Tunable Thermal Conductivity via Domain Structure Engineering in Ferroelectric Thin Films: A Phase-Field Simulation

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Abstract

Effective thermal conductivity as a function of domain structure is studied by solving the heat conduction equation using a spectral iterative perturbation algorithm in materials with inhomogeneous thermal conductivity distribution. Using this proposed algorithm, the experimentally measured effective thermal conductivities of domain-engineered $\{001\}_p$ -BiFeO₃ thin films are quantitatively reproduced. In conjunction with two other testing examples, this proposed algorithm is proven to be an efficient tool for interpreting the relationship between the effective thermal conductivity and micro-/domain-structures. By combining this algorithm with the phase-field model of ferroelectric thin films, the effective thermal conductivity for PbZr_{1-x}Ti_xO₃ films under different composition, thickness, strain, and working conditions is predicted. It is shown that the chemical composition, misfit strain, film thickness, film orientation, and a Piezoresponse Force Microscopy tip can be used to engineer the domain structures and tune the effective thermal conductivity. Therefore, we expect our findings will stimulate future theoretical, experimental and engineering efforts on developing devices based on the tunable effective thermal conductivity in ferroelectric nanostructures.

1. Introduction

The ability to deterministically control the thermal conductivity for semiconductors is of fundamental importance in fields of phononics and thermoelectrics [1,2]. Enhancing scattering during phonon transport provides a means to achieve this control. This can be achieved by engineering the high-densities of interfaces in nanostructured materials such as superlattices [3-6], nanowires [7,8], quantum dots [9-12], and nanocomposites [13-17]. When the size of the nanostructure is smaller than the phonon mean free path, phonons can be strongly scattered, giving rise to a decrease in the thermal conductivity.

In ferroelectrics, such as BaTiO_3 [18] and KDP [19] single crystals and BiFeO_3 [20] and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) [21] thin films, it was found that the ferroelastic domain walls acted as interfaces that can scatter phonons resulting in a net decrease in the effective thermal conductivity. For thin films, the size of ferroelectric domains ranges from several nanometers to hundreds of nanometers depending on the chemical composition, material size, and mechanical and electric boundary conditions of the film [22], which is generally compatible with those phonon mean free paths that carry thermal energy at room temperature [23-26]. Recently, altering the effective thermal conductivity via domain structures engineering either by controlling the film-growing conditions [20] or by applying an electric field [21] has been demonstrated.

In this work, taking BiFeO_3 and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ thin films as examples, we demonstrate that the effective thermal conductivity can be tuned by engineering the ferroelectric domain structure. In order to achieve this, we employ the phase-field model of ferroelectric thin films (see Sec. 2A) to evolve the domain structures of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ [27-29]. We assume that the domain and domain wall can be regarded as two identities with different thermal conductivities

[20,21]. In order to obtain the effective thermal conductivity as function of domain structure, we solve the stationary heat conduction equation with an inhomogeneous thermal conductivity distribution using a spectral iterative perturbation (SIP) method [30-33], as shown in Sec. 2B. Then, the effective thermal conductivity and/or temperature distribution in specific examples are calculated to validate the proposed algorithm (Sec. 3A). For PZT thin films, the film-growing conditions, including the chemical composition [34], substrate-mismatch strain [35,36], film thickness [37-40], and film orientation [41-43], can be controlled to engineer the domain structure. A Piezoresponse Force Microscopy tip also can be used to modify the domain structure [44-49]. The effects of external conditions on domain structure as well as the effective thermal conductivity are studied in Sec. 3B. Before we conclude in Sec. 4, we provide a short discussion (Sec. 3C) on the possible challenges and future perspective in the theoretical prediction of domain wall-tuning of effective thermal conductivity in ferroelectric nanostructures.

2. Method

A. Phase-field Model of a Ferroelectric Thin Film

The phase-field model for ferroelectric thin films has been presented in numerous publications [50-54], and thus we focus on the phase-field description of inhomogeneous conductivity in a domain structure. For determining the domain-wall density in a given domain structure, we introduce a phase-field order parameter $\eta(\mathbf{x})$ to distinguish the domain-wall region and domain. The polarization gradient energy density $f_{\text{grad}}(\mathbf{x})$ is used as a criterion to distinguish the domain interior and domain-wall region because the polarization gradient in the domain wall is much higher than in the domain. The general formulation of the gradient energy density in an anisotropic system can be expressed as

$$f_{\text{grad}}(\mathbf{x}) = \frac{1}{2} \gamma_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}, \quad (2-1)$$

where γ_{ijkl} is the gradient energy coefficient. For an isotropic system, Eq. (2-1) reduces to

$$f_{\text{grad}}(\mathbf{x}) = \frac{1}{2} \gamma_{11} \left[\left(\frac{\partial P_1}{\partial x_1} \right)^2 + \left(\frac{\partial P_2}{\partial x_2} \right)^2 + \left(\frac{\partial P_3}{\partial x_3} \right)^2 + \left(\frac{\partial P_1}{\partial x_2} \right)^2 + \left(\frac{\partial P_2}{\partial x_1} \right)^2 + \left(\frac{\partial P_1}{\partial x_3} \right)^2 + \left(\frac{\partial P_3}{\partial x_1} \right)^2 + \left(\frac{\partial P_2}{\partial x_3} \right)^2 + \left(\frac{\partial P_3}{\partial x_2} \right)^2 \right], \quad (2-2)$$

where γ_{ij} is related to γ_{ijkl} through the Voigt's notation and $\gamma_{12}=0$, $\gamma_{11}=2\gamma_{44}$ in an isotropic system.

For $\eta(\mathbf{x})$, it can be written as follows by considering a diffuse interface

$$\eta(\mathbf{x}) = \frac{1}{2} \left\{ 1.0 + \tanh \left[\beta \left(f_{\text{grad}}(\mathbf{x}) - f_c \right) \right] \right\}, \quad (2-3)$$

where β is a positive parameter controlling the width of the interface, f_c is a critical value of the polarization gradient energy density separating the bulk domain from the domain-wall region. Therefore, in the domain-wall region $\eta(\mathbf{x})=1$, and inside a domain $\eta(\mathbf{x})=0$. In this work, $\beta=500$ and $f_c=0.15 \text{ Jm}^{-3}$ are used for $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ films while assuming isotropic gradient energy coefficient.

The type of a domain wall that separates the two adjacent domains is determined using the product of their polarization vectors. For example, there are two domains, a and b, with respective polarization vectors $\mathbf{P}_a$ and $\mathbf{P}_b$ separated by a domain wall L . The type of domain wall L is determined by $\Theta(L)=\cos^{-1}(\mathbf{P}_a \cdot \mathbf{P}_b)/(P_a P_b)$. For $\Theta(L) = 180^\circ, 90^\circ, 71^\circ$ and 109° , the corresponding domain walls are named $180^\circ, 90^\circ, 71^\circ$ and 109° walls, respectively.

The spatially dependent thermal conductivity in a ferroelectric thin film with domain structure then can be described as follows

$$k_{ij}(\mathbf{x}) = k_{ij}^{\text{fs-wall}} \eta(\mathbf{x}) + k_{ij}^{\text{domain}} (1 - \eta(\mathbf{x})), \quad (2-4)$$

where $k_{ij}^{\text{fs-wall}}$ and k_{ij}^{domain} represent the individual thermal conductivity of the ferroelastic domain wall and domain, respectively. For the 180° ferroelectric domain wall, since the acoustic phonons that carry most of the thermal energy would have identical phonon dispersion spectra on either side of the domain wall, there would be no acoustic mismatch. Also, the amount of strain at a 180° wall is very small, thus the 180° ferroelectric domain wall is assumed to have the same thermal conductivity as the domain interior.

B. Solution of the stationary heat conduction equation

In order to obtain the effective thermal conductivity, it is necessary to solve the stationary heat conduction equation. Heat conduction in a material with inhomogeneous thermal conductivity distribution is governed by

$$\frac{\partial}{\partial x_i} \left(k_{ij}(\mathbf{x}) \frac{\partial T(\mathbf{x})}{\partial x_j} \right) + q(\mathbf{x}) = \rho c_p \frac{\partial T(\mathbf{x})}{\partial t}, \quad (2-5)$$

where $k_{ij}(\mathbf{x})$ is the spatial-dependent thermal conductivity tensor, $T(\mathbf{x})$ is the temperature distribution, ρ , c_p , and $q(\mathbf{x})$ are the mass density, specific heat capacity, and the internal heat source of the material, respectively. Under stationary conditions, which means sufficient time has passed such that the thermal field, $T(\mathbf{x})$, is no longer evolving with time, Eq. (2-5) reduces to

$$\frac{\partial}{\partial x_i} \left(k_{ij}(\mathbf{x}) \frac{\partial T(\mathbf{x})}{\partial x_j} \right) + q(\mathbf{x}) = 0. \quad (2-6)$$

We consider a material system in which the thermal conductivity is periodic on the boundary and the thermal conductivity can be written as

$$k_{ij}(\mathbf{x}) = k_{ij}^0 + \Delta k_{ij}(\mathbf{x}), \quad (2-7)$$

where k_{ij}^0 and $\Delta k_{ij}(\mathbf{x})$ represent the homogeneous and periodically inhomogeneous parts of the thermal conductivity, respectively. The stationary distribution of temperature depends on the boundary condition, and here we consider a homogeneous driving force for heat conduction in the material, *i.e.*,

$$\frac{\partial T(\mathbf{x})}{\partial x_j} = \frac{\partial T^{\text{linear}}(\mathbf{x})}{\partial x_j} + \frac{\partial u(\mathbf{x})}{\partial x_j} = f_j + \frac{\partial u(\mathbf{x})}{\partial x_j}, \quad (2-8)$$

where $T^{\text{linear}}(\mathbf{x})$ represents the linear part of the temperature profile, and $u(\mathbf{x})$ represents the nonlinear part of the temperature profile that originates from the inhomogeneous distribution of the thermal conductivity and has a periodic distribution. Here we use f_j to represent $\partial T^{\text{linear}}(\mathbf{x}) / \partial x_j$ for simplification. Combining Eq. (2-7) and (2-8), Eq. (2-6) can be written as

$$\frac{\partial}{\partial x_i} \left[(k_{ij}^0 + \Delta k_{ij}(\mathbf{x})) \left(f_j + \frac{\partial u(\mathbf{x})}{\partial x_j} \right) \right] + q(\mathbf{x}) = 0. \quad (2-9)$$

Rearranging Eq. (2-9) we get

$$k_{ij}^0 \frac{\partial^2 u(\mathbf{x})}{\partial x_i \partial x_j} = - \frac{\partial}{\partial x_i} \left(\Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u(\mathbf{x})}{\partial x_j} \right) \right) - q(\mathbf{x}). \quad (2-10)$$

Zeroth-order Solution: Assuming the thermal conductivity to be homogeneous so that

$\Delta k_{ij}(\mathbf{x}) = 0$, Eq. (2-10) reduces to

$$k_{ij}^0 \frac{\partial^2 u^0(\mathbf{x})}{\partial x_i \partial x_j} = -q(\mathbf{x}). \quad (2-11)$$

By performing a Fourier transformation on both sides of Eq. (2-11) we have

$$-k_{ij}^0 \xi_i \xi_j u^0(\xi) = -q(\xi), \quad (2-12)$$

where $u^0(\xi)$ and $q(\xi)$ are the Fourier transforms of $u^0(\mathbf{x})$ and $q(\mathbf{x})$, $u^0(\xi) = \int_V u^0(\mathbf{x}) e^{-i\xi \cdot \mathbf{x}} d^3x$,

$q(\xi) = \int_V q(\mathbf{x}) e^{-i\xi \cdot \mathbf{x}} d^3x$, respectively, ξ_j is the j th component of the reciprocal lattice vector, ξ ,

and i is the imaginary unit. From Eq. (2-12), we have the solution for $u^0(\xi)$,

$$u^0(\xi) = G(\xi) q(\xi), \quad (2-13)$$

where $G^{-1}(\xi) = k_{ij}^0 \xi_i \xi_j$. By performing inverse Fourier transforms on both sides of Eq. (2-13), the

zeroth-order approximation of the nonlinear part $u^0(\mathbf{x})$ of the temperature profile is

$$u^0(\mathbf{x}) = \int \frac{d^3\xi}{(2\pi)^3} G(\xi) q(\xi) e^{i\xi \cdot \mathbf{x}}. \quad (2-14)$$

First-order Solution: Substituting the zeroth-order solution of the nonlinear part of the temperature profile (Eq. (2-14)) into the iterative Eq. (2-10), the first-order solution of $u(\mathbf{x})$ can be obtained from

$$k_{ij}^0 \frac{\partial^2 u^1(\mathbf{x})}{\partial x_i \partial x_j} = -\frac{\partial}{\partial x_i} \left[\Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^0(\mathbf{x})}{\partial x_j} \right) \right] - q(\mathbf{x}). \quad (2-15)$$

Similarly, by performing a Fourier transformation on both sides of Eq. (2-15) we have

$$u^1(\xi) = IG\xi_i \left\{ \Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^0(\mathbf{x})}{\partial x_j} \right) \right\}_{\xi} + q(\xi) \quad (2-16)$$

where $\left\{ \Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^0(\mathbf{x})}{\partial x_j} \right) \right\}_{\xi}$ indicates the Fourier transform of $\Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^0(\mathbf{x})}{\partial x_j} \right)$. As a

result, the first-order solution of the nonlinear part of the temperature profile can be obtained using

$$u^1(\mathbf{x}) = \int \frac{d^3\xi}{(2\pi)^3} u^1(\xi) e^{i\xi \cdot \mathbf{x}}. \quad (2-17)$$

Higher-order Solution: The higher-order solutions for $u(\mathbf{x})$ are derived in a similar manner as the first-order solution,

$$k_{ij}^0 \frac{\partial^2 u^n(\mathbf{x})}{\partial x_i \partial x_j} = - \frac{\partial}{\partial x_i} \left[\Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^{n-1}(\mathbf{x})}{\partial x_j} \right) \right] - q(\mathbf{x}) \quad (2-18)$$

Similar to $u^1(\mathbf{x})$, the solution for $u^n(\mathbf{x})$ is solved using Fourier transforms

$$u^n(\xi) = IG\xi_i \left\{ \Delta k_{ij}(\mathbf{x}) \left(f_j + \frac{\partial u^{n-1}(\mathbf{x})}{\partial x_j} \right) \right\}_{\xi} + q(\xi), \quad (2-19)$$

and the n th-order solution of the nonlinear part of the temperature can be obtained by

$$u^n(\mathbf{x}) = \int \frac{d^3\xi}{(2\pi)^3} u^n(\xi) e^{i\xi \cdot \mathbf{x}}. \quad (2-20)$$

As for the total temperature distribution $T(\mathbf{x})$, it can be calculated from

$$T(\mathbf{x}) = u^n(\mathbf{x}) + \int f_j dx_j \quad (2-21)$$

while taking into account the boundary conditions.

According to the Fourier's law, the heat flux density that flows through a unit area per unit time is equal to

$$J_i = -k_{ij}(\mathbf{x}) \partial T(\mathbf{x}) / \partial x_j. \quad (2-22)$$

The effective thermal conductivity tensor k_{ij}^{eff} of the material can be determined from Eq. (2-22)

by solving

$$\langle J_i \rangle = -k_{ij}^{\text{eff}} \langle \partial T(\mathbf{x}) / \partial x_j \rangle, \quad (2-23)$$

where $\langle \rangle$ represents the average property per volume.

3. Results and Discussions

A. Testing Examples

A1. Parallel slabs

As the first test example, we calculate the effective thermal conductivity for a simple microstructure composed of parallel slabs of A and B with isotropic, but different, thermal conductivities, k_A^{iso} and k_B^{iso} , as exhibited in Fig. 1a. In this case, the effective thermal conductivity can be expressed analytically so as to be compared with the numerical results from the SIP method shown in Sec. 2B. Assuming that the heat flux is along the 22 direction, which is parallel to the plane of the slabs, the arrangement is equivalent to a parallel electrical circuit wherein each slab has the same temperature gradient but different heat flux. As a result, the effective thermal conductivity component along the 22 direction is given by $k_{22}^{\text{eff}} = k_A^{\text{iso}} V_A + k_B^{\text{iso}} V_B$,

where V_A and V_B are the volume fractions of component A and B, respectively. Similarly, for heat flux along the 11 direction, which is perpendicular to the plane of the slabs (see Fig. 1a), it is equivalent to a series electrical circuits wherein each slab has the same heat flux but different temperature gradients. As a result, the effective thermal conductivity component along the 11 direction is given by $k_{11}^{\text{eff}} = k_A^{\text{iso}} k_B^{\text{iso}} / (k_A^{\text{iso}} V_B + k_B^{\text{iso}} V_A)$. Fig. 1b shows the comparison of numerical and theoretical $\mathbf{k}^{\text{eff}}$ as a function of volume fraction for these two parallel slab microstructures. As it can be seen from the comparison, the effective thermal conductivity calculated from the SIP method agrees well with those of theoretical solutions, thus validating the proposed spectral method. Additionally, although the thermal conductivity of each composition is isotropic, the effective thermal conductivity is anisotropic due to the anisotropic microstructure.

A2. Square matrix with a circular inclusion

In order to further test the accuracy of SIP method on solving the stationary heat conduction equation with inhomogeneous thermal conductivity distribution, we consider a two-phase microstructure composed of a square matrix and a circular inclusion, as shown in Fig. 2a. These two phases are assumed to have isotropic but different thermal conductivities. The boundary conditions are set as following: temperatures on the left and right boundaries are fixed at 300 K and 500 K, and the bottom and top boundaries are adiabatic, as illustrated in Fig. 2a. The ratio of k^p to k^m has been set to a value of 1:400 and the ratio of the length of the matrix (denoted by d) to the radius of the inclusion (denoted by r) has been set to a value of 10:1. Fig. 2b gives the temperature distribution at the middle cross section of the composite for these conditions (see the red dashed line in Fig. 2a solved from the proposed SIP method, compared with the results obtained from the finite element method (FEM) using COMSOL software. It can be seen that the two solutions are nearly identical, further validating the proposed spectral method.

Fig. 2c and 2d show the numerically calculated effective thermal conductivity as a function of the volume fraction of the inclusion V_p and k^p / k^m , respectively, compared with the results obtained from the Maxwell-Garnett effective medium model [55,56], where the size or the thermal conductivity mismatch between the inclusion and the matrix has been varied. It can be seen that the effective thermal conductivities obtained from these two methods agree well. The advantage of the SIP method is that it is able to compute not only the effective thermal conductivity but also the temperature distribution.

A3. Experimental effective thermal conductivity of BiFeO_3 films

The domain structure in epitaxial BiFeO_3 thin films can be engineered utilizing substrate vicinality to constrain growth and alter the number of domain variants [57-59]. Fig. 3a and 3b show the experimentally measured and simulated out-of-plane effective thermal conductivities at different temperatures for 30nm thick (001)-oriented BiFeO_3 thin films with 2-variant and 4-variant domain structures, respectively [20]. Only 71° domain walls exist in these two domain structures. In the simulation, the thermal conductivity of the domain was taken from the experimental measurements on the sample without domain walls, and the thermal conductivity of the wall was obtained using the experimentally derived Kapitza conductance of these 71° domain walls and multiplying by an estimated domain wall thickness (2.4nm, about 6 unit cells [60,61]), as shown in Fig. 3c. At a temperature of 295 K, the domain has a thermal conductivity of $k^{\text{domain}} = 2.16 \text{ Wm}^{-1}\text{K}^{-1}$, while the ferroelastic domain wall has a value of $k^{\text{fs-wall}} = 0.244 \text{ Wm}^{-1}\text{K}^{-1}$; in other words, the wall has a much higher thermal resistance than the domain interior. For the film with the 2-variant domain structures having a domain-wall volumetric density of 3.3%, the experimental effective thermal conductivity of the film is $1.68 \pm 0.00 \text{ Wm}^{-1}\text{K}^{-1}$, compared with $1.602 \text{ Wm}^{-1}\text{K}^{-1}$ from simulation. While for the film with 4-variant domain structures and a

domain-wall volumetric density of 4.8%, the experimental and simulated effective thermal conductivities are 1.50 ± 0.08 and $1.552 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. Agreement between the experimental and simulated values validates the use of a separate region with finite thickness to define the thermal properties of domain walls in these simulations.

B. Tunable thermal conductivity in PZT films

Based on the above tests on the proposed SIP algorithm for obtaining the effective thermal conductivity in different structures, we can see that the SIP method is an efficient tool for interpreting the relationship between the effective property and microstructure. Hereafter we use it to study the tunable effective thermal conductivity in PZT films by engineering the ferroelectric domain structure. Due to the lack of experimental data or first-principle calculation on the ferroelastic domain-wall thermal conductivity, or Kapitza conductance, for PZT, here a ratio of $k^{\text{domain}} / k^{\text{fs-wall}} = 10$ at room temperature (a ratio of ≈ 9 was used for the (001)-oriented BiFeO_3 film from experiment) is used to evaluate the effective thermal conductivity with different domain structures under various conditions. Although different types of ferroelastic domain walls and different compositions of PZT should have different thermal conductivities, here we assume the same thermal conductivity for all types of ferroelastic domain walls in PZT due to the lack of experimental data. As noted above, the ferroelectric-only 180° domain walls are assumed to have the same thermal conductivity as the domain interior. As a result, the effective thermal conductivity will be mainly determined by the density and arrangement of the ferroelastic domain walls.

B1. Chemical Composition Effect

Here when referring the chemical composition effect, we focus on its effect on the domain structures and, further, the effective thermal conductivity of PZT thin films clamped by a

substrate with a zero mismatch strain. We will not discuss the effect of alloy scattering due to the intermixing of Ti and Zr on the B-site of ABO_3 perovskite. As the Ti composition increases, the ferroelectric state transits from rhombohedral to tetragonal. Fig. 4a shows the domain-wall density and type as function of Ti composition. It can be seen that for compositions with $x_{\text{Ti}} \leq 0.5$, the total domain wall density is small and decreases slightly with composition. However, for $x_{\text{Ti}} > 0.5$, the domain-wall density increases significantly with Ti composition. As a result, the effective thermal conductivity, particularly the out-of-plane component, decreases generally with increasing Ti composition, as illustrated in Fig. 4b. When $x_{\text{Ti}} = 1.0$, *i.e.*, for a PbTiO_3 film, the effective thermal conductivity components along the 11, 22, and 33 directions are 67%, 78%, and 82% of the single domain value, respectively. Such a decrease and anisotropy in the effective thermal conductivity when $x_{\text{Ti}} > 0.5$ can be understood from the domain structure morphologies, as shown in Fig. 4c. When $x_{\text{Ti}} \leq 0.5$, the dominant ferroelectric phase is rhombohedral with low population of domain walls, yet when $x_{\text{Ti}} > 0.5$ the dominant ferroelectric phase is tetragonal with dense populations of 90° ferroelastic domain walls. The large increase of 90° ferroelastic domain walls, oriented at about 45° with respect to the heat flux direction, can significantly scatter phonons and resist the thermal transport.

B2. Misfit Strain Effect

Fig. 5a shows the strain-domain phase diagram for $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films. When the substrate-induced strain is compressive and larger than -0.4% , most of the domains in the film are out-of-plane c domains (see Fig. 5a) and most of the domain walls are 180° -type (see Fig. 5b) non-ferroelastic walls. When the substrate-induced strain is tensile and larger than 1.0% , most of the domains in the film are in-plane aa twinning domains, as shown from the simulated domain structures in the inset of Fig. 5a. This ordered aa twinning domain structure is very similar to the

experimental image for the PbTiO_3 thin film grown on a KTaO_3 substrate [62]. Most of the domain walls in aa twinning domain structures are 90° -type (see Fig. 5b) ferroelastic walls. When the substrate-induced strain is moderate and between -0.4% and 1.0% , out-of-plane c domains and in-plane a domains coexist in the film. When the misfit strain is tensile, the dominant domain walls are 90° type. In general, the total domain wall density increases with the magnitude of misfit strain, as it can be seen from Fig. 5b.

The effective thermal conductivity as a function of misfit strain is shown in Fig. 5c. Generally, with the misfit strain changing from compressive to tensile, the effective thermal conductivity decreases due to the increase of the ferroelastic 90° -type domain-wall density. In most cases the out-of-plane thermal conductivity is different from the in-plane counterpart, exhibiting a strong anisotropy due to the dimensions of the film. The mechanism that strain can increase the domain wall density and further decrease the effective thermal conductivity can be understood from the strain effect on the domain size and, consequently, on the number of ferroelastic domain walls present. With the magnitude of the misfit strain becoming larger, the domain size becomes smaller to introduce more inhomogeneous strain to release the elastic energy, giving rise to high densities of domain walls [63]. It is worth noting that the effective thermal conductivity decreases to a local minimum with the misfit strain varying from compressive to zero (see Fig. 5c), and then increases until the misfit strain becomes 0.6% . This non-monotonic variation of the effective thermal conductivity with strain corresponds to the 90° -type ferroelastic domain wall change (see Fig. 5b), which is caused by the transition of ferroelastic walls from the ac walls to aa walls.

B3. Film Thickness Effect

For $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films epitaxially grown on SrTiO_3 substrates, the ideal strain due to lattice mismatch reaches up to -2.38%, which can generate significant internal stress. With film thickness increasing, such internal stress will be relaxed through the formation of either dislocations or ferroelastic twins. Fig. 6a shows the effective misfit strain as function of film thickness obtained from the People-Bean (PB) model [40,64] which predicts a critical thickness of 8 nm for dislocation formation. According to the PB model, when the film is thinner than 8 nm, the thin film can be regarded as fully constrained by the substrate, giving rise to an ideal misfit strain of -2.38%. With the film thickness increasing to 100 nm, the effective misfit strain decreases to -0.21%. Therefore, the domain structures will be different for films with different thickness although the chemical composition and substrate are the same. Fig. 6b shows the domain structures for films with thickness of 10 nm, 40 nm, and 100 nm, respectively. For the 10 nm-thick and 40 nm-thick films, all domains are out-of-plane c domains separated by 180° domain walls, which are non-ferroelastic, however the domain size of these two films are very different. The thinner the film, the smaller the domain size will be because of the stronger misfit strain. For the 100 nm-thick film, the out-of-plane c domains and in-plane a domains coexist due to the moderate misfit strain. The effects of film thickness on the domain structures are essentially same as the misfit strain effect, as discussed in Sec. 3B2.

Fig. 6c shows the domain wall density as function of film thickness. For films with thicknesses smaller than 40 nm, there are only 180° type ferroelectric domain walls and no ferroelastic domain walls. When the film thickness is thicker than 40 nm, the 90° ferroelastic domain walls begin to emerge and coexist with the 180° ferroelectric domain walls. Fig. 6d shows the effective thermal conductivity for films with different thicknesses. With film thickness increasing, the effective thermal conductivity decreases. It is worth noting here that all data

points for the domain wall density and effective thermal conductivity are obtained by averaging ten different quasi-equilibrium domain structures under a specific condition, and the bar of each data point shows the corresponding standard deviation. For films with thickness smaller than 50 nm, which are severely constrained by the substrate according to the PB model, there are only out-of-plane c domains and thus no ferroelastic domain walls, so the effective thermal conductivity is nearly the same as inside the domains, as exhibited in Fig. 6d.

We note that the film thickness dependent thermal conductivity results presented in this section do not account for size effects due to film boundary scattering [65,66]. Clearly, for thin film systems, phonon-boundary scattering can lead to pronounced size effects in the thermal conductivity depending on the phonon mean free paths relative to the film thickness. However, the goal of this work is to isolate the role of domain boundary resistance on the thermal conductivity of thin films. In experimental data, multiple competing effects will be occurring in addition to this phonon-domain scattering effect. These results presented in this section can begin to help to deconvolve these mechanisms.

B4. Film Orientation Effect

$\{001\}_p$ -, $\{011\}_p$ -, and $\{111\}_p$ -oriented (where the p subscript denotes pseudocubic indices) $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films can be obtained by growing the films on SrTiO_3 substrates with corresponding orientations [43]. Fig. 7a shows the ferroelastic domain wall density as well as the domain structures for the $\{001\}_p$ -, $\{011\}_p$ -, and $\{111\}_p$ -oriented films in the as-grown state. The $\{001\}_p$ -oriented film shows the highest ferroelastic domain wall density, followed by the $\{111\}_p$ -oriented film, and the $\{011\}_p$ -oriented film last. The $\{001\}_p$ -oriented film shows the lowest thermal conductivity value for the in-plane components. The out-of-plane component of the effective thermal conductivity for $\{001\}_p$ - and $\{111\}_p$ -oriented films are similar. The lowest

ferroelastic domain wall density for the $\{011\}_p$ -oriented film results in the highest out-of-plane component of effective thermal conductivity.

B5. Piezoresponse Force Microscopy Tip Effect

Piezoresponse force microscopy (PFM) has been used extensively to image and control the domain structures of ferroelectric thin films [44-49,67,68]. When a PFM tip bias is applied on a ferroelectric thin film, the polarization can be locally or even collectively switched due to the strong coupling between the polarization and electromechanical response. Fig. 8a shows the domain structure evolution for a $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin film (20 nm thickness) under zero mismatch strain and with a_1c^+ tetragonal domain variants. Before applying a PFM tip bias, this simple a_1c^+ domain structure is stable and only has 90° -type domain walls with a volume fraction of 2.7% (see the domain structures and domain-wall density at a time step of 30000 in Fig. 8a). Upon applying a PFM tip with 10 nm radius and 5 V bias on top of the film, c^- domain and a_2 domains are generated, giving rise to an increase to 9.4% in the total domain-wall volumetric density (see the domain structures and domain-wall density at a time step of 60000 in Fig. 8a). Most of this induced domain-wall density increase can be retained after the removal of the PFM tip bias (see the domain structures and domain-wall density at time steps of 90000 in Fig. 8a). This PFM tip bias-induced local 90° and 180° domain switching in tetragonal PZT films can occur in favor of releasing the elastic energy and electric energy, respectively, as analyzed previously in the work of Hong *et al.* [49].

Accompanying the increase in domain-wall density induced by PFM tip bias, the effective thermal conductivity is modified correspondingly. As shown in Fig. 8b, prior to the application of PFM tip bias, the three components of the effective thermal conductivity are 71.1%, 97.2%, and 95.1% of the single domain value (see k values at a time step of 30000 in Fig.

8b), respectively. Under PFM tip bias, the three components of the effective thermal conductivity are changed to 90.9%, 84.2%, and 88.9% of the single domain value, respectively (see k values at a time step of 60000 in Fig. 8b). After the removal of the PFM tip bias, the three components of the effective thermal conductivity are retained at 88.3%, 84.6%, and 88.6% of the domain value, respectively (see k values at a time step of 90000 in Fig. 8b).

C. Discussion

From above simulations we can see that the effective thermal conductivity in ferroelectric thin films can be tuned via domain structure engineering by a number of means. However, we have to acknowledge that the prediction from present simulation needs further verification due to the lack of experimental data for the input parameters such as the thermal conductivity tensors for different types of domains and domain walls. Presently, measurement of thermal properties of a single domain wall presents an experimental challenge. Additionally, the coupling mechanisms between phonons, polarization, and strain at domain walls remain unclear. However, a combination of the density function theory (DFT) calculation and molecular dynamics (MD) simulation may be a feasible way to obtain the thermal conductivity tensors at the domain and domain wall. With the knowledge of the thermal conductivity tensors of the domain (bulk) and domain walls (interfaces), the present proposed spectral iterative perturbation algorithm combined with the phase-field model of ferroelectric films provides an efficient means to predict the effective thermal conductivity as a function of domain structure (microstructures).

4. Conclusions

The heat conduction equation in materials with inhomogeneous thermal conductivity distribution is solved using a spectral iterative perturbation method to obtain the effective thermal conductivity. Based on this method, the effective thermal conductivities for engineered $\{001\}_p$ -

BiFeO₃ thin films are calculated and the obtained results quantitatively agree with the experimentally measured values. By combining this SIP method with the phase-field model of ferroelectric thin films, the effective thermal conductivity as function of domain structure is studied. It is found that for PbZr_{1-x}Ti_xO₃ films, many factors including the chemical composition, misfit strain, film thickness, film orientation, and piezoresponse force microscopy tip can be used to engineer the domains structure and tune the effective thermal conductivity. For chemical composition, increasing PbTiO₃ composition results in increased ferroelastic domain wall concentrations and contributes to decreases in the effective thermal conductivity. For misfit strain, enhancing the tensile misfit strain increases the ferroelastic domain wall density and decreases the effective thermal conductivity. For film thickness, it affects the effective thermal conductivities according to the manner similar to the misfit strain. For film orientation, {001}_p-oriented films show the highest ferroelastic domain wall density and further the lowest effective thermal conductivity. Piezoresponse force microscopy tip bias can also be used to alter the domain structure and the effective thermal conductivity. The present simulation provides not only an efficient way to obtain the effective thermal conductivity as function of microstructure but also an insight on how to tune the effective thermal conductivity of ferroelectric thin films via domain structure engineering.

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Figure 1. (a) Idealized two-phase microstructures composed of parallel slabs of A and B with isotropic but different thermal conductivity: $k_A^{\text{iso}} = 200$ and $k_B^{\text{iso}} = 20$ in same units. (b) Computed and theoretical effective thermal conductivity components as a function of volume fraction of phase A.

Figure 2. (a) Schematic illustration of a two-phase microstructure composed of a square matrix and a circular inclusion with isotropic thermal conductivities and specific boundary conditions. (b) The temperature distributions at the middle cross section of the composite (red dashed line in Fig. 2a) solved from the stationary heat conduction equation using the SIP method and finite element method (FEM), respectively. The effective thermal conductivity of this two-phase microstructure as function of (c) the volume fraction of the inclusion and (d) the ratio of k^p to k^m , compared between the results obtained from the SIP method and the Maxwell-Garnett effective medium model.

Figure 3. Experimental and simulated effective thermal conductivity of (001)-oriented BiFeO₃ thin films with (a) 2-variant domain structures and (b) 4-variant domain structures. (c) Thermal conductivity of the domain and domain wall used as inputs for the simulation. The experimental data is from Ref. [20]. The polarization orientation in each domain indicated by different color is elaborated by the colorwheel of Fig.4c.

Figure 4. Composition-engineering (a) domain wall density, (b) effective thermal conductivity, and (c) domain structures of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ films clamped with zero misfit strain. The colorwheel in (c) shows the corresponding polarization orientation in domains denoted by different colors. The coordinate system of the domain structures is illustrated at the bottom right of (c). The symbols and bars in (a) and (b) represent the corresponding average values and standard deviations, respectively.

Figure 5. Misfit strain-engineering (a) domain structures, (b) domain wall density, and (c) effective thermal conductivity for $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films. The insets of (a) show the domain structures of c domains, ac domains and aa domains. The symbols and bars in (a), (b), and (c) represent the corresponding average values and standard deviations, respectively.

Figure 6. Film thickness-engineering (a) effective misfit strain, (b) domain structures, (c) domain wall density, and (d) effective thermal conductivity for (001)-oriented $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films grown on (001) SrTiO_3 substrate. The effective strain as function of film thickness is calculated from the People-Bean (PB) model which predicts a critical strain of 8nm for the formation of dislocation. The symbols and bars in (c) and (d) represent the corresponding average values and standard deviations, respectively.

Figure 7. Orientation-engineering (a) domain wall density and domain structures, and (b) effective thermal conductivity for $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films grown on different oriented SrTiO_3 substrate. Mismatch strains for these three films are assumed to be the same and with zero value. The polarization direction in domains with different colors are indicated by the colorwheel in Fig. 4c. The symbols and bars in (a) and (b) represent the corresponding average values and standard deviations, respectively.

Figure 8. Piezoresponse Force Microscopy-tuning (a) domain wall density and domain structures, and (b) effective thermal conductivity for a (001)-oriented thin $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ with mismatch strain of zero. The polarization direction in domains with different colors are indicated by the colorwheel in Fig. 4c.