The mechanical equilibrium condition between the T and R layers requires that the tractions at the interface between these layers be equal and opposite at both sides, i.e., $f_{R,\parallel}=-f_{T,\parallel}$.[14] This condition can also be regarded as the elastic coupling between the two films, which "distributes" the total stress due to the lattice mismatch with the underlying substrate between the two layers as a function of their respective thicknesses. Thus,

$$\sigma_{R,\parallel}h_R = -\sigma_{T,\parallel}h_T, \tag{3}$$

and this relation can be expressed in terms of the strains in the layers by using the planar elastic moduli $\hat{\hat{G}}$ such that

$$\hat{\hat{G}}_R\hat{\varepsilon}_R h_R = -\hat{\hat{G}}_T\hat{\varepsilon}_T h_T. \tag{4}$$

Here, $\hat{\hat{G}}$ is a fourth rank tensor and is dependent on the bulk elastic moduli $\hat{\hat{C}}$, as well as the normal vector to the interface plane $\vec{n}$ and is expressed as[17]

$$\hat{\hat{G}} = \hat{\hat{C}} - \hat{\hat{C}}\vec{n}(\vec{n}\hat{\hat{C}}\vec{n})^{-1}\vec{n}\hat{\hat{C}}, \tag{5}$$

where $\vec{n}$ is the normal to the interlayer interface, parallel to the [001] direction.

Furthermore, the interdomain interfaces in the T layer have to be elastically compatible. These conditions can then be utilized to determine the elastic energy densities of the T and R layers,[17–19,22]

$$F_{T,\mathrm{el}} = (1-\alpha)^2 e_{c,T} + \alpha^2 e_{a,T} + \alpha(1-\alpha)(e_{c,T}+e_{a,T}-e^I_{ca,T}), \tag{6}$$

$$F_{R,\mathrm{el}} = [\alpha(e_{a,T}-e_{c,T}+e^I_{cR,T}-e^I_{aR,T}) + (e_{c,T}+e_{R,T}-e^I_{cR,T})]\frac{h_T}{h_R}, \tag{7}$$

where

$$e_{c,T} = \tfrac{1}{2}\hat{\varepsilon}_{T,c}\hat{\hat{G}}_T\hat{\varepsilon}_{T,c}, \quad e_{a,T} = \tfrac{1}{2}\hat{\varepsilon}_{T,a}\hat{\hat{G}}_T\hat{\varepsilon}_{T,a}, \quad e_{R,T} = \tfrac{1}{2}\hat{\varepsilon}_R\hat{\hat{G}}_T\hat{\varepsilon}_R \tag{8}$$

are the elastic energies of the c-domains, a-domains, and the R phase, respectively, and

$$e^I_{ca,T} = \tfrac{1}{2}(\hat{\varepsilon}_{T,c}-\hat{\varepsilon}_{T,a})\hat{\hat{G}}_T(\hat{\varepsilon}_{T,c}-\hat{\varepsilon}_{T,a}),$$

$$e^I_{cR,T} = \tfrac{1}{2}(\hat{\varepsilon}_{T,c}-\hat{\varepsilon}_R)\hat{\hat{G}}_T(\hat{\varepsilon}_{T,c}-\hat{\varepsilon}_R),$$

$$e^I_{aR,T} = \tfrac{1}{2}(\hat{\varepsilon}_{T,a}-\hat{\varepsilon}_R)\hat{\hat{G}}_T(\hat{\varepsilon}_{T,a}-\hat{\varepsilon}_R) \tag{9}$$

are the indirect elastic interaction energies between the phases and domains. Here, $\hat{\hat{G}}$ is given by Eq. (5) with $\vec{n}$ being parallel to the [101] (or [011]) directions for the interdomain interfaces in the $c/a/c/a$ domain pattern that forms in the T layer and normal to the R-T interlayer interface in the R layer, i.e., parallel to [001].[17]

Finally, based on the above definitions and elaborations and after some mathematical rearrangements, the free energy density of the multilayer heterostructure can be expanded as

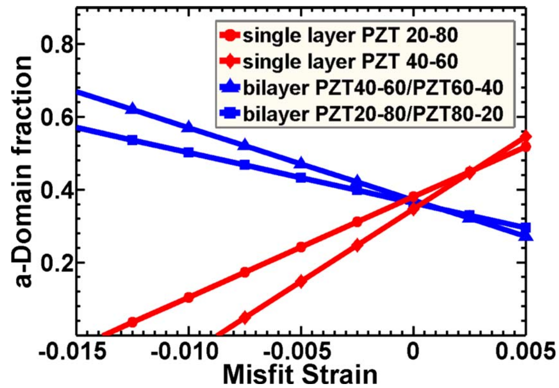

FIG. 3. (Color online) Equilibrium a-domain volume fraction as a function of the effective misfit strain in the T layer.

$$F_{\mathrm{tot}} = \alpha^2 e^I_{ca,T} + \alpha\left(\frac{e_{a,T}-e_{c,T}-2e^I_{ca,T}+e^I_{aR,T}-e^I_{cR,T}}{2}\right) + \frac{e_{c,T}-e_R+e^I_{cR,T}}{2} + F^0_T + F^0_R. \tag{10}$$

Equation (10) differs from the previously developed formulations for the case of single layer systems[18,19,22] in that it contains additional indirect interaction energies ($e^I_{aR,T}$ and $e^I_{cR,T}$), which do not appear for single layered films.[23] Thermodynamic equilibrium requires that $\partial F_{\mathrm{tot}}/\partial\alpha=0$, which yields the equilibrium a-domain fraction

$$\alpha^0 = \frac{e_{c,T}-e_{a,T}+2e^I_{ca,T}+e^I_{cR,T}-e^I_{aR,T}}{4e^I_{ca,T}}. \tag{11}$$

For a tetragonal PZT single layer, the equilibrium a-domain volume fraction is[18]

$$\alpha^0(\text{single layer}) = \frac{e_{c,T}-e_{a,T}+e^I_{ca,T}}{2e^I_{ca,T}}. \tag{12}$$

Both relations are valid only if $e^I_{ca,T}>0$ and $0\leq\alpha^0\leq 1$.

The contribution of the interfaces (i.e., microstrain energies) of the microstructures to the total free energy can be taken into account by introducing the normalized incompatibility parameter $\eta_N=\eta'/\sqrt{h}$, where $\eta'=\sqrt{h_{\mathrm{cr}}}/(1-\beta)$ is the effective incompatibility, h_{cr} is the critical thickness for domain formation, and β is the ratio of the T layer thickness to the total film thickness.[22] Consequently, the equilibrium a-domain fraction will be expressed as

$$\alpha^0 = \frac{e_{c,T}-e_{a,T}+2(1-\eta_N)e^I_{ca,T}+e^I_{cR,T}-e^I_{aR,T}}{4(1-\eta_N)e^I_{ca,T}}. \tag{13}$$

III. RESULTS AND DISCUSSIONS

Figure 3 depicts α^0 as a linear function of the effective misfit strain at the interface of the passive substrate for two key PZT compositions. The misfit strain at the T-R interface is assumed to be fully relaxed. The linear relation between misfit strain and domain fraction shows that the elastic energy is a second order function of strain. Additionally, the change in the equilibrium a-domain fraction in only a T layer grown on a thick substrate is also compared. It is seen that over a considerable interval of effective misfit strains between the film and the passive substrate, the bilayer has a larger *a*-domain fraction. Interestingly, the model shows contrasting trends in the misfit-strain dependence of the *a*-domain volume fraction between the bilayer and the single layer system. In agreement with previous experiments and theoretical predictions, the model predicts increasing the compressive stress reduces the *a*-domain, while increasing tensile strains increase the *a*-domain fractions for the single layer. However, for the bilayer, compressive strains imposed along *R*-substrate interface significantly enhance the *a*-domain fraction. Increasing the interaction energy of *c*-domains (through compressive strain) would lead to an increase in the $e^{I}_{cR,T}$ term and thus an increase in the elastic energy and to an increase in the *a*-domain volume fraction. On the other hand, stabilizing $e^{I}_{aR,T}$ (tensile strain) indicates that *a*-domains are stable, and thus no increase in the *a*-domain volume fraction is necessary to minimize the free elastic energy. Hence, the interaction between the elastic self-strains of the *T* and *R* layers leads to a control parameter that can be easily tuned. Moreover, Fig. 3 also shows that in single layer structure as the Zr concentration is increased, the *a*-domain fraction decreases, in agreement with the available experimental data.[24]

In Fig. 4 the effects of the film thickness on the fraction of ferroelastic domains in both single layer and bilayer structures are compared. Figures 4(a) and 4(b) investigate $PbZr_{0.2}Ti_{0.8}O_3/PbZr_{0.8}Ti_{0.2}O_3$ and $PbZr_{0.4}Ti_{0.6}O_3/PbZr_{0.6}Ti_{0.4}O_3$ bilayers, respectively. Although the model finds that in the single layer the ferroelastic domain fraction increases with increasing thickness (in agreement with previous results[14,18,23,25]), an opposite scenario of decreasing domain fraction is observed for the bilayer films. Increasing the thickness of the structure relaxes the elastic coupling energy, with each layer now behaving almost independently as the thickness increases. This is further evident in the inset in Fig. 4(a), where the effect of increasing effective incompatibility (η') between the *T* and *R* layers on the formation of ferroelastic domains in bilayer structures is shown. Our model finds that as the layers become increasingly incompatible, the *T* layer tends toward the behavior demonstrated by a single layer film, i.e., increasing *a*-domain fraction with increasing thickness.

We note that this analysis does not take into account Clausius–Clapeyron type of effects on the polarization in the *R* and *T* layers due to the respective internal stress states in both layers.[26–28] Furthermore, in these calculations neither long-scale electrostatics nor short-range dipole-dipole interactions between the layers were considered. Our approach presents a methodology based on mechanical equilibrium in the continuum limit. Indeed, experimental results show that for 400 nm thick epitaxial tetragonal (001) $PbZr_{0.2}Ti_{0.8}O_3$ layer on (001) STO substrates with a dense $c/a/c/a$ domain structure, there is no change in the stress state in the film and the domain fraction does not vary regardless of the electrical boundary conditions.[29] As such, ferroelectric polytwin structures may be thought of as purely ferroelastic domains. However, the overall electrostatic coupling may play a significant role in the dielectric properties in ferroelectric bilayers and

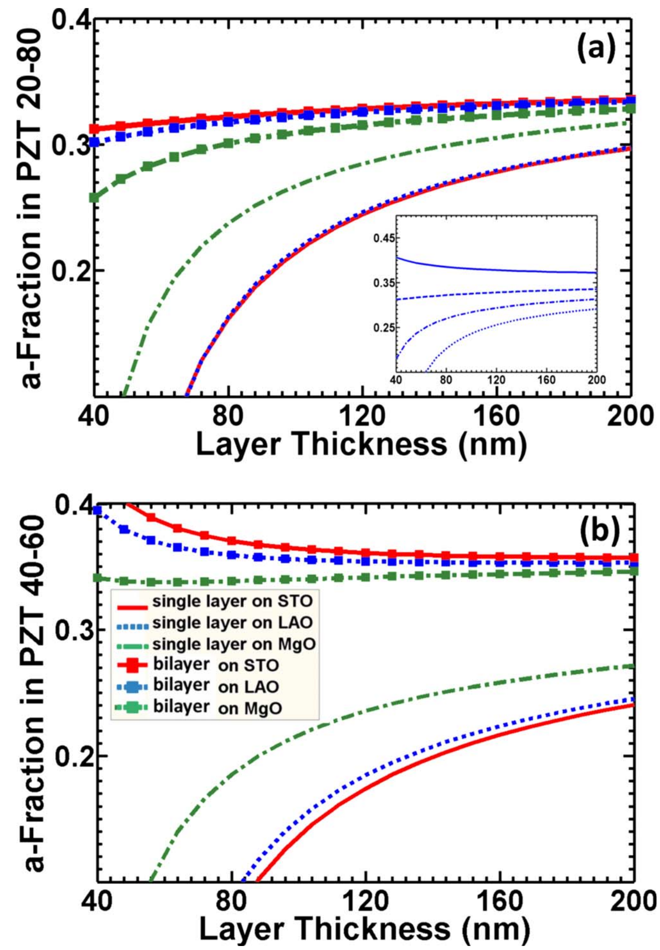

FIG. 4. (Color online) Comparison of *a*-domain fraction in (a) PZT 20/80 and (b) PZT 40/60 bilayer and single layer structures. Key to (a) is the same as (b). The inset in (a) shows *a*-domain fraction in the *T* layer (PZT 20/80) of a bilayer heterostructure as a function of the effective incompatibility parameter (η').

multilayer constructs as shown theoretically by Roytburd *et al.*[9] Recent experimental studies also demonstrate a significant enhancement in the intrinsic polar and piezoelectric response of such multilayered films,[30,31] indicating that there is an electromechanical coupling between the layers due to the polarization gradient and the commensurate internal built-in stress field. Furthermore, the electrostatic interaction due to the polarization mismatch may result in interesting electrical domain patterns that are not feasible in ferroelectric monolayers.[8,31–33] While these contributions might give rise to the formation of unique electrical domain structures within the *R* layer and the $c/a/c/a$ polydomain structure, the mechanical domains in the *T* layer is expected to remain unchanged since there are no variations in the mechanical boundary conditions. On the other hand, the changes in the polarization in the *R* layer with the in-plane strain might produce a deviation from the linear behavior in the in-plane domain fraction in the *T* layer as shown in Fig. 3, especially if the *R* layer is not fully relaxed by the formation of misfit dislocations at the substrate-*R* interface. Such a case corresponding to an ultrathin *R* layer with $h_R \cong h_{cr}$ or h_R slightly larger than h_{cr} was not considered in this study.

IV. CONCLUSIONS

We have theoretically analyzed the formation of domain structures in a bilayer structure consisting of a tetragonal $PbZr_xTi_{1-x}O_3$ and a rhombohedral $PbZr_{1-x}Ti_xO_3$ layer considering the misfit strain between the layers and the substrate, the self-strain of the phase transformation in each layer, and the elastic indirect interaction between the layers. Our results show that these contributions to the total elastic energy density of the system result in a significant increase in the in-plane ferroelastic domain fraction compared to single-layer tetragonal $PbZr_xTi_{1-x}O_3$ films of similar thickness.

ACKNOWLEDGMENTS

We would like acknowledge financial support from ARC Grant No. DP0666231 and UNSW Faculty Research Grant. The work at UConn was supported by the U.S. Army Research Office through Grant No. W911NF-05-1-0528.

[1]M. Dawber, N. Stucki, C. Lichtensteiger, S. Gariglio, P. Ghosez, and J. M. Triscone, Adv. Mater. (Weinheim, Ger.) **19**, 4153 (2007).
[2]H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, Nature (London) **433**, 395 (2005).
[3]Z. H. Zhou, J. M. Xue, W. Z. Li, J. Wang, H. Zhu, and J. M. Miao, J. Appl. Phys. **96**, 5706 (2004).
[4]C. Wang, Q. F. Fang, Z. G. Zhu, A. Q. Jiang, S. Y. Wang, B. L. Cheng, and Z. H. Chen, Appl. Phys. Lett. **82**, 2880 (2003).
[5]S. Zhong, S. P. Alpay, M. W. Cole, E. Ngo, S. Hirsch, and J. D. Demaree, Appl. Phys. Lett. **90**, 092901 (2007).
[6]K. Boldyreva, L. Pintilie, A. Lotnyk, I. B. Misirlioglu, M. Alexe, and D. Hesse, Appl. Phys. Lett. **91**, 122915 (2007).
[7]C. Bungaro and K. M. Rabe, Phys. Rev. B **69**, 184101 (2004).
[8]Y. L. Li, S. Y. Hu, D. Tenne, A. Soukiassian, D. G. Schlom, L. Q. Chen, X. X. Xi, K. J. Choi, C. B. Eom, A. Saxena, T. Lookman, and Q. X. Jia, Appl. Phys. Lett. **91**, 252904 (2007).
[9]A. L. Roytburd, S. Zhong, and S. P. Alpay, Appl. Phys. Lett. **87**, 092902 (2005).
[10]K. Bhattacharya and R. D. James, Science **307**, 53 (2005).
[11]E. Burcsu, G. Ravichandran, and K. Bhattacharya, Appl. Phys. Lett. **77**, 1698 (2000).
[12]N. A. Pertsev and A. Y. Emelyanov, Appl. Phys. Lett. **71**, 3646 (1997).
[13]F. Xu, S. Trolier-McKinstry, W. Ren, B. Xu, Z.-L. Xie, and K. J. Hemker, J. Appl. Phys. **89**, 1336 (2001).
[14]J. S. Speck and W. Pompe, J. Appl. Phys. **76**, 466 (1994).
[15]V. Nagarajan *et al.*, presented at the International Symposium on Integrated Ferroelectrics, Singapore, 2008 (unpublished).
[16]S. K. Streiffer, C. B. Parker, A. E. Romanov, M. J. Lefevre, L. Zhao, J. S. Speck, W. Pompe, C. M. Foster, and G. R. Bai, J. Appl. Phys. **83**, 2742 (1998).
[17]A. L. Roitburd, Phys. Status Solidi A **37**, 329 (1976).
[18]A. L. Roytburd, J. Appl. Phys. **83**, 228 (1998).
[19]S. P. Alpay and A. L. Roytburd, J. Appl. Phys. **83**, 4714 (1998).
[20]Z. G. Ban, S. P. Alpay, F. He, B. O. Wells, and X. X. Xi, Appl. Phys. Lett. **84**, 4848 (2004).
[21]J. Ouyang and A. L. Roytburd, Acta Mater. **54**, 5565 (2006).
[22]A. L. Roytburd, J. Appl. Phys. **83**, 239 (1998).
[23]B. S. Kwak, A. Erbil, J. D. Budai, M. F. Chrisholm, L. A. Boatner, and B. J. Wilkens, Phys. Rev. B **49**, 14865 (1994).
[24]K. Lee and S. Baik, Annu. Rev. Mater. Res. **36**, 81 (2006).
[25]V. Nagarajan, I. G. Jenkins, S. P. Alpay, H. Li, S. Aggarwal, L. Salamanca-Riba, A. L. Roytburd, and R. Ramesh, J. Appl. Phys. **86**, 595 (1999).
[26]A. L. Roytburd, S. P. Alpay, V. Nagarajan, C. S. Ganpule, S. Aggarwal, E. D. Williams, and R. Ramesh, Phys. Rev. Lett. **85**, 190 (2000).
[27]C. Ederer and N. A. Spaldin, Phys. Rev. Lett. **95**, 257601 (2005).
[28]N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[29]S. P. Alpay, V. Nagarajan, L. A. Bendersky, M. D. Vaudin, S. Aggarwal, R. Ramesh, and A. L. Roytburd, J. Appl. Phys. **85**, 3271 (1999).
[30]R. Nath, S. Zhong, S. P. Alpay, B. D. Huey, and M. W. Cole, Appl. Phys. Lett. **92**, 012916 (2008).
[31]W. Tian, J. C. Jiang, X. Q. Pan, J. H. Haeni, Y. L. Li, L. Q. Chen, D. G. Schlom, J. B. Neaton, K. M. Rabe, and Q. X. Jia, Appl. Phys. Lett. **89**, 092905 (2006).
[32]Y. L. Li, S. Choudhury, Z. K. Liu, and L. Q. Chen, Appl. Phys. Lett. **83**, 1608 (2003).
[33]Y. L. Li, S. Y. Hu, D. Tenne, A. Soukiassian, D. G. Schlom, X. X. Xi, K. J. Choi, C. B. Eom, A. Saxena, T. Lookman, Q. X. Jia, and L. Q. Chen, Appl. Phys. Lett. **91**, 112914 (2007).