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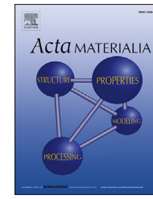

Full length article

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 $\{001\}_p$-$BiFeO_3$ 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 $PbZr_{1-x}Ti_xO_3$ 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 $PbZr_{1-x}Ti_xO_3$ (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 $PbZr_{1-x}Ti_xO_3$ 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. 2.1) to evolve the domain structures of $PbZr_{1-x}Ti_xO_3$ [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. 2.2. Then, the effective thermal conductivity and/or temperature distribution in specific examples are calculated to validate the proposed algorithm (Sec. 3.1). For PZT

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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. 3.2. Before we conclude in Sec. 4, we provide a short discussion (Sec. 3.3) on the possible challenges and future perspective in the theoretical prediction of domain wall-tuning of effective thermal conductivity in ferroelectric nanostructures.

2. Method

2.1. 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 $f_{grad}(\mathbf{x})$ 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

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

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

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

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

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

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 $f_c = 0.15$ J m^{-3} are used for $PbZr_{1-x}Ti_xO_3$ 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 $\theta(L) = 180°, 90°, 71°$ and $109°$, the corresponding domain walls are named 180°, 90°, 71° and 109° walls, respectively.

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

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

where $k_{ij}^{fs-wall}$ 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.

2.2. 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

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

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

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

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

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

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.*,

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

where $T^{linear}(\mathbf{x})$ 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 $\partial T^{linear}(\mathbf{x})/\partial x_j$ for simplification. Combining Eqs. (2-7) and (2-8), Eq. (2-6) can be written as

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

Rearranging Eq. (2-9) we get