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Effect of thickness-mediated misfit strain on the heterophase polydomain structure of epitaxial $BiFeO_3$ films

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A heterophase polydomain structure capable of providing large electromechanical responses was recently discovered in $BiFeO_3$ epitaxial ferroelectric films. In this work, the energetics of such a microstructure are analyzed to predict the equilibrium volume fraction of domains at different film–substrate lattice misfits, which is a function of the substrate lattice parameters as well as the film thickness. The results from this work provide a theoretical starting point for designing and engineering elastic polydomains in $BiFeO_3$ thin film materials.

Keywords: Ferroelectric materials; Thin films; Polyphase microstructure; Domains; Misfit strain

Bismuth ferrite ($BiFeO_3$) is a prototype multiferroic material (ferroelectric and anti-ferromagnetic) that has important implications in many technological applications [1–5]. A recent breakthrough in $BiFeO_3$ thin films is the strain-induced "morphotropic phase boundary" effect [6], which manifests itself through a heterophase polydomain microstructure and the associated extrinsic effects in electromechanical properties.

The morphotropic phase boundary (MPB) effect is usually realized in ferroelectric solid solutions, including lead zirconate titanate (PZT), through control of the composition [7–9]. Unfortunately, the morphotropic phase boundary for a ferroelectric solid solution is always a narrow region in the temperature–composition phase diagram, meaning that any compositional deviation may lead to the disappearance of the MPB effect. This makes it extremely difficult to realize the ideal MPB effect in a ferroelectric solid solution. However, the strain-driven MPB effect in $BiFeO_3$ successfully circumvents this difficulty. The pioneering work of Zeches et al. [6] has proved that a mixture of polymorphic phases in a single-component ferroelectric material can be fabricated through epitaxial growth techniques and the manipulation of misfit strain. Such a microstructure can provide large and stable piezoelectric responses comparable to those in complex relaxor ferroelectric solid solutions [10,11].

Much theoretical work has been undertaken on the as-grown equilibrium microstructures of $BiFeO_3$ thin films. Most studies utilized a modified Landau-type phenomenological theory of ferroelectrics originating from the pioneering work of Pertsev et al. [12]. Misfit strain–temperature phase diagrams [13], phase field simulated domain structures [14] and film properties as functions of film thickness [15] and misfit strains [16,17] for single-phase $BiFeO_3$ films have been successfully obtained through this approach. The density function calculations and phase field simulations in the pioneering work [6] suggested that a critical misfit strain separates two stable ferroelectric phases in $BiFeO_3$, playing the same role as the critical composition in the PZT system to provide the MPB effect.

By applying the theory of elastic domains, our previous work has successfully explained the formation of heterophase polydomains in epitaxial $BiFeO_3$ thin films [18], and their enhanced field-induced response due to domain interface movement [11]. Here, one of the most important aspects of the heterophase polydomain structure, its dependence on misfit strains, is investigated in the present work in the theoretical framework of elastic domains.

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As a result of stress relaxation, a typical equilibrium microstructure of a constrained ferroelectric film is a polydomain, i.e. an alternation of plane-parallel lamellae, or domains [19–22]. A polydomain film can consist of either differently oriented domains of the same phase (twins) [23–25] or domains of different phases [26–28]. In addition, metastable or even unstable phases in bulk materials can form stable epitaxial films in single-domain or polydomain forms. In our recent studies of $BiFeO_3$ [11,18], the model of "dense domains" [19,28] is applied to explain the major thermodynamic mechanism for the formation of a heterophase polydomain microstructure in epitaxial $BiFeO_3$ films. The principal assumption of this model is that the domain size/period is smaller than the film thickness, which was experimentally validated for ferroelectric films with a thickness of ~100 nm or more. On the other hand, the thickness-dependent phenomena, including domain fraction variations and the absence of domains, cannot be understood at a satisfactory level without including the effects of thickness-dependent misfit strains and interface energy terms in the thermodynamic theory. Hence, this is the subject of this article.

A polydomain two-phase $BiFeO_3$ film is illustrated in Figure 1, which shows the domains of different phases in black (a tetragonal-like phase, or "T" phase) and white (a rhombohedral-like phase, or "R" phase). Here the "T" phase is not stable in bulk $BiFeO_3$ materials at room temperature and only exists in films through the effect of strain stabilization [6,28]. It is assumed that domain widths are uniform for both phases. In a (0 0 1) film, there are two equivalent sets of "T/R/T/R..." domains due to the symmetry of the in-plane lattice parameters. The alternatively aligned domains have a period denoted by D, the domain width of the "T" phase is denoted by ω, the film thickness is denoted by h and the domain length is the same for both types of domain. Then the domain fraction of the "T" phase is $\alpha = \omega/D$.

The total free energy for a thick $BiFeO_3$ heterophase polydomain film (>~100 nm) can be expressed as in Eq. (1) [18], where $\Delta e(\mathbf{n}) = e(\mathbf{n})_T - e(\mathbf{n})_R$ is the change in misfit elastic energy density, by transforming a single "R" phase into a single "T" phase:

$$\begin{aligned} F(\alpha, a_s) = F_{\text{bulk}}(\alpha) + F_{\text{macrostress}}(\alpha, a_s) = f_R + \alpha\Delta f \\ + \alpha e(\mathbf{n})_T + (1-\alpha)e(\mathbf{n})_R \\ + \alpha(1-\alpha)[e^{DI}(\mathbf{m_0}) - e^I(\mathbf{n})] \end{aligned} \tag{1}$$

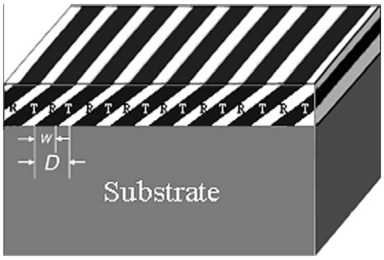

Figure 1. Formation of heterophase polydomains in an epitaxial $BiFeO_3$ film. "T" denotes the tetragonal-like phase while "R" is the rhombohedral-like phase. $\omega/D = \alpha$, where α is the domain fraction of the "T" phase.

Here $\mathbf{m_0} = [1\,1\,2]$. The equilibrium domain fraction α is: $\alpha = \frac{1}{2}\left[1 - \frac{\Delta f + \Delta e(\mathbf{n})}{e^I(\mathbf{n})(1-\eta)}\right]$, where $\eta = \frac{e^{DI}(m_0)}{e^I(\mathbf{n})}$ is the parameter of incompatibility of the polydomain structure [19]. The total free energy density can be numerically calculated through its simplified expression, assuming an isotropic elasticity [18]: $F(\alpha, a_s) \approx f_R + \alpha\Delta f + \frac{E}{1-v}[(1-\alpha)(\varepsilon_R)^2 + \alpha(\varepsilon_T)^2 - \alpha(1-\alpha)(\varepsilon_{aR})^2(1-\eta)]$. Consequently, the equilibrium domain fraction α can be calculated through $\frac{\partial F}{\partial \alpha} = 0$. The increases in free energy density with respect to that of the ground state $R3c$ $BiFeO_3$–f_R are calculated for the three film microstructures, single "T" phase, single "R" phase and "T" + "R" polydomains, as a function of the film–substrate misfit. The results on the three free energies and the equilibrium domain fraction α are presented in Figure 2, which clearly demonstrates the thermodynamic effect of the formation of heterophase polydomains in a $BiFeO_3$ film. First, it can been seen that, when grown on a substrate with a compressive lattice misfit with respect to the "R" phase of ~−5.3% or more ($a_s \leqslant 0.37\,5$ nm), the "T" phase shows a much lower misfit strain energy and consequently a lower total free energy density than that of the "R" phase, although it is not stable in the bulk form. This indicates that the "T" phase is a strain-stabilized phase in thin films. Second, it is shown that, when the effective substrate lattice parameter a_s is within the range of 0.365–0.384, i.e. a lattice misfit range of −7.8% to −3.0% with respect to the "R" phase, the total free energy of the $BiFeO_3$ film is reduced by the formation of heterophase polydomains, as compared with either "T" or "R" single phases. This reduction of total free energy comes from that of the film–substrate misfit energy, which is achieved by a better accommodation of the lattice misfit with substrate of the heterophase polydomains than those of single phases.

The effect of film thickness-mediated misfit strain on equilibrium domain fraction needs to be discussed with the addition of interface energy for very thin films (<100 nm). To do this, the total free energy is expressed as the sum of the bulk, macrostress and interface energies, as shown in Eq. (2) [18]:

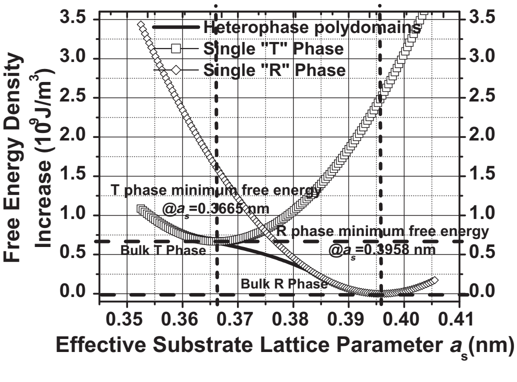

Figure 2. Free energy increase in three types of microstructures, as functions of the effective substrate lattice parameter a_s (hence the film–substrate misfit strain), with respect to the free energy density of the bulk "R" phase.