



# Impact of anisotropic strains on low-frequency dielectric properties and room-temperature polar phases of SrTiO<sub>3</sub> epitaxial thin films

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## ABSTRACT

Impact of anisotropic strains on low-frequency dielectric properties and room-temperature polar phases of SrTiO<sub>3</sub> epitaxial thin films is investigated. The dielectric properties show a remarkable change as a function of anisotropic strains. The number of room-temperature polar phases is as twice as that of isotropically strained SrTiO<sub>3</sub> thin films.

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## 1. Introduction

It has been widely accepted that the thermodynamic theory of ferroelectric thin films can provide effective guidelines on how to control and tailor their physical properties by adjusting substrate-induced misfit strains [1–4]. The ferroelectric thin films show important applications by epitaxially grown on foreign substrates. Specially, ferroelectric thin films/III-nitride heterostructures can lead to promising multifunctional applications which exploit the advantageous properties of both kinds of materials [5–7]. As for usual ferroelectric thin films, their thermodynamic theory descriptions have been established including the two cases of isotropic strain and anisotropic strain [1–4]. Recently, isotropically strained SrTiO<sub>3</sub> epitaxial thin films show important applications in tunable dielectric devices and room-temperature ferroelectric devices [8]. The thermodynamic theory investigations on isotropically strained SrTiO<sub>3</sub> thin films [9] have aroused extensive attentions and advanced the developments in this field [8,10–14]. However, the thermodynamic theory for anisotropic strain has not been established. Contrast to the case of anisotropic strain of usual ferroelectric thin films, SrTiO<sub>3</sub> is particular as a result of an incipient ferroelectric. The energy function expression includes not only the polarization components  $P_i$  but also the structural order param-

eter components  $q_i$ . Thus, the energy function expression of the SrTiO<sub>3</sub> thin films is obviously different from that of usual ferroelectric thin films. Besides, compared with isotropically strained SrTiO<sub>3</sub> epitaxial thin films, more potential applications can be opened for anisotropically strained SrTiO<sub>3</sub> epitaxial thin films because much more equilibrium phases are involved.

Recently, some reports attempt to focus on anisotropically strained SrTiO<sub>3</sub> thin films [15–17]. In the present study, the thermodynamic theory of anisotropically strained SrTiO<sub>3</sub> thin films is developed. The effect of anisotropic strains on low-frequency dielectric properties and room-temperature polar phases of SrTiO<sub>3</sub> epitaxial thin films is investigated. The anisotropic strains make the SrTiO<sub>3</sub> epitaxial thin films produce more room-temperature polar phases, which is crucial importance for room-temperature applications.

## 2. Thermodynamic theory developed

Using the Helmholtz free energy density  $F$  of bulk SrTiO<sub>3</sub> single crystals and the Legendre transformation  $\tilde{F} = F - S_3\sigma_3 - S_4\sigma_4 - S_5\sigma_5$  [9], the renormalized calculations of the Helmholtz free energy density for SrTiO<sub>3</sub> epitaxial thin films can be performed. The thermodynamic equilibrium potential  $\tilde{F}(P_i, q_i, S_1, S_2, T)$  of single-domain (001) SrTiO<sub>3</sub> epitaxial thin films is expressed as power-series expansion in term of polarization components  $P_i$  and structural order-parameter components  $q_i$  including their couplings:

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$$\begin{aligned}
\tilde{F} = & \alpha_1^* P_1^2 + \alpha_2^* P_2^2 + \alpha_3^* P_3^2 + \alpha_{11}^* (P_1^4 + P_2^4) + \alpha_{33}^* P_3^4 \\
& + \alpha_{12}^* P_1^2 P_2^2 + \alpha_{13}^* (P_1^2 + P_2^2) P_3^2 \\
& + \beta_1^* q_1^2 + \beta_2^* q_2^2 + \beta_3^* q_3^2 + \beta_{11}^* (q_1^4 + q_2^4) + \beta_{33}^* q_3^4 \\
& + \beta_{12}^* q_1^2 q_2^2 + \beta_{13}^* (q_1^2 + q_2^2) q_3^2 \\
& - m_{11}^* (P_1^2 q_1^2 + P_2^2 q_2^2) - m_{33}^* P_3^2 q_3^2 - m_{12}^* (P_1^2 q_2^2 + P_2^2 q_1^2) \\
& - m_{13}^* (P_1^2 + P_2^2) q_3^2 - m_{31}^* (q_1^2 + q_2^2) P_3^2 \\
& - m_{44} P_1 P_2 q_1 q_2 - m_{44}^* (P_1 P_3 q_1 q_3 + P_2 P_3 q_2 q_3) \\
& + \frac{c_{11}}{2} \left( S_1^2 + S_2^2 + \frac{c_{12}^2 (S_1 + S_2)^2}{c_{11}^2} \right) \\
& + c_{12} \left( S_1 S_2 - \frac{c_{12} (S_1 + S_2)^2}{c_{11}} \right) \quad (1)
\end{aligned}$$

where the renormalized expansion coefficients are as follows:

$$\begin{aligned}
\alpha_1^* &= \alpha_1 + \frac{g_{12} c_{12}}{c_{11}} (S_1 + S_2) - g_{11} S_1 - g_{12} S_2, \\
\alpha_2^* &= \alpha_1 + \frac{g_{12} c_{12}}{c_{11}} (S_1 + S_2) - g_{11} S_2 - g_{12} S_1, \\
\alpha_3^* &= \alpha_1 + \frac{g_{11} c_{12}}{c_{11}} (S_1 + S_2) - g_{12} (S_1 + S_2), \\
\alpha_{11}^* &= \alpha_{11} - \frac{g_{12}^2}{2c_{11}}, \quad \alpha_{12}^* = \alpha_{12} - \frac{g_{12}^2}{c_{11}}, \\
\alpha_{33}^* &= \alpha_{11} - \frac{g_{11}^2}{2c_{11}}, \quad \alpha_{13}^* = \alpha_{12} - \frac{g_{11} g_{12}}{c_{11}} - \frac{g_{44}^2}{2c_{44}}, \\
\beta_1^* &= \beta_1 + \frac{\lambda_{12} c_{12}}{c_{11}} (S_1 + S_2) - \lambda_{11} S_1 - \lambda_{12} S_2, \\
\beta_2^* &= \beta_1 + \frac{\lambda_{12} c_{12}}{c_{11}} (S_1 + S_2) - \lambda_{11} S_2 - \lambda_{12} S_1, \\
\beta_3^* &= \beta_1 + \frac{\lambda_{11} c_{12}}{c_{11}} (S_1 + S_2) - \lambda_{12} (S_1 + S_2), \\
\beta_{11}^* &= \beta_{11} - \frac{\lambda_{12}^2}{2c_{11}}, \quad \beta_{12}^* = \beta_{12} - \frac{\lambda_{12}^2}{c_{11}}, \\
\beta_{33}^* &= \beta_{11} - \frac{\lambda_{11}^2}{2c_{11}}, \quad \beta_{13}^* = \beta_{12} - \frac{\lambda_{11} \lambda_{12}}{c_{11}} - \frac{\lambda_{44}^2}{2c_{44}}, \\
m_{11}^* &= m_{11} + \frac{g_{12} \lambda_{12}}{c_{11}}, \quad m_{12}^* = m_{12} + \frac{g_{12} \lambda_{12}}{c_{11}}, \\
m_{13}^* &= m_{12} + \frac{g_{12} \lambda_{12}}{c_{11}}, \quad m_{31}^* = m_{12} + \frac{g_{11} \lambda_{12}}{c_{11}}, \\
m_{33}^* &= m_{11} + \frac{g_{11} \lambda_{11}}{c_{11}}, \quad m_{44}^* = m_{44} + \frac{g_{44} \lambda_{44}}{c_{44}}.
\end{aligned}$$

In Eq. (1),  $c_{ij}$  defines the elastic stiffness at constant polarization and order parameter,  $g_{ij}$  defines the electrostrictive constant.  $\lambda_{ij}$  is the linear-quadratic coupling between the strain and structure order parameter, and  $m_{ij}$  describes the interaction between the polarization and order parameter under constant strain. In our calculations, the values of the parameters  $\alpha$ ,  $\beta$ ,  $g_{ij}$ ,  $\lambda_{ij}$  and  $m_{ij}$  are adopted from Ref. [9]. Due to considerations of the couplings between structural order parameters and polarization parameters of the SrTiO<sub>3</sub> thin films, 64 equilibrium phases may occur in the case of anisotropic strain. However, for the cases of anisotropic strain of usual ferroelectric thin films, there is only 8 possible equilibrium phases [3,4]. It means that the SrTiO<sub>3</sub> thin film system is far more complex than usual ferroelectric thin films.

### 3. Results and discussion

In the following calculations, the phase that has minimum free energy is selected as the stable phase. Firstly, we investigate the impact of anisotropic strains on the low-frequency dielectric properties of SrTiO<sub>3</sub> epitaxial thin films. As an example, we give the simulated results of the low-frequency dielectric properties as a function of anisotropic strains, where  $S_2 = 0.005$  is fixed and  $S_1 = -0.015, -0.01, -0.005, 0.010$  and  $0.015$ . By differentiating the thermodynamic potential  $\tilde{F}$ , an explicit expression for the reciprocal dielectric susceptibilities  $\chi_{ij} = \partial^2 \tilde{F} / \partial P_i \partial P_j$  is derived. Using the relations  $\eta_{ij} = \chi_{ij}^{-1}$  and  $\varepsilon_{ij} = 1 + \eta_{ij} / \varepsilon_0$ , the anisotropic strains dependence of low-frequency dielectric constants  $\varepsilon_{11}$ ,  $\varepsilon_{22}$  and  $\varepsilon_{33}$  is calculated and shown in Fig. 1(a), (b) and (c), respectively.

As is seen from Fig. 1(a), (b) and (c), the low-frequency dielectric properties exhibit a remarkable change as a function of the anisotropic strains and temperature. It is attributed to that anisotropic misfit strains induce new equilibrium phases and, thus, remarkably affect the low-frequency dielectric properties. It is obviously different from the two cases of bulk crystal SrTiO<sub>3</sub> and isotropically strained SrTiO<sub>3</sub> thin films. For the bulk crystal SrTiO<sub>3</sub> [18], high dielectric constants are limited to extremely narrow low temperature range. Compared with bulk crystal SrTiO<sub>3</sub>, the high dielectric constants of anisotropically strained SrTiO<sub>3</sub> thin films can present at a wide temperature range from several K to around 310 K, especially at near room temperature. It may be useful for room-temperature applications. Compared with isotropically strained SrTiO<sub>3</sub> thin films, the numerical value change of low-frequency dielectric constants is extremely remarkable as a function of anisotropic strains.

Secondly, the effect of anisotropic strains on room-temperature polar phases is predicted. The anisotropic misfit strains  $S_1$  and  $S_2$  dependence of room-temperature polar phases is calculated and shown in Fig. 2. It clearly demonstrates four room-temperature polar phases, namely,  $F_1$  ( $P_1 \neq 0, P_2 = P_3 = 0$ ),  $F_2$  ( $P_2 \neq 0, P_1 = P_3 = 0$ ),  $F_3$  ( $P_3 \neq 0, P_1 = P_2 = 0$ ),  $F_4$  ( $P_1 \neq 0, P_2 \neq 0, P_3 = 0$ ), and one paraelectric phase ( $P_1 = P_2 = P_3 = 0$ ). The result shows that the anisotropic strains have changed the style of room-temperature polar phases, which is obviously different from the case of isotropic strain. In order to check the validity of the simulation, a diagonal (where, the relationship  $S_1 = S_2 = S_m$  is met) is focused in Fig. 2, which corresponds to room-temperature phase diagram for isotropically strained SrTiO<sub>3</sub> thin films. It is seen from the diagonal in Fig. 2 that  $S_m \in (-0.02, -0.017)$  corresponds to the polar phase  $F_3$ , and  $S_m \in (-0.017, 0.015)$  corresponds to the paraelectric phase, and  $S_m \in (0.015, 0.02)$  corresponds to the polar phase  $F_4$ . One can observe the misfit strain-temperature phase diagram when temperature is fixed at 300 K [9]. It can be found that our results are well consistent with the revised phase diagram at 300 K in Ref. [9]. Note that  $F_4$  ( $P_1 \neq 0, P_2 \neq 0, P_3 = 0$ ) is simplified as  $P_1 = P_2 \neq 0, P_3 = 0$  under the condition of  $S_1 = S_2 = S_m$ . For isotropically strained SrTiO<sub>3</sub> thin films, the styles of room-temperature polar phases are only two, namely, (i)  $P_3 \neq 0, P_1 = P_2 = 0$ ; (ii)  $P_1 = P_2 \neq 0, P_3 = 0$ . It indicates that the number of room-temperature polar phases for anisotropically strained SrTiO<sub>3</sub> thin films is as twice as that of isotropically strained SrTiO<sub>3</sub> thin films. It also means that more chances can be opened to design and manipulate the SrTiO<sub>3</sub> thin films, which is applied at room temperature.

### 4. Conclusion

The thermodynamic theory of anisotropically strained SrTiO<sub>3</sub> thin films is developed to investigate the effect of anisotropic strains on low-frequency dielectric properties and room-temperature polar phases of SrTiO<sub>3</sub> epitaxial thin films. The low-frequency

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