Low-Temperature Monoclinic Phase in Epitaxial (001) Barium Titanate on (001) Cubic Substrates

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ABSTRACT

The possibility of the existence of a low temperature monoclinic phase in epitaxial (001) BaTiO_3 films on a (001) compressive substrate is analyzed theoretically and compared to recent experimental data from literature. There is good agreement between the theoretical findings and the experimentally observed behavior. The formation of the monoclinic phase arises from the point group reduction due to the rotation of the polarization vector commensurate with the variations in the in-plane strain state.

Keywords: Ferroelectric thin films, epitaxy, monoclinic phase, thermodynamics

INTRODUCTION

Ferroelectric perovskites have received considerable interest due to their many unique physical properties. These materials are potential candidates for a variety of applications such as active elements of non-volatile memories (NVRAM), capacitors in dynamic random access memories (DRAMs), tunable dielectric materials for voltage-controlled, frequency-agile phase shifters and filters operating in the microwave regime, and pyroelectric IR detectors. The electrical and electromechanical properties, such as the dielectric, pyroelectric, and piezoelectric response, vary strongly in the vicinity of the ferroelectric-paraelectric phase transformation temperature ($T_C$).

The phase transformation characteristics and thus the electrical properties of ferroelectrics change dramatically in epitaxial films due to the coupling...
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between the internal stresses and the polarization [1, 2]. Recent theoretical studies demonstrate that it is possible to stabilize phases in perovskite ferroelectrics that are not possible in single-crystal or bulk form [3–5]. It has been shown experimentally that ferroelectric state may persist even at \( \sim500^\circ C \) in BaTiO\(_3\) (BT) for which the bulk phase transformation temperature is around \( 120^\circ C \) [1]. Furthermore, experimental results seem to indicate that a ferroelectric state can be induced in SrTiO\(_3\) (an “incipient” ferroelectric) at room temperature [2].

We have recently presented a detailed strain analysis of epitaxial ferroelectric films taking into account multiple sources of strain including the lattice mismatch between the film and the substrate, thermal strains due to differences in the thermal expansion coefficients of the film and the substrate, and relaxation by the formation of interfacial dislocations [6]. The strain state coupled with a thermodynamic model as applied to epitaxial (001) BT films on (001) MgO show that there are successive phase transformations with decreasing temperature that are different than the bulk. We have verified this experimentally for 50 nm thick (001) BT films grown on (001) MgO substrates through synchrotron X-ray diffraction experiments which display two slope changes in the temperature dependence of the out-of-plane lattice constant [6]. This indicates that two phase transformations exist in the film as a function of temperature with transition temperatures and lattice constants that are consistent with the theoretically predicted phases. Theoretical results show that the first transformation at around \( 270^\circ C \) corresponds to a paraelectric-ferroelectric transition. The ferroelectric phase has orthogonal symmetry (Amm\(_2\)) with in-plane polarization components. The transformation at around \( -20^\circ C \) is an Amm\(_2\)\( \leftrightarrow\)Pm transition between two ferroelectric phases. The ferroelectric Pm phase is monoclinic compared to the rhombohedral R3\(_m\) phase in bulk [6].

Two phase transitions have also been identified in (001) BT grown on (001) KTaO\(_3\) (KT) via synchrotron X-ray diffraction [7]. Epitaxy on (001) KT would produce tensile in-plane strains in pseudomorphic (001) BT films compared to compressive in-plane strains of pseudomorphic (001) BT on (001) MgO. In this letter, we present a theoretical analysis to describe the behavior of (001) BT films on (001) KT employing the previously developed thermodynamic methodology and show that the low-temperature phase of BT in low temperatures has again a monoclinic symmetry.

THEORY

The strain state of a (001) epitaxial perovskite ferroelectric film can be expressed as the sum of the elastic strain and the self-strain tensors such that:

\[
\varepsilon^T_{ij} = \varepsilon^m_{ij} + \varepsilon^0_{ij} \tag{1}
\]
where $\varepsilon_{ij}^m$ is the misfit strain of the film in the paraelectric state given by

$$\varepsilon_{ij}^m = \begin{pmatrix} \varepsilon_m & 0 & 0 \\ 0 & \varepsilon_m & 0 \\ 0 & 0 & \left[2S_{12}/(S_{11} + S_{12})\right]\varepsilon_m \end{pmatrix},$$

(2)

and

$$\varepsilon_{ij}^0 = \begin{pmatrix} Q_{11}P_1^2 + Q_{12}(P_2^1 + P_2^2) & Q_{44}P_1P_2 & Q_{44}P_1P_3 \\ Q_{44}P_1P_2 & Q_{11}P_2^2 + Q_{12}(P_1^1 + P_1^2) & Q_{44}P_2P_3 \\ Q_{44}P_1P_3 & Q_{44}P_2P_3 & Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2) \end{pmatrix}$$

(3)

is the self-strain. In the above relations, $Q_{ij}$ and $S_{ij}$ are the electrostrictive coefficients and elastic compliances at constant polarization, respectively, in the contracted notation and $P_i$ are the components of the polarization vector.

In epitaxial films and heterostructures, the strain due to lattice mismatch between the film and the substrate can be partially or even completely relaxed during film growth by the formation of orthogonal arrays of interfacial (or misfit) dislocations at the film-substrate interface. These dislocations are equilibrium defects and their density and spacing depends on the film thickness, the nominal misfit, and the deposition temperature [8]. Due to the relaxation by misfit dislocations, the internal stress state and thus the structural variations become a function of film thickness [9]. Thermal stresses may also arise in the film as it is cooled down due to the differences between the thermal expansion coefficients (TECs) of the film and the substrate. These stresses usually cannot be relaxed by interfacial defects due to kinetic reasons as the film cools down. The ultimate stress state in the film at ambient temperatures evolves due the interplay between dislocation induced relaxation at $T_G$ and thermal stresses that develop afterwards as the film is cooled down.

Taking into account the relaxation of internal stresses via interfacial dislocations and the thermal stresses that develop during cooling down from the deposition temperature, the total strain becomes:

$$\varepsilon_{ij}^T = \varepsilon_{ij}^m + \varepsilon_{ij}^0 + \varepsilon_{ij}^{th} + \varepsilon_{ij}^R.$$  

(4)

In this relation,

$$\varepsilon_{ij}^{th} = \begin{pmatrix} \varepsilon_{th} & 0 & 0 \\ 0 & \varepsilon_{th} & 0 \\ 0 & 0 & \left[2S_{12}/(S_{11} + S_{12})\right]\varepsilon_{th} \end{pmatrix}$$

(5)
and is the strain due to dislocation relaxation which has been neglected in this study due to the small lattice misfit between BT and KT.

Resultant strain tensor in Eq. (4) can be inserted into the Landau-Devonshire (LD) potential for a pseudo-cubic ferroelectric crystal undergoing a paraelectric-to-ferroelectric transformation with a symmetry change from $Pm\overline{3}m$ to $P\overline{4}mm$ at the $T_C$. The LD potential for such a crystal is basically the addition of the polarization related energy terms and the elastic energy:

$$\bar{F}(P,T,\epsilon_{ij}^T) = F(P,T) + F_{\text{Elastic}}(\epsilon_{ij}^T)$$  \hspace{1cm} (8)$$

In Eqn. (8),

$$F(P,T) = F_0 + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6$$  \hspace{1cm} (9)$$

and

$$F_{\text{Elastic}} = \frac{1}{2} \epsilon_{ij}^T \cdot C_{ijkl} \cdot \epsilon_{kl}^T$$  \hspace{1cm} (10)$$

where $C_{ijkl}$ are the elastic moduli at constant polarization.

Minimizing Eqn. (8) with respect to $P_i$ yields the equilibrium spontaneous polarization components as a function of misfit strain and temperature. We plot

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>KT</th>
<th>BT</th>
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<tbody>
<tr>
<td>$a$ at RT (nm)</td>
<td>0.3989</td>
<td>0.4003 (pseudo cubic)</td>
</tr>
<tr>
<td>$a$ at $T_G$ (nm)</td>
<td>0.4009</td>
<td>0.4034</td>
</tr>
<tr>
<td>TEC ($^\circ$C$^{-1}$)</td>
<td>$6.5 \times 10^{-6}$</td>
<td>$9 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value (in SI units)</th>
</tr>
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<tbody>
<tr>
<td>$a_1$</td>
<td>$(T-120)/(2\varepsilon_0 C)$</td>
</tr>
<tr>
<td>$a_{11}$</td>
<td>$-3.52294 \times 10^9$ (curve fit from Ref. [12])</td>
</tr>
<tr>
<td>$a_{111}$</td>
<td>$6.4 \times 10^9$</td>
</tr>
<tr>
<td>$S_{11}$</td>
<td>$8.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>$S_{12}$</td>
<td>$1.97 \times 10^{-12}$</td>
</tr>
<tr>
<td>$Q_{11}$</td>
<td>0.11</td>
</tr>
<tr>
<td>$Q_{12}$</td>
<td>0.43</td>
</tr>
</tbody>
</table>
the polarization components calculated for a 40 nm thick BT film on a KT substrate between 700 K and 20 K in Fig. 1. On the same plot, we also provide the strain state of the film to identify critical misfit strains at which the phase transformations occur. Using these polarization values in Eqns. (3) and (4), we give the lattice parameters as a function of temperature in Fig. 2 together with the values compiled from Ref. [7]. The constants used in the calculations were taken from Refs. [3, 10, 11] as listed in Table 1 and 2.

RESULTS AND DISCUSSION

In Fig. 1, we give the temperature dependence of polarization state in the film together with the strain conditions experimentally determined from the lattice parameters of Ref [9]. Using the same elastic strain in Ref. [7], our thermodynamic method predicts the presence of a paraelectric-to-ferroelectric phase transformation at 530 K with an out-of-plane polarization component giving rise to the tetragonal phase (Fig. 1). This is followed by the appearance of two in-plane polarization components at 275 K that develops further with cooling. In Fig. 2, the theoretical and the experimental lattice parameters are given to display the self-strain dependence of the out-of-plane lattice parameter, \( c \), in particular. We theoretically find two distinct temperatures where the slope of \( c \) changes abruptly due to the self-strain of the polarization components (Fig. 1). In experimental results, \( \partial c/\partial T \) shows a sudden change at \( \sim 500 \) K and the value of \( c \) increases as the film cools down to \( \sim 270 \) K. At 270 K, the slope suddenly changes and gets smaller with decreasing temperature.
Figure 2. Lattice parameters obtained from the total strain tensor. The in-plane lattice parameter of the film is clamped to the substrate without any relaxation (Solid line is the fit to the in-plane lattice parameter in Ref. [9] that is used in this study).

Figure 3. The misfit-strain diagram on which the condition for the current case is shown with the dashed line. The temperatures for the predicted phase transformation to the $c$-phase and the occurrence of the $m$-phase is indicated with the arrows.
Carefully studying the experimental and theoretical data in Fig. 2 and comparing it to Fig. 1, it is clear that the experimentally observed behavior of $c$ is commensurate with the emergence of polarization at 500 K and subsequent rotations of the polarization vector as a function of the in-plane misfit. The slope change around 500 K is related to the out-of-plane polarization, $P_3$ that couples with $c$ via $Q_{11}$. At 275 K, with the formation of in-plane polarization components that results in a rotation of polarization, the polarization-strain coupling becomes somewhat more complicated. At this point, the coupling to the in-plane polarizations, $P_1$ and $P_2$ attempts to lower the $c$ values while the self-strain due to $P_3$ counteracts to stretch $c$. Thus the behavior in Fig. 2 is well defined by the polarization formation and then rotation upon cooling.

Polarization solutions for the system can be utilized to compare the behavior of BT on KT in the light of the temperature-misfit strain diagram for a clamped, pseudomorphic BT film. This diagram has been plotted without any a priori assumption of the phases that are expected to appear. The elastic strain state has been considered to obtain the stable components of the polarization with temperature. In doing so, the $r$-phase identified in previous studies [3] can be considered as a monoclinic phase ($m$-phase) with $P_1 = P_2 \neq P_3 \neq 0$. Looking at the stable phases with the given polarization components, the variation of strain of BT on KT with temperature is given as the dashed line in Fig. 3. The temperatures at which the paraelectric-ferroelectric transformation occurs, stabilizing the tetragonal phase ($c$-phase) and at which the polarization rotation starts, inducing the $m$-phase, are the intersection of the dashed line with the phase boundaries (shown with arrows). These points can also be analytically expressed as

$$T_{C1} = T_C + 2\varepsilon_0 C \left(\frac{Q_{11} + Q_{12}}{S_{11} + S_{12}}\right) \tilde{\varepsilon}_{ij}^m(T)$$  \hspace{1cm} (11)

$$T_{C2} = T_C + 4\varepsilon_0 C \left(\frac{Q_{12}}{S_{11} + S_{12}}\right) \tilde{\varepsilon}_{ij}^m(T)$$  \hspace{1cm} (12)

where $C$ is the Curie constant for BT.

**CONCLUSIONS**

We have analyzed the observed behavior of BT films on KT substrates using experimental data from literature as a starting point of our thermodynamic analysis to show that a monoclinic phase with $P_1 = P_2 \neq P_3 \neq 0$ can indeed exist. A stress induced, low temperature $m$-phase could be stabilized in an epitaxial perovskite ferroelectric film on both tensile and compressive substrates. One major different aspect of the ferroelectrics in thin film compared to bulk form
is that strain prohibits a first order-like phase transformation. Hence, there is no abrupt jump observed in the order parameter as well as the lattice parameters, e.g., in our case of BT on KT, the variation of polarization in a strained film (even close to zero misfit strain) is rather gradual. Therefore, phase transformations in epitaxial ferroelectric films can be described as continuous lattice distortions that result from the rotation of the crystal lattice associated with the rotation of the spontaneous polarization as a function of in-plane misfit strains. On the other hand, we note that, under high compressive strains where the self-strain may be overwhelmed by the large elongation along the out-of-plane direction, the absence of variation in $c$ is not an indication of the lack of spontaneous polarization in the films.

ACKNOWLEDGMENTS

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REFERENCES