here the main parameter governing the trends of the switching fields.

Having established how the texture of our films affects
Figure 4. Comparison between our data and sol-gel/PLD/sputtering samples from literature of switching fields $E_{AFE\rightarrow FE}$ and saturation polarization $P_s$. Details about orientations and other aspects are given in the supplementary information.

Figure 4 reveals some clear trends. Most importantly, for $E_{AFE\rightarrow FE}$ and $P_s$, which are more commonly reported, and defined $P_s$ as the saturation polarization as depicted in Fig. 2a. There is inevitably some uncertainty in the process of defining, reporting and reading those data, and generous error bars have been estimated to be ±10% of the $E_{AFE\rightarrow FE}$ and $P_s$ values. All data are graphically summarized in Fig. 4 and the full list, with the details of references and additional data, is given in the Supporting Information.

Fig. 4 reveals some clear trends. Most importantly, for sol-gel processed films, we notice that orientation effects can account for at least one half of the value distribution. This points to the importance of texture control as the essential way to minimize – or control in general – the AFE switching field. The lowest switching fields, of the order of 150 kV cm$^{-1}$ are indeed obtained for (111)$_{pc}$-oriented films and IDE samples seem to be in the lower range of the switching fields $E_{AFE\rightarrow FE}$ while the (001)$_{pc}$ samples tend to have higher $E_{AFE\rightarrow FE}$. This distribution is coherent with our simple model presented in Fig. 3. The polarization values, on the other hand, do not seem easily comparable. The values are spread without any real noteworthy trend. First, PLD samples tend to have slightly higher $P_s$ values than sol-gel samples. However, polarization should also be maximum in this (111)$_{pc}$-orientation which does not seem to be the case. We attribute this to the fact that the polarization is more difficult to quantify than the switching field, because of different definition chosen, and various sources of spurious currents that modify the shapes of the switching loops.

Finally, let us point out that the rhombohedral structure for the polar phase of PbZrO$_3$ was here hypothesized, and found consistent with the observations. In contrast, the same reasoning with the assumption of a tetragonal, or tetragonal-like polar structure, i.e. with a polarization aligned with or close to a (001)$_{pc}$ direction, would be completely inconsistent with the observations, even at a qualitative level: the lowest fields in our films would be expected in the MIM geometry for the fully oriented films, which is clearly not the case. This gives a strong argument to discard the hypothesis of a tetragonal-like polar phase of PbZrO$_3$. More generally, in the context of antiferroelectrics where switching of oriented single crystals may be difficult to achieve, studies of textured films appear as a promising way to address this structural question.

In summary, we have presented the synthesis and characterization of oriented polycrystalline antiferroelectric PbZrO$_3$ films. X-ray diffraction shows highly-oriented and more randomly oriented PbZrO$_3$ thin films and electrical measurements confirm that a sharpest transition is directly linked to better orientation. AFE switching is demonstrated in a standard MIM geometry, but also more originally by applying the electric field in the plane of the films via IDEs. By comparison with the available data in the literature, we show that film or ceramic texturation can be a major way to control the switching field. Besides, our results are consistent with the generally accepted hypothesis of a rhombohedral, or rhombohedral-like, structure of the field-induced phase of PbZrO$_3$. Studying the switching of oriented films in various geometries therefore appears as a convenient approach to investigate the structure of field-induced polar phases in antiferroelectric materials in general.

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Processing details disclosed in the present contribution are protected by a patent filed in June 2020 (N. Godard, S. Glinšek, A. Blázquez Martínez, E. Defay, patent LU101884, 2020).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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