Finite element analysis of domain structures in epitaxial $PbTiO_3$ thin films

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Equilibrium domain structures commonly observed in epitaxial Pb-based ferroelectric thin films are analyzed by the finite element method (FEM) using a commercial package, ABAQUS (Hibbit, Karlsson & Sorensen, Inc., 1080 Main Street, Pawtucket, RI 02860-4847). Structures of periodic 90° domains in epitaxial $PbTiO_3$ thin films on cubic single crystalline substrates are analyzed as a function of decreasing temperature in order to simulate cooling process after the film deposition at elevated temperature (T_G). The degree of *c*-axis orientation (α) is determined as a function of temperature below the Curie temperature and compared to the experimental results. It is then possible to calculate the magnitude of misfit strain during film growth and its relaxation due to dislocation generation. The effect of PZT composition on *c*-domain abundance is also simulated. FEM simulation is performed with the assumption that the major driving force for such domain formation is thermoelastic strains arising from the film–substrate interaction and the cubic-tetragonal phase transformation. The FEM analysis also suggests that initial misfit stress at T_G is not fully relaxed and the unrelaxed misfit stress is inversely related to final *c*-domain abundance.
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I. INTRODUCTION

Epitaxial ferroelectric thin films attract considerable interest in view of their potential applications in advanced microelectronic and optoelectronic devices, especially as capacitors in high-density random access memories. The fabrication of epitaxial heterostructures is frequently accompanied by the formation of elastic domains (twins) in the films below the Curie temperature. Multiple 90° domain patterns have been observed in lead based perovskite materials such as $PbTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$(PZT) films grown on various cubic substrates.[1–6] These patterns mainly contain alternating domains with the tetragonal *c* axis perpendicular and parallel to the film surface in a periodic sequence that may be termed a *c*/*a*/*c*/*a* domain structure. The understanding of such domain structures and their formation mechanism is essential to control and achieve desirable ferroelectric properties for practical applications.[6–8]

The final domain structures are controlled by various strain factors such as (1) misfit strain due to lattice mismatch between the film and substrate at the growth temperature, T_G, and its relaxation by dislocation generation, (2) thermal strain caused by different thermal expansion coefficients of the film and substrate during cooling, and (3) transformation strain at and below the Curie temperature, T_C.[9,10] As such, it is extremely difficult, if not impossible, to analyze theoretically the final domain structures. Among these strains, thermal and transformation strains can be estimated by experiments. On the other hand, it has not been possible to analyze theoretically or to measure experimentally the magnitude of misfit strain relaxation by the generation of misfit dislocations. Therefore, theoretical considerations have usually assumed that the misfit strains are fully relaxed at T_G.[11,12]

In this article, the misfit strain developed during fabrication of epitaxial $PbTiO_3$ thin films on MgO(001) substrate and its relaxation in the course of cooling down to ambient temperature is analyzed by finite element method (FEM) using a commercial package, ABAQUS. The degree of *c*-domain abundance (α) is determined as a function of temperature below T_C, and compared to the recent experimental results. The final domain structure was found to be a strong function of the degree of initial misfit strain relaxation at T_G. Large residual misfit strain was required in order to satisfy the experimental results. Additionally, the effect of film composition was simulated from the viewpoint of strain relaxation mechanism.

II. FEM MODELING AND ABAQUS SIMULATION

The finite element method is applied to analyze the periodic 90°-domain structures and the initial misfit strain relaxation in $PbTiO_3$ thin film epitaxially grown on MgO(001) substrate. The thickness of film is 200 nm. Figure 1 illustrates finite element meshes and boundary conditions used in this analysis. This modeling consists of 1100 nodes and 990 CPS4T elements, which were selected to simulate 4-node plane stress thermally coupled with quadrilateral, bilinear displacement, and temperature. Since tetragonal ferroelectrics such as $BaTiO_3$, $PbTiO_3$, or $Pb(Zr_xTi_{1-x})O_3$ form 90°-domain twin structures to minimize the elastic energy at and below the Curie temperature, the elements of 45°-parallelograms were adopted for the simulation of domain

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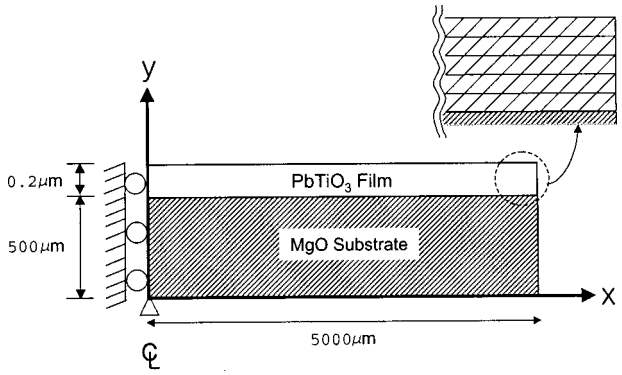


FIG. 1. Finite element mesh used for the ABAQUS simulation of $PbTiO_3$ thin film on MgO(001) substrate.

structure. However, the results were found to be insensitive to the types of discretization elements, and the rectangular-shaped element gave similar results.

In ABAQUS simulation, the point of origin ($x=y=0$) is fixed and the symmetry condition is applied along the y axis. The boundary conditions applied for the film are (1) its top surface is stress free, and (2) the film/substrate interface is coherently constrained.

The initial misfit strain after the film deposition was simulated using the lattice parameters of cubic $PbTiO_3$ and MgO substrate at T_G. The in-plane stresses applied to the film during the cooling process were obtained using the lattice parameters of $PbTiO_3$ at each temperature[13,14] as well as the thermal expansion coefficient of MgO single crystals.[15] The degree of c-domain abundance below T_C was calculated by minimizing the strain energy. Domain wall energy, interfacial energy, and electrostatic factors were assumed to be insignificant. Young's modulus and Poisson's ratio used in the simulation are shown in Table I neglecting slight anisotropy for tetragonal $PbTiO_3$ below T_C.

III. RESULTS AND DISCUSSION

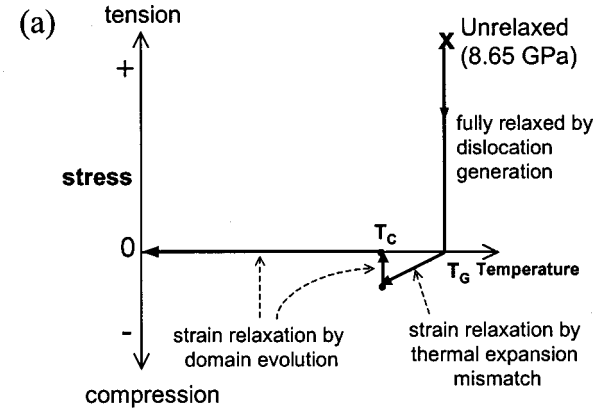
A. Domain structures in fully relaxed $PbTiO_3$ thin film

Because the lattice constant of MgO is larger than that of $PbTiO_3$, in-plane tensile stress is expected in the epitaxial $PbTiO_3$ film on MgO(001) due to large misfit strain. Without misfit strain relaxation by generation of misfit dislocations, a domains should prevail in any temperature because of the large in-plane tensile stress. Although, Lee *et al.*[9] observed experimentally that, just below the Curie temperature, a domains were dominant. As the temperature decreased, the a domains turned into the c domains, which implies clearly that initial misfit strain should be relaxed extensively by the generation of the misfit dislocation. However, it is difficult to estimate or measure quantitatively the extent of such strain relaxation.

TABLE I. Material properties used in ABAQUS simulation.

	$PbTiO_3$[a]	MgO[b]
Young's modulus (GPa)	134	310.5
Poisson's ratio	0.16	0.166
Thickness (μm)	0.2	500

[a]Reference 14.
[b]Reference 15.



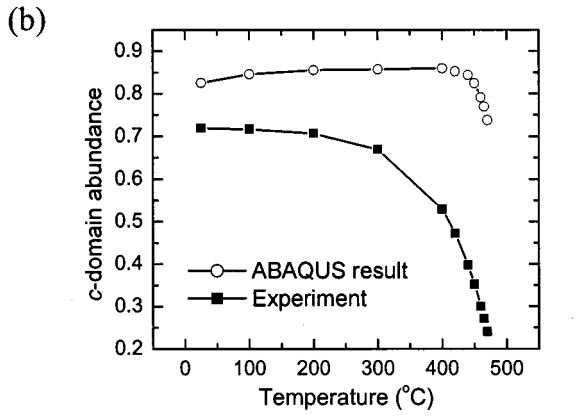


FIG. 2. (a) Schematics showing the change in in-plane stress in fully relaxed $PbTiO_3$ thin film grown on MgO(001) substrate. (b) ABAQUS simulation result on the c-domain abundance in fully relaxed $PbTiO_3$ thin film. Experimental value is taken from Ref. 9.

The first assumption on misfit strain relaxation is that initial misfit strain at T_G is fully relaxed by the generation of misfit dislocations in the epitaxial $PbTiO_3$ thin films.[11,12] Additionally it is assumed that no residual stress is developed as a result of the formation of periodic 90°-domain twin structures below the Curie temperature. As such, relaxation trace follows the schematics shown in Fig. 2(a). In this case, the effective lattice constant of MgO substrate can be considered identical to the lattice constant of cubic $PbTiO_3$ thin film at T_G. Since the thermal expansion coefficient of $PbTiO_3$ is smaller than that of MgO substrate, compressive stress is produced during cooling to T_C. Such compressive thermal stress is beneficial for the enhancement of c-domain abundance as the cubic film transforms to tetragonal structure with $c/a/c/a$ domains.

In Fig. 2(b), the simulation result of fully relaxed $PbTiO_3$ thin film is shown and compared to the experimental result.[9] The simulation overestimates the c-domain abundance. Discrepancy with experimental results is particularly large just below T_C, which implies that initial tensile misfit strain has been relaxed incompletely and tensile strain remained in film above T_C should be significant.

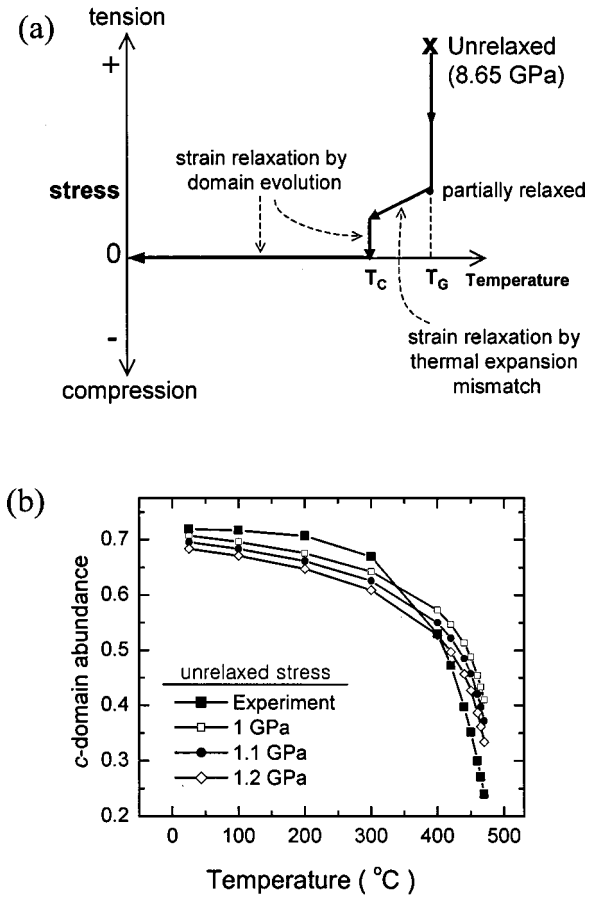


FIG. 3. (a) Schematics showing the change in in-plane stress in partially relaxed $PbTiO_3$ thin film grown on MgO(001) substrate. (b) ABAQUS simulation result on the *c*-domain abundance in partially relaxed $PbTiO_3$ thin film for varying initial misfit stresses. Experimental value is obtained from Ref. 9.

B. Domain structures in partially relaxed $PbTiO_3$ thin film

The initial unrelaxed misfit strain should play a critical role in the subsequent domain structure. In order to estimate the magnitude of the initial misfit strain relaxation, *c*-domain abundance below T_C is determined using ABAQUS simulation as a function of the initial misfit stress remaining in the film at T_G due to insufficient dislocation generation. As such stress relaxation follows the trace illustrated in Fig. 3(a). Even though further stress relaxation is possible due to the thermal expansion mismatch with the substrate, in-plane tensile stress remains in the film at T_C just prior to the cubic-to-tetragonal phase transformation. In the simulation, it is assumed that the residual stress is completely removed below T_C by the phase transformation. Figure 3(b) shows the ABAQUS simulation results on the degree of *c*-domain abundances with varying the initial unrelaxed misfit stresses. Although some discrepancy is obvious between the simulation results of *c*-domain abundances in partially relaxed film and corresponding experimental results near T_C, the behavior of *c*-domain evolution below T_C is reasonably simulated by FEM. As the initial unrelaxed misfit stress increases, the *c*-domain abundance decreases due to the increase in the residual tensile strain. When the initial misfit stress reaches about 1 GPa or above, the estimated *c*-domain abundance shows good agreement with the experimental result.

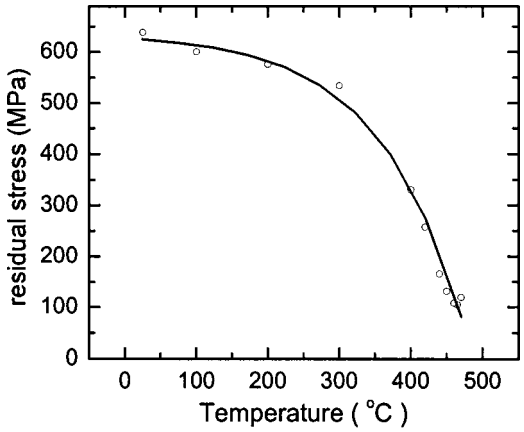


FIG. 4. Residual stress estimated below T_C in epitaxial $PbTiO_3$ thin film grown on MgO(001) substrate.

As mentioned previously, these calculated results are based on the bulk data reported in the literature instead of the data on the film but the thin film grown on bulk substrate is highly constrained; the lattice constants of the film are often different from those of the bulk. For this reason, residual stress in the film below T_C was estimated by considering the differences in lattice constants measured with the film[16] and those for the bulk.[13] As shown in Fig. 4, the residual stress developed in the epitaxial $PbTiO_3$ thin film below T_C is tensile and gradually increases as the temperature decreases.

The *c*-domain abundance taking into account of the residual stress in the film was simulated and the result is shown in Fig. 5. As the ABAQUS simulation is optimized with initial misfit stress of 1.54 GPa, the simulation result shows excellent agreement with the experimental result.

As a consequence, the stress in the 200-nm-thick $PbTiO_3$ thin film grown on MgO(001) substrate follows the trace illustrated in Fig. 6. Initial tensile misfit stress, 8.65 GPa, is relaxed to 1.54 GPa at T_G, and decreased further during cooling to T_C due to the difference in the thermal expansion coefficients. After the phase transformation at T_C, in-plane

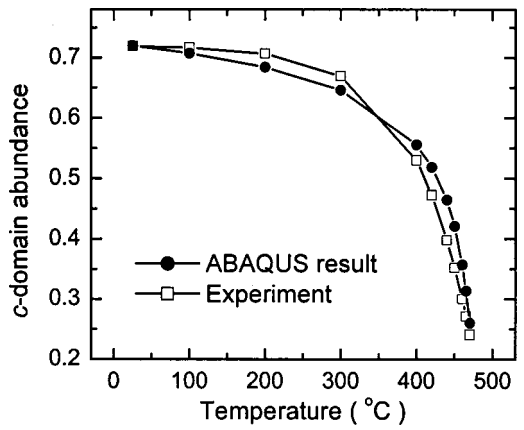


FIG. 5. *c*-domain abundance in $PbTiO_3$ thin film with the initial misfit stress, 1.54 GPa. Experimental result is taken from Ref. 9.

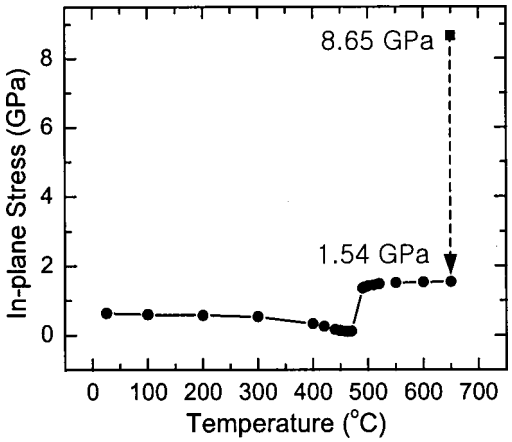


FIG. 6. Trace of in-plane stress experienced by epitaxial $PbTiO_3$ thin film after being fabricated at 650 °C and cooled down to room temperature.

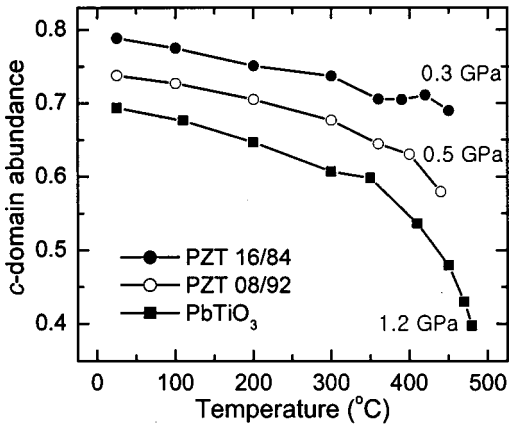


FIG. 7. ABAQUS simulation results on the effect of PZT composition on *c*-domain abundance. Different value of initial misfit stress for $PbTiO_3$ from that in Fig. 6 is due to the use of film data instead of bulk data.

residual stress increases as the tetragonality increases in the course of cooling down to ambient temperature.

C. Effect of PZT composition on *c*-domain abundance

The magnitude of strains developed in the film should be affected by the composition of the film. Lee *et al.*[10] studied experimentally the effect of PZT compositions on domain structures in the epitaxial PZT films on MgO(001) substrate. They reported the lattice constant of PZT thin films measured from x-ray θ–2θ scans as a function of the temperature for various film compositions. As the Zr concentration increases, the lattice constants of *a* axis gradually increase while those of *c* axis exhibit relatively insignificant change. Hence, Zr substitution in $Pb(Zr, Ti)O_3$ for Ti results in reduction in the c/a ratio of tetragonal unit cell.

Pertsev *et al.*[16] have proposed that equilibrium domain fraction of *c* domain is controlled by the relative coherency strain, $(b^*-a)/(c-a)$, where *c*, *a*, and b^* are the lattice constants of film along *c* axis, *a* axis, and the effective lattice constant of substrate, respectively. As the relative coherency strain increases, *c*-domain abundance should decrease according to their model. On the other hand, Lee *et al.*[10] observed that *c*-domain abundance increases with increasing Zr concentration in PZT thin films at T_C as well as at T_R (room temperature), even though the relative coherency strain increases by the reduction of the c/a ratio. A possible explanation of the discrepancy is the increase in compressive stress due to the decreases in T_C as Zr concentration increases. However, the magnitude of such compressive stress in $Pb(Zr_{0.16}Ti_{0.84})O_3$ is about 50 MPa, which is too small to explain such a discrepancy. Another factor that must be considered is the initial misfit stress that remains at T_G after insufficient relaxation by dislocation generation.

The ABAQUS simulation was performed with varying initial misfit stresses in $Pb(Zr_{0.08}Ti_{0.92})O_3$ and $Pb(Zr_{0.16}Ti_{0.84})O_3$ thin films. Unlike the previous simulation, there no reference data exist on the lattice constants of $Pb(Zr_xTi_{1-x})O_3$ as a function of temperature below T_C. Hence, the experimental data by Lee *et al.*[10] were used with the assumption that in-plane stress at the film below T_C is fully compensated by phase transformation. The *c*-domain abundances at T_C and T_R are determined as a function of initial misfit stress. The average values fitting the experimental data at T_C and T_R (Ref. 10) are adopted as the initial misfit stress. The magnitudes of initial misfit stress are about 0.5 GPa in $Pb(Zr_{0.08}Ti_{0.92})O_3$, and 0.3 GPa in $Pb(Zr_{0.16}Ti_{0.84})O_3$ thin films. As the Zr concentration increases, the initial misfit stress of PZT thin films decreases, which in turn enhances *c*-domain abundance. The *c*-domain abundance below T_C for different PZT compositions is shown in Fig. 7 as a result of FEM simulation.

The result is also consistent with the recent experimental observation on the thickness dependence of domain formation in epitaxial $PbTiO_3$ thin film on MgO(001) substrates.[17] The reduction of effective misfit strain as the film grows enhances the degree of *c*-axis orientation.

IV. SUMMARY AND CONCLUSIONS

The unique domain structures observed in epitaxial $PbTiO_3$ thin films grown on MgO(001) substrates were simulated by (FEM) using a commercial package, ABAQUS. Although this simulation is two dimensional and does not consider the domain energy, interface energy, and electrostatic factors, the simulated results showed excellent consistency with the experimental results. For this reason, it is reasonable to conclude that the thermomechanical factors such as misfit strain, thermal strain, and transformation strain have decisive effects on the domain structures in epitaxial $PbTiO_3$ thin films.

Initial misfit strain is not fully relaxed and plays a critical role in the subsequent evolution of final domain structures. When the residual strain in the 200-nm-thick epitaxial $PbTiO_3$ thin film on MgO substrate was considered, the optimized initial misfit stress was as high as 1.54 GPa and the calculated *c*-domain abundance below the Curie temperature was found to be consistent with the experimental observation.

The effect of PZT compositions on *c*-domain abundance was also simulated and compared with the experimental re-

sults. With the Zr concentration increasing, the *c*-domain abundance increased primarily due to the decrease in the initial residual misfit strain.

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