

ELASTIC AND ELECTRIC CONSTRAINTS IN THE FORMATION OF FERROELECTRIC DOMAINS

WENWU CAO

*Intercollege Materials Research Laboratory, Pennsylvania State University,
University Park, PA 16802*

(Received September 6, 1994)

Domain formation in ferroelectric system is a consequence of energy competition between different energy sources, including domain wall energy and the dipole-dipole interaction energy which are internal, and the electrostatic energy from compensating charges and the elastic interaction energy from boundary constraints which are external. The external contributions give the domain patterns in ferroelectrics some distinct features which are different from those in ferromagnetics and ferroelastics.

Keywords: Ferroelectric, ferroelastic, domains, domain walls, elastic constants.

INTRODUCTION

Domain formation is a common feature of ferroic systems, which fascinates scientists not only because its physical complexity, but also because the role of domains in determining many physical properties of ferroic systems. In simple physical arguments, the formation of domains is the manifestation of the coexistence of multi-variants in the ferroic phase. There are two distinct groups, i.e., coherent and incoherent domains. The latter is the result of multi-nucleation centers for the ferroic transition associated with structural defects, such as cracks, dislocations, surfaces, etc., domains of this kind can not be switched easily from one to the other since they have strong ties with defects. The formation of coherent domain patterns is controlled by the intrinsic properties of the system and the boundary conditions, it can be described from the view point of energy balance between different sources.

The simplest and the most thoroughly studied ferroic system is ferromagnetic system in which the domain formation is dominated by two energy sources, i.e., the domain wall energy and the demagnetization energy.^{1,2} Since there are no free magnetic monopoles, the magnetization in the domain structures must form a closed loop. In a ferroelastic case, the domain formation is determined by the balance of domain wall energy and the elastic interaction energy with the surrounding medium.³ Domain formation in ferroelastics is more involved than in ferromagnetics because the inclusion of the surrounding medium in the energy minimization process and the tensorial nature of the elastic interactions. Ferroelectric system is the most complicated among all three types of ferroic systems, which combines the characteristics of both ferromagnetic and ferroelastic systems. In addition, there is a new complication of free charge carriers which accumulate at the interfaces and the surfaces of a finite system to compensate the internal electric field. In order

to understand the influence of electric boundary conditions and the elastic constraints on the formation of domain patterns, we need to analyze each energy contributions in more detail.

DOMAIN WALL ENERGY

Domain wall is the coherent transition region in a twin structure. In the spirit of Landau-Ginzburg theory, the domain wall can be described by a continuum model consisting both nonlinear and nonlocal contributions.^{2,5} The mathematic formulation of the continuum theory allows solitary wave solutions which describe the twin and twin band structures in ferroelectrics. From these solutions one can calculate all the physical properties of domains and domain walls, such as the width of domains, the thickness of domain walls and the energy associated with domain walls. It can be easily verified from the solution of continuum theory that the energy associated with a domain wall is positive definite and the interaction between walls is repulsive.⁵ Because of the positive energy associated with these domain walls, single domain state would be the most desirable configuration when the depolarization field is compensated.

ELECTROSTATIC ENERGY AND 180° DOMAINS

There are two sources for the electrostatic energy. One is the interaction energy among the dipoles generated in each unit cell, which tends to align the dipoles in the forwarding direction (along the poling direction) but flip over all neighboring dipoles in the transverse direction (perpendicular to the poling direction). When this dipole-dipole interaction energy is used to balance the domain wall energy, the result will be a regularly spaced 180° domains with planar domain walls.^{6,7} The other electrostatic energy contribution is from the free charge accumulations, mostly on the surfaces and interfaces as a mean to compensate nonvanishing electric fields. Because of these compensating charges, ferroelectric domain patterns do not have to arrange the polarization vector in the domains to form a closed loop like in ferromagnetics. These two electrostatic energy contributions plus the domain wall energy contribution make the formation of 180° domains very complicated. In certain cases, the effects of compensating charges may be neglected due to the relatively lone relaxation time, especially when the charges are captured from external sources, but one must include the contributions from the internal charge carriers in calculating the stable domain patterns in ferroelectrics.^{8,9} When the compensating charges are neglected, the 180° domain pattern in ferroelectrics is similar to that of the ferromagnetic case, i.e., regularly spaced domains with planar domain walls. However, with the compensating charge effects, the 180° domains will not be regularly spaced and may not even be planar depending on the charge carrier concentration and the conductivity of the system. Figure 1(a) is for the case of regularly spaced 180° domain pattern where no free charges are present. Figure 1(b) is the irregular 180° domain pattern for which the depolarization field is compensated in each of the domains and the free charge carriers trapped on the

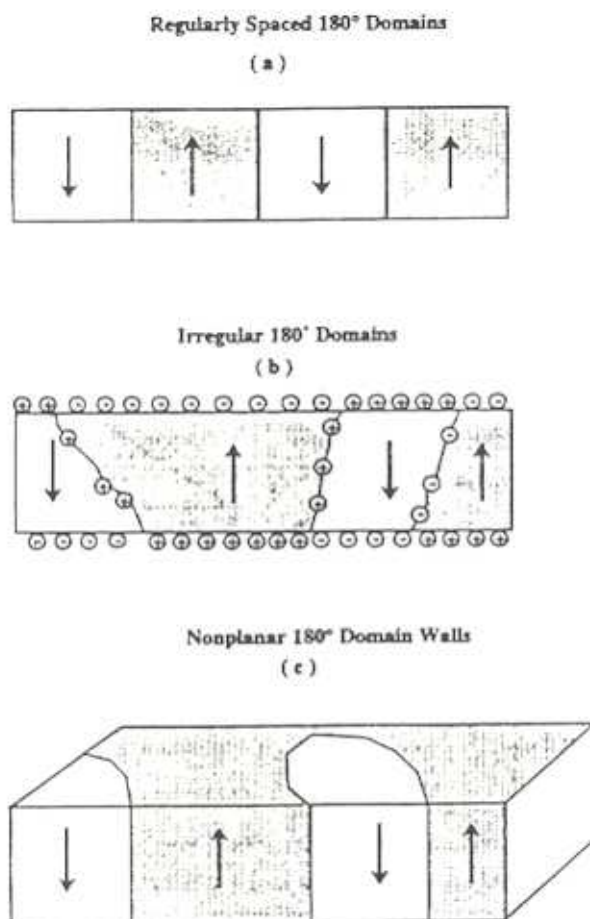


FIGURE 1 (a) Regularly spaced 180° ferroelectric domains without free charges, (b) irregularly spaced 180° domain pattern caused by the charge compensation on the surface and interfaces, and (c) nonplanar domain walls.

domain walls cause the wall to bend, this pattern may eventually settle down to the situation illustrated in Figure 1(c) which shows the nonplanar 180° domain walls commonly observed in ferroelectrics.

ELASTIC ENERGY AND NON-180° DOMAINS

The formation of non-180° domains, such as 90° domains in tetragonal ferroelectrics, is controlled by the elastic boundary conditions. The elastic interaction energy between the system and the surrounding medium depends on the geometry of the system and the size of the medium. There are 1-D, 2-D and 3-D cases in terms of elastic energy calculation. Figure 2(a) is the 1-D case in which the vertical dimension of the medium along the domain wall is relatively small and the horizontal dimension and the dimension perpendicular to the drawing plane are very large, Figure 2(b) is the 2-D case in which the dimension of the system is much larger perpendicular to the drawing plane than that in the plane, and Figure 2(c) is the 3-D case in which the system is simply merged in a large three dimensional medium.

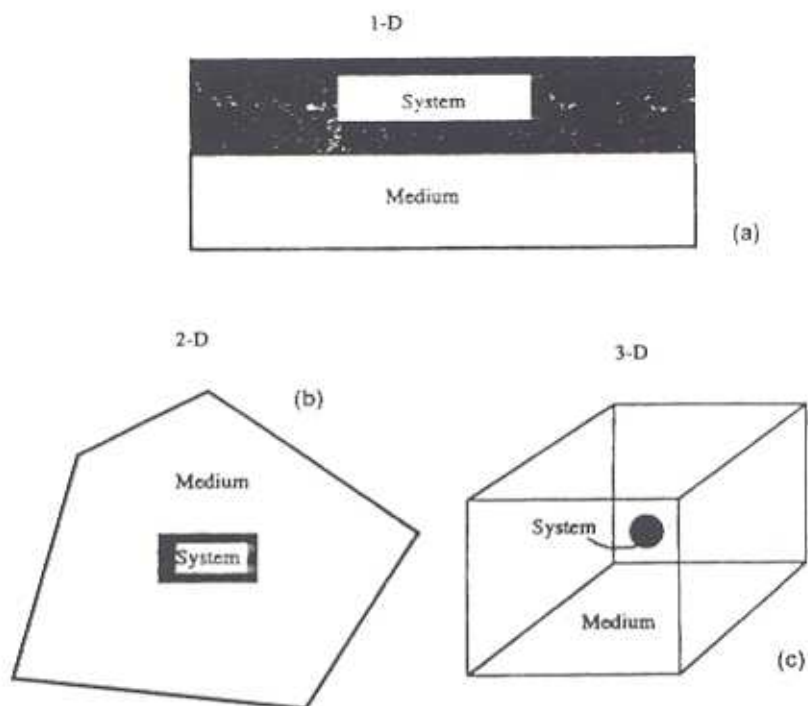


FIGURE 2 The definition of 1-D, 2-D and 3-D stress situation used in the analysis for a ferroelectric in an elastic medium.

In thin film case, the ferroelectrics is attached to the substrate only on one side, if we look at the cross section the stress field generated at the interface is either 1-D or 2-D, while the domains inside ceramic is an example of 3-D case. As a consequence of the stress field difference, domain size can be quite different for thin film with substrate, thin samples for TEM observations and a grain inside a large ceramic. Previous analyses^{3,7} on ferroelastic domains all give the same square-root relationship between the domain size l_d , and the grain size L_g , i.e.,

$$l_d \propto \sqrt{L_g} \quad (1)$$

which is the same as for ferromagnetic domains. However, no concrete experimental data are available to verify this relationship up to date.

Of course, all theories were based on certain assumptions which may not always be applicable. There are circumstances when this relation does not hold, for example, let us take a simple 1-D case as shown in Figure 3 for a cubic-tetragonal phase transition. Figure 3(a) is a section of a ferroelectric system which will form one of the 90° domains below the transition temperature with the polarization pointing to the $[010]$ direction, the system is free on one side and attached to an elastic medium on the other side, the medium is fixed at its bottom to simplify our calculation. Assuming we can make an imaginary separation of the system and the medium, the system will transform freely to the tetragonal phase making a shear deformation in $[\bar{1} 1 0]$ as illustrated at the top portion of Figure 3(b), if we now apply a virtual stress in the vertical direction which is a linear function of the horizontal axis so that the system and the medium will have the same slope along their interface and rejoin the two together afterwards, the whole structure will

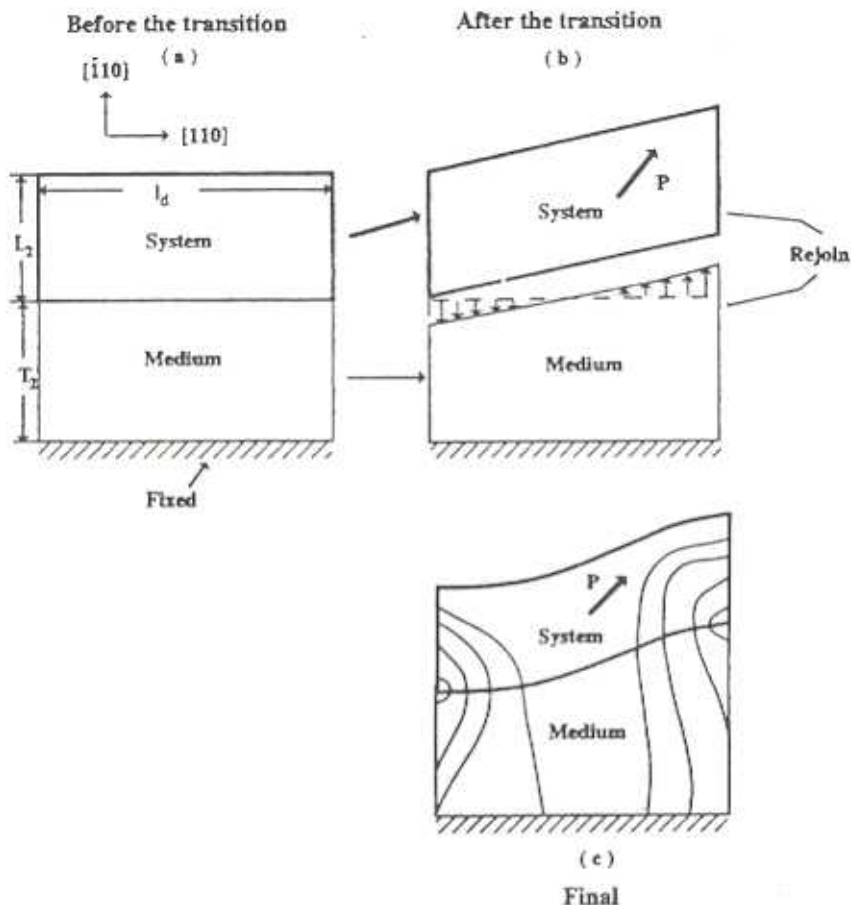


FIGURE 3 A section of a ferroelectric attached to a medium whose bottom is fixed. (a) before the phase transition, (b) after the cubic-tetragonal transition and (c) the final stable configuration and the stress contour.

readjust to the new equilibrium position as shown in Figure 3(c), where the surface of the system will be bent and the stress field is illustrated by the contour curves with the high stress concentrated near the domain wall regions. When the elastic constant of the medium is the same as the ferroelectric system, we can approximate the elastic energy of Figure 3(c) by taking one-half of the energy calculated in Figure 3(b) using the equal partition principle since the kinetic energy will be damped out during the relaxation process from Figure 3(b) to Figure 3(c). When the elastic constant of the medium is different from the system, the elastic energy of Figure 3(c) will be proportional to the elastic energy of Figure 3(b) but not equal to one-half. This elastic interaction energy between the medium and the system gives an additional effective contribution to the system, which if used to balance the domain wall energy will lead to the following equilibrium domain size l_d ,

$$l_d = \sqrt[3]{\frac{24\sigma_w T_2 L_2}{C\alpha^2}} \quad (2)$$

where the quantity σ_w is area density of the domain wall energy, C is the effective normal elastic constant of the medium in $[\bar{1}10]$ direction and α is the deformation

angle caused by the shear in the $[\bar{1} 1 0]$ direction. Considering L_2 to be the grain size, the relationship between the domain size and the grain size will be cubic-root instead of square-root as Equation (1).

The inclusion of the medium dimension T_2 in the expression is a consequence of the global energy minimization and the fact that the 1-D like stress will extend into the whole medium. In most of practical cases, the medium is much larger compared to the system, therefore, the stress field becomes 2-D or 3-D, which will decay in the inverse powers of distance from the system-medium interface. In the 2- and 3-D cases the medium dimension T_2 is integrated out to become a characteristic length for the stress field, but the cubic relation Equation (2) still hold. Compared with the experimental data of Arlt¹⁰ for BaTiO_3 , the cubical relation fits much better than the quadratic relation for the larger grain tetragonal phase.

SUMMARY AND CONCLUSIONS

The formation of coherent ferroelectric domains is the result of global energy minimization which not only involves the ferroelectric but also the free charges and the elastic medium that is directly in contact with the ferroelectric. The competition between three energy sources determines the formation of 180° domains, the domain wall energy, the dipole-dipole interaction energy and the free charges at the surfaces and interfaces. The presence of free charges causes the formation of irregular 180° domain patterns, and the walls may even be curved in certain cases. Since the free charges can flow through the system, the 180° domains can not have "memory" when the temperature is cycled through the ferroelectric phase transition.

The formation of coherent non- 180° domains is mainly a consequence of the elastic interaction of the system with the surrounding medium. The stress field produced at the interface could have 1-D, 2-D or 3-D nature for different geometry as shown in Figure 2. For the 2-D and 3-D cases, the interface stress will decay in the inverse power law so that the domain size will be independent of the medium size for a relative large medium. But for system with 1-D like stress, the dimension of the medium will also influence the domain size. A simple derivation shows that the domain size-grain size relationship for the ferroelastic walls is cubical instead of quadratic for the 1-D model. Compared with existing experimental data on BaTiO_3 , the cubic-root relation fits better than the square-root relation systems with grain size larger than $10 \mu\text{m}$.

ACKNOWLEDGEMENTS

The author wishes to thank Drs. L. E. Cross, C. R. Randall, R. E. Newnham and J. R. Banavar for beneficiary discussions. This research was sponsored by the Office of Naval Research and the National Science Foundation.

REFERENCES

1. L. Landau and F. Lifshits, *Sov. Phys.*, **8**, 153 (1935).
2. J. Fousek and M. Safrankova, *Japan J. Appl. Phys.*, **4**, 406 (1965).

3. B. Horovitz, G. R. Barsch and J. A. Krumhansl, *Phys. Rev. B*, **43**, 1021 (1991).
4. V. A. Zhirnov, *Sov. Phys. JETP*, **35**, 822 (1959).
5. W. Cao and L. E. Cross, *Phys. Rev. B*, **44**, 5 (1991).
6. C. Kittel, *Phys. Rev.*, **70**, 965 (1946).
7. G. Arlt, *J. Mat. Sci.*, **25**, 2655 (1990).
8. B. V. Selyuk, *Soviet Phys. Crys.*, **16**, 292 (1971).
9. M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, Oxford, 1977).
10. G. Arlt, *Ferroelectrics*, **104**, 217 (1990).