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The arrangement of domains and domain walls is a crucial factor in determining the functional properties of ferroelectric materials. Here, we track the ferroelectric domain formation mechanism in ultrathin PbTiO$_3$ films in real time during epitaxial growth using in-situ optical second harmonic generation (ISHG). In combination with complementary ex-situ piezoresponse force microscopy and SHG imaging, we unambiguously identify the tensile-epitaxial-strain-induced partial conversion of out-of-plane-polarized $a$-domains into in-plane-polarized $c$-domains. We further show that in the strongly compressive epitaxial regime the $c$-to-$a$ conversion can be shifted to the early stage of the growth to favor a remarkable randomization in the distribution of $a$- and $c$-domains. This unprecedented access to the domain-formation dynamics constitutes an important step towards deterministic domain architectures in technologically relevant ultrathin ferroelectrics which, in turn, is valuable for the development of functional ferroelectric and piezoelectric structures.

In ferroelectric materials, the morphology of domains and domain walls considerably influences both local nanoscale properties, as well as the macroscopic response to external electric fields.$^{1-4}$ For instance, domains walls separating regions with different spontaneous polarization are currently explored for their locally deviating electrical conductance and field effects with an outreach towards re-writable nano-circuitry.$^{5-8}$ In addition, the lattice-polarization coupling in ferroelectrics allows for the presence of secondary, so-called ferroelastic domains, characterized by their different strain states. This has made ferroelastic domain engineering a factor in the advancement of electromechanical device applications.$^{3,9}$

In the technologically most relevant tetragonal ferroelectric thin films, like BaTiO$_3$ and Pb(Zr,Ti)$_2$O$_3$ (PZT), the domain morphology consists of a mixture of so-called ferroelectric (and ferroelastic) $a$- and $c$-domains with an in-plane and out-of-plane polarization, respectively.$^{9,2}$ Their formation is governed by a complex interplay of strain and electrostatics$^{12-15}$. Furthermore, cross-correlations between the nucleation of $a$- and $c$-domains complicate their formation mechanism. Specifically, the charge accumulation at the domain walls of emerging $a$-domains$^{9,2}$ leads to an electrostatic influence on the $c$-domain growth. Also, strain relaxation may induce inter-conversion of $c$- and $a$-domains. This often leads to non-deterministic domain patterns and hence understanding and control of domain nucleation and evolution have been posing a challenge. Because the $a$-$c$-$c$-domain formation occurs during the epitaxial growth process itself, in-situ investigations are key to shedding light on the topic of domain formation. The extreme environment of the epitaxial growth has, however, remained incompatible with conventional ferroelectric characterization techniques thus far.

Here, we track, in real time, the formation of domains during the epitaxial growth of thin films of the tetragonal ferroelectric model system PbTiO$_3$ (PTO) using in-situ optical second harmonic generation (ISHG)$^{17}$. We complement the thickness-dependent ISHG experiments with spatially resolved ex-situ SHG and piezoresponse force microscopy (PFM) investigations to identify the strain-driven partial conversion of $c$-domains into randomly oriented $a$-domains during the deposition. We further find that triggering $a$-domain formation during the early stage of the growth via substrate-controlled strain tuning results in an extraordinarily randomized distribution of $a$- and $c$-domains. This suggest a handle towards the control of the domain and domain-wall distribution as an alternative to compositionally driven polar disorder at morphotropic phase boundaries.$^{18}$

We start our investigation on PTO as model system for tetragonal ferroelectrics. Epitaxial films with a thickness of 25 nm are grown with pulsed laser deposition on metallic SrRuO$_3$-(SRO)-buffered (001)$_z$-oriented SrTiO$_3$ (STO) and on (110)$_z$-oriented DyScO$_3$ (DSO) substrates. (The c and o subscripts refer to the cubic and orthorhombic structures of STO and DSO, respectively.) These substrates exert $-0.25 ~\%$ (DSO) and $-1.40 ~\%$ (STO) compressive strain with respect to the extrapolated paraelectric PTO unit cell$^{19}$, respectively and therefore offer a platform for analyzing the strain dependent interplay of $a$- and $c$-domain formation.$^{11,20,21}$ The crystalline quality and the strain state of the tetragonal films were characterized by X-ray diffraction (XRD). Fig. 1(a) shows the reciprocal space map (RSM) around the STO (103), reflex, yielding a single PTO peak at an in-plane lattice constant equal to that of STO (equal $Q_a$), consistent with a fully strained film in a pure $c$-domain configuration, as expected from the compressive lattice mismatch.$^{19}$ In contrast, for the PTO film on DSO, the RSM around the DSO (420)$_o$ reflex in Fig. 1(b) exhibits an additional PTO peak at a reduced out-of-plane lattice constant (increased $Q_o$), confirming the presence of $a$-domains in a $c$-oriented matrix.$^{11,20,21}$ The PFM scans for the two films in Fig. 1(c,d) support these findings. Fig. 1(c) depicts an as-grown single-domain state of PTO on SRO-buffered STO with an upwards out-of-plane polarization that can be reversibly switched by applying $\pm 4$ V between the scanning tip and the SRO electrode. For the film on DSO, however, the as-grown state in the PFM scan in Fig. 1(d) reveals an additional typical cross-hatched pattern of $a$-domains polarized along the [001], and [110], directions of the orthorhombic DSO substrate.$^{22}$
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Epitaxial strain can favor lattice distortions and therefore leads to an increased ferroelectric Curie temperature (T\textsubscript{C}) for many ferroelectric systems\textsuperscript{23-25}. In particular for PTO in the thickness range considered here, the strain imposed by STO\textsuperscript{23} and DSO raises the T\textsubscript{C} of bulk PTO (≈875°C) above the growth temperature of T\textsubscript{growth}= 550°C (see Fig. S3). Thus, the PTO/STO/STO and PTO/STO/DSO heterostructures are ideal systems to elucidate the mechanisms behind the formation of domains during epitaxial deposition. Because the PTO growth takes place in the ferroelectric phase, one needs to consider the PTO strain state with respect to the ferroelectric tetragonal (T) unit cell. This results in a higher tensile strain on DSO compared to STO substrates favouring in-plane oriented \(\alpha\)-domains \((\varepsilon_\alpha = +1.04\% \text { and } \varepsilon_\alpha = +0.03\% \text { for DSO and STO, respectively.})\) In order to directly access the polarization of our thin films during growth, we used ISHG as a noninvasive detection technique\textsuperscript{25}. ISHG is a non-linear optical process and describes the frequency doubling of light in matter. SHG emission from a material is only allowed when space-inversion symmetry is broken and therefore makes SHG sensitive to the emergence of ferroelectric order\textsuperscript{17,26,27}. In-situ reflection-high-energy-electron-diffraction (RHEED) monitoring is performed simultaneously in order to relate the ISHG yield to the PTO film thickness with unit cell accuracy.

In Fig. 2, we compare the measured ISHG signal during the deposition of PTO on both of the SRO-buffered substrates. On SRO/STO, the onset of an ISHG signal after 1 nm (4 a.u.) of PTO growth (close-up in Fig. S6) followed by a continuous signal rise is observed, which corresponds to the expected formation of a ferroelectric single-\(c\)-domain state PTO (Fig. 1(a,c)). We note the excellent agreement with the reported critical thickness of PTO of 3 u.c., obtained using in-situ x-ray diffraction experiments\textsuperscript{25}. In contrast to the earlier results, however, the charge screening metallic SRO matrix. Hence, partial conversion of \(c\)-domains to randomly polarized \(a\)-domains poses the most likely explanation for the decrease of ISHG intensity in Fig. 2.

To validate the proposed PTO/STO/DSO multi-domain architecture within the film, we moved to spatially resolved post-growth ex-situ SHG measurements. Since SHG light is only emitted for polarization components in a plane perpendicular to the incident light\textsuperscript{31}, it is possible to select the domain states contributing to SHG by adjusting the sample tilt \(\theta\) as depicted schematically in Fig. 3(a,b) (see also Supplementary Materials Fig. S1).\textsuperscript{33,34} For the case of normal incidence, only in-plane polarization components can contribute (\(c\)-SHG for \(a\)-domains). When introducing a non-zero sample tilt, out-of-plane-polarized components (\(c\)-SHG for \(c\)-domains) come into play as well, with increasing weight for larger angles \(\theta\). On both PTO/STO/STO and PTO/STO/DSO, we applied an electric field using the PFM tip in order to locally reverse the out-of-plane-polarization of the \(c\)-oriented matrix in a square area of 20\(\times\)20\(\mu\text{m}^2\), shown in Fig. 3(c)-e). In addition to the out-of-plane switch, an effective trailing field aligns the in-plane polarized \(a\)-domains along the slow scanning direction\textsuperscript{33,34}.

For the PTO/STO/STO sample the \(\alpha\)-SHG (\(\theta = 0^\circ\)) and (\(c\oplus\alpha\))-SHG (\(\theta = 15^\circ\)) images are shown in Fig. 3(c,d). The lack of \(\alpha\)-SHG in normal incidence in Fig. 3(c) verifies the absence of any macroscopic in-plane polarization for both the as-grown and the switched state. When tilting the sample, the out-of-plane-polarized \(c\)-domains become SHG-active in the as-grown and switched regions with equal amplitude, yet with a 180° relative phase shift. In the vicinity of the written 180° domain wall, destructive interference between SHG light from the oppositely polarized regions manifests as a dark line [Figs. 3(d), S2].\textsuperscript{35}

For the PTO/SRO/DSO film, both \(\alpha\)-SHG and \((c\oplus\alpha\))-SHG images are significantly different. In the \(\alpha\)-SHG image, shown in Fig. 3(e), only the switched region appears bright, indicating the presence of the aforementioned net in-plane polarization induced by the trailing field. The as-grown region, on the other hand, lacks a net \(\alpha\)-SHG response, which points to a random orientation of \(a\)-domains in the pristine state [see Figs. S2, 1(d)]. When tilting the sample to add the \(c\)-SHG contribution, see Fig. 3(f), the dark lines indicating interference at the \(c\)-domain walls appear in addition. We thus conclude that in the pristine state, \(a\)-domains are randomly polarized along ±[001], and ±[110], and embedded in a uniformly polarized \(c\)-oriented matrix as sketched in the insets. Therefore, the ISHG signal evolution in Fig. 2 reveals the partial re-orientation of \(c\)- into \(a\)-domains during the epitaxial depo-
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The intermediate ISHG signal drops in the range between 8 and 18 nm, we have a growing volume fraction of randomly oriented $a$-domains forming at the expense of the originally grown $c$-domains.

Thus, we have shown the conversion of $c$- to $a$-domains during the early stages of ferroelectric PTO thin-film growth caused by tensile epitaxial strain. This domain conversion is absent on lattice-matched SRO-buffered STO and starts on passing a PTO thickness of 8 nm for SRO-buffered DSO, which is in agreement with previous XRD studies on PTO/DSO$^{24,29}$. The possibility to observe the onset of the $c$-to-$a$ conversion directly and immediately via ISHG provides us with a handle on deterministic domain nucleation in ultra-thin PTO layers. For instance, by shifting the $c$-to-$a$ conversion threshold to the very start of the growth, we can prevent the early formation of the single-$c$-domain state and favor instead a mixed $c/a$-domain pattern right from the beginning of the deposition. The resulting domain architecture with an increased domain heterogeneity is of fundamental interest for many practical applications$^{20,21}$. When the ferroelectric domain or domain-wall density is high, small increments in the applied voltage can lead to enormous changes in ferroelectric net polarization$^{20,21}$.

There are several strategies to act on the thickness threshold for the $c$-to-$a$ domain conversion. Increasing tensile strain, for example, would enforce a pure $a$-domain-based configuration and prevent the occurrence of the $c$-domain state altogether$^{21,20}$. However, to enforce the coexistence of $c$- and $a$-domains, we move to the strongly compressive epitaxial regime$^{20}$. For extreme compression, i.e. $>3\%$,$^{20}$ strain relaxation at the substrate interface becomes inevitable and can thus trigger the undelayed nucleation of both $a$- and $c$-domains.

To investigate the domain-formation mechanisms in a system prone to an early onset of $a/c$-domain coexistence, we probe the growth of PTO on DSO (110), with a 8 nm thick conducting C$_{0.05}$Co$_{0.95}$MnO$_3$ (CCMO) buffer layer$^{19}$. The PTO film exhibits a $-4.3\%$ compressive lattice mismatch with the CCMO buffer, where the CCMO is fully relaxed on DSO$^{20}$ as confirmed by XRD (see Fig. S4).

The ISHG data during growth of PTO on CCMO/DSO are shown in Fig. 4(a) with the PTO growth on SRO/DSO for comparison. Strikingly, the ISHG yield stays close to the paraelectric background signal during the early stage of the growth up to a thickness of 20 nm with a signal rise only thereafter. One may suspect that the elastic boundary conditions on the CCMO-buffer results in a lowering of $T_c$ below the growth temperature. However, the strain state of PTO (Fig. S4(d)), the continued absence of an ISHG onset during cooling (Fig. S5), and the observed ISHG rise in the late stages of the growth, where a sudden increase in lattice compression is unlikely, makes a drop of $T_c$ below $T_{growth}$ improbable. Thus leaves the growth of a multi-domain pattern of $a$- and $c$-domains and the corresponding SHG light-wave cancellation (see Supplementary Materials Fig. S2) as an obvious explanation for the initial absence of the ISHG signal in Fig. 4(a).

To verify the suspected multi-domain state of $a$- and $c$-domains in the PTO/CCMO/DSO heterostructure, we used bulk-sensitive ex-situ $a$-SHG and $(c\oplus a)$-SHG imaging. In Fig. 4(b,c) the $a$-SHG and $(c\oplus a)$-SHG images are shown after electrically poling a square of $20\times20\mu$m$^2$.

Within the poled region, the trailing field aligns the polarization of the $a$-domains and allows for their detection in the $a$-SHG image [Fig. 4(b)]. The surrounding area, however, shows no SHG signal, which points to a random distribution of $a$-domains in the pristine state.

In order to make the $c$-domains SHG-active, a sample tilt of $\theta = 15^\circ$ is introduced in Fig. 4(c). The poling field uniformly polarizes the $c$-domains inside the $20\times20\mu$m$^2$ area, which manifests as a bright square in Fig. 4(c). In contrast to the as-grown single-$c$-domain state in PTO/SRO/STO in Fig. 3(c), however, there is no domain-wall contrast at the borders of the poled area in $c$-SHG. The domain-wall contrast in Fig. 3(c) is a consequence of destructive interference between single-$c$-domain states with opposite polarization inside and outside the poled region. Therefore, the absence of this domain-wall contrast on PTO/CCMO/DSO in Fig. 4(c) excludes the presence of a $c+ c$ or $c- c$-single-domain state and confirms $180^\circ$ multi-domain split $c$-domains in the as-grown state assumed from ISHG in Fig. 4(a).

To further characterize the multi-$c/a$-domain distribution, the out-of-plane PFM signal after switching a box-in-box structure by applying $\pm 4$ V is shown in Fig. 4(d). The PFM profile along the red dashed line, shown in Fig. 4(e), reveals three distinct PFM signal levels. The top and bottom levels correspond to field-induced $c$-domains inwards and downwards polarized states, respectively. For the pristine state, the PFM signal is clearly distinct from the poled states and thus confirms the presence of a multi-$c$-domain pattern concluded from the SHG imaging experiments in Fig. 4(b,c). We note that the absence of the typical cross-hatched $a$-domain pattern in the PFM scan points to either an $a$-domain size below the PFM resolution limit or to an accumulation of $a$-domains near the interface towards CCMO that are inaccessible by surface-sensitive PFM.

We therefore demonstrate the coexistence of both $a$- and $c$-domains in a multi-domain configuration. The random polarization distribution in both in-plane and out-of-plane components is corroborated by the lack of ISHG yield during growth [see Fig. 4(a)]. For a PTO thickness above 20 nm an imbalance of upwards and downwards polarized $c$-domains, which may be attributed to the built-in electric field$^{21}$, causes a delayed onset of an ISHG signal [Fig. 4(a)].

One question that remains to be answered is, why both $c$- and $c$-domains are formed in the CCMO bottom electrode, although the charge-screening buffer should favor a single-$c$-domain state. Here, we suspect that $a$-domains forming in the early stages of the growth isolate the nucleating $c$-domains from the conducting buffer. Thus, uncompensated charges from the $c$-oriented PTO accumulate and domain splitting occurs due the resulting depolarizing field$^{15,31,42}$.

In summary, we have investigated the mechanism of ferroelectric domain formation in tetragonal ultrathin PbTiO$_3$ films during epitaxial growth. We are able to control the final domain distribution between a pure single-domain state and fully randomized $a/c$-domain mixtures by tracking
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the domain evolution in-situ during growth by ISHG. The observed extraordinary domain heterogeneity in the strongly compressive regime, similar to the one reported to occur at the morphotropic phase boundary in PZT, highlights the potential of controlling the distribution and inter-conversion of c- and α-domains with respect to technological applications.

See the supplementary materials for more details on SHG and XRD experiments.

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All authors discussed the results and contributed to the completion of the manuscript. M.F.S. performed the thin film growth, ISHG measurements, XRD characterization, PFM analysis, SHG imaging, and wrote the manuscript with M.T. and M.F. M.T. designed the experiment and supervised the work jointly with M.F.

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

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FIG. 1. (a,b) Reciprocal space maps (out-of-plane $Q_{\perp}$ and in-plane $Q_{\parallel}$) around the STO (103) and DSO (420) reflections for a purely $c$-oriented PTO on SRO/STO (a) and for a mixed state of $a$- and $c$-domains of PTO on SRO/DSO (b). The insets show the heterostructures with the polarization direction (open arrows). (c,d) Corresponding out-of-plane PFM scans showing a single-$c$-domain state for PTO on SRO/STO (c), and a typical cross-hatched $a$-domain pattern in a $c$-matrix for PTO on SRO/DSO (d). In (c) ±4 V was reversibly applied to the tip to generate the box-in-box distribution of ±$c$-polarized single-domain regions.

FIG. 2. ISHG signal during the growth of PTO on SRO/STO (black) and on SRO/DSO (red). The light polarization of both the incoming fundamental beam and the reflected SHG light are fixed at 90°. The thickness calibration of the ISHG is performed using RHEED and post-growth x-ray reflectivity, as explained in the main text. The paraelectric background level shown as grey region results from the surface SHG signal from the nonpolar substrate/buffer interface. We attribute the increased ISHG noise between 8 and 20 nm to the ongoing domain conversion during the measurement.
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FIG. 3. (a,b) Optical configuration for spatially resolved ex-situ SHG measurements. Normal-incidence measurements are sensitive to the in-plane polarization components $P_{∥}$ (a-SHG) (a), while a sample tilt ($\theta$) allows for the detection of additional out-of-plane polarized components $P_{⊥}$ through projection on the plane perpendicular to the incident light beam ($\pi$-SHG) (b). (c,d) SHG images of the PFM-tip-induced poling applied to the PTO/SRO/STO structure under normal incidence (c) and tilted incidence (d). (e,f) Corresponding measurements as in (c) and (d) for the PTO/SRO/DSO film. The light polarization of both the incoming fundamental and the reflected SHG light are fixed at 90°. Insets illustrate the direction of the incident fundamental light and the extracted domain architecture.

FIG. 4. (a) ISHG signal during PTO growth on CCMO/DSO (blue). The ISHG for the growth of PTO on SRO/DSO (red) is added for comparison. (b,c) Spatially resolved SHG measurements under normal (b) and tilted (c) incidence. Here, polarizer and analyzer were fixed at 60° to maximize the SHG contrast. The insets show the direction of the incident fundamental light and the extracted domain configuration. (d) Out-of-plane PFM response for the PTO film grown on CCMO-buffered DSO. (e) Signal profile along the red dashed line in (d). The black arrows indicate the out-of-plane polarization state of the film.
Normal incidence ($\theta = 0^\circ$) Tilted incidence ($\theta = 15^\circ$)

(c) (d) (e) (f)
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