

ENERGY RELEASE DUE TO DOMAIN FORMATION IN THE STRAINED EPITAXY OF MULTIVARIANT FILMS

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ABSTRACT

Twin related domain formation is examined as a strain relaxation mechanism for a heteroepitaxial tetragonal film on a cubic substrate. Elastic relaxations are calculated for a single twin band in which the c-axis of the tetragonal domains is either related by a 90° rotation about an axis in the plane of the film or by a 90° rotation about the surface normal. In all cases, the strain energy change is evaluated for both the film and the substrate. A domain pattern map is developed that predicts single domain and multiple domain fields depending on the relative misfit strains and domain wall energy. The concept of a critical thickness, h_c , for domain formation is developed. For cases in which the c-axis is rotated 90° about an axis in the plane of the film, the critical thickness depends only on the relative coherency strain between the substrate and film and the ratio of the domain wall energy to the stored elastic energy. For the case of a pattern consisting of energetically equivalent domains with the c-axis in plane, the equilibrium distance of multiple domains is derived. For such multiple domains, a minimum wall separation distance exists which depends non-linearly on the film thickness.

INTRODUCTION

In this paper, the possibility of twin related domain formation is examined as a mechanism of strain energy release in the heteroepitaxial growth of thin films. For this to be possible, there must be at least two possible orientations (variants or twins) in which the strained film can align with respect to the substrate. The interest in this problem is motivated by current activity in the growth of thin film ferroelectrics [1, 2, 3] and thin film ferroelastics [4]. Domains must be considered as a mechanism of strain energy release in the heteroepitaxial growth of tetragonal ferroelectrics such as lead titanate or barium titanate on single crystal cubic substrates such as strontium titanate. The stability of monovariant films is a critical issue for ferroelectric applications such as sensors or memory. Therefore, not only the formation of periodic domain arrangements, but also single embedded domain segments require study.

Lattice-matched epitaxy provides a continuous elastic constraint for the thin film in two dimensions, the film may freely relax in the surface normal direction. The elastic constraint is achieved by matching the two-dimensional film periodicity to the two-dimensional periodic potential of the substrate. Therefore, elastic relaxations can only be concentrated in the film and substrate near discontinuities such as edges or domain boundaries, as demonstrated in extensive elasticity calculations by Hu [5] and by Freund and Hu [6].

RESULTS AND DISCUSSION

Definition of the Problem and Physical Model

The problem considered here involves the strained epitaxy of a thin tetragonal film on a cubic substrate. Domain formation is driven by minimizing the stored elastic energy and in ferroelectrics by additionally reducing the electrostatic energy. For the sake of simplicity of the elasticity analysis, we consider 90° boundaries which are normal to the film/substrate

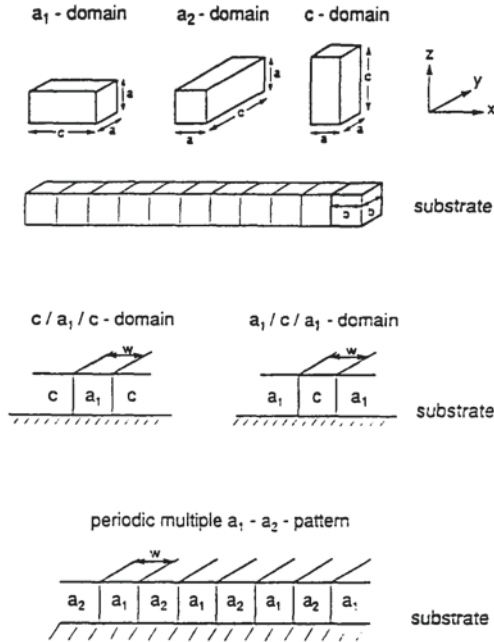


Figure 1 Characteristic configurations of multivariant tetragonal domains on an (001) cubic substrate.

interface and the domain boundary energy will be estimated by the twin boundary energy. We believe that the elastic effects of normal and inclined boundaries qualitatively show the same behavior. (In ferroelectric films the domain boundaries may be inclined to preserve the normal component of the polarization vector across the boundary, thus avoiding space charges.) The analysis is correct for ferroelastics or other non-polar multivariant materials.

We consider cases in which either the (001) plane (c -axis normal) or (100) plane of the film are parallel to the film/substrate interface. The substrate plane corresponds to (001) of a cubic crystal. The lattice parameter of the substrate square lattice is b and the lattice parameters of the film are a and c . The coordinate system used is shown in Fig. 1. For the present problem the interface is assumed to be fully coherent and thus free of misfit dislocations. It is important to note that generation of misfit dislocations represents a competitive process for strain relaxation for all misfitting films.

The film thickness is h and the x and y axes lie in the plane of the interface. We have to distinguish three different domain orientations. For one orientation, referred to as the c -domain in the following, the (001) plane of the tetragonal crystal is aligned along the interface with the substrate. Far from any lateral interfaces, the misfit strains of this domain are given as $\epsilon_{xx} = \epsilon_{yy} = \epsilon_a = \frac{(b-a)}{b}$. Additionally, the two variants of the film in which the (100) plane lies in the interface are relevant. Variant 1 of the a -domain has misfit strains $\epsilon_{xx} = \epsilon_c = \frac{(b-c)}{b}$, $\epsilon_{yy} = \epsilon_a$ and will be referred to as the a_1 domain. For the variant 2 of the a -domain, we select an orientation with misfit strains $\epsilon_{xx} = \epsilon_a$, $\epsilon_{yy} = \epsilon_c$ and refer to this domain as a_2 .

We begin by considering a thin misfitting film on a semi-infinite substrate. Initially the film has infinite lateral extent. Two cases are considered. In Case I, the film is loaded in tension in the x -direction, in Case II the film is loaded in compression in the x -direction. Because the substrate is semi-infinite all stress and strain is concentrated in the film. Now consider the effect of finite size domains. Far from any boundaries, we anticipate that the film and substrate have the same stresses and elastic displacements as a laterally infinite film. At the boundaries however, the film can no longer sustain a normal stress σ_{xx} , and there are resulting elastic relaxations in both the film and the substrate. There is a characteristic stress relaxation length in the film of the order of the film thickness h . If we bring islands together with different epitaxial misfits, then the net strain and displacement fields can be described by a superposition of the stress and displacement fields of isolated islands. When band-like domains with a large extension along the y -axis are considered, there will be a long-range stress relaxation with a logarithmic singularity in energy for a single boundary [7]. Thus, domain boundaries, and the material near the boundary, act as displacement "absorbers" in heteroepitaxial systems. This process of mutual elastic accommodation provides the basis for domain patterning as a mechanism of strain energy release in multivariant thin films.

Equilibrium Domain Structures

From this phenomenological description of stress relaxation along domain boundaries, some general results may be established concerning the stability of different misfitting thin film structures. The film forms three variants relative to the substrate: the c -axis is either normal to the film/substrate interface (c variant), or parallel to the interface (a_1 and a_2 variants). The variants may coexist to form domains; a few patterns are shown in Fig. 1. Here we analyze the equilibrium domain patterns which result from the competition between the strain energy reduction and the domain wall energy. Thus, both the film thickness, h , and domain width, w , are regarded as variables in minimizing the combined strain and domain wall energy.

Our analysis indicates that a diagram of equilibrium domain patterns may be developed by using two non-dimensional variables: the relative coherency strain e_r given by the ratio of one misfit strain, $\epsilon_a = \frac{b-a}{b}$, to the tetragonality strain, $\epsilon_T = \frac{c-a}{b}$, $e_r = \frac{b-a}{c-a}$

and the ratio of the strain energy over the domain wall energy $hE\epsilon_T^2/\gamma$, where γ is the specific domain wall energy, and E is Young's modulus of the film. A calculated equilibrium diagram is presented in Fig. 2.

When $b < a$, or $e_r < 0$, all variants are under biaxial compression; the film tends to make an a -to- c switch to stabilize as a single c -domain. When $b > c$, or $e_r > 1$, all variants are under biaxial tension; the film tends to make a c -to- a switch to stabilize with alternating a_1 and a_2 domains. A value $e_r = e_c$ exists where the epitaxy causes the same strain energy in the a and c variants. This is the vertical line in Fig. 2; the c variant dominates on the left, and the a variants dominate on the right. A multi-domain region appears near $e_c - \Delta e \leq e_r \leq e_c + \Delta e$. For example, when $e_r < e_c$, the strain energy of a large c -domain may be diminished by embedding small a -domains. Similarly, when $e_r > e_c$, small c -domains may be stable within a large a -domain. The mechanism is efficient for thicker films, because the coexisting variants in the film add domain walls and deform the substrate. Thus the range of stable multiple domain structures increases with increasing film thickness.

Epitaxial, monovariant films of either type a or c provide the reference for the energy change to be considered in the later sections. Because the film is much thinner than the substrate, the substrate is undeformed and, to match the undeformed lattice of the substrate, the film is strained by $\epsilon_a = \frac{b-a}{b}$, $\epsilon_c = \frac{b-c}{b}$. The stresses in the film for the c -variant and for the a -variants are determined by Hooke's law. The strain energy per unit volume can be readily computed for both the a -variants and the c -variant. Note that the a_1 and a_2 variants have the same strain energy. It follows by equating the energy densities of monovariant a and c domains that both variants are energetically equivalent when

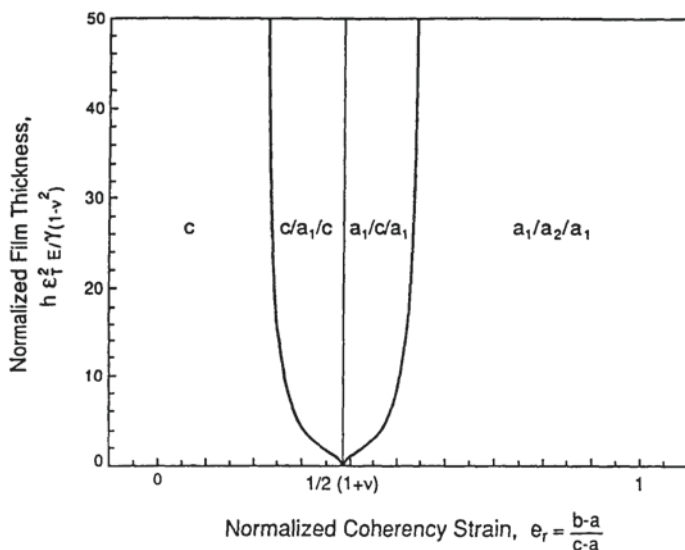


Figure 2 Equilibrium diagram of domain patterns. The domain pattern fields are computed on the basis of idealized configurations discussed in the text.

$e_r = e_c = \frac{\epsilon_a}{\epsilon_a - \epsilon_c} = \frac{1}{2(1+\nu)}$. This is the vertical line in Fig. 2, $e_c = 0.385$ (for $\nu = 0.3$). The c -variant has the lower strain energy on the left of the line, and the a -variants have the lower strain energy on the right.

Further simplifications will be invoked to calculate the strain energy. The film and the substrate are taken to be elastically isotropic and homogeneous with Young's modulus E and Poisson's ratio ν . (A value $\nu = 0.3$ will be used in the plots.) Domain walls are assumed to be perpendicular to the film/substrate interface. Each domain is long in the y -direction compared to the film thickness, so that stresses everywhere are invariant with respect to y . To simplify some of the calculations, the film is sandwiched between two thick substrates, so that Green's functions for an infinite space under plane strain conditions can be used, as described elsewhere [8].

Formation of Domain Bands

When $e_r < e_c$, even though the c -variant has a lower strain energy than the a -variant, a small a -domain may emerge in a large c -domain to reduce the elastic energy in the film. This is done at the expense of adding the domain walls and deforming the substrate. Proper energy accounting requires that the elasticity problem be solved rigorously. In what follows a specific configuration, a long a_1 -band in a large c -domain (Fig. 3), is analyzed. We will determine (i) the equilibrium band width, and (ii) the stability range for domain formation. The a_1 -bands, disrupting a perfect c -variant film, bear much similarity with other strain-relaxing mechanisms in thin films. Familiar examples include misfit dislocations [9] and channeling cracks [10].

The lattice misfits among the variants and the substrate cause a complicated stress field. We solve the elasticity problem by linear superposition. Consider Problem A first, shown schematically in Fig. 3. Starting from the unbonded a_1 -band, c -domain and substrate, the a_1 -band is deformed to match the 3D lattice of the c -domain. Compared with the strain

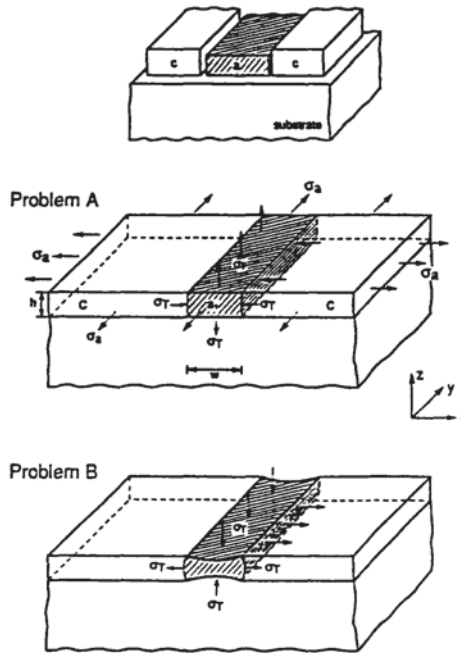


Figure 3 Micromechanical model of an embedded domain band. In Problem A clamping tractions are applied to match the variants and the substrate. In Problem B tractions σ_T in the opposite directions are applied to remove σ_T in Problem A.

energy per unit domain band length in an epitaxially bonded c -monovariant, Problem A increases the strain energy by $U_A = \frac{E}{1-\nu} \epsilon_T^2 h w \left(\frac{1-\nu}{1+\nu} - e_r \right)$.

Problem A differs from the problem of a c -monovariant one aspect: the clamping tractions σ_T that prevent relaxation. Upon removing the tractions, the lattice mismatches deform the system. On the basis of linear superposition, the displacement field, after removing σ_T from Problem A, is the same as that induced solely by the negative tractions without the lattice misfits, as illustrated by Problem B. The strain energy is reduced and the change in the strain energy scales as $U_B = -\epsilon_T^2 h^2 g \left(\frac{w}{h} \right)$, where g is a dimensionless function of w/h . The displacements in Problem B are obtained by integrating Green's functions; U_B is the work done per unit band length by tractions σ_T through the associated displacements. Both are described in elsewhere [8].

The difference in the strain energies in a large c -domain with and without the a_1 -band, $U_A + U_B$, is shown in Fig. 4, varying with both w and e_r . Two types of behaviors emerge. When $e_r < e_c - \Delta e = 0.2149$, embedding an a_1 -band of any w increases the strain energy, so that the c -monovariant is favored. When $e_c - \Delta e < e_r < e_c$, an a_1 -band over a limited range of width decreases the strain energy. The equilibrium band width w_{eq} minimizes the strain energy, which is indicated in Fig. 4 for one value of e_r . Also indicated is U_{eq} , the strain energy reduction due to embedding the a_1 -band.

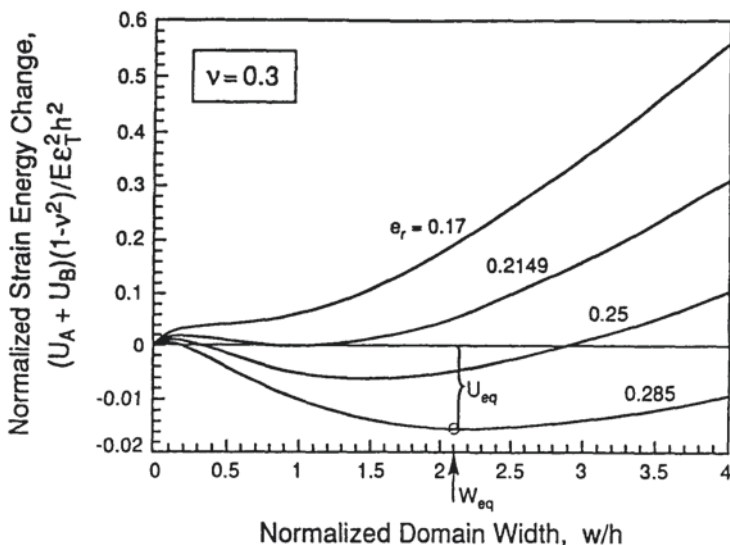


Figure 4 Calculated difference in the strain energies between a large c -domain with and without the a_1 -band for various relative coherency strains e_r . The equilibrium band width and the associated reduction in the strain energy are indicated for one curve.

Embedding an a_1 -band into a c -domain adds two domain walls. The a_1 -band forms when the strain energy reduction U_{eq} compensates the domain wall energy, *i.e.*, $U_{eq} + 2\gamma h \leq 0$. Because U_{eq} scales as h^2 , this condition defines a critical film thickness, below which the a_1 -band is unstable, and the film stabilizes as a c -monovariant. The critical thickness, obtained from the calculated U_{eq} , is plotted in Fig. 2, separating two regions of equilibrium domain patterns: the c -monovariant prevails below the curve, and a_1 -bands form above the curve.

When $e_r > e_c$, an epitaxial a -monovariant has lower strain energy than c -monovariant. Similar calculations lead to the symmetric pattern in Fig. 2 which separates the region of coexisting a and c domains from the region of only a variants.

Patterning of Equivalent Variants

Now consider the region in the equilibrium diagram where the c -variant completely disappears. Epitaxial films of single a_1 or a_2 variant have the same strain energy. We will show that the film stabilizes with alternating a_1 and a_2 domains - that is, a monovariant film. say of a_1 -type, is unstable for any film thickness. Our conclusion thus differs from that of Roytburd [11].

The two variants are assumed to form alternating bands with the same width w (Fig. 1). The two variants accommodate each other, reducing the strain energy, causing a complicated stress distribution. The elasticity problem is solved by linear superposition described elsewhere [8].

Including both the change in the strain energy and the domain wall energy (with respect to a monovariant), the average energy change in the system, per unit length in both x and y

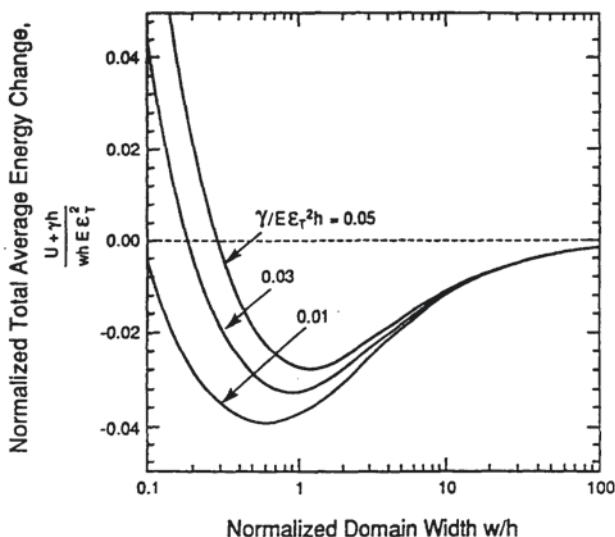


Figure 5 Total energy changes as a result of the competition between domain wall energy and strain energy reduction due to patterning (note the log-linear scales employed).

directions, is $\frac{(U + \gamma t)}{w}$. The computed results are plotted in Fig. 5, varying with the domain width and the domain wall energy. Note that the "energy change" is with respect to the strain energy in an a_1 -monovariant. When w/h is small, the domain wall energy dominates so that the energy change is positive. When w/h exceeds some finite value, the strain energy reduction dominates so that the energy change becomes negative. The average energy becomes indistinguishable from that of a monovariant film for large w/h . Consequently, *an equilibrium domain width exists for any film thickness which minimizes the total energy below the strain energy of the a -monovariant. That is, the alternating pattern is always energetically favored over an a -monovariant.*

CONCLUSIONS

By minimizing the combined strain energy and domain wall energy, we have developed a diagram of equilibrium domain patterns for a tetragonal film epitaxially grown on a cubic substrate (Fig. 2). The c and a variants dominate over the two sides of the diagram, separated by a critical value of the misfit parameter, $e_r = e_c$. When $e_c - \Delta e < e_r < e_c$, a critical film thickness exists below which the film stabilizes as a perfect c -variant. Above the critical thickness, bands of a_1 variant traverse the c -variant to reduce the strain energy. When $e_c < e_r < e_c + \Delta e$, a critical film thickness exists below which the c -variant disappears completely. In this region, the film can only stabilize with alternating a_1 and a_2 domains, but not a monovariant. The dependence of the stability ranges on the relative coherency strain of the film/substrate system opens a way for the engineering of domain configurations. Many parameters may be varied to control the domain structure, including choice of substrate, and alloying the substrate and film to control lattice parameters.

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