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# A modified Landau–Devonshire thermodynamic potential for strontium titanate

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The range of reported values of the Landau energy coefficients of bulk $SrTiO_3$ leads to uncertainty in not only the magnitude but also the direction of the calculated spontaneous polarization in $SrTiO_3$ thin films in a state of biaxial tension. In this study, we use experimental results from strained $SrTiO_3$ films together with phase-field simulations to refine the values of the Landau energy coefficients and report a modified thermodynamic potential for bulk strontium titanate. The transition temperatures and ferroelectric/antiferrodistortive domain stabilities predicted from this modified potential agree well with measurements on biaxially strained $SrTiO_3$ thin films. © *2010 American Institute of Physics*. [doi:10.1063/1.3442915]

$SrTiO_3$ has received considerable interest due to its low temperature properties, such as high dielectric constants and low microwave losses, as well as its room temperature applications.[1] Bulk $SrTiO_3$ is an incipient ferroelectric in its pure unstressed form and undergoes a cubic to tetragonal antiferrodistortive (AFD) transition at 105 K.[2–5] It has been predicted[6–10] and experimentally verified[10–15] that strain can induce room temperature ferroelectricity in $SrTiO_3$ thin films. Both ferroelectric and AFD domain stabilities in strained $SrTiO_3$ thin films have been investigated extensively using Landau–Devonshire thermodynamic theory,[6,7,9,10] where the spontaneous polarization $p=(p_1,p_2,p_3)$ and the structural order parameter $q=(q_1,q_2,q_3)$ are chosen as the order parameters to describe the ferroelectric transition and the AFD transition, respectively. The ferroelectric and AFD domain structures of $SrTiO_3$ thin films have also been predicted by the phase-field method.[9,10] In all existing thermodynamic analyses[6,7,9] and phase-field simulations,[9,10] a fourth-order polynomial is employed to describe the bulk stress-free free energy density $f_{\text{bulk}}(p_i,q_i)$, as follows:

$$\begin{aligned} f_{\text{bulk}}(p_i,q_i) &= \alpha_1(p_1^2+p_2^2+p_3^2)+\alpha_{11}(p_1^4+p_2^4+p_3^4)\\ &\quad+\alpha_{12}(p_1^2p_2^2+p_2^2p_3^2+p_3^2p_1^2)+\beta_1(q_1^2+q_2^2+q_3^2)\\ &\quad+\beta_{11}(q_1^4+q_2^4+q_3^4)+\beta_{12}(q_1^2q_2^2+q_2^2q_3^2\\ &\quad+q_3^2q_1^2)-t_{11}(p_1^2q_1^2+p_2^2q_2^2+p_3^2q_3^2)-t_{12}[p_1^2(q_2^2\\ &\quad+q_3^2)+p_2^2(q_1^2+q_3^2)+p_3^2(q_1^2+q_2^2)]\\ &\quad-t_{44}(p_1p_2q_1q_2+p_2p_3q_2q_3+p_3p_1q_3q_1), \qquad (1)\end{aligned}$$

where $\alpha_{ij}$ and $\beta_{ij}$ are the Landau coefficients and $t_{ij}$ is the coupling coefficient between $p$ and $q$. The range in the Landau energy coefficients leads, however, to significantly different predictions of domain states, and thus different domain structures, under biaxial tensile strain. For example, the uncertainty of the fourth-order coefficient $\alpha_{12}$ in Eq. (1) will result in two completely different polar states under tensile strains. An $\alpha_{12}$ value of $5.5\times10^{-12}$ $\text{cm}^6\ \text{dyn/esu}^4$ [the average of the experimental value, $\alpha_{12}=9.28$ at $T=8$ K,[16] and the value used in a previous calculation[7] $\alpha_{12}=1.7$ (both in cgs units $10^{-12}$ $\text{cm}^6\ \text{dyn/esu}^4$)] favors the ferroelectric polarization along pseudocubic (subscript $p$) $[010]_p/[100]_p$.[9] A smaller value, e.g., $\alpha_{12}=1.7$ (Refs. 7 and 9) or 1.5 (Ref. 6) stabilizes a ferroelectric polarization along $[110]_p/[1\bar{1}0]_p$.

To find the appropriate $\alpha_{12}$ value, we compared the simulation results using two existing $\alpha_{12}$ values with available experimental measurements of polarization directions. Optical second harmonic generation measurements demonstrated that a (001) $SrTiO_3$ thin film grown on (110) $DyScO_3$ substrate with biaxial strain $e_{s1}=e_{s2}=0.94\%$ (Ref. 12) ($e_{s1}$ stands for the misfit strain between the substrate and thin film along $[100]_p$ while $e_{s2}$ is along the $[010]_p$ axis) exhibited a $[110]_p/[1\bar{1}0]_p$ polar state, which is consistent with both thermodynamic calculations[6,7] and phase-field simulations[9] using $\alpha_{12}=1.7$ or 1.5. The $[110]_p/[1\bar{1}0]_p$ polar state, an orthorhombic *Amm*2 structure, also agrees with first-principle calculations.[8] In contrast, samples with anisotropic in-plane strains, (001) $SrTiO_3$ on (110) $DyScO_3$ (Ref. 10) ($e_{s1}=1.03\%$, $e_{s2}=1.06\%$) and (001) $SrTiO_3$ on (110) $GdScO_3$ (Ref. 15) ($e_{s1}=1.46\%$, $e_{s2}=1.59\%$) develop ferroelectric polarization along both in-plane $[010]_p$ and $[100]_p$ axes, leading to domain twinning at lower temperatures. To be consistent with these experimental findings $\alpha_{12}=5.5$ should be employed[10] instead of 1.7 or 1.5 in order to produce the $[010]_p/[100]_p$ polar states in these two films.

From these simulations it is obvious that the coefficient $\alpha_{12}$ affects the relative thermodynamic stability of the $[110]_p$ and $[100]_p$ polar states under a biaxial tensile strain. In the early electric field induced Raman scattering measurement,[16] the value of $\alpha_{12}$ is determined from $\omega_s^{\perp}$, the measured components perpendicular to an applied electric field along the (001)-direction. This phonon frequency $\omega_s^{\perp}$ is the only mea-

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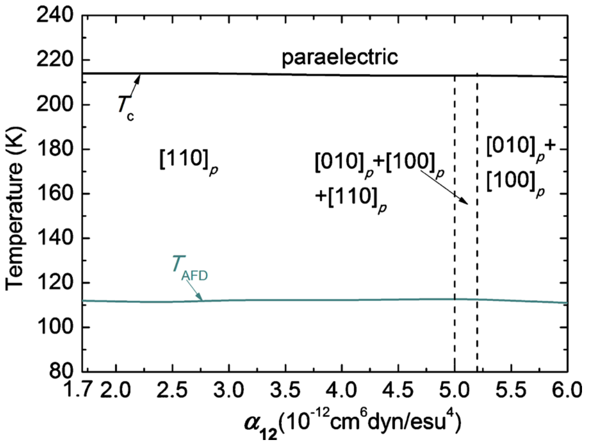

FIG. 1. (Color online) Predicted transition temperatures and polarizations as a function of $\alpha_{12}$ for SrTiO$_3$ thin films deposited onto (110) DyScO$_3$ substrates under a symmetric strain of $e_{s1}=e_{s2}=0.94\%$.

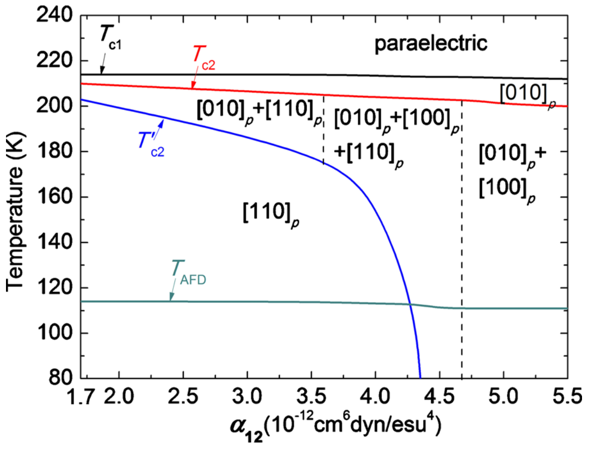

FIG. 2. (Color online) Predicted transition temperatures and polarizations as a function of $\alpha_{12}$ for SrTiO$_3$ thin film deposited onto (110) DyScO$_3$ substrates under asymmetric biaxial strains of $e_{s1}=1.03\%$ and $e_{s2}=1.06\%$.

sured physical property to determine $\alpha_{12}$ and at the same time, $\omega_s^{\perp}$ is not used to determine other coefficients. Therefore, $\alpha_{12}$ does not affect other physical quantities of SrTiO$_3$. Thus we are able to adjust $\alpha_{12}$ without changing the other parameters to improve the potential for SrTiO$_3$.

In this paper, we perform a series of simulations repeating the experimental cooling process in three films with different strain states. In all these simulations we vary $\alpha_{12}$ from 1.7 to 5.5, while fixing all other parameters. After examining the transition temperatures and polarization states as a function of different $\alpha_{12}$, we identify the most appropriate $\alpha_{12}$ as that satisfying all the existing experimental observations.

In the phase-field model of (001) SrTiO$_3$ thin films, the temporal and spatial evolutions of the two order parameters $p$ and $q$ are governed by the three-dimensional time dependent Ginzburg–Landau equations, as follows:[9]

$$\frac{\partial p_i(x,t)}{\partial t} = -L_p \frac{\delta F}{\delta p_i(x,t)}, i=1,2,3, \tag{2}$$

$$\frac{\partial q_i(x,t)}{\partial t} = -L_q \frac{\delta F}{\delta q_i(x,t)}, i=1,2,3, \tag{3}$$

where $L_p$ and $L_q$ are the kinetic coefficients. $F$ is the total energy, including the bulk energy, elastic energy, electrostatic energy, and domain wall energy, i.e.,

$$F=\int_V [f_{\text{bulk}}+f_{\text{elas}}+f_{\text{grad}}+f_{\text{elec}}]dV, \tag{4}$$

where $f_{\text{bulk}}(p_i,q_i)$ is same as Eq. (1). The calculation details of other energy terms are addressed in Refs. 9, 17, and 18.

In this work, a (001)-oriented SrTiO$_3$ thin film on an orthorhombic substrate is considered. The average film/substrate misfit strains $e_{s1}=\bar{\varepsilon}_{11}$ and $e_{s2}=\bar{\varepsilon}_{22}$ are along the in-plane $[100]_p$ and $[010]_p$ axes, respectively. We took a $128\Delta x\times 128\Delta x\times 40\Delta x$ model size where $\Delta x$ is the grid spacing. The thickness of the film is $25\Delta x$. The kinetic coefficient in Eq. (1) is taken as $L_q/L_p=180$. The material constants used in the simulation are from the literature[6,7,9,19] and listed in Ref. 20. These calculations use a background dielectric constant of 10.[21] Each simulation proceeded for 60 000 time steps (a normalized time step is 0.05).

The transition temperatures and corresponding stable ferroelectric polarization states as a function of $\alpha_{12}$ determined from our simulations are summarized in Figs. 1–3 for the three different strains. For symmetric strain $e_{s1}=e_{s2}=0.94\%$ (Fig. 1), there are two transition temperatures on cooling from room temperature: $T_c$ stands for the paraelectric-to-ferroelectric transition temperature and $T_{\text{AFD}}$ for the structural transition temperature. The stable ferroelectric polarization directions corresponding to different $\alpha_{12}$ values and temperatures are labeled on the diagram. The stable AFD domains, which appear at temperatures lower than $T_{\text{AFD}}$, are not labeled since they have the same symmetry as earlier formed ferroelectric domains. It can be seen that both $T_c$ and $T_{\text{AFD}}$ are nearly independent of $\alpha_{12}$ but the stable direction of the ferroelectric polarization depends strongly on $\alpha_{12}$. Furthermore the $[110]_p/[1\bar{1}0]_p$ ferroelectric state, the experimentally observed state at symmetric strain, can be obtained by using $\alpha_{12}$ values from 1.7 to as large as 5.0. The $[100]_p/[010]_p$ polar states were predicted with $\alpha_{12}$ values between 5.2 and 6.0, while values between 5.0 and 5.2 resulted in a mixture of the two phases.

For the other two anisotropically strained thin films ($e_{s1}=1.03\%$, $e_{s2}=1.06\%$ in Fig. 2 and $e_{s1}=1.46\%$, $e_{s2}=1.59\%$ in Fig. 3), there are three transition temperatures. The first ferroelectric transition ($T_{c1}$) corresponds to the development of a polarization along the longer in-plane direc-

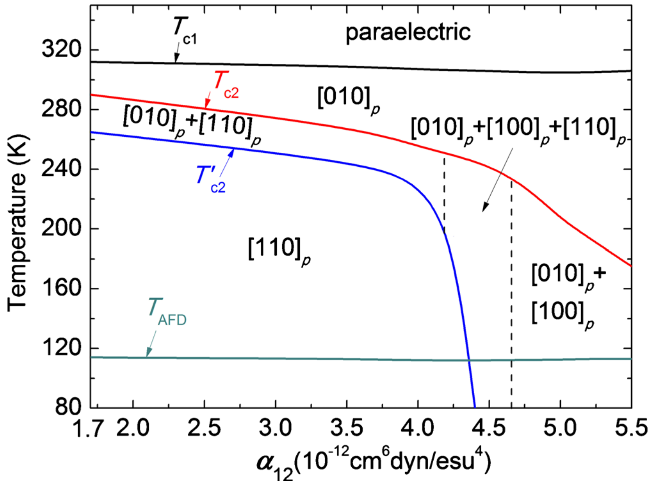

FIG. 3. (Color online) Predicted transition temperatures and polarizations as a function of $\alpha_{12}$ for SrTiO$_3$ thin film deposited onto (110) GdScO$_3$ substrates under the asymmetric strains of $e_{s1}=1.46\%$ and $e_{s2}=1.59\%$.

TABLE I. Predicted transition temperatures of $SrTiO_3$ thin films under the same biaxial strain states utilized in experiments from phase-field simulations using $\alpha_{12}=4.85\times 10^{-12}\ \text{cm}^6\ \text{dyn/esu}^4$.

| | $e_{s1}=e_{s2}=0.94\%$ | | | $e_{s1}=1.03\%,\ e_{s2}=1.06\%$ | | $e_{s1}=1.46\%,\ e_{s2}=1.59\%$ | |
|---|---|---|---|---|---|---|---|
| | Experiment | This work | | Experiment[c] | This work | Experiment[d] | This work |
| $T_c$ | $\sim$293 K [a]<br>$\sim$270 K [b]<br>$(p_1,p_2,0)$ | 213 K<br>$(p_1,p_2,0)$ | $T_{c1}$ | $\sim$260 K<br>$(0,p_2,0)$ | 215 K<br>$(0,p_2,0)$ | $\sim$400 K<br>$(p_1,0,0)+(0,p_2,0)$ | 310 K<br>$(0,p_2,0)$ |
| | | | $T_{c2}$ | $\sim$210 K<br>$(p_1,0,0)+(0,p_2,0)$ | 210 K<br>$(p_1,0,0)+(0,p_2,0)$ | | 210 K<br>$(p_1,0,0)+(0,p_2,0)$ |
| $T_{\text{AFD}}$ | $\sim$180 K [b]<br>$(p_1,p_2,0)$<br>$(q_1,q_2,0)$ | $\sim$112 K<br>$(p_1,p_2,0)$<br>$(q_1,q_2,0)$ | $T_{\text{AFD}}$ | $\sim$160 K<br>$(p_1,0,0)+(0,p_2,0)$<br>$(q_2,0,0)+(0,q_1,0)$ | 114 K<br>$(p_1,0,0)+(0,p_2,0)$<br>$(q_2,0,0)+(0,q_1,0)$ | $\sim$150–175 K<br>$(p_1,0,0)+(0,p_2,0)$<br>$(q_2,0,0)+(0,q_1,0)$ | 115 K<br>$(p_1,0,0)+(0,p_2,0)$<br>$(q_2,0,0)+(0,q_1,0)$ |

[a] Reference 12.
[b] Reference 14.
[c] Reference 10.
[d] Reference 15.

tion (i.e., the higher strain axis, here [010]) while the lowest transition temperature ($T_{\text{AFD}}$) corresponds to the AFD transition. The intermediate transition temperature ($T_{c2}$) produces either twinning from a single variant $[010]_p$ to $[010]_p/[100]_p$ domain structure (with a large $\alpha_{12}$ such as 5.5) or rotation from $[010]_p$ to the $[110]_p$ direction (with smaller $\alpha_{12}$ values such as 1.7). Strictly speaking, the $[010]_p$ to $[110]_p$ transition should be divided into two stages, corresponding to the two intermediate transition temperatures: $T_{c2}$ for the beginning of the transition while $T'_{c2}$, for the end. As shown in Figs. 2 and 3, an $\alpha_{12}$ value larger than 4.7 is sufficient to stabilize the $[010]_p/[100]_p$ twin structure.

After examining the transition temperatures and polarization states as a function of $\alpha_{12}$ shown in Figs. 1–3, we found that the polarization states predicted from $\alpha_{12}$ values between 4.7 and 5.0 are consistent with all of these recent experiments. An average of 4.85 is then chosen for $\alpha_{12}$ and the transition temperatures determined from this updated $\alpha_{12}$ are summarized in Table I together with experimental measurements. The predicted ferroelectric and AFD domain stabilities are in reasonable agreement with experiments, although the transition temperatures from simulations are always lower than those measured. Such discrepancies, likely, arise from the uncertainties in the electrostriction and thermal expansion coefficients used in the modeling as well as the relaxor character of the films.[22]

In summary, we report an improved coefficient $\alpha_{12}$ in the Landau–Devonshire thermodynamic potential for $SrTiO_3$ utilizing recent experimental data and phase-field simulations. The transition temperatures and ferroelectric/AFD domain stabilities predicted from this modified potential agree well with experimental measurements. It is expected this modified potential will stimulate future experimental measurements of $\alpha_{12}$ and lead to a better understanding of the ferroelectric/AFD domain stabilities in $SrTiO_3$ thin films.

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