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Influence of lateral size on dielectric properties of ferroelectric thin films with structure transition zones

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By taking into account structural transition zones near the lateral and thickness direction edges, this paper uses a modified transverse Ising model to study dielectric properties of a finite size ferroelectric thin film in the framework of the mean-field approximation. The results indicate that the influence of the lateral size on the dielectric susceptibility cannot be neglected and lateral structural transition zones could be a crucial factor that improves the mean susceptibility of the fixed size film.

Keywords: ferroelectric thin film, transverse Ising model, dielectric properties
PACC: 7755, 7780B, 7780D

1. Introduction

Ferroelectric thin films have gained considerable attention in recent years because of their potential in memory applications.[1−3] In order to achieve very high-density storage devices, it is crucial to downscale lateral (along surface of film) dimensions of ferroelectric capacitors. But there are two fundamental questions, one is how small a ferroelectric capacitor can be, the other is how the lateral size of the capacitor can affect its ferroelectric properties. Therefore, the finite size effects on phase transition properties and dielectric properties of ferroelectric thin films have been extensively studied both experimentally[4−10] and theoretically.[11−22]

Experimentally, Ganpule *et al*[4] fabricated $Pb_{1.0}(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3$ submicron capacitors by using a focused ion-beam milling method. They found that the capacitors still exhibited ferroelectric properties when their lateral dimensions were reduced to 100 nm, which meant that the memories with storage densities in the range of 4–16 Gbits were successfully fabricated. Bühlmann *et al*[5] observed a steep increase of the piezoelectric response below 200 nm lateral dimensions for an epitaxial 200 nm thick $Pb(Zr,Ti)O_3$ (PZT) film. Additionally, $SrTiO_3$ thin films deposited on Ru have been processed by Ahn *et al*[6] by using a plasma-enhanced atomic layer deposition. The results showed that when $SrTiO_3$ films were deposited on Ru directly, the dielectric constants of $SrTiO_3$ films decreased abruptly as film thicknesses dwindled below 20 nm. Interestingly, when $SrTiO_3$ films were deposited on Ru with a SrO interlayer, the dielectric constants of $SrTiO_3$ films were obviously improved. Recently, Park *et al*[7] discussed the influence of the film thickness and Sc doping on the dielectric response of epitaxial $(Ba,Sr)TiO_3$ (BST) thin films grown on epitaxial $Pt/SrTiO_3$ substrates. They found that the dielectric constant of the BST film decreased as the film thickness decreased, whereas a maximum of the dielectric constant of the Sc-doped BST film occurred at a certain thickness with a larger dielectric constant in comparison with the BST thin film.

Theoretically, two approaches have been frequently used to study size effects in ferroelectrics. One is the Ginzburg-Landau-Devonshire phenomenological theory,[11−15] another is the transverse Ising model (TIM).[16−22] Using the phenomenological theory, Zhong *et al*[11] demonstrated the film thickness dependence of the dielectric susceptibility of the ferroelectric thin film. The results show that the mean susceptibility of the thin film increases or decreases with the decrease of the film thickness when the spontaneous polarization is reduced or enhanced in the sur-

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face layer (compared to the interior of the film). On the microscopic level, the traditional TIM has also been successful in studying size effects in the order–disorder and displaceable type ferroelectrics. Utilizing the Green's function technique, Wesselinowa[16] discussed the dependence of the film thickness on the dielectric susceptibility of the thin film. The results reveal that the dielectric susceptibility can increase or decrease with the decrease of the film thickness depending on the surface interaction. Additionally, the influence of particle sizes on static and dynamic properties of ferroelectric nanoparticles was evaluated convincingly by Michael *et al* [17,18] and Wang *et al.*[19] Other works have also been reported. The lateral size dependence of the dielectric susceptibility, the pyroelectric coefficient and the Curie temperature has been systematically discussed by Xin *et al* [20] in a monolayer ferroelectric square lattice. It is shown that the maximum of the dielectric distribution is found in the edge area of the lattice and its position can be varied by the interaction range.

According to investigations mentioned above, it is indicated that variations of the lateral and thickness dimensions can result in many interesting phenomena. And the lateral size effects play an important role in deciding the physical properties of high-density ferroelectric memories. By using the TIM method, the influence of film thicknesses on properties of ferroelectric thin films has been discussed adequately, while theoretical studies on lateral size effects in ferroelectric thin films are scarce. Though Xin *et al* [20] discussed the influence of the lateral size on dielectric properties of a monolayer ferroelectric square lattice by using TIM, thickness direction size effects have not been considered due to the model limitation. Therefore, on the basis of TIM, it is indispensable to study a more realistic model which can take into account not only lateral size effects but also thickness direction size effects. Furthermore, the inhomogeneous structural distribution along the lateral and thickness direction may exist in thin films due to the limitations of processing techniques. Based on TIM, the traditional method that describes the structural difference between surface layers and the interior of the film is to mainly modify the pseudo-spin interaction J_{ij}, namely J_{ij} is treated to be uniform in surface layers and only differs from that of the interior. However, the structural change from the surface layer to the interior of the film is gradual for a realistic thin film. It is not practical to employ a 'single-step' model to study ferroelectric characteristics of a finite size film. Additionally, the influence of the inhomogeneous structural distribution near the lateral edges on ferroelectric properties of thin films may become more remarkable for miniature electronic devices. Therefore, we put forward a multistep model, i.e., an inhomogeneous structural transition is introduced along the lateral and thickness directions. Such a model reflects a more realistic situation of the film than the previous 'single-step' model. In this paper, distribution functions representing the interactions between pseudo-spins are introduced to reflect the structural difference from the inhomogeneous structural transition zones to the interior of the film. By considering the Coulomb interaction nature of ferroelectrics, it is widely thought that the number of dipole moments increases with the increase of film dimensions. Hence, the interactions between pseudo-spins are also described as a function of film dimensions, which can more realistically reflect the influence of the change of film dimensions on the properties of thin films.

The aim of the present paper is to introduce the multistep structural change near the lateral edges and surfaces of the film and to study the influence of the film thickness and lateral structural transition zones on the susceptibility of the film based on such a modified TIM.

2. The model

A schematic of a finite size ferroelectric thin film with two symmetrical surfaces is shown in Fig.1. All pseudo-spin layers are parallel to the xy plane and pseudo-spins are located at a simple cubic lattice. The z-direction is perpendicular to the film surface and is also the polarization direction. The film volume is $N \times N \times L$ where N and L stand for the lateral dimension and the thickness of the film, respectively. In Fig.1(a), every pseudo-spin layer is divided into a series of square loops, whose size gradually becomes smaller from the outside to the centre. The location of each square loop is labeled by $m = 1, 2, \ldots s$, where s [$s = N/2$ or $(N + 1)/2$] is the number of square loops in a pseudo-spin layer, $m = s$ stands for the edge loop, and s_t represents the number of transition square loops in lateral edge zones of the film, including edge loops. In Fig.1(b), the position of each pseudo-spin layer is labeled by $k = 1, 2, \ldots L$, where $k = 1$ and $k = L$ denote surface layers of the film along the z-direction.

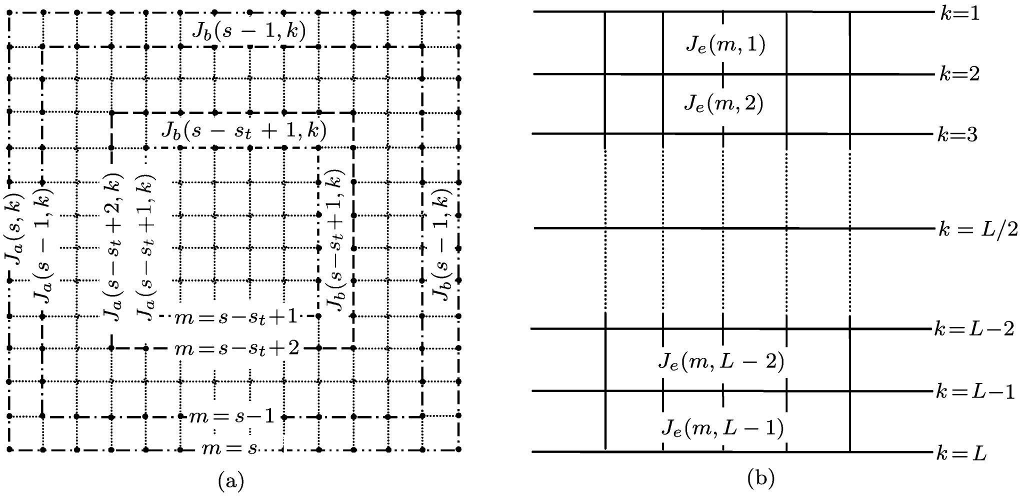

Fig.1. Schematic diagram of a ferroelectric thin film with $N \times N \times L$ size: (a) the distribution of the square loop in the pseudo-spin plane; (b) the distribution of the pseudo-spin layer along the z direction.

The system is described by the Ising Hamiltonian under a transverse field:

$$H = -\sum_i \Omega_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - 2\mu E \sum_i S_i^z, \tag{1}$$

where Ω_i is the transverse field at site i, S_i^x and S_i^z are the x and z components of a spin-1/2 operator at site i, J_{ij} is the exchange interaction between sites i and j, the sum $\sum_{ij}$ runs over only nearest-neighbour pairs, μ is the dipole moment of the pseudo-spin, and E is the applied electric field. $J_{ij} = J_a(m,k)$, if sites i and j locate in the same square loop (m is fixed); $J_{ij} = J_b(m,k)$, if two sites are in the mth and the $(m+1)$th square loops, respectively; $J_{ij} = J_e(m,k)$ if two sites situate in the kth and the $(k+1)$th pseudo-spin layers, respectively.

Since pseudo-spin interactions in ferroelectrics are very complicated and there are no available experimental data to accurately describe characteristics of structural transition zones, we introduce the exponential function to reflect interaction changes due to the inhomogeneous structural distribution near the edge of a film. For simplicity but without loss of generality, it is assumed that the film is symmetric along the z-direction. So the expressions of exchange interactions J_{ij} for the upper half-film containing $L/2$ [or $(L+1)/2$ including the middle layer] are as follows:

$$J_a(m,k) = J_\infty \mathrm{e}^{-1/(\alpha_1 \times N \times L \times k)}, \quad 1 \le m \le s - s_t, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{2a}$$

$$J_a(m,k) = J_s \mathrm{e}^{-1/(\alpha_1 \times N \times L \times k)}, \quad m = s, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{2b}$$

$$J_a(m,k) = J_a(s,k) + [J_a(2,k) - J_a(s,k)] \times (1 - \mathrm{e}^{-\beta_1 (m_t - 1)/s_t}),$$
$$m = s + 1 - m_t, \quad 1 \le m_t \le s_t, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{2c}$$

$$J_b(m,k) = J_\infty \mathrm{e}^{-1/(\alpha_1 \times N \times L \times k)}, \quad 1 \le m \le (s - s_t), \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{3a}$$

$$J_b(m,k) = J_a(s,k) + [J_a(2,k) - J_a(s,k)] \times (1 - \mathrm{e}^{-\beta_2 m_t / s_t}),$$
$$m = s - m_t, \quad 1 \le m_t \le s_t - 1, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{3b}$$

$$J_e(m,k) = J_\infty \mathrm{e}^{-1/(\alpha_2 \times N \times L \times k)}, \quad 1 \le m \le s - s_t, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{4a}$$

$$J_e(m,k) = J_{es} \mathrm{e}^{-1/(\alpha_2 \times N \times L \times k)}, \quad m = s, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{4b}$$

$$J_e(m,k) = J_e(s,k) + [J_e(1,k) - J_e(s,k)] \times (1 - \mathrm{e}^{-\beta_3 (m_t - 1)/s_t}),$$
$$m = s + 1 - m_t, \quad 1 \le m_t \le s_t, \quad 1 \le k \le L/2 \text{ or } 1 \le k \le (L+1)/2, \tag{4c}$$

where m_t labels the location of each transition square loop, $\alpha_1(\alpha_2)$ represents the interaction intensity parameter when two pseudo-spins do not locate in lateral structural transition zones but in the same (different) layer, $\beta_1(\beta_2)$ is the interaction intensity parameter when two pseudo-spins locate in the same (different) transition square loop, β_3 is the interaction intensity parameter when two pseudo-spins situate in different layers and in lateral structural transition zones, J_∞ stands for the interaction between pseudo-spins in an infinite pseudo-spin plane, J_s and J_{es} denote the interactions between pseudo-spins in the same edge loop and in different layers when the film thickness is infinite and when $m = s$, respectively. In addition, $J_a(1, k) = 0$ if the lateral size N is an odd number. It must be noted that the form of the distribution function does not affect the generality of the results and conclusions.[14]

Using the mean-field approximation (MFA), we can express the spin average along the z-direction at site i as

$$\langle S_i^z \rangle = (\langle H_i^z \rangle / 2\,|\boldsymbol{H}_i|) \tanh(|\boldsymbol{H}_i|/2k_{\rm B}T), \quad (5)$$

where $\boldsymbol{H}_i = \left(\Omega_i, 0, \sum_j J_{ij} \langle S_j^z \rangle + 2\mu E \right)$ is the mean field acting on the ith pseudo-spin, and $|\boldsymbol{H}_i| = \sqrt{\Omega_i^2 + (\langle H_i^z \rangle)^2}$. $\langle H_i^z \rangle = \sum_j J_{ij} \langle S_j^z \rangle + 2\mu E$, where H_i^z is the z-component of $\boldsymbol{H}_i$. $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature.

The polarization P_i at site i is

$$P_i = 2n\mu \langle S_i^z \rangle, \quad (6)$$

where n is the number of pseudo-spins in an unit volume.

The static susceptibility χ_i at site i can be formulated as

$$\chi_i = \left.\frac{\partial P_i}{\partial E}\right|_{E=0} = 2n\mu \left.\frac{\partial \langle S_i^z \rangle}{\partial E}\right|_{E=0}. \quad (7)$$

The mean susceptibility of the thin film is determined by

$$\bar{\chi} = \frac{1}{(N^2 \times L)} \sum_{i=1}^{N^2 \times L} \chi_i. \quad (8)$$

For a bulk material with a second-order phase transformation, the transverse field Ω_i and the exchange interaction J_{ij} are constant. The Curie temperature $T_{\rm b}$ can be obtained from the following equation:[22]

$$\tanh(\Omega/2k_{\rm B}T_{\rm b}) = 2\Omega/rJ, \quad (9)$$

where r is the coordination number. In our calculations, the corresponding variables are renormalized to dimensionless units by utilizing the bulk material parameters.

3. Numerical results and discussions

According to Eqs.(7) and (8), we present the numerical results in the following figures. For simplicity, the transverse field at all sites is treated identically in our calculations, and we assign $\Omega_i/J = 0.1$ and $\beta_3 = \beta_1$. We set $t = T/T_{\rm b}$.

Figure 2 shows the dielectric susceptibility dependence of the temperature $T/T_{\rm b}$ with different parameters J_∞ and α_1. We set $\alpha_1 = \alpha_2$ in Fig.2. Each curve exhibits a susceptibility peak at a certain temperature, which means that a phase transformation will take place from the ferroelectric phase to the paraelectric phase. One can also see from Fig.2 that the susceptibility peak shifts to the higher temperature with the increase of J_∞ (or α_1). This is rational because the interactions are strengthened everywhere except the edge loop with the increase of J_∞ (or α_1), and the stronger interactions can push the susceptibility peak to the higher temperature. Evidently, the Curie temperature of a fixed size film is chiefly determined by the interaction intensity near the centre of the film, which shows that the requirement of a fixed size film on the work environment can be reduced by strengthening the interaction intensity near the centre of the film.

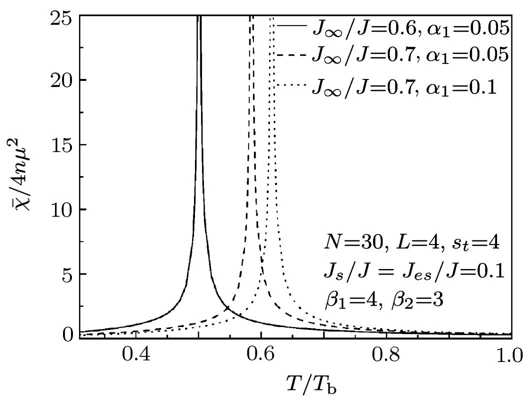

Fig.2. The mean susceptibility of the film as a function of the temperature with different α_1 and J_∞.

Figure 3 presents the dependence of the mean susceptibility on the temperature $T/T_{\rm b}$ with different film sizes. For comparison, we also plot the susceptibility versus temperature curves for the bulk material and the four-layer thick film with the infinite lateral size. Similar to the result in Fig.2, the maximum of the mean susceptibility occurs at the temperature where the polarization should become zero. One can also see from Fig.3 that the susceptibility peak shifts to the higher temperature and the peak width increases with the increase of the lateral size of the film when the film thickness is fixed (here $L = 3$). Likewise, the susceptibility peak shifts to the higher temperature and the peak width is enhanced with the increase of the film thickness when the lateral size of the film is fixed (here $N = 40$). This feature qualitatively agrees with experimentally measured results for $PbTiO_3$ (PTO)[8] particles. This can be ascribed to the fact that the number of pseudo-spins in favour of the ferroelectricity of the film increases with the enhancement of film sizes, and the effective interactions between pseudo-spins in the film are strengthened. For the film with $N = 20$ and $L = 3$, the Curie temperature of the film is $T_{\mathrm{C}} \approx 0.35T_{\mathrm{b}}$. If the Curie temperature of the bulk material is $T_{\mathrm{b}} = 659$ K (the bulk Curie temperature of PZT that is a favourite material for ferroelectric memories), the Curie temperature of the PZT film with finite sizes is $T_{\mathrm{C}} \approx 230$ K. It is demonstrated that when a smaller lateral size and thinner film is at the ferroelectric phase, the film has difficultly working at higher temperatures (over room temperature) unless the pseudo-spin interactions in the smaller size film are much stronger. Therefore, the smaller size film may put forward a rigorous standard of the working environment when the film works at the ferroelectric phase. On the other hand, it can also be seen that the position of the susceptibility peak of the finite size thin film is much lower than those of the bulk material and the four-layer thick film with the infinite lateral size.

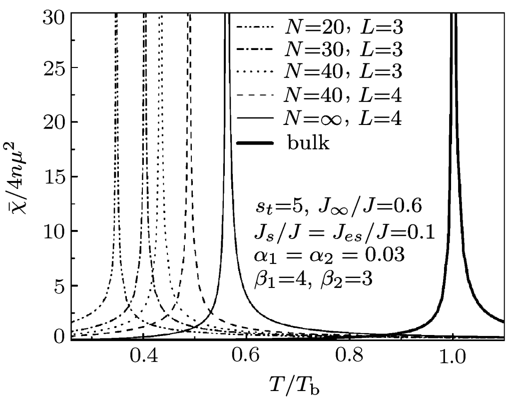

Fig.3. The mean susceptibility of the film as a function of the temperature with different N and L.

Evidently, the weak pseudo-spin interactions push the susceptibility peak to the lower temperature when the lateral size or the thickness of the film changes from the infinity to a finite value. Therefore, film dimensions including the lateral size and thickness play a crucial role in determining the dielectric susceptibility of the film.

Figure 4 presents the relation of the lateral size of the thin film to the mean susceptibility for several different film thicknesses in detail. Each curve presents a susceptibility peak, which implies that a lateral size-driven phase transformation from the paraelectric phase to the ferroelectric phase will occur with the increase of lateral size of the thin film. This kind of feature has already been observed experimentally in the studies of PTO[9] and Ba(Zr,Ti)O_3[10] particles. Interestingly, this is a unique phenomenon in ferroelectric thin films with finite sizes in three dimensions, and it can not occur in bulk materials and thin films with infinite lateral size. One can also see from Fig.4 that the susceptibility peak occurs at a larger lateral size with the decrease of the film thickness, which indicates that the decrease of the film thickness comes with an apparent increase of the critical lateral size. It is demonstrated that if a high-storage-density memory fabricated by the downscaling of the lateral size of the film can work at a higher temperature, the thickness of the film should be larger. This is understandable because the thinner the thin film, the weaker the interlayer interaction.

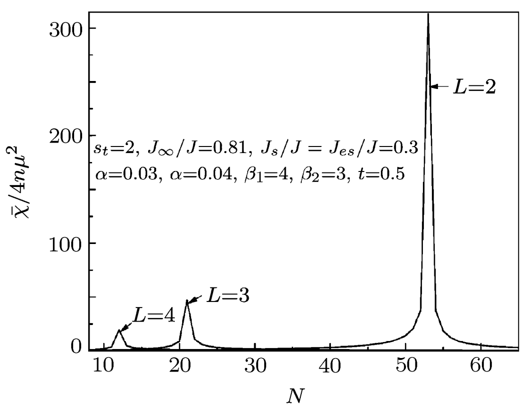

Fig.4. The lateral size dependence of the mean susceptibility with different film thicknesses.

Figure 5 shows the lateral size dependence of the mean susceptibility of the thin film with different J_∞ and α_1 when $t = 0.5$. Here we set $\alpha_1 = \alpha_2$. The susceptibility peak shifts to the larger lateral size with the decrease of J_∞ when α_1 is fixed (here $\alpha_1 = 0.1$).

Similarly, the susceptibility peak shifts to the larger lateral size with the decrease of α_1 when J_∞ is definite (here $J_\infty/J = 0.75$). Evidently, the position of the susceptibility peak shows a strong dependence of parameters J_∞ and α_1. This is an indication of the fact that the change of the interaction intensity near the centre of the film can push the transfer of the susceptibility peak, i.e. the critical lateral size varies. Therefore, if the fixed thickness film at the ferroelectric phase can work at room temperature, the lateral size of the film can dwindle by strengthening the interaction intensity near the centre of the film, which provides a way to downscale the dimensions of electric devices.

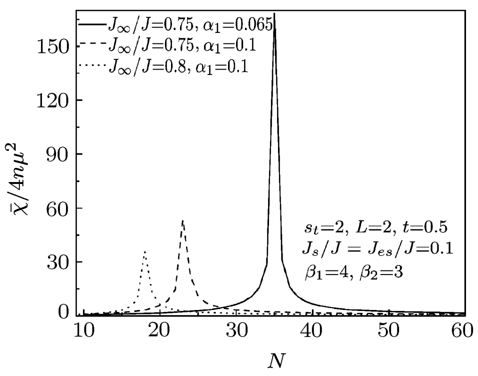

Fig.5. The lateral size dependence of the mean susceptibility of the thin film with different α_1 and J_∞.

Figure 6 shows the spatial distribution of the susceptibility for the second layer ($k = 2$) of the film with different s_t and β_1. Here we set $\beta_1 = \beta_2$. In contrast with Fig.6(a), Fig.6(b) shows that the increase of susceptibility extends into the centre of the film with the widening of the lateral structural transition zones of the film when the parameter β_1 is fixed (here $\beta_1 = 1$). Therefore, the widening of the lateral structural transition zones of the film could be an effective way to increase the mean susceptibility of a fixed size film. Compared with Fig.6(b), Fig.6(c) indicates that the susceptibility is reduced with the increase of β_1 when s_t is definite (here $s_t = 7$). This feature is an indication of the fact that the stronger interactions between pseudo-spins in lateral structural transition zones suppress the mean susceptibility of the film. In conclusion, the mean susceptibility of the fixed size film could be elevated by widening lateral structural transition zones and weakening pseudo-spin interactions in these regions, which may be a reference to the future experimental work in the fabrication of ferroelectric thin films with the giant susceptibility.

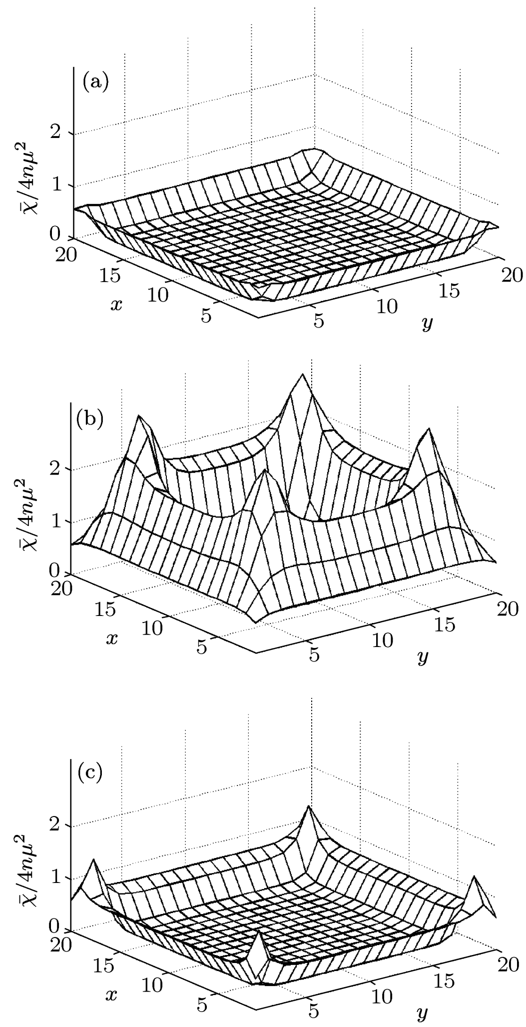

Fig.6. The profile of the susceptibility for the second layer of the film: (a) $s_t = 1$ and $\beta_1 = 1$; (b) $s_t = 5$ and $\beta_1 = 1$ and (c) $s_t = 5$ and $\beta_1 = 5$. The corresponding parameters are $N = 20$, $L = 3$, $t = 0.35$, $J_s/J = J_{es}/J = 0.1$, $J_\infty/J = 0.8$, $\alpha_1 = 0.1$ and $\alpha_2 = 0.2$.

4. Summary and conclusions

To sum up, dielectric properties of a finite size ferroelectric thin film have been studied by a modified TIM in the framework of MFA. The conclusions obtained are as following. (1) The influence of the lateral size on dielectric properties of the film cannot be ignored. The position of the susceptibility peak driven by the lateral size of the film depends sensitively on the film thickness and the interaction intensities near the centre of film. (2) The mean susceptibility of the fixed size could be improved by widening lateral structural transition zones and weakening pseudo-spin interactions in these regions. Our theoretical results here provide some useful guidance for future experiments in view of the rapid development in the miniaturization of ferroelectric thin films.

References

[1] Auciello O, Scott J F and Ramesh R 1998 *Phys. Today* **51** 22

[2] Scott J F 2000 *Ferroelectric Memories* (Berlin: Springer)

[3] Dawber M, Rabe K M and Scott J F 2005 *Rev. Mod. Phys.* **77** 1083

[4] Ganpule C S, Stanishevsky A, Su Q, Aggarwal S, Melngailis J, Williams E and Ramesh R 1999 *Appl. Phys. Lett.* **75** 409

[5] Bühlmann S, Dwir B, Baborowski J and Muralt P 2002 *Appl. Phys. Lett.* **80** 3195

[6] Ahn J H, Kim J Y and Kang S W 2007 *Appl. Phys. Lett.* **91** 62910

[7] Park W Y, Hwang C S, Baniecki J D, Ishii M, Kurihara K and Yamanaka K 2008 *Appl. Phys. Lett.* **92** 102902

[8] Grigalaitis R, Banys J, Lapinskas S, Erdem E, Böttcher R, Gläsel H J and Hartmann E 2006 *IEEE Trans. Ultrason. Ferr.* **53** 2270

[9] Qu B D, Jiang B, Wang Y G, Zhang P L and Zhong W L 1994 *Chin. Phys. Lett.* **11** 514

[10] Ohno T, Suzuki D, Ishikawa K, Horiuchi M, Matsuda T and Suzuki H 2006 *Ferroelectrics* **337** 25

[11] Zhong W L, Qu B D, Zhang P L and Wang Y G 1994 *Phys. Rev.* B **50** 12375

[12] Oh S H and Jang H M 2000 *Phys. Rev.* B **62** 14757

[13] Wong C K and Shin F G 2006 *Appl. Phys. Lett.* **88** 72901

[14] Lü T Q and Cao W W 2002 *Phys. Rev.* B **66** 24102

[15] Wang Y L, Wei T R, Liu B T and Deng Z C *Acta Phys. Sin.* **56** 2931 (in Chinese)

[16] Wesselinowa J M 2002 *Solid State Commun.* **121** 489

[17] Michael Th, Trimper S and Wesselinowa J M 2007 *Phys. Rev.* B **76** 94107

[18] Michael Th, Trimper S and Wesselinowa J M 2006 *Phys. Rev.* B **74** 214113

[19] Wang C L, Xin Y, Wang X S and Zhong W L 2000 *Phys. Rev.* B **62** 11423

[20] Xin Y, Wang C L, Zhong W L and Zhang P L 1999 *Phys. Lett.* A **260** 411

[21] Qu B D, Zhong W L and Zhang P L 1995 *Phys. Rev.* B **52** 766

[22] Wang X G, Pan S H and Yang G Z 1999 *J. Phys.: Condens. Matter* **11** 6581