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Abstract

The use of domain stability maps for epitaxial perovskite ferroelectric films is illustrated with some examples. The equilibrium domain structure and domain fractions as a function of temperature are predicted for $PbTiO_3(001)$ films grown epitaxially on three different substrates: $MgO(001)$, $KTaO_3(001)$, and $SrTiO_3(001)$. Misfit dislocation formation at the growth temperature is found to have a profound effect on both the domain selection and relative domain populations. Theoretical predictions are compared with available experimental data.

1. Introduction

In Part I [1] of this series we analyzed the domain formation as a strain relaxation mechanism in epitaxial ferroelectric films deposited on a cubic substrate and developed domain stability maps showing not only the regions of stability for possible domain configurations but also the relative populations of each domain in coordinates of the misfit strain $\epsilon_M = (a - a_s)/a_s$ and the tetragonality $\epsilon_T = (c - a)/a$, where a_s is the lattice parameter of the cubic substrate and a and c are the lattice parameters of the tetragonal film. The fraction of c-domains in a (1,3)/(2,3) structure was found to be [1]:

$$\alpha_3^0 = \frac{(1+v)\epsilon_M + (\epsilon_M + 1)\epsilon_T}{(\epsilon_M + 1)\epsilon_T}, \tag{1}$$

where v is Poisson's ratio. However, if the formation of domain structures containing all possible tetragonal variants is possible, i.e., the (12,3) heterostructure, then the volume

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fraction of c-domains in such a configuration is given by [1]:

$$\alpha_3^0 = \frac{2\epsilon_M + (\epsilon_M + 1)\epsilon_T}{(\epsilon_M + 1)\epsilon_T}. \tag{2}$$

The relative domain population in a polydomain structure is an important quantity because it strongly affects the polarization hysteresis loop and the dielectric response of epitaxial films.

In this paper we demonstrate the use of domain stability maps developed in Part I [1] with some examples of epitaxial ferroelectric film-substrate systems. For the details on the theoretical approach used to construct these maps and the notation used in this paper, the reader is referred to the original paper [1]. To analyze experimental data, we take into account the possibility of misfit dislocation formation at the growth temperature.

2. Relaxation at the Parastate by Misfit Dislocations

Deposition of films usually takes place at temperatures greater than the Curie temperature where the film is cubic. A mechanism that relaxes the strain due to lattice mismatch between the layers at the growth temperature is misfit dislocation formation. This classical phenomenon [2,3] can be included in the map by using an effective substrate parameter [4] given by:

$$a_s^{eff}(T) = \frac{a_s(T)}{\rho a_s(T) + 1}, \tag{3}$$

where

$$\rho \cong \frac{\epsilon}{a_0}\left(1 - \frac{h_\rho}{h}\right) \tag{4}$$

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 with a thickness h, 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 calculate the misfit strain ϵ_M at any temperature given the substrate lattice parameter as a function of temperature or the thermal expansion coefficient of the substrate. Otherwise, the knowledge of the actual dislocation density at the growth temperature is required.

3. Domain Stability Maps for Various Epitaxial Systems

3.1. $PbTiO_3$ on MgO(001)

To calculate the misfit strain and the tetragonality, the bulk values [5] of the lattice parameters of the film and the substrate as a function of temperature are used. The values of ϵ_M and ϵ_T are calculated in 25°C intervals, starting from 0°C up to T=485°C, and the data is superimposed on the domain stability map in Figure 2 of Part I [1].

The reason to avoid the map which shows all possible domain states is that there is no experimental evidence for the formation of 3-domain heterostructures in this system. The stability map for the $PbTiO_3$/MgO system is shown in Figure 1 (solid squares), on which the metastability line was omitted. From this figure, it can be concluded that the expected domain structure for this system in this temperature range is the (1,2) pattern. However, this contradicts with experimental studies [6-9] where usually a (1,3)/(2,3) domain pattern is observed. The reason for this discrepancy is probably strain relaxation at growth temperature by misfit dislocations.

To take into account misfit dislocation formation at the growth temperature and to compare our predictions with experimental results of Kwak et.al. [6], we assume a film thickness of 280 nm and a deposition temperature of 550°C. The critical thickness for dislocation generation is calculated to be ∼0.3-0.5 nm for this system from the Matthews-Blakeslee [2-4] criteria. For a film of 280 nm thickness at T=550°C, the dislocation density is $1.68 \cdot 10^6$ cm^{-1} according to Eq. (2.2) which corresponds to full relaxation. Therefore, an effective substrate parameter as a function of temperature is obtained using the relation given in Eq. (2.1), and the misfit strain is modified accordingly. The data taking into account this relaxation is shown as open squares in Figure 1.

The domain fraction of c-domains, Eq. (1.1), at different temperatures is also calculated and shown in Fig. 2 together with experimental observations of Kwak et.al. [6]. The fitting is within reasonable accuracy up to ~ 400°C. Unfortunately, there is no other experimental data on temperature dependence of c-domain fraction.

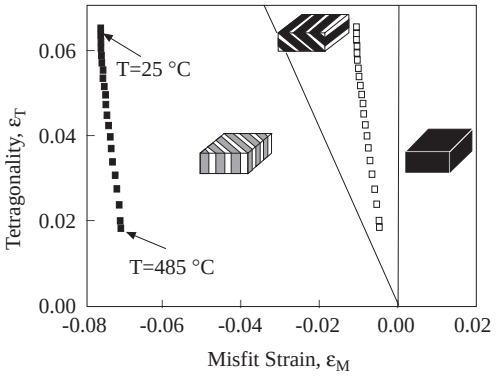

Figure 1. Domain stability map for $PbTiO_3$/MgO(001). Solid squares show data for an unrelaxed film from 0°C to 485°C and the open squares are for a film completely relaxed by misfit dislocations at the deposition temperature.

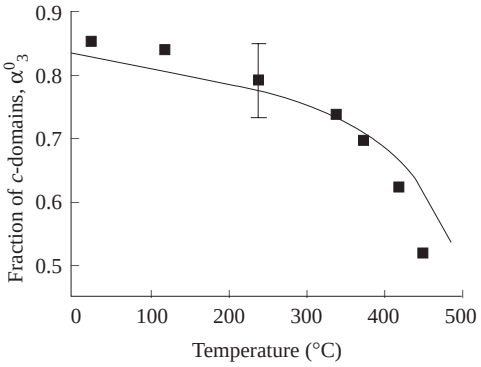

Figure 2. Plot of theoretical (solid line) and experimental (solid squares) fraction of c-domains, α_3^0, as a function of temperature for $PbTiO_3$/MgO(001). Experimental values of α_3^0 are taken from Ref. 6. α_3^0 is related to the normalized c-domain amount N_c measured in Ref. 6 through $\alpha_3^0 = 2N_c/(1 + N_c)$.

In a detailed series of experimental research, Foster et.al. [7, 8] obtained a relative coherency strain ($e_r \cong -\epsilon_M/(\epsilon_T + 1)$ in our notation) of 0.178 from c-domain tilt angle measurements and 0.180 from integrated x-ray intensities at room temperature for a 720 nm thick $PbTiO_3$ on MgO grown at 700-750°C by metalorganic chemical vapor deposition (MOCVD). For a fully relaxed film, we predict a theoretical relative coherency strain of 0.1712 at room temperature which is fairly close to experimental results, the minor difference between experimental and theoretical values indicating that the film is not completely but practically completely relaxed by misfit dislocations. This has also been verified by the magnitude of the tilting of the c-axis grains away from the MgO[001] surface normal [7]. In addition, Foster et.al. [8] measure average domain width and domain period as ∼30 nm and 160 nm, respectively. The c-domain fraction is thus ∼0.81 and our theory estimates 0.79 at room temperature. The c-domain fraction has been found to be $(70 \pm 6)\%$ in another experimental study [9] from integrated intensities of $(00l)$ and $(h00)$ peaks for a 20 μm thick $PbTiO_3$ film on MgO(001) substrate deposited at $580 - 630$°C by rf sputtering.

3.2. $PbTiO_3$ on $KTaO_3$(001)

Although the formation of three-domain heterostructures has not been observed experimentally until now mainly because of experimental difficulties in distinguishing a_1-domains from a_2-domains in x-ray diffraction, the co-existence of all possible variants of the tetragonal phase has been observed for the $PbTiO_3/KTaO_3(001)$ system for thicknesses exceeding ∼150 nm from a ϕ-scan of the $PbTiO_3(220)$ reflection [6]. This, however, does not provide enough evidence for the presence of a perfect three-dimensionally arranged heterostructure consisting of all variants as shown in Figure 1 of Part I [1]. By assuming that the three-domain structure is not possible, as in the case of $PbTiO_3$/MgO, we obtain c-domain fractions of 0.50 and 0.99 for the unrelaxed and the 95% relaxed 250 nm $PbTiO_3$ film on a $KTaO_3$ substrate grown at 550°C, respectively from Eq. (1.1). The film is only 95% relaxed by misfit dislocation formation because h_ρ is around 13 nm. The experimental value of 0.55 for the c-domain fraction [6] suggests that either no misfit dislocations were formed during deposition or, together with the x-ray data, all variants of the ferroelectric phase are present.

With this in mind, we develop a domain stability map for this system, illustrated in Figure 3, by superimposing the misfit strain and the tetragonality at various temperatures on the universal map for all possible domain states given in Figure 3 of Part I [1]. The unrelaxed film switches from the (1,3)/(2,3) pattern to the (1,2) pattern at temperatures close to the Curie temperature. When the relaxation of 95% by misfit dislocations is taken into account, the curve shifts to lower values of the misfit strain and the (12,3) structure is stable at all temperatures up to the transition temperature. The c-domain fraction, given by Eq. (1.2), as function of temperature for the relaxed film is shown in Figure 4 together with the experimental results of Kwak et.al. [6] and there is an excellent agreement between the theory and the experiment for the relaxed film, especially in the low-temperature regime where the experimental data is more reliable. This implicitly

points out to the presence of three-domain heterostructures in this system for films of thicknesses greater than 250 nm, and further experimental study is worthwhile not only to prove the existence of a theoretical curiosity but also because of unique physical properties that can be expected from these kind of structures.

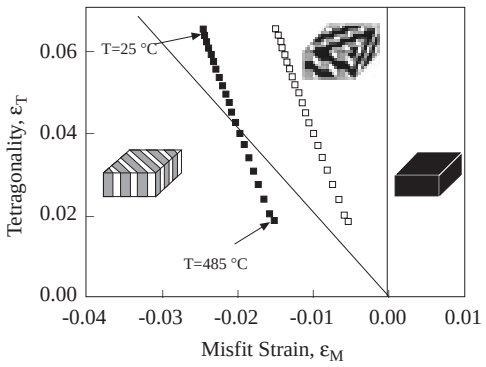

Figure 3. Domain stability map for $PbTiO_3/KTaO_3(001)$. Solid squares show data for a unrelaxed film from 0°C to 485°C and the open squares are for a film 95% relaxed by misfit dislocations at the deposition temperature.

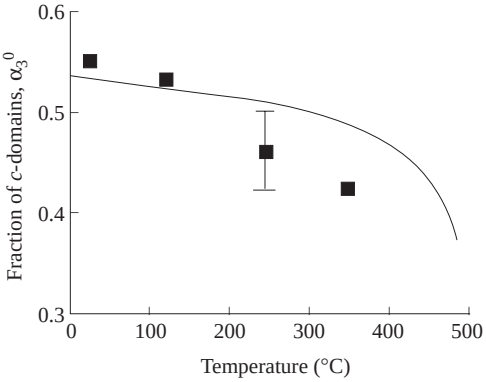

Figure 4. Plot of theoretical (solid line) and experimental (solid squares) fraction of c-domains, α_3^0, as a function of temperature for $PbTiO_3/KTaO_3(001)$. Experimental values of α_3^0 are taken from Ref. 6. α_3° is related to the normalized c-domain amount N_c measured in Ref. 6 through $\alpha_3^0 = 2N_c/(1+N_c)$.

3.3. $PbTiO_3$ on $SrTiO_3(001)$

The $PbTiO_3/SrTiO_3$ system has been studied experimentally extensively [6-8,10] because of the excellent lattice parameter match between the $PbTiO_3$ and $SrTiO_3$. Similar to the case for $PbTiO_3/MgO$, we proceed by superimposing the data on misfit strain and tetragonality on Figure 2 of Part I [1], which gives the domain stability map shown in Figure 5. As in the case for the MgO substrate, there is no experimental observation of the 3-domain heterostructure for this system.

The unrelaxed film switches from the (1,3)/(2,3) structure to single-domain state (3) at around 300°C by gradually increasing its c-domain fraction. When relaxation by misfit dislocations at the growth temperature for a film of thickness of 700 nm deposited at 700°C is considered, it can be seen that the curve for the unrelaxed film shifts to the left ($h_\rho = 10$ nm). At the growth temperature the film is in tension and the stress is relaxed by introducing "extra planes" to the substrate as opposed to the previous case for MgO. The misfit strain changes sign at 300°C, and the misfit dislocations introduced during the deposition no longer relax the stress and further increase the compressive misfit strain. The theoretical c-domain fractions for the completely relaxed and unrelaxed film at room temperature are found to be 0.72 and 0.93, respectively from Eq. (1.1). There is good

agreement between the theoretical c-domain fraction and the experimental study of Hsu and Raj [10] where a c-domain fraction of 0.75 is found for a 350 nm thick film deposited at 645°C by pulsed laser ablation.

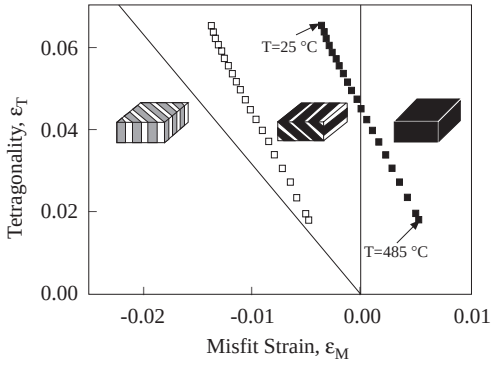

Figure 5. Domain stability map for $PbTiO_3/SrTiO_3(001)$. Solid squares show data for a unrelaxed film from 0°C to 485°C and the open squares are for a film completely relaxed by misfit dislocations at the deposition temperature.

However, there are significant differences when these theoretical values are compared to experimental observations of Faster *et.al.* [8]. Depending on the cooling rate from the deposition temperature (700°C), they obtain c-domain fractions of 0.93, 0.87 and 0.85 and corresponding relative coherency strains 0.062, 0.132, and 0.150 for fast cooling (FC), normal cooling (NC), and slow cooling (SC), respectively for a film of 770 nm thickness. Were the film completely relaxed as expected by misfit dislocations at the growth temperature, e_r would have attained the value of 0.238 at room temperature. The observed values of e_r correspond to 5%, 43% and 53% relaxation for FC, NC, and SC, respectively, when traced back to the deposition temperature. For these amounts of relaxation, the theoretical c-domain fraction is 0.92, 0.83 and 0.80 for FC, NC and SC, respectively.

3.4. $BaTiO_3$ on MgO(001), Si(001), and $SrTiO_3$(001)

The effects of substrate selection and various deposition techniques and conditions on the domain selection of $BaTiO_3$ films have been experimentally investigated [11-16]. To provide some theoretical insight, we present in Figure 6 domain stability maps for a 500 nm thick $BaTiO_3$ film grown at 600°C on MgO(001), Si(001), and $SrTiO_3$(001) substrates. The data shown in Figure 6 corresponds to films completely relaxed by misfit dislocations at the growth temperature. It should be noted that were the films not relaxed at all, the expected equilibrium domain structure for $BaTiO_3/MgO(001)$ and $BaTiO_3/Si(001)$ would be the a_1/a_2 pattern whereas the unrelaxed $BaTiO_3/SrTiO_3(001)$ system would have a single-domain c-structure. It has been experimentally verified [11] that $BaTiO_3$ films grown on MgO(001) by pulsed laser deposition indeed are highly oriented along

(00l) and the film is completely relaxed. This is in accordance with our map shown in Figure 6 (open circles).

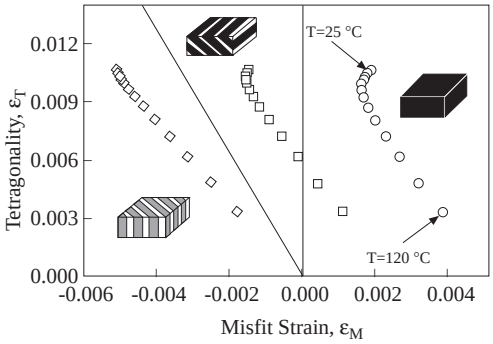

Figure 6. Domain stability maps for completely relaxed $BaTiO_3$ films on MgO(001) (circles), Si(001) (diamonds) and $SrTiO_3$(001) (squares) in the 0°C to 120°C temperature range.

4. Discussion and Conclusion

The theory developed Part I [1] is based on the concepts of linear elasticity. Its application to the ferroelectric transformation becomes doubtful near the critical temperature. For the transformations which are close to 2nd order type, the elastic properties near the Curie point are strongly temperature dependent and nonlinear. However, the positions of the boundaries on the stability map do not depend on elastic moduli. Therefore, it is likely that these diagrams are applicable at least qualitatively even near critical temperature. This assumption, of course, should be checked through nonlinear elastic theory calculations. The analysis of electrostatic effects is also necessary to improve the applicability of the theory to ferroelectrics.

In this paper, we have illustrated the applications of the domain stability maps for epitaxial perovskite films. Although simple in its nature, the theoretical approach is in excellent agreement with several experimental results for epitaxial ferroelectric films. We have shown that these maps are very dependable practical tools to interpret experimental observations and to predict and to control the microstructure in epitaxial systems. Experimental evidence for the $PbTiO_3/KTaO_3$(001) system indicates to the presence of a more complex hierarchical domain structure. Although a perfect three-dimensional arrangement of domains is not observed experimentally, we believe that this type of domain structures should be studied extensively.

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