Thickness Dependence of c/a Polytwin Structures Observed in Epitaxial Oxide Ferroelectric Thin Films

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Abstract

Ferroelectric or ferroelastic epitaxial films undergoing a cubic-to-tetragonal phase transformation usually relax the resultant strain energy due to lattice misfit by forming a polytwin (polydomain) structure. Polydomain formation occurs at the expense of building interdomain interfaces and microstresses which develop at the film-substrate interface due to the periodic deviation of the strain. The interplay between these components results in a critical thickness for domain formation below which the polydomain structure is not stable. In this article, we investigate the film thickness dependence of a polydomain structure using a thermodynamical approach.

1. Introduction

During the past decade, epitaxial ferroelectric thin films have received considerable interest because of their potential applications as elements of non-volatile random access memories (NVRAM) and static random access memories (SRAM), high dielectric constant capacitors, optical waveguides, and pyroelectric detectors. Improvements in the deposition techniques have made it possible to deposit ferroelectric films with good compositional control on various substrates.

Experimental studies indicate that epitaxial ferroelectric films usually form a polytwin (or polydomain) structures. The polydomain structure usually consists of two of the three possible orientational variants (or ferroelastic domains) separated from each other by 90° domain walls. The most common structure is the c/a polydomain pattern, which consists of alternating c-domains with the tetragonal axis (and thus the direction of the spontaneous polarization) perpendicular to the film-substrate interface and a-domains with the c-axis of the tetragonal film along either the [100] or [010] plane of the substrate (Fig. 1). This structure is commonly observed in BaTiO$_3$ [1-5], PbTiO$_3$ [6-10], $Pb(Ti_{1-x}Zr_x)$O$_3$ (PZT) [11-14], Pb$_{1-x}$La$_x$TiO$_3$ (PLT) [15-17] and KNbO$_3$ [18] epitax-

ial films on various cubic and pseudo-cubic substrates. Transmission electron microscopy and x-ray diffraction studies indicate that the interdomain interface is usually along (110) or ($\bar{1}$10).
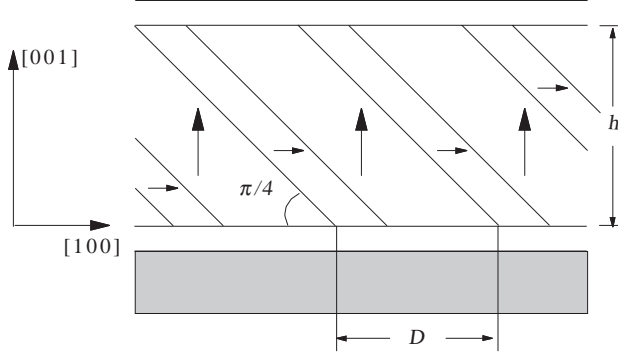

Figure 1. The c/a polytwin structure on a cubic substrate sandwiched between top and bottom cubic electrode layers. The top and the bottom electrode layers are assumed to be coherently strained to fit the ferroelectric film and the substrate, respectively. The arrows in the film indicate the direction of the spontaneous polarization (i.e., the direction of the tetragonal axis). c-domains are along [001] direction and a-domains are along [100] direction.

The formation of 90° domains as a mechanism of strain energy relaxation was predicted as early as 1976 [19]. During the past years, together with the experimental data, there has been an increase in the theoretical description of polydomain formation in constrained ferroelectric films [6,20-23] and multilayer heterostructures containing ferroelectric layers as active components [24,25]. Recently, we have developed domain stability maps (or phase diagrams) that show stable polydomain and single-domain structures as a function of the misfit and the tetragonality strain [25-26] and verified their applicability and accuracy with available experimental data from the literature [25,27]. These maps predict the stable domain structure and the fractions of domains in polydomain states. In this article, we address the dependence of the volume fractions of the constituent domains of a c/a polytwin structure on the film thickness.

2. Theory

When ferroelectrics with a perovskite structure undergo a cubic-tetragonal phase transformation, three different orientational variants (or domains) with self-strains

$$\hat{\epsilon}_1 = \begin{pmatrix} \epsilon'_0 & 0 & 0 \\ 0 & \epsilon_0 & 0 \\ 0 & 0 & \epsilon_0 \end{pmatrix} \hat{\epsilon}_2 = \begin{pmatrix} \epsilon_0 & 0 & 0 \\ 0 & \epsilon'_0 & 0 \\ 0 & 0 & \epsilon_0 \end{pmatrix} \hat{\epsilon}_3 = \begin{pmatrix} \epsilon_0 & 0 & 0 \\ 0 & \epsilon_0 & 0 \\ 0 & 0 & \epsilon'_0 \end{pmatrix} \tag{1}$$

may form where $\epsilon'_0 = (c - a_0)/a_0, \epsilon_0 = (a - a_0)/a_0$, a and c are the lattice parameters of the film in the ferroelectric state and a_0 is the lattice parameter of the film in the

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paraelectric state.

If a ferroelectric film is grown epitaxially on a cubic substrate such that $(001)_{\text{Film}}//$ $(001)_{\text{Subst.}}$, the misfit due to the difference in lattice parameters of the active and the passive layer may be described by the following misfit strain tensors for each domain as:

$$\hat{\epsilon}_1^M = \begin{pmatrix} \epsilon_T' & 0 & 0 \\ 0 & \epsilon_M & 0 \\ 0 & 0 & \epsilon_M \end{pmatrix} \quad \hat{\epsilon}_2^M = \begin{pmatrix} \epsilon_M & 0 & 0 \\ 0 & \epsilon_T' & 0 \\ 0 & 0 & \epsilon_M \end{pmatrix} \quad \hat{\epsilon}_3^M = \begin{pmatrix} \epsilon_M & 0 & 0 \\ 0 & \epsilon_M & 0 \\ 0 & 0 & \epsilon_T' \end{pmatrix} \tag{2}$$

where, $\epsilon_T' = \epsilon_M + \epsilon_T, \epsilon_M = (a - a_s)/a_s$ is the misfit strain between the substrate and one side of the base of the tetragonal film; $\epsilon_T = (c - a)/a$ is the tetragonality of the film; and a_s is the lattice parameter of the substrate. The above tensors are obtained from the linear relation between the self-strain and the misfit strain for each variant since the strains are small [24].

It has been shown that if the film thickness h is greater than a critical thickness h_{cr}, formation of polydomain structures with twinning planes along {110} reduces the total energy of the system. The free energy density of a polydomain film consisting of variants with self-strains and $\hat{\epsilon}_1$ and $\hat{\epsilon}_3$, i.e., a c/a polydomain as shown in Fig. 1, consists of three components [24,25]:

$$f_{c/a} = f_{\text{Macro}} + f_{\text{Micro}} + f_\gamma. \tag{3}$$

The first term of the above equation, f_{Macro}, is the elastic energy density of the polydomain structure and is given by the relation

$$f_{\text{Macro}} = \left[(1 - \alpha)e_1^M + \alpha e_3^M - \alpha(1 - \alpha)e_{13}^I\right] \tag{4}$$

if the thickness of the substrate is much larger than the film thickness. In the above equation, α is the volume fraction of c-domains; $e_1^M = 1/2\hat{\epsilon}_1^M \cdot \mathbf{G} \cdot \hat{\epsilon}_1^M$ and $e_3^M = 1/2\hat{\epsilon}_3^M \cdot \mathbf{G} \cdot \hat{\epsilon}_3^M$; $\mathbf{G}$ is the planar elastic modulus; and $e_{13}^I = 1/2\Delta\hat{\epsilon}_{13} \cdot \mathbf{G} \cdot \Delta\hat{\epsilon}_{13}$ and $\Delta\hat{\epsilon}_{13} = \hat{\epsilon}_3 - \hat{\epsilon}_1$. The misfit energies e_1^M and e_3^M, and the energy of indirect interaction e_{13}^I can be determined in terms of the misfit strain, tetragonality and the elastic constants of the film if the film is assumed to be elastically isotropic as [25]:

$$e_1^M = \frac{Y}{2(1 - \nu^2)}\left[2\epsilon_M^2(1 + \nu)\,\epsilon_M\epsilon_T(1 + \nu) + \epsilon_T^2\right], e_3^M = \frac{Y}{(1 - \nu)}\epsilon_M^2 \tag{5a}$$

$$e_{13}^I = \frac{Y}{2(1 - \nu^2)}\epsilon_T^2, \tag{5b}$$

where Y is the Youngs modulus and ν is the Poissons ratio of the film.

The second term of Eq. (3), f_{Micro}, is the energy of the microstresses. Microstresses arise due to the periodic deviation of the actual misfit from the average misfit on the film-substrate interface. This energy can be approximated as [24]:

$$f_{\text{Micro}} = \xi \alpha^2 (1-\alpha)^2 e_{13}^I \frac{D}{h}, \tag{6}$$

for $D/h \le 1$, where D is the domain period and ξ is a numerical coefficient equal to 0.27.

The last term in Eq. (3) is the energy of the interdomain interfaces and is given by:

$$f_\gamma = 2\sqrt{2}\frac{\gamma}{D}, \tag{7}$$

where γ is the specific surface energy of the interdomain interface per unit area.

The equilibrium domain period can be obtained by the solution of $\partial f_{c/a}/\partial D = 0$ as:

$$D^0 = \frac{\sqrt{lh}}{\alpha(1-\alpha)}, \tag{8}$$

where $l = (2\sqrt{2}\gamma)/(\xi e_{13}^I)$. Substitution of Eq. (8) back into Eq. (3) and minimization with respect to α yields the equilibrium c-domain fraction:

$$\alpha^0 = \frac{1}{2}\left[1 - \frac{\Delta e_{13}^M}{(1-\eta)e_{13}^I}\right], \tag{9}$$

where $\Delta e_{13}^M = e_1^M$, $\eta = \sqrt{h_{cr}/h}$, and $h_{cr} = (8\sqrt{2}\xi\gamma)/e_{13}^I$ is the critical thickness for polydomain formation of the c/a structure below which this structure is not energetically favored and the film consists of c-domains only. The critical thickness may range from 10 to 150 nm [6,8,10], depending on the film-substrate system.

3. Discussion

Before we compare theoretical expectations with experimental data, it should be noted that epitaxial films relax the internal strain at the growth (or deposition) temperature by forming misfit dislocations. This classical phenomenon was discussed earlier [21,25,27] and it has been demonstrated that the generation of misfit dislocations during film growth can be taken into account using an effective substrate lattice parameter and thus an effective misfit strain given by:

$$a_s^{eff}(T) = \frac{a_s(T)}{\rho a_s(T) + 1}; \quad \epsilon_M^{eff} = \frac{a(T) - a_s^{eff}(T)}{a_s^{eff}(T)}, \tag{10}$$

where

$$\rho \cong \frac{\epsilon}{a_0}\left(1 - \frac{h_\rho}{h}\right) \tag{11}$$

is the equilibrium linear dislocation density at the deposition temperature, $\epsilon = (a_s - a_0)/a_s$ is the misfit strain at the growth temperature, a_0 is the lattice parameter of the cubic film at the growth temperature, and h_ρ is the critical thickness for dislocation generation below which dislocation formation is not feasible. With the assumption that no additional dislocations form during cooling the above equations may be utilized to calcu-

late the effective misfit strain ϵ_M^{eff} at any temperature if the substrate lattice parameter is given as a function of temperature or the thermal expansion coefficient of the substrate.

With this in mind, utilizing the bulk lattice parameters of PbTiO$_3$ and SrTiO$_3$ as a function of temperature [28], the c-domain fraction of epitaxial PbTiO$_3$ films with different thicknesses on (001) SrTiO$_3$ substrate grown at 645°C can be calculated if the lead titanate film is assumed to be fully relaxed by misfit dislocation formation (h_ρ=10 nm at 645°C [21]) at the deposition temperature and the critical thickness for domain formation h_{cr} is assumed to be 30 nm [10]. This is achieved by using Eqs. (9-11) and the results are shown in Fig. 2, together with the experimental observations of Hsu and Raj [10]. It can be seen that theoretical predictions are in agreement with experimental results. There is a slight deviation at film thicknesses close to h_{cr} because the approximation for the microstresses, Eq. (6), no longer holds (the assumption $D/h \leq 1$ becomes invalid) and its more accurate form, given by the relation
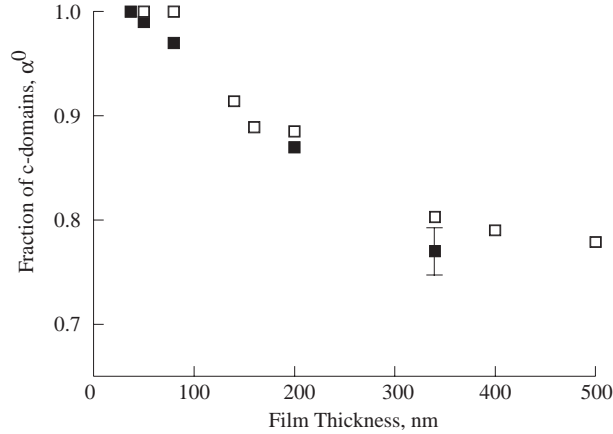

Figure 2. Thickness dependence of the c-domain fraction for PbTiO$_3$/ SrTiO$_3$(001) deposited at 645°C. Solid squares are experimental values from Ref. 10 and the open squares are calculated values with h$_{cr}$ ≅30 nm. For theoretical calculations, the film was assumed to be completely relaxed at the growth temperature by misfit dislocation generation.

$$f_{\mathrm{Micro}}\left(\alpha, \frac{D}{h}\right) = \frac{1}{2\pi^3}\frac{D}{h}e_{13}^I \sum_{n=1}^{\infty}\frac{1}{n^3}\sin^2(n\pi\alpha)\left[1 - \exp\left(-2n\pi\frac{h}{D}\right)\right] \qquad (12)$$

must be used. This equation is obtained from the Fourier series solution of the periodic deviation of the strain tensors at the film-substrate interface [23] and has a similar form for the expression for the energy of the stray field of a ferromagnetic material with plane-parallel 180° domains developed in a classical paper by Kooy and Enz [29].

4. Conclusion

In this article, we have demonstrated the thickness dependence of the domain fractions

of a c/a type polytwin structure commonly observed in epitaxial ferroelectric-ferroelastic thin films undergoing a cubic-to-tetragonal phase transformation. The equilibrium domain period follows a $\sqrt{h}$ dependence. We have shown that the c-domain fraction hyperbolically decreases with increasing film thickness and levels out for very thick films. The theoretical approach is in good agreement with experimental observations except for film thicknesses very close to the critical film thickness for domain formation.

Acknowledgement

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