Critical thickness for dislocation generation during ferroelectric transition in thin film on a compliant substrate

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The formation energy of misfit dislocations in a ferroelectric thin film grown on compliant substrate is calculated based on the Landau-Devonshire formalism and Timosheko's method for thermal stresses. The critical thickness is shown to change significantly according to the polarization in the film, leading to serious concerns, particularly for thick substrates, in the device design stage. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338515]

It is well known that the presence of dislocations in thin films may adversely affect their functionality.[1,2] The existence of a minimum thickness for nonferroelectric films, below which misfit dislocations are absent, has been observed and extensively investigated in many nonferroelectric thin films.[3–9] Thus, Zubia *et al.*[3] use the equilibrium criterion to establish the critical conditions. Matthews and Blakeslee[4] and People and Bean[5] show that the critical thickness increases with increasing substrate thickness under many different conditions. Freund and Nix[6] use the so-called energy approach to derive the critical thickness. Zhang *et al.*[7] and Zhang and Su[8] established the criteria for the formation of interface dislocations in an epilayer of finite thickness deposited on a compliant substrate. Kastner and Gosele[9] established principles of strain in heteroepitaxial films growing on compliant substrate. Yet, the case of misfit dislocations in a ferroelectric thin film on a compliant substrate has not been studied due to the complication of the polarization.

In this letter, based on the Landau-Devonshire formalism and Timosheko's method for thermal stresses, the critical thickness for misfit dislocation generation is established. The effects of the polarization and the film/substrate thicknesses on the critical thickness are discussed.

A ferroelectric thin film deposited on a compliant substrate incorporated on a thick viscous borophosphorosilicate glass (BPSG) layer is considered (Fig. 1).[10] h and H are the thicknesses of the film and substrate, respectively. The substrate on BPSG can either shrink or expand to minimize the strain energy. For this setup, it has been shown that the observed final strains agree well with that predicted by stress balance, and the bending of the film/substrate system can be neglected.[9,10] The origin of our coordinate system is put at the lower surface of the ferroelectric thin film. We also consider the x plane and y plane to be infinite, so that all the associated fields are functions of z only. We suppose that the polarization P is only along the z direction.

Without the elastic interactions, the free energy can be expressed in terms of the Ginsburg-Landau functional as[11,12]

$$F_P = \int_0^h \left\{ \frac{1}{2}A(T-T_{c0})P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{2}D\left(\frac{dP}{dz}\right)^2 - \frac{1}{2}E_dP - E_{\text{ext}}P \right\} dz + \frac{1}{2}\left(\frac{DP_0^2}{\delta} + \frac{DP_h^2}{\delta}\right), \quad (1)$$

where A, B, C, and D are phenomenological coefficients. T_{c0} is the cooling phase-transition temperature of the bulk crystal. P_0 and P_h are the polarization at the surface and the interface of thin film, respectively. δ is the extrapolation length. E_d is the depolarization field.[11,13] E_{ext} is the external electric field.

For a ferroelectric thin film grown on a compliant substrate of finite thickness, the total elastic energy can be derived following Timosheko's method for calculating thermal stresses.[14] For a coherent interface between the film and substrate, we define the biaxial in-plane misfit strains in the film as $\varepsilon_{11}^m=\varepsilon_{22}^m=\varepsilon^m=(a_s-a_f)/a_f$, in which a_s and a_f are the lattice constant of the substrate and film, respectively. We note that the critical thickness refers to the point just before dislocation formation, at which the interface is still coherent. In addition to the misfit strain, there is also in-plane electrostrictive strain given by $\varepsilon_{11}^T=\varepsilon_{22}^T=\varepsilon^T=QP^2$, where Q is the electrostrictive coefficient. Both the film and the substrate are treated as cubic elastic bodies with elastic moduli C_{11}, C_{12} and $\bar{C}_{11}$, $\bar{C}_{22}$, respectively. Appling the misfit stresses and the electrostrictive stresses on the ferroelectric thin film $\sigma_{\text{appl}}=G(\varepsilon^m-QP^2)$, where $G=C_{11}+C_{12}-2C_{12}^2/C_{11}$, keeps the lattice constant of the film equal to that of the unstressed substrate. The resultant force (per unit length) due to σ_{appl} is given by

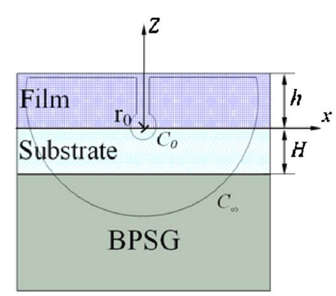

FIG. 1. (Color online) Schematics diagram of a ferroelctric thin film on a compliant substrate.

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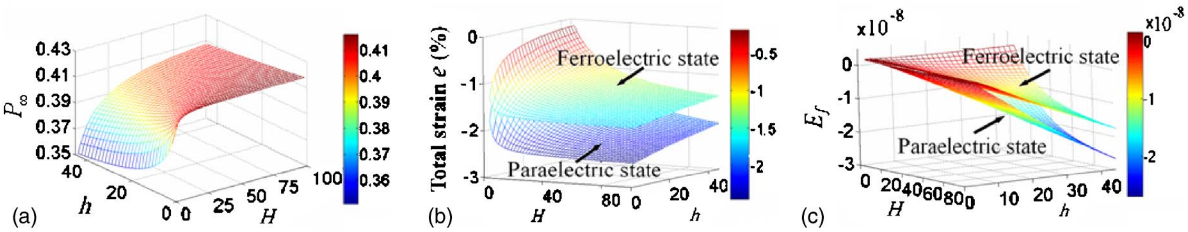

FIG. 2. (Color online) (a) Polarization distribution (T=300 K). (b) Distribution of the total strain. (c) Dislocation formation energy as a function of the film and substrate thicknesses in the paraelectric ($T>T_c$) and ferroelectric phases (T=300 K).

$$N_1 = N_2 = N = \int_0^h \sigma_{\text{appl}} dz = \int_0^h G(\varepsilon^m - QP^2)dz. \quad (2)$$

Equilibrium of the film/substrate system requires an equal and opposite force ($-N$) to balance the effect of σ_{appl}. The uniform strain ε^b produced by the force is given by

$$\sigma_{11}^b = \sigma_{22}^b = \sigma^b = G\varepsilon^b, \quad \bar{\sigma}_{11}^b = \bar{\sigma}_{22}^b = \bar{\sigma}^b = \bar{G}\varepsilon^b,$$
$$h\sigma_{11}^b + H\bar{\sigma}_{11}^b = h\sigma_{22}^b + H\bar{\sigma}_{22}^b = -N, \quad (3)$$

where $\bar{G}=\bar{C}_{11}+\bar{C}_{12}-2\bar{C}_{12}^2/\bar{C}_{11}$, and the barred quantities refer to the substrate. Equations (2) and (3) can be solved to give ε^b as $\varepsilon^b=-N/(hG+H\bar{G})$.

The total elastic energy of the film/substrate system is then given by

$$F_{\text{elastic}} = \int_0^h G(\varepsilon^m - QP^2 + \varepsilon^b)(\varepsilon^m - QP^2 + \varepsilon^b)dz + \int_h^{h+H} \bar{G}\varepsilon^b\varepsilon^b dz. \quad (4)$$

The stationary polarization state corresponding to the minimum total free energy $F=F_P+F_{\text{elastic}}$ can be obtained by solving the variational equation $\delta F/\delta P=0$.[12,15] To focus on the critical thickness of the misfit dislocation generation, we simplify the boundary conditions on the upper and lower surfaces to $\partial P/\partial z=0$ at $z=0$ and $z = h$, with $\delta_0=\delta_h\to\infty$.[1,2] The corresponding polarization state is uniform along the z direction. If P_∞ is the stationary value of the polarization, the strains in the film and substrate are given, respectively, by

$$\varepsilon_{11} = \varepsilon_{22} = e = \varepsilon^m - QP_\infty^2 + \varepsilon^b,$$
$$\bar{\varepsilon}_{11} = \bar{\varepsilon}_{22} = \bar{e} = \varepsilon^b. \quad (5)$$

We now introduce a dislocation $\mathbf{b}=[b_1,b_2,b_3]$ at the coherent interface. The formation energy E_f of the dislocation at the coherent interface is given by[9,10]

$$E_f = \frac{1}{2}\int\int_\Sigma (\sigma_{\text{dis}} + \sigma_c)(\varepsilon_{\text{dis}} + \varepsilon_c)dxdz - \frac{1}{2}\int\int_\Sigma \sigma_c\varepsilon_c dxdz = E_{\text{dis}} + E_{\text{int}}, \quad (6)$$

where $E_{\text{dis}}=\frac{1}{2}\iint_\Sigma \sigma_{\text{dis}}\varepsilon_{\text{dis}}dxdz$ and $E_{\text{int}}=\frac{1}{2}\iint_\Sigma(\sigma_c\varepsilon_{\text{dis}}+\sigma_{\text{dis}}\varepsilon_c)dxdz$. σ_{dis} and ε_{dis} are the stress and strain fields of the dislocation respectively, σ_c and ε_c are the stress and strain in the film/substrate system, respectively, from Eq. (5), i.e., without the dislocation. E_{dis} and E_{int} are the self-energy of the dislocation and the elastic interaction between the strain fields of the dislocation, the misfit, and the spontaneous polarization respectively. Σ is the integration domain that encloses the whole system (Fig. 1). Using contour integration and considering the traction-free condition along the surface $z=h$ and the vanishing far field of the dislocation E_{dis} in Eq. (6) can be rewritten as $E_{\text{dis}}=E_0+E_c=-\frac{1}{2}\int_{r_0}^L \sigma_{ij}^{\text{dis}} n_j b_i ds + \frac{1}{2}\int_{C_0}\sigma_{ij}^{\text{dis}} n_j u_{\text{dis},i} ds$,[8] where r_0 is the atomic-scale core cutoff radius and L is the length of the cut. At the same time, $E_{\text{int}}=-\int_0^L \sigma_{ij}^c n_j b_i ds$. For simplicity, we replace in the present calculation $M=2\mu(1+\nu)/(1-\nu)$ and $\bar{M}=2\bar{\mu}(1+\bar{\nu})/(1-\bar{\nu})$, where μ and $\bar{\mu}$ are shear moduli and ν and $\bar{\nu}$ are Poisson's ratio of the film and the substrate, respectively. E_0 can be evaluated as

$$E_0 = \frac{\mu}{4\pi(1-\upsilon)}[b_1^2 + b_2^2 + (1-\upsilon)b_3^2]\ln\left[\frac{4hH}{(h+2H)r_0}\right] - \frac{\mu(b_1^2+b_2^2)}{4\pi(1-\upsilon)}\left[1 - \frac{2H}{h+2H} + \frac{2H^2}{(h+2H)^2}\right] + E_{0,4s} + E_{0,4e}, \quad (7)$$

where $E_{0,4e}$ and $E_{0,4s}$ are caused by the stress fields of the edge and screw components of the dislocation.[8] The interaction energy can be calculated by integrating from the film surface to the dislocation core. For the ferroelectric thin film, $E_{\text{int}}=-Mb_1h(\varepsilon^m-QP_\infty^2+\varepsilon^b)$.

The spontaneous formation of the dislocation is energetically viable when the formation energy satisfies $E_f<0$. Solutions of Eq. (6) for $E_f=0$ then give the minimum film thickness for misfit dislocation formation. For an infinite substrate, the condition for zero formation energy can be rewritten as

$$\frac{\mu}{4\pi(1-\upsilon)}[b_1^2 + b_2^2 + (1-\upsilon)b_3^2]\ln\left[\frac{2h}{r_0}\right] - \frac{\mu(b_1^2+b_2^2)}{8\pi(1-\upsilon)} + E_c = Mb_1h(\varepsilon^m - QP_\infty^2 + \varepsilon^b) \quad (8)$$

We now apply the foregoing to consider the case of a $BaTiO_3$ thin film. Two kinds of substrates are considered: compressive substrates (e.g., $SrTiO_3$ and $LaAlO_3$) and tensile substrates (e.g., $KTaO_3$ and MgO). The material constants are taken from Refs. 8, 12, and 15. We assume here that the dislocation lies on the {1,1,1} plane, with Burgers vectors $\mathbf{b}=\pm b\left[\frac{1}{2},\frac{\bar{1}}{\sqrt{2}},\frac{1}{2}\right]$ for tensile and compressive substrates. We note that the Burgers vector may change with the polarization.[16]

For a $BaTiO_3/SrTiO_3$ system, P_∞ and e are calculated and shown in Figs. 2(a) and 2(b), respectively, as a function of the film and substrate thicknesses. In Fig. 2(b) we compare e in the paraelectric phase ($T>T_c$) and ferroelectric phase (T=300 K). Using Eq. (7), the dislocation formation

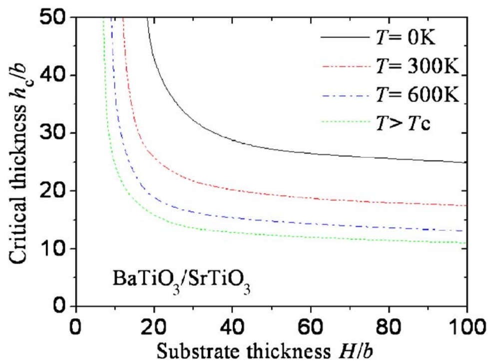

FIG. 3. (Color online) Critical thickness for misfit dislocation generation h_c at different temperatures plotted as a function of substrate thickness.

energy E_f for films in the paraelectric and ferroelectric phases can be expressed as a function of the film and substrate thicknesses, as shown in Fig. 2(c). The corresponding critical thickness as a function of the substrate thickness are shown in Fig. 3, where it can be seen to be larger in the ferroelectric phase ($T=0$, 300, and 600 K) than in the paraelectric phase, showing the effect of the electrostriction on the dislocation formation energy E_f.

In Fig. 4, we consider critical thickness h_c as a function of misfit strain for various values of P_∞ (0, 0.2, 0.4, and 0.6 C/m^2) in the important case of thick substrates. We consider cases with both compressive misfit strains ($\varepsilon^m<0$), such as in the $BaTiO_3/SrTiO_3$ system, and tensile ones ($\varepsilon^m>0$), such as in the $BaTiO_3/KTaO_3$ system. In this regard, we note that the polarization depends on variables such as the ambient temperature and the external field, while the misfit strain varies with the substrate. Figure 4(a) shows h_c in the compressive misfit case. In general, h_c increases as the magnitude of the misfit strain decreases, as expected. This is exactly the case for $P_\infty=0$. For nonzero values of P_∞ the transition from the cubic to tetragonal phase causes a reduction of the lattice constant of the film, and polarization leads to a reduction of the effective misfit between the film and the substrate, causing an increase in the critical thickness. As the polarization increases, the cancellation between the misfit strain by the electrostriction increases, producing an infinite critical thickness when the cancellation is complete. This can be seen in the cases of $P_\infty=0.4$ and 0.6, in which the electrostiction exactly cancels the misfit strain at about -0.7% and -1.6%, respectively. If the misfit strain is smaller than these values, the misfit becomes effectively tensile under the polarization instead of compressive, and h_c will decrease, instead of increase, as the magnitude of the misfit strain decreases. In Fig. 4(a), interception of the curves with $P_\infty=0$ and $P_\infty\neq 0$ are also observed. It shows that even if there is a polarization, with the same misfit strain, h_c can be equal. Figure 4(b) shows results for positive misfit strains (tensile). It can be seen that when the polarization increases, h_c decreases as expected, showing much less complexity compared to the case where the epitaxial stress is in the same direction as the electrostriction.

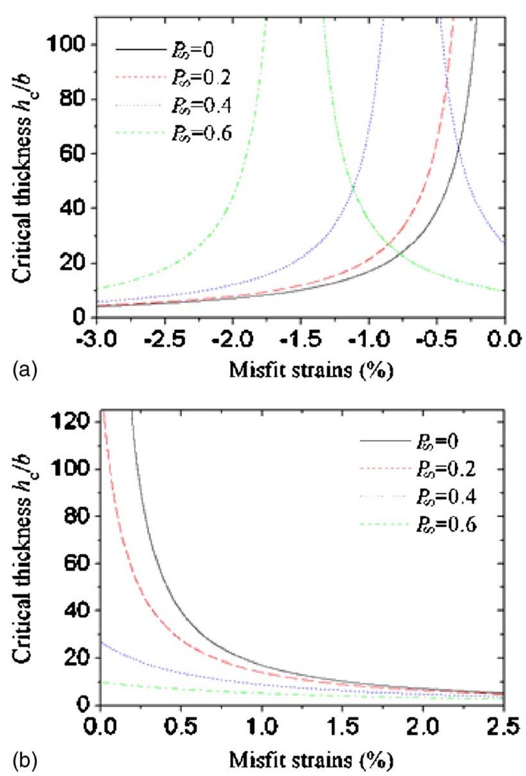

FIG. 4. (Color online) Critical thickness h_c of misfit dislocation generation for films grown on thick (a) compressive substrates and (b) tensile substrates with different polarizations.

To summarize, from an energy perspective within the Landau-Devonshire formalism, the critical thickness of spontaneous formation of misfit dislocations in a ferroelectric thin film on a compliant substrate is calculated. It is found to depend on the substrate thickness, the polarization state, and the misfit strain, particularly its sign. Of particular importance, the generation of misfit dislocations during transitions between different ferroelectric states should be a design concern. This effect is particularly serious for thick substrates when the critical thickness increases. For compliant substrates, the critical thickness increases as the substrate thickness decreases and becomes more compliant.

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