Thickness effect on ferroelectric domain formation in compressively strained K_{0.65}Na_{0.35}NbO₃ epitaxial films

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In this paper, the influence of thickness in epitaxial $K_{0.65}$ Na_{0.35}NbO₃ ferroelectric thin films grown on a (110) TbScO₃ substrate was systematically studied. Detailed atomic force microscopy revealed a complex change in growth mode with increasing film thickness, with the surface roughness remaining <0.30 nm throughout. By combining piezoresponse force microscopy and high-resolution x-ray diffraction, the occurrence of 90° stripe domains was demonstrated for the films with a thickness of ≥ 11 nm, while the domain periodicity is in good agreement with Kittel's law. Furthermore, up to the thickness of 93 nm, elastic strain relaxation induced by the formation of ferroelectric domains was observed, whereas plastic strain relaxation plays only a minor role. As the film thickness increases, three successive phases of ferroelectric domains were observed: (i) irregularly arranged orthorhombic *c* domains in the thinnest film, (ii) periodically arranged 90° monoclinic M_C domains up to a thickness of 25 nm, and (iii) a flux closure vortexlike structure in thicker films to achieve the lowest equilibrium energy. These results demonstrate the importance of understanding the lattice relaxation mechanism for intentional tuning of ferroelectric thin film properties.

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I. INTRODUCTION

Ferroelectrics are of increasing interest for a broad range of applications such as nonvolatile memory devices, transducers, and micro-electromechanical system sensors [1–4]. Ferroelectric phases with monoclinic symmetry, in which the polarization vector can rotate continuously within particular mirror planes of the monoclinic unit cell, are noteworthy since they provide enhanced ferroelectric and piezoelectric properties [5,6].

A typical feature of ferroelectric materials is the formation of domains driven by the minimization of the total free energy, including the chemical, electrostatic, elastic, and domain wall energy of the system [7–9]. In thin films, the domain sizes are typically in the range of the film thickness, and the volume fraction of the domain walls is significantly more pronounced than in bulk materials. The domain configuration in ferroelectric thin films can be tuned by the film orientation, elastic constraints, and electrical boundary conditions [10,11]. Especially due to the inherent coupling between structure and ferroelectricity in perovskite oxides, lattice strain and film thickness have a strong impact on the ferroelectric properties both on local and macroscopic scales [12]. Therefore, regarding technological applications, the precise control of domain formation is necessary and therefore requires a fundamental understanding of how film properties can be specifically tailored through strain engineering.

In previous work, we have investigated in detail the influence of lattice stress on domain formation in ferroelectric $K_r Na_{1-r} NbO_3$ thin films subjected to both compressive and tensile strain [13–17]. However, the effect of film thickness on strain has not been investigated in these studies. In this context, it must be considered that lattice strain can only be applied in a very limited thickness range. If a critical film thickness is exceeded during the epitaxial growth, misfit dislocations can form, leading to plastic strain relaxation [18,19]. In ferroelectric thin films, however, the formation of domains can also reduce the elastic strain energy [20]. For example, Pompe *et al.* [21] have reported that, in tetragonal films on a cubic substrate, the strain energy of a large c domain can be diminished by embedding small a domains. Li et al. [22] reported that the elastic misfit strain relaxation in PbTiO₃ film was mainly ruled by the formation of multiple domain patterns and vortex domains. These strain relaxation mechanisms depend on the film thickness and strongly influence the morphology of the domain configuration [23]. In addition to the impact on domain morphology, some experiments suggest that the film thickness also changes the domain width and domain periodicity. Most previous studies have revealed that the relationship between domain width D and film thickness t follows Kittel's law, with D proportional to the square root of t [24,25]. For an intentional tuning of film properties, it is of great significance to gain an in-depth understanding of the effect of film thickness on domain configuration in

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epitaxial films, which has not yet been investigated in sufficient detail for the environmentally friendly lead-free ferroelectric $K_x Na_{1-x} NbO_3$ material.

In this paper, we have studied in-depth the influence of the film thickness on the domain formation in fully strained epitaxial $K_{0.65}Na_{0.35}NbO_3$ films on (110) TbScO_3 substrates, which provide strongly anisotropic biaxial in-plane compressive strain. Atomic force microscopy (AFM) revealed a complex change in growth mode with film thickness. By combining piezoresponse force microscopy (PFM) and high-resolution x-ray diffraction (HRXRD), for film with a minimum thickness of 11 nm, the occurrence of 90° stripe domains with a periodicity which agrees well with the Kittel's law was demonstrated. Three different domain structures were observed as a function of film thickness, with a transition from the orthorhombic *c*-domain structure to M_C domains and, finally, to a flux closure vortexlike structure.

II. EXPERIMENTAL SECTION

All $K_{0.65}Na_{0.35}NbO_3$ films with a thickness range from 6 to 93 nm were epitaxially grown on 0.1° off-oriented (110) TbScO_3 (TSO) substrates by liquid-delivery spin metal-organic vapor phase epitaxy, which is a chemical deposition method close to thermodynamic equilibrium and at elevated oxygen partial pressure. Epitaxial growth was performed at a substrate temperature of 700°C and a gas pressure of 2.5×10^3 Pa with an argon: oxygen ratio of 5. K(tmhd), Na(tmhd) (thd = 2, 2, 6,6-tetramethyl-3,5-heptanedione), and Nb(EtO)₅ [(EtO)₅ = pentaethoxide] dissolved in dry toluene were used as the metal-organic source materials. Further details of the deposition process were described in Ref. [13].

At room temperature (RT), TbScO₃ exhibits orthorhombic symmetry (a = 5.466 Å, b = 5.731 Å, and c = 7.917 Å) and displays a nearly quadratic (110) surface unit cell with inplane lattice parameters of 2 × 3.960 and 2 × 3.959 Å along with the $[1\bar{1}0]_{TSO}$ and $[001]_{TSO}$ directions, respectively [26]. For more convenience, we use the pseudocubic (pc) notation to describe the K_{0.65}Na_{0.35}NbO₃ structure. With Vegard's law, the lattice parameters for K_{0.65}Na_{0.35}NbO₃ are calculated to be $a_{pc} = 3.952$ Å and $b_{pc} = c_{pc} = 4.012$ Å with an angle of $\alpha = 89.70^{\circ}$ between the b_{pc} and c_{pc} axes [27–30]. A comparison of the substrate and thin film unit cell leads to the expectation of a c_{pc} out-of-plane orientation of the films with strong compressive strain along the b_{pc} axis of -1.31% and slight tensile strain along the a_{pc} axis of +0.17% (more details can be found in Ref. [31]).

The surface morphology was examined using AFM (Dimension Icon, Bruker). A PFM equipped with a dual AC resonance tracking (DART) model (MFP3D, Asylum) was used to image the lateral and vertical polarization state in the ferroelectric domains of the K_{0.65}Na_{0.35}NbO₃ films. To analyze film thickness, strain state, and domain morphology of the K_{0.65}Na_{0.35}NbO₃ thin films, HRXRD was carried out on a 9 kW SmartLab system (Rigaku) using Cu K α_1 radiation ($\lambda = 1.54056$ Å). Fast two-dimensional (2D) x-ray reciprocal space mapping (RSM) was carried out using a 2D area detector (HyPix-3000).

III. RESULTS AND DISCUSSION

AFM images in Fig. 1 reveal a thickness-dependent evolution of surface morphology of the K_{0.65}Na_{0.35}NbO₃ films. It should be noted that the film thickness denoted in the following is evaluated from HRXRD data (described in more detail below) with an accuracy of ± 1 nm. A careful investigation of the growth mode was performed by analyzing the height profiles of selected line scans which are shown below each AFM image. Randomly distributed three-dimensional (3D) islands with 1- or 2-monolayer (ML) step height are observed in the thinnest film of 6 nm [Fig. 1(a)]. When the thickness is increased to 25 nm [Fig. 1(c)], only islands with a height of 1 ML were detected, indicating that the growth changes to a 2D layer-by-layer mode. With further increasing thickness, the growth mode is still 2D, but film growth seems to start at the step edges; the growth mode again changes [Fig. 1(d)], which would indicate a step-flow growth mode. However, since the step edges are no longer as straight as on the pure substrate (the morphology of the pure substrate can be found in Fig. S1 in the Supplemental Material [32]), the growth mode is better described as a transition region between 2D island nucleation and step flow. Such an evolution from small 3D islands via the 2D growth mode to a step-flow growth mode has been observed for several oxide heteroepitaxial systems like in SrRuO₃/SrTiO₃ [33], BiFeO₃/SrRuO₃ [34], and $Ga_{2-x}Fe_xO_3/SrTiO_3$ [35]. However, for films with even higher film thickness of 57 nm [Fig. 1(e)] and 93 nm [Fig. 1(f)], the growth mode switches back to the 3D islands with island heights of several monolayers, which is often observed in lattice mismatched heterosystems [36]. It is worth noting that all films have a smooth surface with a root-meansquare (rms) roughness of maximum 0.30 nm.

PFM images in Fig. 2 show the influence of the film thickness on the formation of ferroelectric domains in the films. Pronounced stripe domains were observed for all films with the thickness ≥ 11 nm exhibiting both an in-plane and an out-of-plane PFM amplitude signal, while for the thinnest film (6 nm), no regular domain formation could be defined. In the case of the 11-nm-thick thin film, stripe domains are only clearly detected in the lateral PFM image [Fig. 2(b)], while they are hardly observed in vertical PFM [Fig. 2(h)]. This can be explained by the lower sensitivity of the vertical measurements and the crosstalk of the small vertical signal with the film morphology. The stripe domains are periodically arranged with domain walls running along the diagonal $[1\overline{1}1]_{TSO}$ or $[\overline{1}11]_{TSO}$ directions, comparable with what we have previously observed in 35nm-thick K_{0.70}Na_{0.3}NbO₃ films on TbScO₃ [13]. According to Ref. [13], up to four different types of superdomains can be identified in Figs. 2(b)-2(f), which are superimposed on the fine stripe domains.

For more detailed structural analysis, HRXRD has been performed. Strain-sensitive 2θ - ω HRXRD results of the K_{0.65}Na_{0.35}NbO₃ films of the thickness series displayed in Fig. 2 were presented in the vicinity of the symmetrical (110) Bragg reflection of the TbScO₃ substrate in Fig. 3(a). The occurrence of pronounced thickness fringes for all samples indicates smooth surfaces and sharp interfaces. All diffraction patterns exhibit film peaks at lower 2θ angles than



FIG. 1. Surface morphology images $(4 \times 4 \mu m)$ of (a) 6 nm, (b) 11nm, (c) 25 nm, (d) 37 nm, (e) 57 nm, and (f) 93 nm K_{0.65}Na_{0.35}NbO₃ films on (110) TbScO₃ substrate, and corresponding line scans along the green dashed lines are shown below each image. The length of the red arrows in each line scan corresponds to the vertical dimensions of a pseudocubic unit cell of K_{0.65}Na_{0.35}NbO₃.

the sharp substrate reflection. The expected positions of unstrained $K_{0.65}Na_{0.35}NbO_3$ in a_{pc} and c_{pc} orientation are shown in Fig. 3(a) as vertical solid lines. The x-ray data reveal a compressive in-plane strain of c_{pc} -oriented K_{0.65}Na_{0.35}NbO₃ films. This is also to be expected, as the lattice mismatch is much smaller with c_{pc} orientation than with a_{pc} orientation.



FIG. 2. Lateral and vertical piezoresponse force microscopy (PFM) amplitude images $(2 \times 2 \mu m)$ for the K_{0.65}Na_{0.35}NbO₃ films grown on (110) TbScO₃ substrates with different film thicknesses: (a) and (g) 6 nm, (b) and (h) 11 nm, (c) and (i) 25 nm, (d) and (j) 37 nm, (e) and (k) 57 nm, and (f) and (l) 93 nm, respectively.



FIG. 3. (a) High-resolution x-ray diffraction (HRXRD) 2θ - ω scans of 6, 11, 25, 37, 57, and 93 nm K_{0.65}Na_{0.35}NbO₃ films in the vicinity of the (110) TbScO₃ substrate Bragg reflection. The blue and yellow lines represent the expected angular positions of unstrained K_{0.65}Na_{0.35}NbO₃ films as a function of film thickness.

Obviously, with increasing film thickness, the angular distance between film and substrate Bragg peak, which was used to evaluate the vertical lattice parameter of the film, decreases. It is noted that film peak position is calculated by fitting the positions of several oscillation minima, which increased approximately linearly [37]. This was displayed in Fig. 3(b) which reveals a slight decrease of the vertical lattice parameter with increasing film thickness except for the thinnest 6-nm film.

X-ray RSMs were measured in the vicinity of the asymmetric (444) Bragg reflection of the TbScO₃ substrate (see Fig. 4). The film peak appears at smaller values of Q_Z than the sharp Bragg reflection of the TbScO₃ substrate ($Q_Z = 6.36 \text{ Å}^{-1}$). For a film thickness of 6 nm [Fig. 4(a)], a vertically elongated film Bragg reflection is observed. With increasing film thickness [Figs. 4(b)–4(d)] (11, 25, and 37 nm), an intense satellite reflection pattern evolves, which is caused by a periodic arrangement of the domain walls. At the same time, a vertical splitting can be observed [marked as up and down arrows in Fig. 4(d)], which is caused by opposite monoclinic shearing of the unit cells along the \pm [001]_{TSO} directions. For the RSM in the vicinity of the (620) TbScO₃ Bragg reflection (not shown here), we observed a similar behavior, which indicates the additional occurrence of unit cells sheared in \pm [1 $\overline{10}$]_{TSO} directions. Furthermore, different domain wall orientations can be detected, as schematically illustrated by the two white dotted lines in Fig. 4(d). In combination with the PFM images in Fig. 2, it proves the occurrence of the well-known M_C ferroelectric phase with monoclinic crystal symmetry; a detailed structural model can be found in Ref. [13].

The PFM and x-ray diffraction (XRD) results shown in Figs. 2 and 4, respectively, reveal that both strain state and domain configuration in the films are a function of the film thickness, however, with significant differences. These can be summarized as follows:

(i) The vertical lattice parameters are almost identical for the 11, 25, and 37 nm films and correspond to the value expected for the fully strained film. The vertical lattice parameter in fully strained films with a K content of $\sim 65\%$ is estimated to 4.042 Å with a Poisson ratio of 0.38 [38] (see Note 1 in the Supplemental Material [32] for more statements), which fits quite well with the measured values shown in Fig. 3(b). However, both for the thinnest film (6 nm) and the thicker films, the vertical lattice parameters are reduced.

(ii) For films with a thickness up to 37 nm, the superimposed superdomains are relatively large, typically in the range of several micrometers (for a better overview, additional PFM images in a larger scan range are shown in Fig. 5).



FIG. 4. X-ray reciprocal space maps (RSMs) in the vicinity of the asymmetric (444) Bragg reflection of the TbScO₃ substrate of the (a) 6 nm, (b) 11nm, (c) 25 nm, (d) 37 nm, (e) 57 nm, and (f) 93 nm $K_{0.65}Na_{0.35}NbO_3$ films.



FIG. 5. Large area lateral piezoresponse force microscopy (PFM) images $(4 \times 4 \ \mu m)$ for the $K_{0.65}Na_{0.35}NbO_3$ films grown on (110) TbScO₃ substrate with film thickness ranging from 25 to 93 nm. The blue arrows mark the net in-plane electrical polarization direction forming flux closure vortexlike structures.

For the 11 nm film, one superdomain variant dominates, and the 90°-rotated variant occurs only within very small areas. With increasing thickness, the superdomain size remarkably decreases [Figs. 2(e) and 2(f)].

(iii) The periodicity of the stripe domains increases with increasing film thickness. The stripe domain width was extracted directly from the lateral PFM images and from x-ray RSMs—derived from the horizontal distance of the satellite peaks—and plotted in Fig. 6 as a function of the film thickness (black squares and red circles, respectively). The change trend of the domain width D with the film thickness t can be well de-



FIG. 6. Lateral domain width D derived from piezoresponse force microscopy (PFM; black square) and reciprocal space mapping (RSM; red circle) as a function of film thickness t. The dashed line represents the best fit using Kittel's law.

scribed by Kittel's law with $D \propto t^{0.5}$, as shown in Fig. 6 with the black dashed line [39]. This agrees well with the literature data for tetragonal domains [25] as well as for monoclinic domains [40] and can be explained by the energy costs of a domain wall which are proportional to the domain wall area. Consequently, the domain wall density has to diminish with increasing film thickness.

It is worth noting that, for all films with the thickness of \geq 57 nm, the film Bragg reflections (Fig. 4) appear at the same Q_X value as the substrate reflection, verifying fully strained epitaxial growth on the TbScO₃ substrate. However, the center of gravity of the Bragg contribution of the 93 nm film [Fig. 4(f)] is apparently shifted to larger Q_X and Q_Z values. Furthermore, the diffuse scattering background in the vicinity of the film contribution is remarkably increased for the 57 and 93 nm films, indicating the onset of defect formation. Due to the periodic domain structure at RT, the RSMs show a correspondingly complex satellite reflection pattern. Therefore, it is difficult to elucidate the reason for the observed peak shifts, especially for the thicker films. To clarify the role of possible plastic relaxation, we performed in situ XRD at elevated temperatures below and above the phase transition temperature to the well-known orthorhombic c phase [41]. In Fig. 7, we exemplarily show a temperature-dependent series of RSMs for the 93 nm film. At $\sim 190^{\circ}$ C, the periodic satellite peaks have disappeared, and according to our former results for $K_{0.70}Na_{0.30}NbO_3$ thin films, the monoclinic M_C phase has been transferred to an orthorhombic c phase [41]. Similar behaviors related to phase transition temperature were observed in the other films of different thicknesses except for the 6 nm film. Meanwhile, the temperature-dependent XRD result did not show a clear mutation of lattice parameter, perhaps indicating there is no phase transition occurring in 6 nm film from RT to 250°C. Due to the absence of the periodically arranged domain walls and the corresponding satellite peaks, Figs. 7(d)-7(f) display a single film peak below the substrate contribution at the same Q_X value. However, two weak satellite reflections [marked as S1 and S2 in Fig. 7(f)] can be noticed in the direction perpendicular to the scattering vector. These satellite peaks are a fingerprint of the very early stages of plastic relaxation with correspondingly misfit dislocation density [42], but most of the 93 nm film is still fully strained on the TbScO₃ substrate. The satellite peaks S1 and S2 were only observed for the thickest film of 93 nm, while in the other samples, they are absent (not shown here), proving the absence of plastic relaxation in these samples. This in turn means that the observed peak shifts in the RSMs at RT [Figs. 4(e) and 4(f)] cannot be explained by plastic relaxation. Obviously, elastic strain relaxation takes place here through the formation of ferroelectric domains.

For the two thicker films, the decrease of the vertical lattice parameter seems to be correlated to the formation of superdomains (walls). This assumption is supported by the significant increase of superdomain wall density in these films [Figs. 2(e) and 2(f)]. In contrast to the stripe domains, which are 90° domains, adjacent superdomains exhibit only a 90° domain wall in thin films up to a thickness of 25 nm. For thicker films, additional flux closure vortexlike structures are observed [see Figs. 5(b)–5(d), marked by the blue arrows], the



FIG. 7. Temperature-dependent reciprocal space maps (RSMs) in the vicinity of the asymmetric (444) Bragg reflection of the (110) TbScO₃ substrate of the 93 nm $K_{0.65}Na_{0.35}NbO_3$ films.

fraction of which increases with increasing film thickness. It is therefore assumed that such vortexlike structures are formed to minimize the energy generated by large local stress and charge variations [43].

In contrast, the reduced vertical lattice parameter in the thinnest film (6 nm) is attributed to a symmetry mismatch effect. While in TbScO3 an antiphase tilting of adjacent O_6 octahedra occurs ($a^-a^-c^+$ in Glazer's notation [44]), in $K_x Na_{1-x} NbO_3$, no octahedral tilting is observed for x > 0.5[45]. As a result, we assume that lattice strain is accommodated in very thin films by adapting the symmetry of the substrate through oxygen octahedra rotation within the first few monolayers in the film. This would result in a reduced vertical lattice parameter. The inverse effect has been observed for very thin La_{0.67}Sr_{0.33}MnO₃ $(a^+a^+c^0)$ films grown on (100) SrTiO₃ $(a^0a^0a^0)$ substrates [46]. Additionally, no vertical splitting of the film peak shown in Fig. 4(a) is observed. It is assumed that the film unit cell is adapted to the rectangular surface unit cell of the TbScO₃ substrate, revealing an orthorhombic *c* phase in the thinnest film.

Based on these results, it is concluded that pure elastic strain relaxation occurs in compressively strained $K_{0.65}Na_{0.35}NbO_3$ for films with the thickness of 93 nm by ferroelectric domain formation. The elastic strain relaxation occurs in three successive phases: (i) irregularly arranged orthorhombic *c* domains, (ii) periodically arranged 90° monoclinic M_C domains, and finally, (iii) a flux closure vortexlike structure in thicker films to achieve the lowest equilibrium energy.

IV. CONCLUSIONS

In this paper, we have systematically studied the thickness effect in epitaxial $K_{0.65}Na_{0.35}NbO_3$ films grown on (110) TbScO₃ substrate, which experience anisotropic biaxial inplane compressive strain. A complex change in growth mode as a function of film thickness was evaluated with AFM measurement, in which the growth model changes from 3D islands to a 2D layer and finally to 3D islands. All the films show smooth surfaces with a rms roughness of <0.30 nm. Moreover, by combining PFM with corresponding XRD data, we have shown that, only from a minimum film thickness of 11 nm, the monoclinic M_C phase is formed in periodically arranged 90° M_C domains. The relation between (stripe) domain width D and the film thickness t agrees with Kittel's law, i.e., $D \propto t^{0.5}$. For thinner films, an orthorhombic c phase with irregularly arranged domains is obtained. The formation of stripe domains as well as superdomains provides pure elastic strain relaxation which is imposed by the pseudomorphic growth of the films on TbScO₃ substrates. No remarkable plastic lattice relaxation could be observed throughout. Only for the thickest film, very early stages of plastic relaxation are visible. In thicker films, a flux closure vortexlike domain structure was observed, which is known to minimize the total free energy. Our result underlines the importance of understanding the mechanisms of lattice relaxation in ferroelectric thin films for an intentional tuning of the film properties. It is encouraging to achieve excellent piezoelectric properties through strain engineering and exploiting them for nanoscale piezoelectric applications.

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