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Monte Carlo simulations of polycrystalline ferroelectrics: Effects of electric field and grain size on dynamic electric polarization

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ABSTRACT

The present work incorporates a two dimensional Monte Carlo based polycrystalline simulation analysis for ferroelectric thin films. In the two stage process; first, grain growth is simulated via a traditional Q-State Monte Carlo method, taking into account isotropic grain boundary energies. Second, the grain growth results are incorporated within an electric polarization model, combining contributions from a three component Hamiltonian, including the electrostatic potential, nearest neighbor electrical interactions, and electrostatic energy. Among other findings, the results suggest a strong correlation between electric polarization and grain size, particularly at relatively large electric field frequencies.

1. Introduction

Increased demand for the miniaturization of various technological devices has resulted in significant advancements in the fabrication of multiscale ferroelectric systems, including those at the meso and nano scales. By definition, ferroelectric materials are particularly attractive due to the fact that unlike their dielectric or paraelectric counterparts, they demonstrate the capacity for spontaneous non-zero polarization that can be reversed by the application of an electric field. In fact, it is the exploitation of this unique characteristic, that of electric domain switching and the consequential hysteresis effect, that has given ferroelectrics a prominent role in such applications as micro-electronics and electro-optical devices [1–5]. In particular, this includes the design of high speed, nonvolatile random access memory devices, including Ferroelectric Random Access Memories (FeRAM) and Dynamic RAM [6,7].

As its name implies, dynamic hysteresis is concerned with the hysteretic response of a material to a time varying electric field. In particular this is often characterized by such features as the hysteresis shape, area, remanent polarization, and coercive field strength. It is well known for example, that the hysteresis area directly corresponds to energy dissipation during one cycle of domain switching, and that the remanent polarization, and coercive field strength characterize the stability of the spin alignment and the resistance of domain switching to external field fluctuations, respectively. Aside from a time varying electric field, grain size is another factor that has been shown to influence the electric polarization. In Barium Titanate ($BaTiO_3$), for example, the grain size has been reported to have substantial influence on the dielectric permittivity [8–15] and piezoelectric constant [16,17]. Numerous experimental studies have been conducted on another well known ferroelectric, Lead Zirconate Titanate (PZT), and have considered the effects of temperature, stress, dopants, and various other quantities with respect to polarization and electrical hysteresis [18,19].

Apart from the aforementioned experimental research relating to polarization and hysteresis of ferroelectric materials, less common are the complementary numerical studies. These include numerical techniques based on ab initio calculations [20–22], the solution of the Landau-Ginzburg energy relations [23–25], Q-State Monte Carlo simulations [26,27], and phase-field models [28].

In this work, we develop a two-dimensional, two-stage Monte Carlo model designed to simulate both the effects of grain size evolution and dynamic polarization in ferroelectric thin films. In particular, the first stage relies on a traditional Q-State Monte Carlo approach in which the grain size evolution is modeled through the use of isotropic grain boundary energies. In the second stage, the dynamic electrical polarization is modeled through a three-component Hamiltonian, accounting for electrostatic potential, nearest neighbor electrical interactions, and electrostatic energy. To our knowledge, this coupling of grain size effects to a three component polarization model is uniquely distinctive to the present work. Analyses are conducted with respect to the dependency of dynamic hysteresis on electric field frequency, including investigations relating to the hysteresis shape, the remanent polarization (P_r), and the coercive field strength (E_c). Additionally,

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simulations demonstrating the effects of isotropic grain size evolution on the electric polarization are performed. Where possible, qualitative comparisons with experiments taken from the literature are conducted.

2. Method

As stated previously, the Solution method presented herein proceeds in a two-step process. First, grain growth is simulated via the traditional Q-State Monte Carlo method, taking into account isotropic grain boundary energy. Second, these results are used to initialize the electric polarization model, wherein contributions from electrostatic potential, nearest neighbor electrical interactions, and electrostatic energy are included. Both models rely heavily on acceptance-rejection criteria that are based on the well-known Metropolis algorithm [29].

2.1. Grain growth model

Within the Q-State Monte Carlo model, the simulation space is discretized into a set of lattice points onto which a continuum microstructure is mapped so that each lattice point represents an individual grain with a specific orientation. The grain boundaries, instead of being tracked explicitly, are implicitly defined as existing between lattice sites of neighboring grains. The total energy of the system may be defined by the following Hamiltonian, which sums the interfacial energy of the system:

$$\mathcal{H} = 1/2\sum_{N^2}\sum_{\langle i,j\rangle} J_{ij}(1-\delta_{q_i q_j}) \tag{1}$$

where N^2 is the total number of lattice points, q_i is the orientation (state) of grain i, $\langle i,j\rangle$ represents summation over nearest neighbors (eight in the case of two-dimensions), $\delta_{q_i q_j}$ is the Kronecker delta function ($\delta_{q_i q_j} = 1$ if $q_i = q_j$; and 0 otherwise), and J_{ij} is the grain boundary energy associated with grains i and j. In this work, J_{ij}, is assumed constant (set to $0.33k_BT$) as appropriate for isotropic conditions.

Grain growth is simulated using the method developed in several previous works [30–32]. To summarize, first a lattice site is chosen at random from the simulation space. Then a new state q_i is chosen at random from the Q_{Total} possible states of the system (in this work $Q_{Total} = 24$). The change in energy ($\Delta\mathcal{H}$) is computed using Eq. (1) and the probability, P, that the site will change orientation is then determined from the Metropolis algorithm [29]:

$$P = \begin{cases} M\exp\left(-\frac{\Delta\mathcal{H}}{k_BT}\right) & \Delta H > 0 \\ M & \Delta H \leqslant 0 \end{cases} \tag{2}$$

where $\Delta\mathcal{H}$ is the change in energy associated with the reorientation event, M is the grain boundary mobility, and k_BT is the simulation temperature. We note that the grain boundary mobility is typically dependent on the misorientation angle (θ), (i.e., $M_{ij} = M_0\left[1-\exp\left(-B\left(\frac{\theta}{15}\right)^m\right)\right]$), where M_0 is the maximum mobility. In this work, given that we are assuming isotropic conditions, we set the mobility to a constant, equal to its maximum value; $M_0 = 1$.

In this work, the grain growth simulations were performed on a two-dimensional microstructure represented by an $N \times N$ array of square elements ($N = 128$). Periodic boundary conditions were applied along all domain boundaries, and as customary, the simulation time was measured in Monte Carlo Steps (MCS), wherein one MCS is equivalent to $N \times N$ reorientation attempts. The average grain size, $\langle R\rangle$ was computed as:

$$\langle R\rangle = \sqrt{N \times N/\#Grains} \tag{3}$$

2.2. Electric polarization model

For the polarization model, each lattice site is allowed two order parameters, q_i, and u_i, where $q_i = 1, 2, \ldots Q_{Total}$ represents the orientation of the electrical polar at site i (with total number of orientations, Q_{Total}), and u_i represents the magnitude of the electrical displacement. Similar to grain boundaries, domain boundaries delineate lattice regions with equivalent polar orientations (albeit with potentially different polar magnitudes). The system Hamiltonian may be written as [33]:

$$\mathcal{H} = \sum_i\left(\frac{p_i^2}{2m} - \frac{\alpha}{2}u_i^2 + \frac{\beta}{4}u_i^4\right) - \sum_{\langle i,j\rangle} U\cdot u_i u_j\cdot[q_i,q_j] - \sum_i E\cdot u_i\cdot[1,q_i] \tag{4}$$

where the three corresponding terms represent the electrostatic potential at site i (assumes a double well potential), the nearest neighbor electrical interactions, and the electrostatic energy, respectively. p_i is the momentum at site i, U is the ferroelectric ordering factor, m is the mass, E is the electric field (directed throughout this work along $q_i = 1$), α and β are parameters defining the double well potential [33], $\langle i, j\rangle$ represents summation over nearest neighbor sites, and $[q_i, q_j]$ is the difference in polar orientation between i and j. Assuming no symmetry, this last term can be represented as:

$$[q_i q_j] = \cos\left(2\pi\cdot\frac{q_i - q_j}{Q_{Total}}\right) \tag{5}$$

Since this work conforms to a dynamic study of hysteresis, a time-varying electric field was used:

$$E = E_0\sin(2\pi f t) \tag{6}$$

where E_0 is the maximum electric field strength, t is the time measured in MCS units, and f is the frequency (MCS^{-1}). The polarization (global) and electrical susceptibility (χ) are shown in Eqs. (7) and (8), respectively [34]:

$$P = \frac{\sum_i u_i\cdot\cos(\theta_i)}{N^2} \tag{7}$$

$$\chi = \langle P^2\rangle - \langle P^2\rangle \tag{8}$$

where θ_i is the angle between the electric field vector and q_i.

Similar to Liu et al. [35], in this work, we utilize two types of polar switching mechanisms, both with equal probabilities of occurrence. The first; polar reversal, involves a 180° change in electric polarization that is induced by the externally imposed electric field. That is, each domain may only possess two possible polar orientations, approximating two-fold crystalline anisotropy. The polar magnitude, u_i, associated with site i and polarization orientation, q_i, may take any random value between 0 and u_m, where u_m is the maximum electrical displacement. The second mechanism, responsible for domain growth, is activated by the interaction energy between the nearest neighbor polars. While the selection process for the polar magnitude is identical to the polar reversal mechanism, the polar orientation selection involves a random selection from one of its nearest neighbor sites. As in the earlier procedure for grain growth, the probability for any polar reversal or domain growth event is based on the Metropolis algorithm [29]. Fig. 1 outlines the flow algorithm pertaining to one complete cycle (one MCS) of the electric polarization model, where for clarity; $\mathcal{R}$ indicates a random number [0, 1], and NN represents a nearest neighbor selection.

All simulations were performed in reduced units with length defined by a simulation lattice constant (i.e., the lattice unit, LU) and the dipole moment defined to be 1 charge-LU. Temperature