Design and preparation of stress-free epitaxial BaTiO$_3$ polydomain films by RF magnetron sputtering

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Abstract
Domain structures of BaTiO$_3$ thick films grown on (100) SrTiO$_3$ single-crystal substrates were engineered using an RF magnetron sputtering deposition process. By tuning the sputtering power and cooling rate and using an off-axis sputtering technique to prepare conducting perovskite oxide bottom electrode with heteroepitaxial quality, we have deposited epitaxial tetragonal single-domain and polydomain BaTiO$_3$ films with a self-assembled three-domain architecture. The electrical properties and microstructure of the BaTiO$_3$ films were characterized, and a $c/a_1/a_2$ cellular polydomain structure was clearly observed in as-grown films by optical microscopy. Such a polydomain structure was a consequence of a complete relaxation of misfit stresses of the film. Engineering of this self-assembled microstructure has great potential in providing large, field-tunable pyroelectric and electromechanical responses in next-generation microelectronic devices and micro-electro-mechanical systems (MEMS).

Keywords: epitaxial films, BaTiO$_3$, self-assembly, domain, magnetron sputtering, polydomain

1. Introduction

BaTiO$_3$ is one of the most intensively studied perovskite ferroelectrics due to its many useful electrical properties. The absence of lead and physiological inertness of BaTiO$_3$ has made it an ideal material for transducer applications in environment-friendly electronic systems, as well as in biosensing and biomechanical systems [1]. Furthermore, owing to the large anisotropies existing in its physical properties [2], engineering of differently oriented domains (so-called ‘domain engineering’) of BaTiO$_3$ may result in novel or improved functionalities in its device applications. For example, a large, field-tunable dielectric property may be achieved in a BaTiO$_3$ material with $c/a$ type of polydomains, when the domain structure evolves under an applied electric field. Recently, BaTiO$_3$ ceramics and single crystals have shown significantly enhanced electromechanical properties by domain engineering [3–5], and hence stimulated intensive research on this material in the fields of lead-free ferroelectric dielectrics and piezoelectrics. However, to the best of our knowledge, there have been very few reports on the preparation of domain-engineered BaTiO$_3$ films aimed at innovating or improving their physical

4 The notations of $c$ and $a$ domains are made with respect to the orientation of the long axis (also named $c$-axis) of the tetragonal phase. When a domain’s $c$-axis is parallel to the applied field or the surface normal, it is called a ‘$c$-domain’. On the other hand, an ‘$a$-domain’ has its $c$-axis perpendicular to the applied field or the surface normal (see figure 3(b)). The dielectric constant is 33 times larger for $a$ than for $c$ domains in BaTiO$_3$ [2].
Table 1. Crystalline structures and thermal expansion coefficients of involved materials.

| Material       | BaTiO$_3$ | SrTiO$_3$ | La$_{0.5}$Sr$_{0.5}$CoO$_3$ |
|----------------|-----------|-----------|-----------------------------|
| Room-temperature crystalline structure | ABO$_3$ tetragonal perovskite | ABO$_3$ cubic perovskite | Pseudo-cubic perovskite |
| Lattice parameters (Å) | $a = 3.993$ | 3.905 | 3.835 |
| $c = 4.034$ | | | |
| Thermal expansion coefficient ($\times 10^{-6}$ K$^{-1}$) | $\sim 10.7$ [10] | $\sim 11$ [11–12] | $\sim 20^a$ |

$^a$ Thermal stresses are mainly induced by the difference in thermal expansion coefficients between film and substrate.

Table 2. Film deposition parameters

| Sputtering parameters | Single-domain BaTiO$_3$ | Polydomain BaTiO$_3$ |
|-----------------------|--------------------------|----------------------|
| Sputtering power (W)  | 65                       | 105                  |
| Post-deposition cooling rate (°C min$^{-1}$) | 6–7                       | 10–12               |
| Substrate temperature (°C) | 700                       |                     |
| Base pressure (Pa)    | $2.0 \times 10^{-4}$     |                     |
| Sputtering pressure (Pa) | 1.9                      |                     |
| Target–substrate distance (mm) | 60                       |                     |
| Deposition time (min) | 60                       |                     |

properties. In this paper, we present experimental results of the preparation and microstructural characterization of self-assembled polydomains in epitaxial BaTiO$_3$ thin films. Such a structure-engineered thin film material has great potential in realizing large, field-tunable pyroelectric [6] and electromechanical [7–9] responses in next-generation microelectronic devices and micro-electro-mechanical systems (MEMS).

Generally, the formation of self-assembled polydomains in a ferroelectric film is closely related to the evolution of its stress status during preparation, on which the initial lattice misfit, thermal expansion and a thickness and temperature-mediated relaxation processes play central roles. In the present work, the engineering of polydomains was simplified by selecting substrate and electrode materials with similar structure, closely-matched lattice parameters and thermal expansion coefficients [10–12] (see table 1). The major driving factor is the misfit strain relaxation process dictated by thermal history and thickness of the epitaxial films.

It is well known that the formation of elastic polydomains and misfit dislocations are two stress relaxation mechanisms in epitaxial films. The former requires a minimum film thickness above which the formation of polydomains is thermodynamically stable [13], while the latter takes places at elevated temperatures. By tuning the film thickness via sputtering power and post-deposition cooling rate, the stress relaxation mechanisms in epitaxial films can be engineered, which will result in different domain structures. In the present work, BaTiO$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$/SrTiO$_3$ (BTO/LSCO/STO) heterostructures showing two kinds of domain structure (single-domain and polydomain) in the BaTiO$_3$ layer were fabricated based on the above design method for sputtering deposition. Low sputtering power and slow cooling rate led to the formation of single-domain BaTiO$_3$ films ($\sim 300$ nm), while polydomain BaTiO$_3$ films ($\sim 500$ nm) were prepared at a high sputtering power and a fast cooling rate. These observations are consistent with the literature on lead zirconate titanate solid solutions [11, 12, 14, 15]. Details of the deposition process are described in the Experimental section and illustrated in figure 1. The deposition parameters are summarized in table 2.

2. Experimental section

The (100) single-crystal SrTiO$_3$ substrates ($10 \times 10 \times 0.5$ mm$^3$) were ultrasonically cleaned in acetone, followed by two 10 min washing steps, firstly by ethanol and then deionized water. To clean up residual contaminants, a pre-sputtering of 6 min was applied to these substrates in the loading chamber just before they were placed into the deposition chamber. A base pressure of $2.0 \times 10^{-4}$ Pa was achieved before the film deposition. A 50-nm-thick
La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) bottom electrode layer was sputtered from an LSCO ceramic target by using a 90° off-axis RF magnetron sputtering technique, which is capable of producing epitaxial thin films with smooth surfaces [16]. Then, BaTiO$_3$ thin films were deposited by on-axis RF magnetron sputtering from a BaTiO$_3$ ceramic target. Both sputtering targets had a cylinder shape ($\Phi = 50$ mm, $L = 5$ mm) and a purity of 99.99%. The off-axis and on-axis sputtering geometries for the BaTiO$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$/SrTiO$_3$ heterostructures are schematically shown in figure 1. During the film deposition, the substrate temperature was set at 700°C, and the chamber pressure was kept at 1.9 Pa in a pure argon atmosphere. The crystalline orientations and lattice spacings of the BaTiO$_3$ and La$_{0.5}$Sr$_{0.5}$CoO$_3$ thin film layers were analyzed by x-ray diffraction (XRD; $\theta$–2$\theta$ scans in a commercial Rigaku Dmax-rc XRD diffractometer equipped with a Ni-filtered Cu-K\alpha radiation source). The surface morphology and the polydomain pattern of the BaTiO$_3$ films were observed with an Olympus BX51M optical microscope. Domain size was measured by tapping-mode atomic force microscopy (AFM) in a commercial MicroNano\textsuperscript{TM} D-5A setup using CSC37-AIBS AFM tips CSC37-AIBS (MikroMasch, Estonia). The ferroelectric hysteresis loops and leakage currents of the BaTiO$_3$ films were measured with an RT-66 ferroelectric tester and a Keithley 4200-SCS semiconductor characterization system, respectively.

3. Results and discussion

The crystalline structure and orientation of the films were analyzed by conventional x-ray $\theta$–2$\theta$ scans. Figures 2(a) and (b) show the XRD patterns for the single-domain and polydomain BaTiO$_3$ films, respectively. Both films are highly $c$-axis oriented, showing a dominant cube-on-cube growth of BaTiO$_3$ (001)/La$_{0.5}$Sr$_{0.5}$CoO$_3$ (100)/SrTiO$_3$ (100). The values of full width at half maximum (FWHM) of the BaTiO$_3$ (002) peaks are $0.342^\circ$ and $0.388^\circ$ for the single-domain and polydomain films, respectively. No other peaks are present in the XRD patterns of the BaTiO$_3$ and La$_{0.5}$Sr$_{0.5}$CoO$_3$ layers, except for a characteristic peak of BaTiO$_3$ (200) ($a$ domains) in figure 2(b). By comparing the integrals of the (200) and (002) diffraction peaks, the abundance of $a$-domains in the polydomain BaTiO$_3$ film was estimated at $\sim$8%.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{XRD $\theta$–2$\theta$ scans of (a) single-domain and (b) polydomain BaTiO$_3$ thin films; the corresponding BTO/LSCO/STO heterostructures are illustrated in (c) and (d), respectively.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Temperature-microstructure evolution of a thick epitaxial ferroelectric film, where it undergoes (a) a cube-on-cube growth at a temperature above its Curie point; (b) a paraelectric–ferroelectric phase transition at its Curie point, which corresponds to a cubic-tetragonal transformation of the crystalline lattice and is representative of BaTiO$_3$ and many other perovskites; (c) formation of different domain architectures at room temperature [13, 14].}
\end{figure}

The corresponding heterostructures are illustrated in figures 2(c) and (d) for the two types of BaTiO$_3$ films.

A typical temperature-microstructure evolution of a thick epitaxial ferroelectric film is schematically shown in figure 3 [17]. The paraelectric–ferroelectric phase transition corresponds to a cubic–tetragonal transformation of the crystalline lattice, which is the case for the BaTiO$_3$ film and is representative of many other perovskites. In figure 3(c), a lattice misfit close to zero leads to the formation of the cellular polydomains, corresponding to the case of a thick BaTiO$_3$ film epitaxially grown on (100) SrTiO$_3$ substrates. Such a polydomain structure consists of all three possible elastic twins of the tetragonal phase to reach a complete relaxation of the misfit stresses [13]. These elastic twins or domains self-assemble into a network of plane-parallel lamellae, separated by elastically compatible 90° domain walls. To verify that the polydomain films are indeed fully relaxed, a calculation of effective misfit strain was performed using equation (1) [13]:

$$\bar{\varepsilon}_M = \frac{(\alpha_c - 1) \cdot \varepsilon_T}{2}.$$  \hspace{1cm} (1)

Here, $\alpha_c$ is the fraction of $c$-domains (92% in this work), and $\varepsilon_T$ is the tetragonality of the ferroelectric material (for BaTiO$_3$, $\varepsilon_T = 1.027%$); $\bar{\varepsilon}_M$ is estimated as $\sim -0.04\%$, i.e. the polydomain film is virtually ‘stress free’. Such a polydomain structure usually has highly mobile domain walls and can be very adaptive to an applied field [7, 18].

The main methods of studying the domain structures of ferroelectric thin films include surface modification [19], optical microscopy [19, 20], scanning electron microscopy [19, 21] and scanning probe microscopy [19, 21–23]. Many researchers used advanced optical microscopy techniques to observe domain structures in ferroelectric films, including polarization optical microscopy [3, 24], near-field
which is caused by the interface steps across every \( c/a/c \) unit of the polydomains [27]. An illustration of the periodic \( c/a/c \) interface steps of the \( c/a_1/a_2 \) cellular polydomain structure is given in figure 4(c). The interface step between two adjacent \( c \)-domains separated by an \( a \)-domain is a result of surface relief associated with the formation of \( c/a \) interfaces. Its height \( \Delta Z \) can be calculated as [27]

\[
\Delta Z \approx t_a \times \tan^{-1} \left( \frac{c}{a} - 1 \right),
\]

where \( t_a \) is the width of \( a \)-domain, and \( a \) and \( c \) are the lattice parameters of the film. For a tetragonal \( BaTiO_3 \) film, the theoretical value of \( \Delta Z \) calculated from equation (2) is \( \sim 10 \) nm. It should be noted that the ‘orthogonal grid’ is a virtual image of the polydomains, which consists of information collected not only by optical microscopy (500× magnification in this case), but also by the reflection and refraction of light due to the periodic surface steps. Therefore, the exact dimension of the polydomain structure, including the width (usually in the 100 nm scale for films several hundred nm thick) and height of interface steps (\( \sim 10 \) nm), should be confirmed by instruments capable of nanoscale analysis. For this purpose, AFM was employed as a supplemental tool to measure the width and height of interface steps.

Figure 5(a) is the tapping-mode AFM image of the surface of the polydomain film, which clearly shows the \( c/a_1/a_2 \) cellular polydomain structure. The two sets of parallel strips, which intersect with each other at a 90° angle, are surface images of the \( a_1 \) and \( a_2 \) domains, respectively, while the remaining area represents the \( c \)-domain matrix. A high-contrast version of the same AFM image (figure 5(b)) clearly differentiates the two types of domains (bright area: \( a \)-domains, dark area: \( c \)-domains).

Figures 5(c) and (d) show AFM line scans across representative \( a_1 \) and \( a_2 \) domains, respectively. Figure 5(c) reveals that the widths of two adjacent \( a_1 \) domains are 165 nm (marked with AB) and 160 nm (marked with CD). The corresponding heights of the interface steps are 5.3 nm for AB and 4.9 nm for CD. Figure 5(d) shows the wider \( a_2 \) domains. The domain width (marked with EF) is about 280 nm and the height of the interface step is 21 nm. On average, the \( a \)-domains are \( \sim 200 \) nm wide and the interface step is \( \sim 12 \) nm in height, the latter agreeing fairly well with the theoretical value of \( \sim 10 \) nm calculated from equation (2). The asymmetry in the physical dimensions of \( a_1 \) and \( a_2 \) domains is possibly due to an inclined substrate alignment with respect to the sputtering flux of \( BaTiO_3 \).

The ferroelectric properties of the \( BaTiO_3 \) films were characterized and reported earlier [28]. The \( 2P_r \) value of the single-domain \( BaTiO_3 \) films was \( \sim 7 \) \( \mu \)C cm\(^{-2} \) and was improved to 27 \( \mu \)C cm\(^{-2} \) when oxygen was added to the sputtering atmosphere. Figure 6 shows the \( J-V \) leakage current curves obtained by using different voltage ranges. The minimum leakage current densities are \( \sim 10^{-8}–10^{-9} \) A cm\(^{-2} \) in all the measurements. The \( J-V \) curves are not symmetrical versus the origin and the minimum leakage current density is shifted towards the positive voltages. This may be explained by the existence of an internal electrical field across the film.
due to the use of asymmetrical electrodes (Pt top electrode and LSCO bottom electrode). In the future, we will investigate the electromechanical properties of the polydomain films, which are expected to have large extrinsic contributions from field-driven domain-wall movements [7, 18].

4. Conclusions

In summary, epitaxial BaTiO$_3$ films with different domain structures and good electrical properties were prepared by an RF magnetron sputtering process consisting of both off-axis and on-axis deposition steps. The crystalline and domain structures of the BaTiO$_3$ films were characterized by XRD analysis, conventional optical microscopy and atomic force microscopy. This work establishes a simple processing route to fabricate high-quality epitaxial BaTiO$_3$ films, whose domain structure can be engineered by tuning the sputtering parameters and observed by XRD, optical microscopy and AFM.

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