Three Dimensional Domain Structure in Epitaxial Barium Titanate Thin Films

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Abstract. The three dimensional domain structure of barium titanate thin films was determined using a serial sectioning technique. The domain structure varied sharply through the film thickness, being primarily a-oriented near the substrate and increasingly c-oriented away from this interface. The variation in domain structure is explained in terms of a strain gradient due to partial relaxation of epitaxial coherency strains. The refractive index also varied through the film thickness. A simple relationship based on areal fraction of each domain type aptly described the changes in refractive index with domain structure. These results indicate the importance of understanding three-dimensional domain structure and its impact on film properties.

Keywords: ferroelectric, domain, thin film

1. Introduction

Heteroepitaxial ferroelectric thin films are under consideration for a number of promising technologies, ranging from non-volatile memory for information storage to high speed, low power electro-optic modulators for optical communications [1]. The microstructure and the ferroelectric domain structure of these thin films is critical to the observed properties and ultimate performance. For example, Gopalan and Raj [2] have demonstrated that the measured second-harmonic generation coefficient depended on the volume fraction of each domain type. The strain state of the film can also affect the Curie transition temperature and induce relaxor-type behavior [3]. Furthermore, Hoerman et al. [4] have shown that the dynamics of the electro-optic response in polydomain films are dependent on domain structure. Thus understanding of the detailed relationships between domain structure and properties is critical to utilization of ferroelectric thin films for maximum functionality.

Domain structure in heteroepitaxial ferroelectric thin films depends on the minimization of electro-static energy from the spontaneous polarization and strain energy due to epitaxy with the substrate balanced against the energy of domain wall formation [5]. Phase diagrams have been derived that predict the equilibrium domain structure for a given strain state and temperature [6]. Recent modeling efforts using a phase field approach have predicted equilibrium domain structures for the simplifying assumption of uniform strain, with the calculated three-dimensional domain structures being strongly dependent on the strain state [7, 8]. These structures vary through the film thickness due to interface effects, dipole-dipole interactions and electrical boundary conditions [9]. Additionally, heteroepitaxial films exhibit strain relaxation away from the film/substrate interface, resulting in a strain gradient [3].

Determination of domain structure in ferroelectric films requires specialized analytical methods that can treat the three-dimensional nature of the problem. Current domain characterization techniques fall into two main groups. The first group provides information about domain structure averaged over a volume of the thin film. Techniques based on X-ray diffraction [10] and second harmonic generation [11] fall into this category. Although the relative amounts of each domain type can be ascertained, no information about spatial distribution or size is obtained. The second

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group consists of a large number of scanning surface probe techniques [12], which can provide the two-dimensional spatial distribution of domains with high resolution, but are limited to surfaces. Due to these limitations, characterization of the three-dimensional domain structure of ferroelectric thin films has not been accomplished to date. Quantitative serial sectioning analysis has long been used for the similar problem of evaluating complex metallic microstructures [13, 14]. In this technique, two-dimensional images of thin planar sections from the sample are combined to reconstruct the three-dimensional microstructure.

In this paper, we report initial work to examine the three-dimensional domain structure in epitaxial BaTiO$_3$ thin films using quantitative serial sectioning analysis. The films were polydomain, with the domain fraction dependent on the distance from the film-substrate interface. The measured in-plane optical refractive index also depended on distance from the substrate/film interface.

2.   Experimental

BaTiO$_3$ thin films heteroepitaxially grown on MgO (100) substrates via metal-organic chemical vapor deposition (MOCVD) [15] were used for this study. Films were 0.5–2.0 microns thick. The films were sectioned using a chemical mechanical polishing process (50 g load, 60 RPM, Buehler Microcloth pad, ∼5 nm/min polish rate) with a colloidal silica suspension (80 nm diameter; pH = 9), which resulted in a domain dependent surface topography. Similar domain dependent topography has been observed for certain wet etch chemistries on BaTiO$_3$ single crystals [16], with the preferential etching ascribed to the unique surface chemistry of the different domain types [17]. The differential polishing rate observed here is attributed to interaction of the negatively charged silica nanoparticles with the charged c-oriented domain surfaces. Care was taken to hold the sample temperature below 60°C during all processing, well below the expected Curie temperature, to stabilize the as-grown domain structure.

Following each polishing step, the film was examined with a Digital Instruments Nanoscope III atomic force microscope (AFM) using contact mode. Quantitative analysis of the observed two-dimensional domain structures was performed using a thresholded gray-scale spectrum in ImageJ (public domain software) to separate the domain types observed and calculate their respective areas. Once AFM imaging was completed, the sample was polished again to create a new "slice" through the film thickness.

A Metricon 2010 prism coupler using 632.8 nm light measured the thickness and in-plane refractive index of the film after each polishing iteration. For thicknesses below ∼300 nm, only one prism coupling peak was found and the refractive index was assumed in order to measure the thickness.

3.   Results and Discussion

The domain dependent topography created by the chemical mechanical polishing process can be seen in the AFM micrograph shown as Fig. 1. The very dark and the very light regions are attributed to c-oriented domains, due to the wavy 180-degree domain walls. The needle-like gray regions are a-oriented domains, with their 90-degree domain walls running along ⟨100⟩ directions. The imaging technique is able to differentiate between c-oriented domains, but provides little detail about domains with their polarization in the plane of the film. The high spatial resolution of the technique is apparent from the narrow widths of the a-oriented domains and the sharp appearance of the 180-degree domain walls between c-orientations. Domain dimensions as small as 15 nm have been clearly resolved.

Detailed information about the domain structure can be ascertained from the two-dimensional image shown as Fig. 1. The film is polydomain, with both c domains and a domains present. The areal fraction of c domains is 0.8. The continuity of c-oriented domains across a-oriented domains suggests the c-oriented domains formed first, as is expected when a compressive strain is present at the initial transition from paraelectric to ferroelectric [8]. Domain dimensions range from less than 50 nm to greater than 1000 nm. A fractal distribution of domains sizes is observed. The fractal dimension of the domain structure depicted in Fig. 1 (using the box counting method) is $D_f = 2.53$, in excellent agreement with the theory of Hoerman et al. [4].

The dependence of the domain structure on the distance from the substrate/film interface for epitaxial BaTiO$_3$ on MgO is examined in Fig. 2. The areal fraction of c-oriented domains is plotted as a function of distance from the substrate. Near the film surface (700 nm), the areal fraction of c-oriented
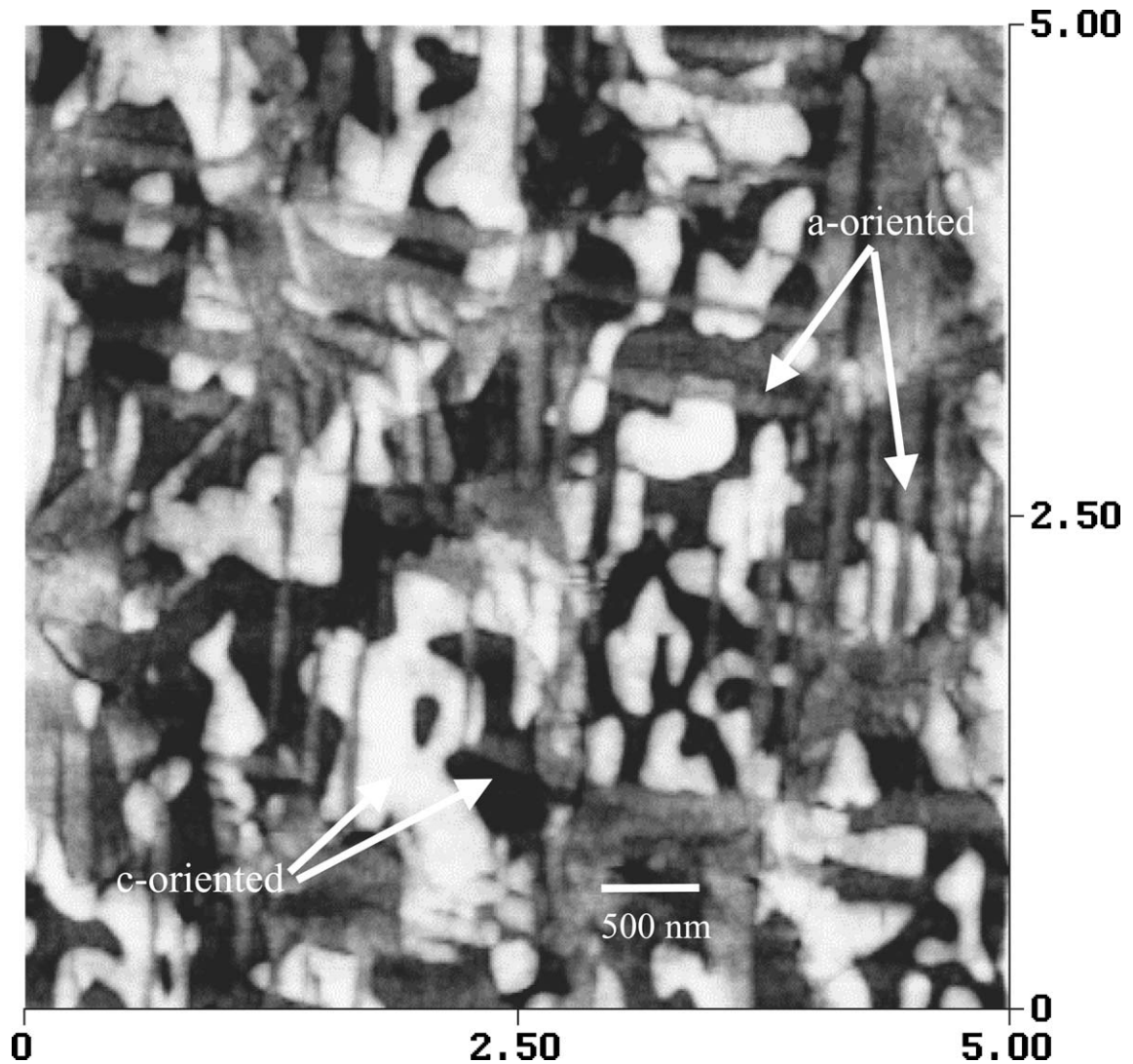
Fig. 1. Contact mode AFM micrograph of a polydomain BaTiO₃ film surface polished to create domain dependent topography.

domains is near 0.5. As the film/substrate interface is approached, the domain structure becomes predominantly *a*-oriented. Based on theoretical domain phase diagrams for uniform strain [6], this suggests the film is under a steep strain/domain gradient. The polydomain surface structure corresponds to a compressive strain ($\sim -0.25\%$), while the purely *a*-oriented region nearer the substrate corresponds to a tensile strain ($>0.20\%$) as the MgO interface is approached. The large domain gradient for relatively modest strains is due to the weak tetragonality of BaTiO₃. The strain/domain gradient through the film thickness could help explain the broad

phase transitions and relaxor-like behavior often observed in epitaxial thin films [3].

The range of strain from compressive to tensile suggests the strain relaxation mechanisms at work in these films are thickness dependent. At the growth temperature of 900°C, the cubic BaTiO₃ lattice (4.027 Å) must be strained 5.9% in tension to be commensurate with the MgO lattice (4.265 Å), where the high temperature lattice constants are calculated using the temperature dependent coefficients of thermal expansion for each material. Upon cooling to room temperature ($\Delta T \sim -875°C$) after film growth, the difference in
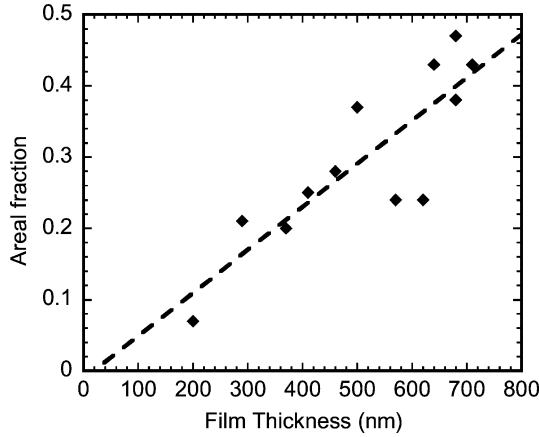
Fig. 2. Measured areal fraction of c-oriented domains through the thickness of a BaTiO$_3$ thin film, with zero thickness representing the interface with the MgO substrate.

Fig. 3. Measured in-plane refractive index for BaTiO$_3$ as a function of areal fraction of *c*-domains determined from AFM images. Error ovals indicate one standard deviation. The dotted line represents the expected refractive index assuming an area fraction model based on bulk property values.

thermal expansions between film and substrate creates compressive strains in the BaTiO$_3$ thin film of 0.51%. If the lattice misfit strain is totally relaxed at the growth temperature, as is often assumed, the residual strain should therefore be compressive throughout the film. The domain structures observed, however, indicate a tensile strain remains near the film/substrate interface, and that the compressive strain near the surface is less than expected. The observed domain gradient is most readily explained by the presence of a graded tensile strain in the film prior to cooling to room temperature, which is then superimposed on the uniform compressive strain due to thermal expansion mismatch. While the polishing process could contribute to the film strain, any such contribution is expected to be small and compressive [18], opposite the trend of increasing in-plane tension observed here. Because the sample was held far below the Curie temperature at all times, any induced changes in the thin film strain would need to surmount the coercive strain field for any reconfiguration of domain structure to occur.

Optical Properties

Gradients in domain structure should directly impact the observed thin film properties. The magnitudes of tensor properties, such as the refractive index, depend upon the type and concentration of domains in the thin film [2]. Figure 3 plots the measured in-plane refrac-
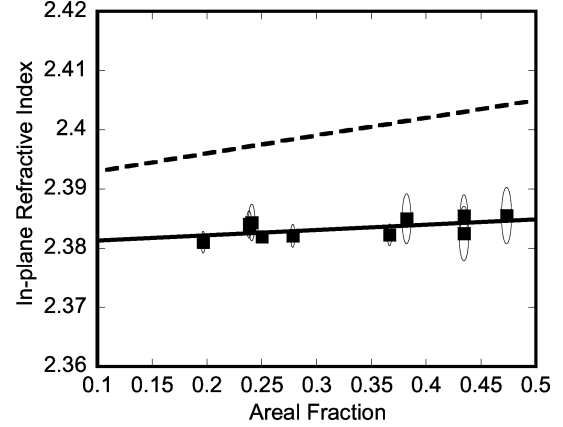
tive index as a function of areal domain fraction in the accompanying AFM measurement. The dashed line in the graph shows the expected behavior based strictly on bulk refractive index values and the given domain configuration. If the sampling electric field is aligned to *a* $\langle 100 \rangle$ direction in the film plane, we expect that the *c*-oriented domains will exhibit the ordinary refractive index, n_o, while half the *a*-oriented domains will contribute as n_o and the other half as extraordinary, n_e. The effective refractive index is then given by

$$n_{\text{eff}} = (c)n_o + \left(\frac{1}{2}\right)(a)n_o + (1/2)(a)n_e$$

where n_{eff} is the effective refractive index of the film, *c* is the fraction of *c*-oriented domains, *a* is the fraction of *a*-oriented domains, and n_o and n_e are the ordinary and extraordinary refractive indices, respectively. The solid line shows the observed trend from these experiments. The slopes of the two lines are similar, indicating the trend with domain structure closely follows the areal fraction model. However, the refractive index values for the domain variants in the thin film are shifted from the bulk, which accounts for the offset between the two lines. Since the domains in the thin film are strained, this is not unexpected. Using the equation for the line fit and extrapolating to the *y*-intercepts at $c = 0$ and $c = 1$, we find $n_e = 2.37$ and $n_o = 2.39$, comparable to the bulk values of 2.36 and 2.42.

4. Conclusions

The domain-dependent surface topography of ferro-electric BaTiO$_3$ thin films was examined, and the three-dimensional domain structure was obtained. In contrast to what is commonly assumed, domain orientations observed at the surface do not extend through the entire film thickness. A gradient in the domain structure was observed, with the films being primarily a-oriented near the film/substrate interface and increasingly c-oriented toward the film surface. The gradient in domain structure indicates a strain gradient in the film, which we attribute to difference in the degree of coherency strain relaxation through the film thickness.

The measured thin film properties changed with domain structure through the film thickness. The in-plane refractive index depended linearly on the areal fraction of c-oriented domains. Gradients in measured properties can explain the relaxor-like behavior often observed in ferroelectric thin films.

This work indicates that further studies of the three-dimensional domain structure and its relation to ferroelectric properties will need to go beyond the fraction of each domain present. In particular, the volume and three-dimensional arrangement of domains are expected to strongly affect the property dynamics.

Acknowledgments

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