Front. Phys. China, 2007, 2(3): 318—321
DOI 10.1007/s11467-007-0042-3

RESEARCH ARTICLE

LI Li-ben, YOU Jing-han, CHEN Qing-dong

Gradient-stress on polarization in $Ba_{1-x}Sr_xTiO_3$ films

© Higher Education Press and Springer-Verlag 2007

Abstract A group of position-thickness-dependent stresses are used to modified Landau-Devonshire theory to investigate the second-order phase transition in $Ba_{1-x}Sr_xTiO_3$ films. The result shows that the short-range interaction between the unit cells of the film and the substrate induces the phase transition dispersion and the rise of the transition temperature in the films. The dependence of the effective dielectric constant on the temperature and the average spontaneous polarization on the film thickness are computed, which qualitatively agree with the experiments.

Keywords ferroelectricity, thin film, stress, phase transition

PACS numbers 77.80.-e, 77.55.+f, 62.40.+i, 77.80.Bh

1 Introduction

$Ba_{1-x}Sr_xTiO_3$ (BST) is the most common ferroelectric material used for high-storage-density capacitor structures such as dynamic random access memory (DRAM) [1] because of its high static dielectric constant. However, the dielectric/ferroelectric properties of the films differ markedly from those of bulk ferroelectrics. The investigations have indicated that the first-order transition takes place in bulk BST [2]. In the BST films, the dielectric anomalies are substantially diffuse [3, 4] and the transition temperature is higher than that of the corresponding bulk [5]. The experimental results showed that the remnant polarization increases at room temperature and the dielectric constant decreases at 400 K when the film thickness of the $Ba_{0.5}Sr_{0.5}TiO_3$ films decreases [3]. Pertsev *et al.* developed a thermodynamic theory to investigate the properties of the ferroelectric thin films with a constant strain [6, 7]. However, Sinnamon et al. [3] pointed out that the out-of-plane strain in the BST film is of an exponential form with the film thickness. In this paper, we will apply a group of position-thickness-dependent stress distribution functions to the Modified Landau-Devonshire phenomenological theory to explain the phase transition characteristics of the BST film mentioned above.

LI Li-ben (✉), YOU Jing-han, CHEN Qing-dong
School of Science, Henan University of Science and Technology, Luoyang 471003, China
E-mail: liliben2001@sina.com

Received January 20, 2007

2 Methods

Consider a two-dimensional ferroelectric film at high temperature with thickness $2D$ grown on a cubic substrate. The interface between the film and the substrate is “strained incommensurate” [8]. The x and z axes are chosen parallel and perpendicular to the interface, respectively, shown in Fig.1. A set of position-thickness-dependent stress, which originates from the interaction of unit cells between the substrate and the film, can be obtained by solving the elastic mechanical equations [9]:

$$\sigma_{xx}(x,z) = -\sigma_0 \cos(2\pi x/L_s) \cdot \cosh(2\pi z/L_s)/\sinh(2\pi D/L_s) = \sigma_1 \tag{1}$$

$$\sigma_{zz}(x,z) = -\sigma_{xx} = \sigma_3 \tag{2}$$

$$\sigma_{xz}(x,z) = -\sigma_0 \sin(2\pi x/L_s) \cdot \sinh(2\pi z/L_s)/\sinh(2\pi D/L_s) = \sigma_5 \tag{3}$$

and

$$L_s = b_f b_s / |b_s - b_f| \tag{4}$$

where b_f and b_s are the lattice constants of the film and the substrate, respectively; σ_i (i=1,3,5) is the Voigt matrix notation, and σ_0 is a constant. The elastic Gibbs function can be expanded in powers of the polarizations P_i (i=x, z) and stresses σ_{ij} (i, j=x ,z) [10]:

$$G = [\alpha_1 - (Q_{11} - Q_{12})\sigma_1]P_x^2 + \alpha_{11}P_x^4 + \alpha_{111}P_x^6 + \alpha_{12}P_x^2P_z^2 + \alpha_{112}(P_x^4P_z^2 + P_x^2P_z^4) - Q_{44}\sigma_5 P_x P_z + [\alpha_1 + (Q_{11} - Q_{12})\sigma_1]P_z^2 + \alpha_{11}P_z^4 + \alpha_{111}P_z^6 + G_0 \tag{5}$$

where

$$G_0 = (s_{12} - s_{11})\sigma_1^2 - s_{44}\sigma_5^2 / 2$$

and α_1 is the dielectric stiffness, α_{ij}, α_{ijk} (i, j=1,2) the high-order stiffness coefficients at a constant stress, s_{ij} (i, j=1, 2, 4) the elastic compliances of the film measured at a constant polarization, Q_{ij} (i, j=1, 2, 4) the electrostrictive coupling between stress and polarization. α_1 equals to $(T-T_c)/(2C\varepsilon_0)$, in which ε_0 is the dielectric permittivity of free space and T_c is the transition temperature of bulk ferroelectric [11].

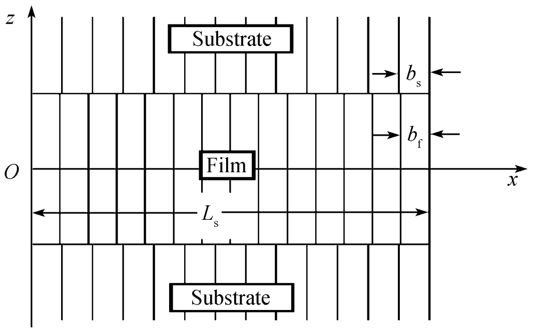

Fig.1 The structure and coordinate frame of the strained incommensurate film on cubic substrate.

We apply the model developed above to BST-0.5 films. The parameters are taken from Ref. [3] as follows (in SI unit, T is °C): C =1.24×10^5; T_c=−50°C; $\alpha_{11} = 2.8\times10^8$; $Q_{11}-Q_{12}$= 0.055. The terms of P_x^6 and P_z^6 in Eq. (5) can be neglected since $\alpha_{11} > 0$ [3, 12]. Two low-temperature phases are possibly present in the film when the film undergoes a high-temperature cubic phase to a low-temperature tetragonal phase. The following notation is used to describe the two phases: c-phase for $P_z \neq 0$ and $P_x = 0$; a-phase for $P_x \neq 0$ and $P_z = 0$. Between the two low-temperature phases, the one with the minimum elastic Gibbs function with respect to the polarization and stress corresponds to the equilibrium thermodynamic state of the film. From Eq. (5) we know that the region with a tensile stress is in favor of the a-phase, and the region with a compressive stress is in favor of the c-phase under the condition of $(Q_{11}-Q_{12}) > 0$. Considering c-phase with $P_z \neq 0$ and P_x=0, the expression for the spontaneous polarization can be derived from the elastic Gibbs function in terms of the stability criterion of the first derivative ($\partial G / \partial P_z = 0$). The dielectric susceptibility (χ_{ij}) can be determined by $\frac{1}{\chi_{33}} = \partial^2 G / \partial P_z^2$. The transition temperature(T_c^*) in the film can be obtained from the criterion $G = G_0$. We have

$$T_c^*(x,z) = T_c + 2C\varepsilon_0(Q_{11} - Q_{12})\,|\sigma_1| \tag{6}$$

When $T < T_c^*$,

$$P_z^2(x,z) = -\frac{\alpha_1 - (Q_{11} - Q_{12})\,|\sigma_1|}{2\alpha_{11}} \tag{7}$$

and

$$\chi_{33}(x,z) = \frac{C}{2(T_c^* - T)} \tag{8}$$

When $T > T_c^*$,

$$P_z(x,z) = 0, \quad \chi_{33}(x,z) = \frac{C}{T - T_c^*} \tag{9}$$

Total effective dielectric constant of the film is derived from:

$$\varepsilon_{33}(T) = \frac{2D}{L_s}\int_0^{L_s/2}\left(\int_0^D \frac{1}{1+\chi_{33}(x,z)}\mathrm{d}z\right)^{-1}\mathrm{d}x \tag{10}$$

Let $q = 2\varepsilon_0\sigma_0 L_s(Q_{11}-Q_{12})/(\pi D)$ and $r = 2(T_c - T)/C$. When $T < T_c$ and $\chi_{33}(x,z) >> 1$, $\varepsilon_{33}(T)$ can be given as follows:

$$\varepsilon_{33}(T) = \frac{2}{\pi\sqrt{q^2 - r^2}}\arctan\left(\frac{\sqrt{q^2 - r^2}}{q}\right) \tag{11}$$

under $r < q$ and

$$\varepsilon_{33}(T) = \frac{2}{\pi\sqrt{r^2 - q^2}}\arctan\left(\frac{\sqrt{r^2 - q^2}}{q}\right) \tag{12}$$

under $r > q$.

The transition temperature in BST film, T_c^*, is always higher than that in bulk BST (T_c) as shown in Eq. (6), which agrees with the experiment by Yuzyuk *et al.* [13]. The range of T_c^* covers from T_c to $T_{c\max}^* = T_c + 2C\varepsilon_0(Q_{11}-Q_{12})\sigma_0 \cot(2\pi D/L_s)$. It means that the phase transition in the BST film is diffuse. As the film cools from high temperature (such as deposited temperature) to low temperature, the PE-FE phase transition will take place continuously from the center to the interface of the film.

The curves of $\varepsilon_{33}(T)$ for the c-phase in BST-0.5 films are shown in Fig. 2, for various thickness, where we take $\sigma_0 = 3.7$ GPa and L_s is about 100nm from the lattice parameters in Ref. [3]. The dielectric anomalies are substantially diffuse. The peak value of $\varepsilon_{33}(T)$ decreases as the film thickness decreases. The dependence of $\varepsilon_{33}(T)$ on the thick

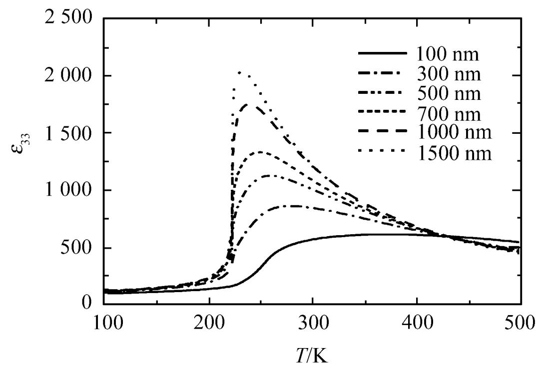

Fig. 2 Dependence of effective dielectric constant on the temperature T for c-phase under various thickness. L_s = 100 nm, σ_0 = 3.7 GPa.

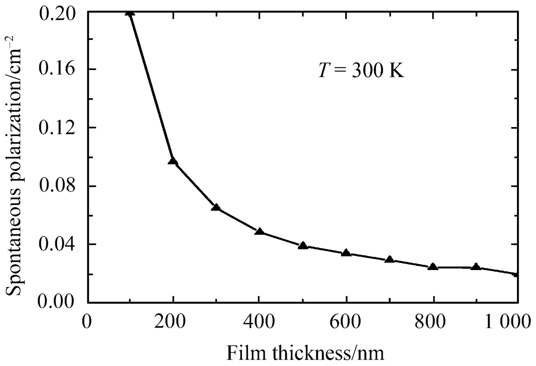

Fig. 3 Dependence of average spontaneous polarization on film thickness at room temperature for *c*-phase. L_s = 100nm, σ_0 = 3.7 GPa.

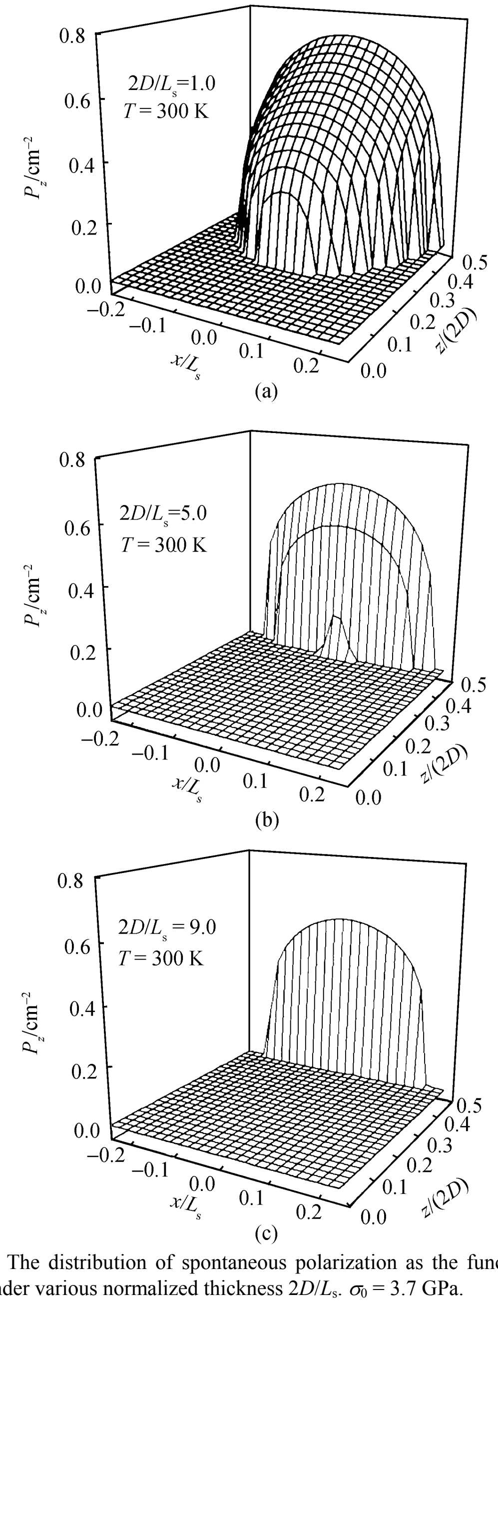

Fig. 4 The distribution of spontaneous polarization as the function of *x* and *z* under various normalized thickness $2D/L_s$. σ_0 = 3.7 GPa.

ness agrees with the experiment results when the temperature is lower than 400 K and higher than 223 K [3]. The theoretical value is lower than the experiment results when $T < T_c$. The (average) spontaneous polarization on the film thickness at 300 K which is higher than T_c of bulk BST has been computed, as shown in Fig. 3. It decreases with the increase of the film thickness, which is in qualitative agreement with the results observed by Sinnamon *et al.* [3]. The result can be explained by the change of the ferroelectric region with the normalized film thickness $2D/L_s$, as shown in Fig.4. The ferroelectric region of the film with $2D/L_s$=5.0 is smaller than that of the film with $2D/L_s$=1.0 and larger than that of the film with $2D/L_s$= 9.0. According to Eqs. (1) and (6), the thinner a film, the bigger the stress exists in it and the higher the transition temperature the film will be with. Thus, the (average) spontaneous polarization of a thin film is relatively large compared with that of a thick film.

3 Summary

In the application of position-thickness-dependent stress to the Modified Landau-Devonshire phenomenological theory, the dielectric/ferroelectric properties in the BST films are investigated. For *c*-phase, the phase transition is substantially diffuse in the film, which originates from the short-range interaction between the unit cells of the film and the substrate. The dependence of the dielectric constant on the temperature and the dependence of the average spontaneous polarization on film thickness are computed, which are in qualitative agreement with the experiment results.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 10574066).

References

1. Scott J. F., Morrison F. D., Miyake M., et al., J. Am. Ceram. Soc., 2005, 88(7): 1691
2. Hilton A. D. and Ricketts B. W., Phys. D: Appl. Phys., 2002, 29: 1321
3. Sinnamon L. J., Bowman R. M., and Gregg J. M., Appl. Phys. Lett., 2002, 81(5): 889
4. Boikov Y. A. and Claeson T., Appl. Phys. Lett., 2001, 79(13): 2052
5. Yuzyuk Y. I., Simon P., Zakharchenko I. N., Alyoshin V. A., and Sviridov E. V., Phys. Rev. B. , 2002, 66(5): 052103-1
6. Pertsev N. A., Zembilgotov A. G., and Tagantsev A. K., Phys. Rev. Lett., 1998, 80(9): 1988
7. Pertsev N. A., Zembilgotov A. G., Hoffmann S., Waser R., and Tagantsev A. K., J. Appl. Phys., 1999, 85(3): 1698
8. Kwak B. S., Erbil A., Budai J. D., Chisholm M. F., Boatner L. A.,

and Wilkens B. J., Phys. Rev. B., 1994, 49(21): 14865

9. Li L. B., Zhang J., Yin Z., and Zhang M. S., Phys. Lett. A, 2004, 321 (1): 67
10. Kim H. J., Oh S. H., and Jang H. M., Appl. Phys. Lett., 1999, 75(20): 3195
11. Oh S. H. and Jang H. M., Phys. Rev. B, 2000, 62(22): 14757
12. Basceri C., Streiffer S. K., Kingon A. I., and Waser R., J. Appl. Phys. 1997, 82(5): 2407
13. Yuzyuk Yu. I., Simon P., Zakharchenko I. N., Alyoshin V. A., and Sviridov E. V., Phys. Rev. B, 2002, 66(5): 052103