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DOMAIN FORMATION IN THIN FERROELECTRIC FILMS: THE ROLE OF DEPOLARIZATION ENERGY

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Abstract Formulae for equlibrium stripe domain width W_{eq} in a nonductive ferroelectric plate of thickness d are deduced, taking into account electrostatic interaction of surfaces. It is shown that the classical formula giving $W_{eq} \propto d^{1/2}$ is not applicable when the sample thickness decreases below the value d_{crit} which is a function of dielectric properties and domain wall energy density. For many ferroelectrics the value of d_{crit} lies in a range which can be easily reached far below the transition point by contemporary thin film techniques; it further increases as the transition point is approached. In the region $d < d_{crit}$ the width W_{eq} increases with decreasing d. For samples with thickness $d << d_{crit}$ the domain structure becomes insensitive to electrical boundary conditions and will be primarily determined by other factors.

INTRODUCTION

Shapes and size of ferroelectric domains are determined by electrical and elastic boundary conditions and greatly influenced by crystal defects which codetermine the local direction of polarization and the position of domain walls. For high quality samples treated in a way minimizing stresses and effects of electric conduction, very regular antiparallel domain pattern can be observed in plate-like ferroelectric samples with P_0 perpendicular to the major plane. The existence and form of such structures have been intensively studied for a number of materials[1-7] and the results were discussed using the concept of equilibrium domain structures which minimize the total free energy. In calculating its electrostatic part the assumptions were often made that compensation of the bound charge $\mathrm{div}\boldsymbol{P}_0(\boldsymbol{r})$ by free carriers does not substantially influence the electrostatic energy in the *early stages* of the development of the domain pattern and that crystal plates are thick enough to substantiate the neglection of mutual electrostatic interaction

of the plate surfaces.

The problem of equilibrium domain structures has recently emerged again, in connection with ferroelectric thin films. In most cases films of multiaxial ferroelectrics are fabricated and it is the occurrence of ferroelastic domain pairs (a- and c-domains) which is of primary interest. Since we have no free standing films, structures in these systems are primarily determined by elastic considerations.[8] An analysis of the problem was offered by Pompe et al.[9] They considered several domain arrangements in a film with tetragonal symmetry deposited on a cubic substrate: homogeneous a-oriented film, c-oriented film (which eventually may still contain antiparallel domains), alternating c- and a-domains, a-domains with alternating polar-axis orientations. The arrangement which relaxes the elastic energy most effectively depends on the film thickness d and the relative coherency strain e_r. The relative stability of these arrangements can be represented graphically by maps in the d,e_r space. Now, the depolarization energy may become significant in non-electroded films deposited on an insulating substrate. For this case the situation was discussed by Speck and Pompe[10] who consider the simultaneous role of elastic and electrostatic energies, using again the assumption of noninteracting surfaces (thick plates).

In the present paper we give more general formulae for domain structures in uniaxial ferroelectric plates, taking the surface interaction into account, discuss when the thick plate approximation is not valid and show that in thin samples the thickness dependence of domain width changes substantially its character.

GEOMETRY, VARIABLES AND ENERGY OF THE SYSTEM

We consider a plate-like sample (medium II) of infinite area and thickness d with major surfaces perpendicular to the ferroelectric axis z, surrounded by vacuum (media I and III). Domains of alternating polarization $\pm P_0$ are lamellae of the width W_+ and W_-, resp., with walls perpendicular to the x-axis. We resort to the idealized case assuming that i) the crystal plate is defect-free, ii) the domain walls are infinitely thin and iii) the depolarizing field are not screened by free charges. Then the structure which will be formed is expected to correspond to the minimum of the free energy F which in the following will

be expressed per unit area of the plate. It is useful to introduce several parameters characterizing the material and the domain structure:

$$c = \sqrt{\varepsilon_x / \varepsilon_z}, \qquad g = \sqrt{\varepsilon_x \varepsilon_z} = c\varepsilon_z \tag{1a}$$

$$k = 2\pi / (W_+ + W_-), \qquad A = (W_+ - W_-) / (W_+ + W_-) \tag{1b}$$

$$R = \pi cd / (W_+ + W_-) = kcd / 2 \tag{1c}$$

We have intentionally introduced the asymmetry parameter A although we expect that neutral structuress with $A = 0$ will correspond to equilibrium states. The free energy is considered in the form

$$F = F_0 + F_{dep} + F_w \tag{2}$$

where F_0 relates to the single domain state. Here F_{dep} is the energy of depolarizing field

$$F_{dep} = \frac{1}{2}\int_{-\infty}^{+\infty} \mathbf{E}(\mathbf{D} - \mathbf{P}_0)dz \tag{3}$$

and F_w is the energy of domain walls characterized by energy density σ_w:

$$F_w = \frac{2}{\pi}\sigma_w \frac{R}{c}. \tag{4}$$

We first solve the Laplace equation for potential inside and outside the plate, observing the requirement of potential continuity as well as conditions of continuity of normal components of $\boldsymbol{D}$ and tangential components of $\boldsymbol{E}$. We do not reproduce here the resulting expressions for the electric field. Integration of eq. (3) gives

$$F_{dep} = \frac{1}{2}\frac{P_0^2 d}{\varepsilon_0 \varepsilon_z}\left(A^2 + \frac{8g}{\pi^2 R}\sum_{n=1,2,\ldots}^{\infty}\frac{1}{n^3}\sin^2\left(n\pi\frac{A+1}{2}\right)\frac{1}{1+g\coth nR}\right). \tag{5}$$

We note that the expression

$$\frac{1}{2}\frac{P_0^2}{\varepsilon_0 \varepsilon_z}d \equiv F_{cap} \tag{6}$$

on the right hand side of eq. (5) represents the energy of a plate condenser of unit area and thickness d, filled by a dielectric with permittivity ε_z and carrying surface charges $\pm P_0$. The expression in brackets then represents the dimensionless factor K which modifies the energy of the plate-like condenser into the electrostatic energy of the domain texture. K is a function of material and geometrical parameters A, g and R. Thus

$$F_{dep} = F_{cap} K(A, g.R). \tag{7}$$

For neutral structures ($A = 0$) and plates with thickness satisfying the condition

$$d >> d_{crit} = 5\pi\sigma_w \varepsilon_0 \varepsilon_z^{3/2} / P_0^2 \varepsilon_x^{1/2} \tag{8}$$

(approximation of "thick" plates) the electrostatic interaction of the surfaces can be neglected. Then eq.(5) simplifies to

$$F_{dep} = \frac{8{,}42}{\pi^3} \frac{P_0^2 W}{\varepsilon_0 (1 + \sqrt{\varepsilon_x \varepsilon_z})} \tag{9}$$

which has been used in previous literature on the subject.

EQUILIBRIUM DOMAIN PATTERN

Here we consider neutral structures, $A = 0$; the role of A will be treated in the next section. The domain pattern is then characterized by the single parameter $W = W_+ = W$. Its equilibrium value W_{eq} is determined by the energy minimum condition $\partial F/\partial W = 0$. In the thick plate approximation we obtain from eqs. (4) and (9) the classical formula

$$W_{eq} = \left(\frac{\pi^3 \varepsilon_0 \sigma_w (1 + \sqrt{\varepsilon_x \varepsilon_z})}{8.42 P_0^2} \right)^{1/2} d^{1/2}. \tag{10}$$

For the general case (no approximation) it is useful to characterize the domain structure by the parameter R.. The condition $\partial F/\partial R = 0$ yields, making use of eqs. (4) and (5)

$$\frac{1}{2}\sigma_w \frac{\varepsilon_0 \pi}{P_o^2 c^2} \frac{1}{d} = \frac{1}{R^2} \sum_{n=1,3,..}^{\infty} \frac{1}{n^3} \frac{1}{1 + g \coth nR} - \frac{g}{R} \sum_{n=1,3,5..}^{\infty} \frac{1}{n^3} \frac{1}{(\sinh nR + g \cosh nR)^2} \tag{11}$$

This relation can be considered an implicit equation for the value of R that corresponds to the equilibrium domain structure. We introduce the symbol $f(g,R)$ for the right hand side of this equation, so that it now reads

$$\frac{1}{2}\sigma_w \frac{\varepsilon_0 \pi}{P_o^2 c^2} \frac{1}{d} = f(g, R) \tag{12}$$

The expression on the left hand side is given by the material properties and plate thickness. For a given value of g the function f on the right-hand side can be calculated numerically and presented in a plot. From the latter the value of R can be determined

fulfilling the condition (12), and thus also the required value of W_{eq}. This general procedure is applicable for any plate thickness d, i.e. also for thin films where formula (10) gives incorrect results.

DISCUSSION

In the present theory we neglect the effect of free carriers which are expected to contribute to the reduction of electrostatic energy. A number of obervations[1-4,11] showed that while in short-circuited crystals domain structures arise which are far from neutrality ($0.5 < A \leq 1$), in carefully treated samples cooled in insulating media always $A \cong 0$. This proves beyond any doubt the vital role of depolarization energy. The influence of free carriers was discussed theoretically.[12,13] It was shown that domain pattern minimizing $F_{dep}+F_w$ is expected to exist in some temperature interval below T_c. At lower temperatures this multidomain state becomes unstable and the crystal plate tends to reach a single domain state. Because the time evolution is a slow process which may take hundreds of hours in almost perfect crystals[4,11] and in less perfect crystals may never be completed, it can be expected[12,13] that patterns in high quality crystals will tend to equlibrium structures treated above.

Let us now consider when the condition (8) is violated and the classical formula (10) giving $W_{eq} \propto d^{1/2}$ can no longer be used. Inserting material coefficients at room temperature,[14] we obtain for TGS $d_{crit} \cong 4\text{x}10^{-5}$ cm, for $BaTiO_3$ $d_{crit} \cong 5\text{x}10^{-8}$ cm, for GMO $d_{crit} \cong 2\text{x}10^{-4}$ cm, for $Pb_5Ge_3O_{11}$ $d_{crit} \cong 7\text{x}10^{-6}$ cm. For Rochelle Salt at 0°C we get $d_{crit} \cong 1\text{x}10^{-4}$ cm and for KDP at 100 K $d_{crit} \cong 1\text{x}10^{-5}$ cm. In all these estimations we put $\sigma_w \cong 10^{-2}$ Jm^{-2} Thus for common ferroelectric samples and far from T_c the criterion (8) is satisfied; however, at present thin films are fabricated with thicknesses that are comparable to or smaller than d_{crit}. It is interesting to estimate how d_{crit} may depend on temperature. For proper ferroelectrics with a second order phase transition we expect $P_s^2 \propto (T_0-T)$, $\varepsilon_z \propto (T_0-T)^{-1}$ and $\sigma_w \propto (T_0-T)^{3/2}$ so that $d_{crit} \propto (T_0-T)^{-1}$. For improper ferroelectrics we expect $P_s \propto (T_0-T)$, $\varepsilon_z = \text{const}$ and $\sigma_w \propto (T_0-T)^{3/2}$; from here d_{crit} scales like $(T_0-T)^{-1/2}$. Thus the value of d_{crit} may be large close to the transition point where the domain structure is first formed. However, very close to T_c the dielectric nonlinearity

neglected in this paper may become essential[15]. In any case this analysis shows that d_{crit} must be critically assessed for each particular material and temperature and that experimental situations with $d \leq d_{crit}$ are not rare. Then the equilibrium pattern is expected to follow eq. (11) rather than eq. (10).

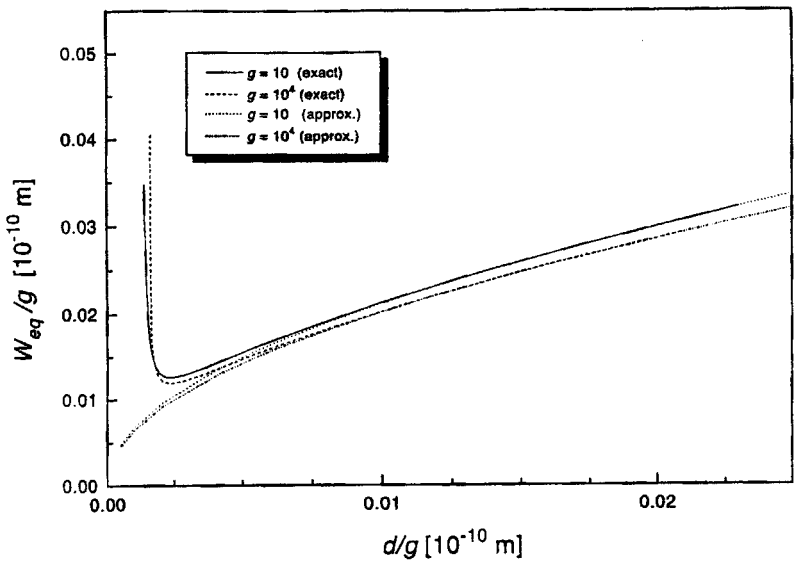

Fig.1 Example of the dependence of reduced equilibrium domain width W_{eq} on reduced sample thickness d. Calculated for arbitrarily chosen parameters $\sigma_w = 5 \cdot 10^{-3}$ Jm^{-2}, $P_0 = 0.2$ Cm^{-2}, $c = 5$. Shown are exact solution of eq.(11) as well as solution based on the approximation of thick sample, for two values of the parameter g.

We now point out some basic features of the above solutions. Laminar domains are characterized by parameters A and R. Let us first treat pattern with $A = 0$ which is intuitively considered advantageous. The equilibrium value W_{eq} fulfilling eq. (11) can be determined graphically. For given values of material parameters σ_w, P_0 and c the left-hand of eqs. (11) is calculated. For a chosen value of g the right-hand side of eq. (11) is calculated numerically and presented as a plot $f(R)$. From the latter the value of R can be determined, fulfilling the equation (12), and thus also the required width W_{eq} of the equilibrium pattern. In a similar way we can generate a plot showing W_{eq} as a function of d in any range of thicknesses.

To illustrate qualitatively novel features of solutions obtained in this manner, fig.1 shows the dependences of W_{eq}/g on d/g for arbitrarily chosen values of parameters (σ_w = $5 \cdot 10^{-3}$ Jm^{-2}, $P_0 = 0.2$ Cm^{-2}, $c = 5$). The curves marked "approx." were calculated from the formula (10) valid for "thick" samples; here in the whole range of values of d the proportionality $W_{eq} \propto d^{1/2}$ is satisfied. The curves marked "exact" were obtained by graphically solving eq. (11) as described above. We see that for $d \cong d_{crit}$ the correct

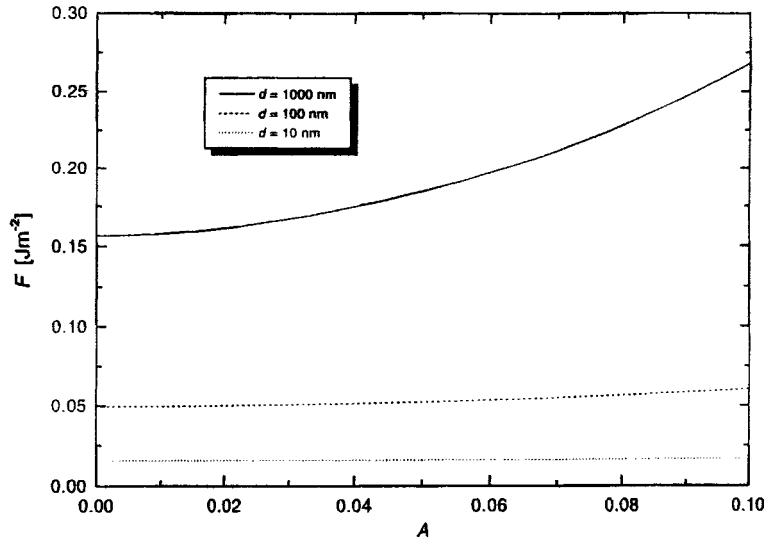

Fig.2 Energy density F as a function of the asymmetry parameter A at the point W_{eq} for different values of the thickness. Calculated for arbitrarily chosen parameters $\sigma_w = 5 \cdot 10^{-3}$ Jm^{-2}, $P_0 = 0.2$ Cm^{-2}, $c = 5$, $g = 1000$.

solution starts to depart from the approximative formula (10). These curves are almost independent of g if $g \gg 1$; this fact follows from the expansion of the function $f(g,R)$ in powers of $1/g$. On decreasing d, the value of W_{eq} reaches a minimum and begins to increase. This means that the parameter R is approaching zero. It can be shown easily that $\lim_{(R \to 0)} K(0,g,R) = 1$; thus as R tends to zero the energy of the structure approaches that of a plate capacitor. Correspondingly, the minimum of $F(W)$ is becoming exceedingly flat.

As for the asymmetry parameter A, it follows from eq. (7) that at $A = 0$ the energy F reaches minimum. Further, the function $(\partial^2 F/\partial A^2)_{A=0}$ shows that as d decreases below

d_{crit}, this minimum becomes flatter. Fig.2. gives an illustration of this fact.

Thus the behaviour of the function $F(W,A)$ around the equilibrium parameters $W = W_{eq}$ and $A = 0$ indicates that for very thin samples the total energy is approaching the energy of a plate capacitor and becomes insensitive to both parameters.

To summarize, we have shown that in ferroelectric plate-like samples the solution (10) for equilibrium domain pattern is not applicable when the sample thickness approaches d_{crit} given by eq.(8). For many ferroelectrics the value of d_{crit} lies in a range which can be easily reached far below the transition point by contemporary thin film technologies. For both proper and improper ferroelectrics d_{crit} tends to increase as the temperature T_c is approached. New formulae valid for plate of any thickness show that as the plate thickness decreases below d_{crit} the proportionality $W_{eq} \propto d^{1/2}$ no longer holds and the equilibrium domain width starts to increase. For samples with thickness $d << d_{crit}$ the domain structure becomes insensitive to electric boundary conditions and will be primarily determined by other factors.

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