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Physica A 387 (2008) 1963–1971
PHYSICA A
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Dielectric properties of ferroelectric thin films with surface transition layers

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Received 21 April 2007; received in revised form 30 October 2007
Available online 5 November 2007

Abstract

By taking into account surface transition layers (STL), the dielectric properties of ferroelectric thin films described by the transverse Ising model are discussed in the framework of the mean-field approximation. Functions of the intra-layer and inter-layer couplings are introduced to characterize STL, which makes the model more realistic compared to the previous treatment of surface layers using uniform surface exchange interactions and a transverse field. The effects of physical parameters on the dielectric properties are quantified. The results obtained indicate that STL has a very strong influence on the dielectric properties of ferroelectric thin films. Some of our theoretical results are in accordance with the available experimental data.
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PACS: 77.80.Bh; 77.55. +f; 77.80.Dj

Keywords: Ferroelectric thin film; Transverse Ising model; Dielectric properties

1. Introduction

With rapid progress in material preparation techniques, the qualities of ferroelectric thin films and composite materials have improved greatly, which has made the study of ferroelectric thin films a subject of great practical importance. However, surface and size effects are two important phenomena observed in ferroelectric thin films which have been known since the early 1950s, still beset by many problems yet to be answered. In recent years the finite-size and surface effects on the phase transition temperature, spontaneous polarization, and dielectric susceptibility of ferroelectric thin films have been extensively studied both experimentally [1–4] and theoretically [5–20]. The dielectric properties have been reported for Pb(Zr, Ti)O_3(PZT) [21,22], $PbTiO_3$ [23], $BaTiO_3$ [24], and (Ba, Sr)TiO_3 (BST) [25,26] thin films by many groups. The low frequency dielectric permittivity measurements were performed on the KH_2PO_4 (KDP) nanosize particle systems. The significant shift of the transition temperature, compared to the bulk value, as well as the broadening of the transition region for KDP particle samples was observed by Colla et al. [27]. The origin of the reduced dielectric response in $SrTiO_3$ thin films was discussed by Ostapchuk et al. [28]. Using the

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doi:10.1016/j.physa.2007.10.070

phenomenological theory, Zhong et al. [29] and Chen et al. [30] have calculated the size and surface effects on the dielectric susceptibility of ferroelectric thin films and found that the peak of dielectric susceptibility shifts to lower temperature due to the presence of the surface layers. Wang et al. [31] and Qu et al. [32] have studied the ferroelectric thin films described by the transverse Ising model (TIM) under the mean-field approximation. The results showed that the film susceptibility diverges at the film Curie temperature, similar to the bulk susceptibility, but its magnitude is much reduced. Wesselinowa [33] has investigated the dielectric susceptibility of FE thin films using a Green's function technique and found that depending on the interaction constants on the surface and on the bulk, the dielectric susceptibility can increase or decrease as the film thickness decreases.

The TIM with the mean-field approximation has been widely applied to study properties of ferroelectric thin films containing surface layers. In the TIM model mentioned above, the method to describe the lowing symmetry at the surface is to make a modification of Ω_i and J_{ij} (the transverse field and the two-spin exchange interaction) compared with their bulk values. The modified Ω_i and J_{ij} are treated to be uniform in surface layers, and the structural difference between surface layers and the interior of film is a "step" model. But in reality, the film surface is a transition layer with properties continuously changing. A more realistic treatment is to consider multilayer structures of many ferroelectric materials. It is therefore more interesting to investigate the role of intra-layer (within layer) and inter-layer (cross layers) interactions [$J_a(m)$ and $J_e(m)$] and their influence on the physical behaviors of ferroelectric thin films. From such a more realistic model, one may get a better explanation of the experimental facts and find the way to better control the properties of artificially fabricated films by controlling the STL, such as its thickness, the intensity of exchange interactions near the surface, etc. In this article, we introduce functions of the intra-layer and inter-layer interaction between two spins, $J_a(m)$ and $J_e(m)$, to describe the structure change from the imperfect surface to the perfect interior of the film. Such a model reflects a more realistic situation of the film than that previous step-function type model. The dielectric properties of ferroelectric thin films under such a model will be investigated theoretically. Our theoretical predictions will be compared with the available experimental results, which may be a reference for future experimental work in the study of surface effects or fabrication of ferroelectric thin films.

Effects of the transverse field Ω_i on the phase transition properties of ultra-thin ferroelectric films have been studied in Ref. [32]. When the exchange interaction parameter J_s is defined to characterize the film surface layer, the deviation of Ω_i from the corresponding bulk value Ω can only lead to different shapes of the profiles, but will not influence the change of the Curie temperature (see group Fig. 3(I), 3(II) and group Fig. 3(III), 3(IV) in Ref. [32]). For simplicity, the transverse field is taken as a constant $\Omega/J = 1.0$ across the whole film in our calculations.

2. The model

To study the dielectric property of the film, we apply a weak uniform electric field along the spontaneous polarization direction. The Hamiltonian of the TIM [5–10] is

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

where Ω_i is the transverse field (for H-bond ferroelectrics, it represents the proton tunneling between the two equilibrium positions on the H bonds), S_i^x and S_i^z are the x and z components of a spin $\frac{1}{2}$ operator at site i (the thermal average of S_i^z is related to the polarization), J_{ij} is the two-spin exchange interaction constant between site i and site j, and the sum $\sum_{ij}$ runs over all sites. E is the applied electric field and μ is the dipole moment.

The model used to describe the ferroelectric properties of the thin film is shown in Fig. 1. For simplicity but without loss of generality, we assume that the z-direction is perpendicular to the surface and the polarization is along the z-direction. An N-layer film with symmetrical surface is studied. The number of pseudo-spin layers included in the STL is n_s. The simplest assumption is to take J_{ij} non-zero only for nearest-neighbor sites i and j. We assumed that $J_{ij} = J_a(m)$ if sides i and j are within one pseudo-spin layer; $J_{ij} = J_e(m)$ if two sites are across two different pseudo-spin layers; when both sites lie inside the film but out of STL, the exchange interaction $J_{ij}$is taken to be the same as the bulk constant J, i.e., $J_{ij} = J_a(m) = J_e(m) = J$ (see Eqs. (2) and (3)).

Since we do not have any experimentally measured data available on the surface imperfection, two simple functions are assumed to describe the inhomogeneous distribution of the intra-layer and inter-layer exchange interactions. As a continuous structure, the property of the STL continuously changes to match the properties of imperfect surface at

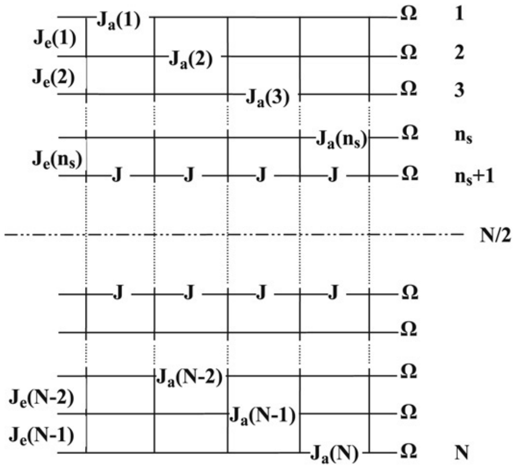

Fig. 1. Geometric structure of the thin film under study, where $J_a(m)$ is the intra-layer interaction, $J_e(m)$ is the inter-layer interaction and J is the bulk interaction strength.

one end and perfect interior at the other end. Thus, as the main factors to characterize the STL, the intra-layer and inter-layer exchange interaction are position dependent. This particular choice of $J_a(m)$ and $J_e(m)$ do not affect the generality of the results and conclusions. Since the film is symmetric, only the functions for the upper film with $N/2$ layers are given:

$$\begin{cases} J_a(m) = \alpha \left(\frac{2m}{N}\right)^{\sigma} J & m = 1 \sim n_s \left(n_s \le \frac{N}{2}\right) \quad \text{(a)} \\ J_a(m) = J & \frac{N}{2} \ge m > n_s \quad \text{(b)} \end{cases} \tag{2}$$

$$\begin{cases} J_e(m) = \beta \left(\frac{2m}{N}\right)^{\sigma} J & m = 1 \sim n_s \left(n_s \le \frac{N}{2}\right) \quad \text{(a)} \\ J_e(m) = J & \frac{N}{2} \ge m > n_s \quad \text{(b)} \end{cases} \tag{3}$$

where m is the sequence number of the film layer, N is the total number of film layers across the film, n_s is the number of pseudo-spin layers included in the STL. The parameter σ reflects the variable intensity of the intra-layer and inter-layer interactions near the upper surface. The parameters α and β are adjustable parameters representing the strength difference between the intra-layer and inter-layer interactions.

Using mean-field approximation and assuming that the pseudo-spins in the same layer have the same values, the spin average along the z-direction in the ith layer can be expressed by:

$$\langle S_i^z \rangle = (\langle H_i^z \rangle / 2|\mathbf{H}_i|) \tanh(|\mathbf{H}_i|/2k_B T) \tag{4}$$

where $\mathbf{H}_i = (\Omega_i, 0, \sum_j J_{ij}\langle S_j^z \rangle + 2\mu E)$ is the mean field acting on the ith spin, $\langle H_i^z \rangle = \sum_j J_{ij}\langle S_j^z \rangle + 2\mu E$, k_B is the Boltzmann constant. The spontaneous polarization P_s is proportional to $\langle S_i^z \rangle$. Let R_m denote the value of $\langle S_i^z \rangle$ in the mth layer, then

$$R_m = \frac{\langle H_m^z \rangle}{2|\mathbf{H}_m|} \tanh(\mathbf{H}_m/2k_B T) \tag{5}$$

where

$$\langle H_m^z \rangle = 4J_m R_m + J_{m+1} R_{m+1} + J_{m-1} R_{m-1} + 2\mu E, \tag{6}$$

$$|\mathbf{H}_m| = \sqrt{\Omega_m^2 + (\langle H_m^z \rangle)^2}. \tag{7}$$

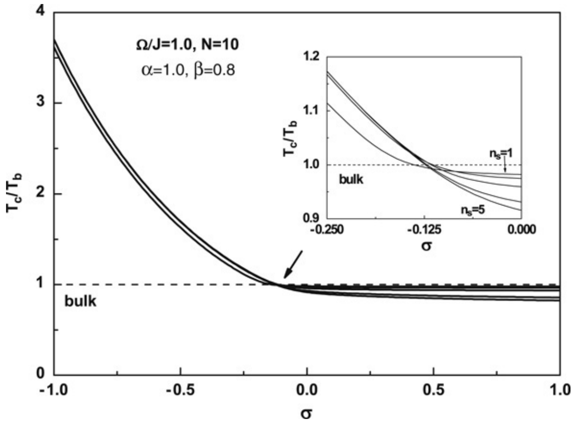

Fig. 2. Curie temperature vs σ for ten-layer films with n_s from 1 to 5.

Eq. (5) represents a set of simultaneous equations from which R_m can be calculated iteratively. The polarization of the mth layer is proportional to the thermal average of R_m, i.e.

$$P_m = 2n\mu R_m \tag{8}$$

where n is the number of pseudo-spins per volume, and $\mu$is the dipole moment.

The mean polarization $\bar{P}$ is determined by

$$\bar{P} = \frac{1}{N}\sum_{m=1}^{N} P_m = 2n\mu\frac{1}{N}\sum_{m=1}^{N} R_m. \tag{9}$$

The static susceptibility of the film can be calculated from the formula below:

$$\chi_m = \left.\frac{\partial P_m}{\partial E}\right|_{E=0} = 2n\mu \left.\frac{\partial R_m}{\partial E}\right|_{E=0}. \tag{10}$$

Define

$$k_m = \frac{1}{4n\mu^2}\chi_m = \frac{1}{2\mu}\left.\frac{\partial R_m}{\partial E}\right|_{E=0} \tag{11}$$

then k_m satisfies the following equation:

$$k_m = (4J_m k_m + J_{m+1}k_{m+1} + J_{m-1}k_{m-1} + 1)\frac{\partial R_m}{\partial H_m^z} \tag{12}$$

where $\partial R_m/\partial H_m^z$ is a function of R_m and can be obtained based on the calculation of Eq. (5).

The mean susceptibility χ of the film is determined by

$$\chi = \frac{1}{N}\sum_{m=1}^{N}\chi_m = \frac{4n\mu^2}{N}\sum_{m=1}^{N} k_m. \tag{13}$$

3. Numerical results and discussions

First, in Fig. 2 we show the influence of parameter σ on the phase transition temperatures for a ten-layer film with the number n_s taking a value from 1 to 5. The parameters α and β are taken to be 1.0 and 0.8 for these calculations. One can see that with the increase of σ, the transition temperature decreases and every curve has a critical σ_c (When $T_c = T_b, \sigma = \sigma_c, T_b$ is the bulk transition temperature.). Films with different thicknesses of STL have different critical intra-layer and inter-layer interactions' strengths (J_{ac} and J_{ec}). When $\sigma < \sigma_c$, the film Curie temperature T_c is higher

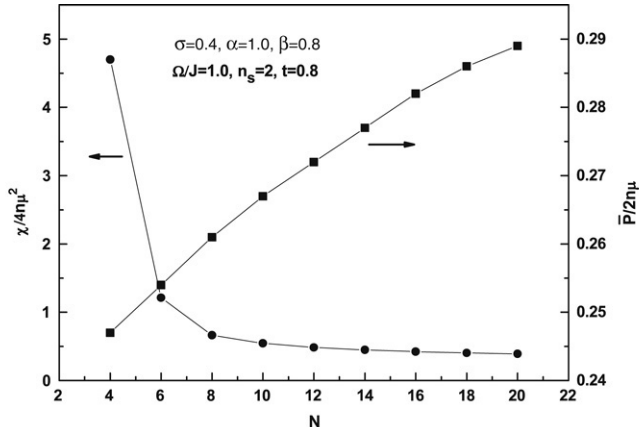

Fig. 3. Thickness dependence of the mean polarization and dielectric susceptibility when $T_c < T_b$.

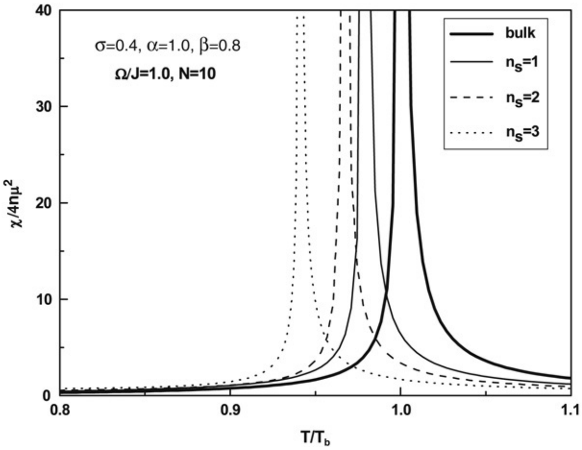

Fig. 4. Mean susceptibility as a function of temperature for a ten-layer film with different thicknesses of the STL when $T_c < T_b$.

than the bulk transition temperature T_b. When $\sigma > \sigma_c$, the weak coupling will suppress the phase transition so that $T_c < T_b$. That is to say, STL can make the Curie temperature of the film higher or lower than that of the corresponding bulk material.

The result is different from the result obtained in Ref. [7], which mentioned that except for the single-surface-layer film which has the critical surface interaction strength given by $J_{sc}/J = 1.25$, the multisurface-layer films have the same critical surface interaction strength given by $J_{sc}/J = 1.078$. In other words, adding the STL to the model gives us some new results, we now discuss two different cases in more detail below.

3.1. The film Curie temperature T_c is lower than the bulk transition temperature T_b

The film thickness dependence of the mean polarization and dielectric susceptibility is shown in Fig. 3. With decreasing film thickness, the mean polarization decreases, while the mean susceptibility increases, then goes up rapidly accompanied by a dielectric divergence, which is in agreement with the experimental data of KDP [34], $BaTiO_3$ [35] and $PbTiO_3$ fine particles [36,37]. For ferroelectric thin films, when the thickness is smaller than the critical value, the polarization cannot line up under thermoequilibrium because of the weakened long-range interaction by the sample size, but when a weak electric field is applied, they line up easily and show a large dielectric susceptibility.

The mean susceptibility as a function of temperature for a ten-layer film with different thicknesses of STL is plotted in Fig. 4. Compared to the bulk, the Curie temperature and the integrated intensity of the phase transition peak have changed due to the contribution of the STL. With the increase of n_s, the peak position shifts to lower temperature and

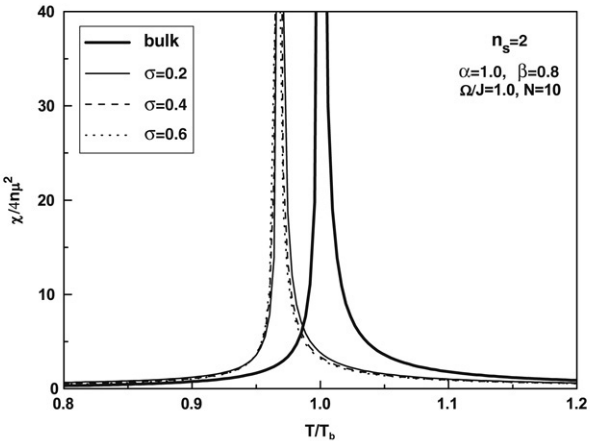

Fig. 5. Influence of parameter σ on the dielectric properties of a ten-layer ferroelectric film when $T_c < T_b$.

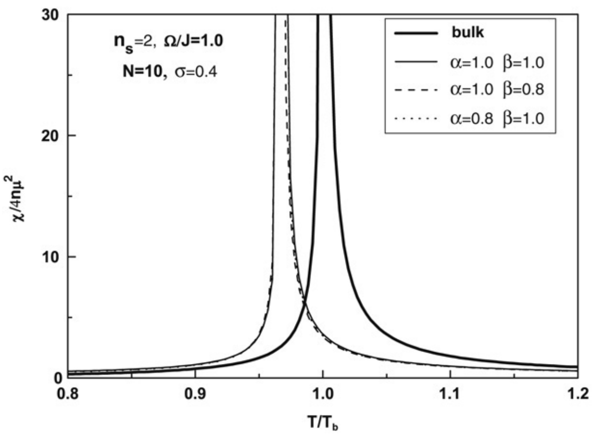

Fig. 6. Influence of α and β parameters on the dielectric properties of a ten-layer ferroelectric film when $T_c < T_b$.

the dielectric susceptibility at room temperature is effectively increased, but its half-peak width is reduced. In other words, thicker STL has lower transition temperature and narrower half-peak width.

Figs. 5 and 6 show the influence of parameters σ, α and β on the dielectric properties of ten-layer ferroelectric films, respectively. Similar to the results in Fig. 4, the mean susceptibility diverges at the temperature where the polarization becomes zero, the peaks shift to lower temperature and the half-peak width decreases when σ increases or α, β decrease, i.e., lower σ, larger α and β values correspond to higher Curie temperature.

3.2. The film Curie temperature T_c is higher than the bulk transition temperature T_b

The film thickness dependence of the average spontaneous polarization and susceptibility is depicted in Fig. 7. It can be seen that as the film thickness decreases, the average polarization and transition temperature increases while susceptibility decreases, which is in agreement with the experimental data for the TGS film [38]. In this case, the surface layer of the film has induced transition temperature even above that of the bulk. This is an opposite behavior compared to the previous case in part 3.1, which occurs due to the reduced properties of the STL. The properties of the whole system are highly dependent upon the STL conditions.

The mean susceptibility as a function of temperature with different n_s values for films with increased Curie temperature is depicted in Fig. 8. The results are different from those obtained in part 3.1. There are two peaks in the temperature dependence of susceptibility. One is around the bulk Curie point (bulk-related), but its magnitude is much reduced and its integrated intensity decreases with increasing n_s. The other one (surface-related) is at a higher temperature caused by the disappearance of the spin average, which can be understood more clearly from Fig. 9,

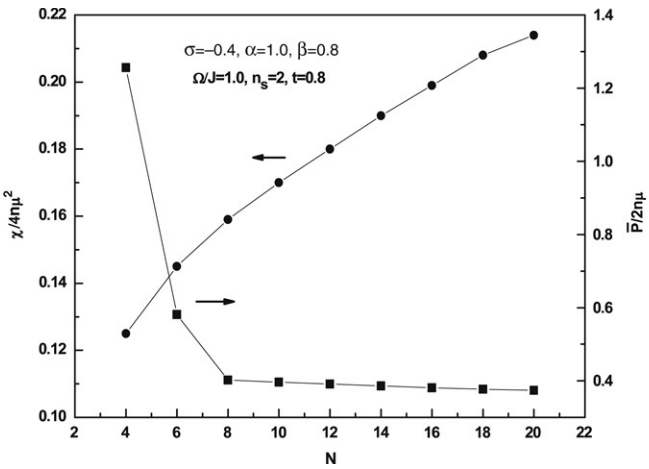

Fig. 7. Thickness dependence of the mean polarization and dielectric susceptibility when $T_c > T_b$.

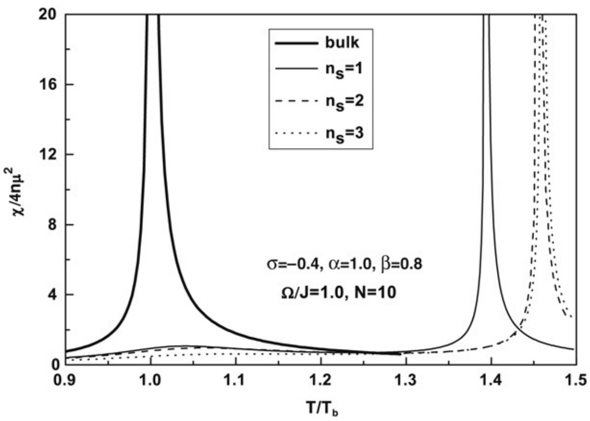

Fig. 8. Mean susceptibility as a function of temperature for a ten-layer film with different thickness of the STL when $T_c > T_b$.

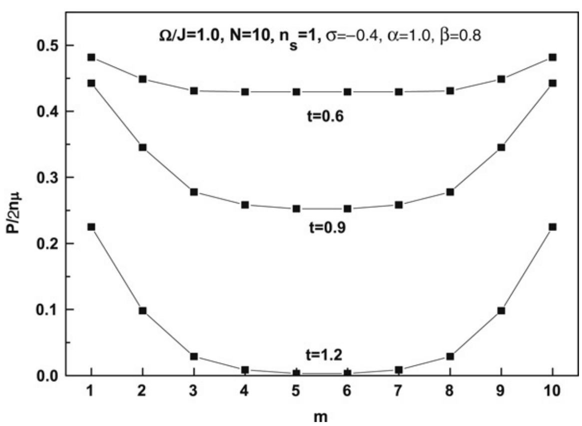

Fig. 9. Spontaneous polarization distribution of a ten-layer film at different temperatures.

which depicts the spontaneous polarization distribution at different temperatures for a film with ten layers. We can see that with increasing temperature, the polarization decreases and tends to zero when $T \rightarrow T_c$. Larger n_s corresponds to a greater peak shift, and its integrated intensity also decreases with the increase of n_s.

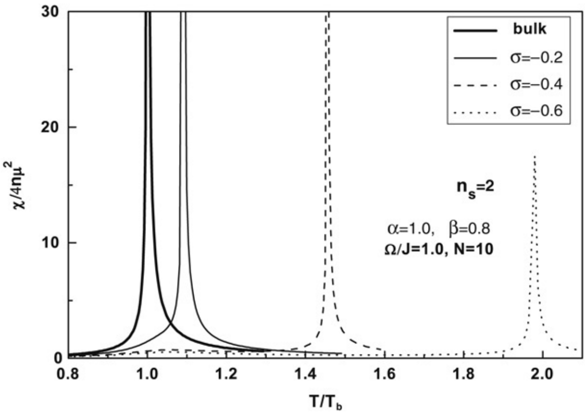

Fig. 10. Influence of parameter σ on the dielectric properties of a ten-layer ferroelectric film when $T_c > T_b$.

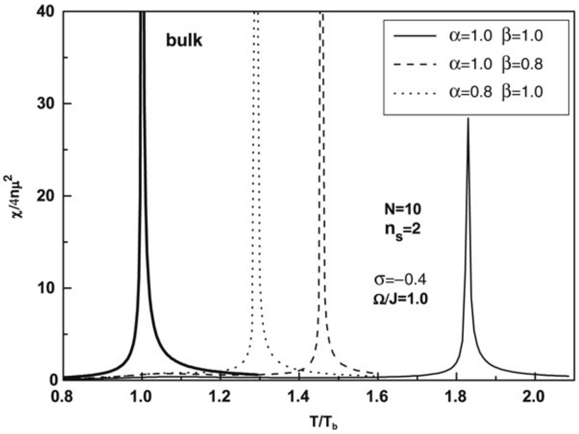

Fig. 11. Influence of α and β parameters on the dielectric properties of a ten-layer ferroelectric film when $T_c > T_b$.

The influence of σ, α and β on the dielectric properties of ten-layer ferroelectric films are respectively plotted in Figs. 10 and 11. The peak position obviously shifts to higher temperature and the magnitude of the peak is greatly suppressed as σ decreases or α, β increase. Lower σ, larger α and β values correspond to more shift of susceptibility peak and larger reduction in peak magnitude. In Fig. 11 several groups of α and β values are calculated. We can see that both α and β parameters have influence on the dielectric susceptibility, but in comparison, α has stronger influence than β. This is to say, controlling the exchange interaction parameter between two nearest spins on the same layer has more effect on the film dielectric properties than controlling the exchange interaction parameter across nearest-neighbor layers. This conclusion can also be obtained from the results in Fig. 6, which is less obvious than that in Fig. 11 due to the choices of the functional forms of $J_a(m)$ and $J_e(m)$.

It should be mentioned that Wesselinowa and Dimitrov [39] have studied the influence of substrates on dielectric properties of ferroelectric thin films. The obtained results indicated that the influence of the substrates have similar effects as that of STL. The substrates can also make the susceptibility peak position and Curie temperature to occur at either lower or higher temperatures, and decrease the susceptibility peak.

4. Conclusion

Considering surface transition layers (STL), the dielectric property of ferroelectric thin films was studied based on the transverse Ising model in the framework of the mean-field approximation. Inhomogeneous distribution functions of the intra-layer and inter-layer interactions $J_a(m)$ and $J_e(m)$ are introduced to characterize the STL. The following conclusions are obtained from our study: (1) STL has great influence on dielectric properties of ferroelectric thin films, which can shift the Curie temperature to either lower or higher temperatures compared to the corresponding bulk value. (2) Two susceptibility peaks appear when the film Curie temperature is higher than that of the bulk, and the bulk-related peak is less pronounced than the surface-related peak. (3) Intra-layer interactions have more effects than inter-layer interactions on the dielectric behavior. These results are consistent with the experimental fact observed in ferroelectric thin films, and they may provide some guidance for future experiments in view of the rapid development in the fabrication of ferroelectric thin films.

References

[1] I. Kanno, S. Hayashi, R. Takayama, T. Hirao, Appl. Phys. Lett. 68 (1996) 382.
[2] A. Erbil, Y. Kim, R.A. Gerhardt, Phys. Rev. Lett. 77 (1996) 1628.
[3] H. Tabata, T. Kawai, Appl. Phys. Lett. 70 (1997) 20.
[4] B.D. Qu, M. Evstigneev, D.J. Johnson, R.H. Prince, Appl. Phys. Lett. 72 (1998) 1394.
[5] H.K. Sy, Phys. Rev. B 46 (1992) 9220.
[6] H.K. Sy, J. Phys.: Condens. Matter 5 (1993) 1231.
[7] C.L. Wang, W.L. Zhong, P.L. Zhang, J. Phys.:Condens. Matter 3 (1992) 4743.
[8] C.L. Wang, Y. Xin, X.S. Wang, W.L. Zhong, P.L. Zhang, Phys. Lett. A 268 (2000) 117.
[9] B.D. Qu, W.L. Zhong, P.L. Zhang, Ferroelectrics 197 (1997) 23.
[10] X.G. Wang, S.H. Pan, G.Z. Yang, Solid State Commun. 113 (2000) 807.
[11] D.L. Yao, Y.Z. Wu, Z.Y. Li, Phys. Status Solidi B 231 (2002) 3.
[12] T. Kaneyoshi, Physica A 319 (2003) 355.
[13] J.M. Wesselinowa, Phys. Status Solidi B 223 (2001) 737.
[14] J.M. Wesselinowa, Phys. Status Solidi B 231 (2002) 187.
[15] J.M. Wesselinowa, Internat. J. Modern Phys. B 16 (2002) 473.
[16] J.M. Wesselinowa, Solid State Commun. 121 (2002) 89.
[17] T. Kaneyoshi, J. Magn. Magn. Mater. 264 (2003) 30.
[18] T. Kaneyoshi, Phys. Status Solidi (b) 2 (2003) 592.
[19] T. Kaneyoshi, Physica A 319 (2003) 355.
[20] B.H. Teng, H.K. Sy, Phys. B 348 (2004) 485.
[21] Y. Sakashita, H. Segawa, J. Appl. Phys. 73 (1993) 7857.
[22] K. Amanuma, T. Mori, T. Hase, T. Sakuma, Jpn. J. Appl. Phys. 32 (1993) 4150.
[23] H. Funakubo, T. Hioki, M. Otsu, K. Shinozaki, Jpn. J. Appl. Phys. 32 (1993) 4175.
[24] T. Hayashi, N. Oji, H. Maiwa, Jpn. J. Appl. Phys. 33 (1994) 5277.
[25] C.B. Parker, J.P. Maria, A.I. Kingon, Appl. Phys. Lett. 81 (2002) 340.
[26] J.C. Shin, J. Park, C.S. Hwang, H.J. Kim, J. Appl. Phys. 86 (1999) 506.
[27] E.V. Colla, A.V. Fokin, Yu.A. Kumzerov, Solid State Commun. 103 (1997) 127.
[28] T. Ostapchuk, J. Petzelt, V. Zelezny, Phys. Rev. B 66 (2002) 235406.
[29] W.L. Zhong, B.D. Qu, P.L. Zhang, Y.G. Wang, Phys. Rev. B 50 (1994) 12375.
[30] H. Chen, T.Q. Lü, W.W. Cao, Phys. B 373 (2006) 177.
[31] X.S. Wang, C.L. Wang, W.L. Zhong, X.Y. Xue, Mater. Sci. Eng. B 99 (2003) 576.
[32] B.D. Qu, W.L. Zhong, P.L. Zhang, Phys. Rev. B 52 (1994) 766.
[33] J.M. Wesselinowa, Solid State Commun. 121 (2002) 489.
[34] A. Jaccard, W. Kaenzig, M. Peter, Helv. Acta 26 (1953) 521.
[35] T. Kanata, T. Yoshikawa, K. Kubota, Solid State Commun. 62 (1987) 765.
[36] K. Ishikawa, K. Yoshikawa, N. Okada, Phys. Rev. B 37 (1988) 5852.
[37] S. Chattopadhyay, P. Ayyub, V.R. Palkar, M. Multani, Phys. Rev. B 52 (1995) 13177.
[38] A. Hadni, R. Thomas, Ferroelectrics 59 (1984) 221.
[39] J.M. Wesselinowa, Al.B. Dimitrov, Phys. Status Solidi B 244 (2007) 2242.