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Switching Properties of Finite-Sized Ferroelectrics

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1. Introduction

The characteristic property of ferroelectric materials, which is the reversal of polarization by an external electric field, is of technological importance in device applications, particularly in nonvolatile ferroelectric random access memories (NV-FeRAMs). These binary coded NV-FeRAMs can be fabricated by using ferroelectric materials in which the polarization direction can be switched between two stable states when a minimum electric field is applied. To fabricate good quality NV-FeRAMs to meet the demands of the current market, the ability to achieve low coercive field $E_c$ (the minimum external field required to reverse the direction of remnant polarization), short switching time $t_s$ and high packing density (Scott, 2000; Dawber et al., 2005) in the memory chips are great challenges. These challenging factors are closely knitted with the underlying physics on the switching properties of ferroelectric materials. Though the subject of interest has been elucidated both theoretically and experimentally over the past sixty years and the achievements are enormous, but the challenging factors mentioned are still current. Auciello, Scott and Ramesh (1998) have explicitly outlined four main problems in NV-FeRAMs fabrication which are related to basic physics. Firstly, what is the ultimate polarization switching speed? Secondly, what is the thinnest ferroelectric layer which sustains stable polarization? Thirdly, how do switching parameters, such as coercive field, depend on frequency? Lastly, how small can a ferroelectric capacitor be and still maintain in ferroelectric phase? These are fundamental problems which should be tackled through continuous experimental and theoretical efforts.

From the theoretical perspective on this area of studies, a few models (Duiker and Beale, 1990; Orihara et al., 1994; Hashimoto et al., 1994; Shur et al., 1998) were proposed to study the switching properties of ferroelectric thin film based on the Kolmogorov-Avrami theory of crystallization kinetics (Avrami, 1939, 1940 and 1941). In these models, the authors focused on statistics of domain coalescence. Tagantsev et al. (2002) proposed another model based on the experimental work of a few groups (Lohse et al. 2001; Colla et al., 1998a; Ganpule et al., 2000). Their model also focuses on statistics of domains nucleation. Another approach, which is different from the classical nucleation reversal mechanism, is based on the Landau-type-free energy for inhomogeneous ferroelectric system as discrete lattices of electric
dipoles (Ishibashi, 1990). However, all these models neglect the surface effect, which is shown to have influence on phase transitions of ferroelectric films, and as the films get thinner the surface effect becomes more significant.

The continuum Landau free energy for a ferroelectric film, extended by Tilley and Zeks (Tilley and Zeks, 1984), incorporates the surface parameter $\delta$ (extrapolation length). Positive $\delta$ models a decrease in local polarization at surface, and negative $\delta$ an increase, with a smaller absolute value of $\delta$ giving a stronger surface effect. This model has been used to elucidate phase transition and dielectric properties of FE thin films with great success (Wang C. L. et al., 1993; Zhong et al., 1994; Wang Y. G. et al., 1994; Wang C. L. and Smith, 1995; Ishibashi et al., 1998; Tan et al., 2000; Ong et al., 2001; Ishibashi et al., 2007) and the results of phase transition and dielectric properties of ferroelectric thin films obtained are well accepted. In this chapter, we outline the progress of theoretical and experimental work on switching phenomena of ferroelectric thin films, and the main focus is on the results of switching properties of ferroelectric thin film obtained from the Tilley – Zeks continuum Landau free energy and Landau-Khalatnikov (LK) dynamic equation (Ahmad et al., 2009; Ong and Ahmad, 2009; Ahmad and Ong, 2009; 2011a; 2011b). The surface effects, represented by $\pm \delta$ on properties of polarization reversal, namely, coercive field $E_c$ and switching time $t_s$ will be discussed (Ahmad et al., 2009). For positive $\delta$, $E_c$ and $t_s$ decrease with decreasing $|\delta|$, while for negative $\delta$, $E_c$ and $t_s$ increase with decreasing $|\delta|$. Strong surface effects represented by smaller $|\delta|$ are more profound in thin ferroelectric films. As the film size increases, the delay in switching at the centre relative to switching near the edges is more remarkable for systems of zero or small polarization at the edges ($\delta \approx 0$). It is found that the dipole moments at the centre and near the edges switch almost together in small-sized systems of any magnitudes of $\delta$. (Ong et al., 2008a; 2008b). We also elucidated the phenomena of polarization reversal of second-order ferroelectric films, particularly the characteristics of hysteresis loops by an applied sinusoidal field. It is shown that at a constant temperature, the size of hysteresis loops increases with increasing film thickness for $\delta > 0$ and the reverse is true for $\delta < 0$. For a film of fixed thickness, the size of hysteresis loop decreases with increasing temperature for cases of $\delta > 0$ and $\delta < 0$. We have demonstrated that the effect of magnitude of the applied field on the hysteresis loops is similar to the experimental results (Ong and Ahmad, 2009). Our numerical data also show that switching time $t_s$ is an exponential function of the applied field and the function implies that there is a definite coercive field in switching for various thicknesses of FE films (Ahmad and Ong, 2011b). Lastly, since in reality, ferroelectric thin films are fabricated on conductive materials (such as SrRuO$_3$) as electrodes, hence, we shall include the effects of misfit strain on switching phenomenon of epitaxial film of BaTiO$_3$ (Ahmad and Ong, 2010a) and conclude with some remarks.

2. Ferroelectric thin film and Tilley-Zeks model

The behaviour of ferroelectric thin films is significantly different from that of the bulk. The arrangement of atoms or molecules at the surface is different from that of the bulk material. Due to the process of surface assuming a different structure than that of the bulk, which is known as surface reconstruction, polarization at the surface is not the same as that in the bulk; and it affects the properties of the material. This so called surface effect may have little influence on the properties of material if the material is thick enough. However, when the
material becomes thinner, the surface effect becomes significant. The demand by current technological applicants on material thickness of ferroelectric thin film is now in the range of nano-scale. Hence, surface effect in ferroelectric thin film is a significant phenomenon and how it can affect switching must be understood.

The Landau free energy for a ferroelectric film, extended by Tilley and Zeks (Tilley and Zeks, 1984), incorporates the surface parameter $\delta$ (also named the extrapolation length) and for convenient, we named it TZ model. Positive $\delta$ models a decrease in local polarization at the surface, and negative $\delta$ an increase; with a smaller absolute value of $\delta$ giving a stronger surface effect. This is important since both forms of behavior have been observed in experiments on different materials. With this surface parameter $\delta$, the inherent material properties at the surfaces of a ferroelectric film which can be either of the two cases are explained. This Landau free energy is given by

$$F = \frac{L}{2S} \left[ \frac{\alpha}{0} \left( \frac{p^2}{2} + \frac{\beta}{4} p^4 + \frac{\kappa}{2} \left( \frac{dP}{dz} \right)^2 \right) dz + \frac{\kappa}{2\epsilon \delta} \left( \frac{p^2}{2} + p^2 \right) \right],$$

(1)

where $S$ is the area of the film with plane surfaces at $z = \pm L/2$ and $P_z = P(\pm L/2)$. $\alpha$ is temperature dependent, taken in the form $\alpha = \alpha_0(T - T_{c0})$ with $T_{c0}$ the critical temperature of the bulk material and the constants $\alpha_0, \beta$ and $\kappa$ are positive. $\epsilon_0$ is the dielectric permittivity of the material and the $\kappa$ term inside the integral in Eq. (1), represents the additional free energy due to spatial variation of $P$. Whereas the $\kappa$ term outside the integral in Eq. (1), represents the free energy due to the surface ordering.

### 3. Phase transition in ferroelectric thin film

We (Ong et al., 2000; 2001) reinvestigated the TZ model and obtained much simpler expressions, compared with previous work (Tilley and Zeks, 1984), for the polarization profiles of ferroelectric thin films in Jacobian elliptic functions for both positive and negative $\delta$. Variation of Eq. (1) about the equilibrium form $P(z)$ shows that this satisfies the Euler-Lagrange equation (Ong et al., 2001)

$$\frac{\alpha}{\epsilon_0} p + \frac{\beta}{\epsilon_0^2} p^3 + \frac{\kappa}{\epsilon_0} \frac{d^2P}{dz^2} = 0,$$

(2)

with the following boundary conditions:

$$\frac{dP}{dz} = \pm \frac{p}{\delta} \quad \text{at} \quad z = \pm L/2.$$

(3)

It follows from Eq. (3) that if the extrapolation length $\delta$ is positive, $P(z)$ decreases near the surface, and if it is negative, $P(z)$ increases. In consequence, the critical temperature $T_c$ of the film is reduced below $T_{c0}$ for positive $\delta$ and increased for negative $\delta$. The first integration of Eq. (2) leads to

$$\frac{dP}{dz} = \pm \left( \frac{\beta}{2\kappa} \right)^{\frac{1}{2}} \left[ \frac{1}{\epsilon_0} p^4 + \frac{2\alpha}{\epsilon_0 \beta} p^2 + \frac{4G}{\beta} \right]^{\frac{1}{2}},$$

(4)
where $G$ is the constant of integration. The extremum of $P(z)$ is at $z = 0$ so that the central value $P(0)$ is a solution of the quadratic equation corresponding to $dP/dz = 0:

\[ P^4 + \frac{2e_0\alpha}{\beta}p^2 + \frac{4e_0^2G}{\beta} = \left(p^2 - p_1^2\right)\left(p^2 - p_2^2\right) = 0, \quad (5) \]

where the roots $P_1$ and $P_2$ are introduced for later use; and the roots are such that $P_2^2 > P_1^2$. It follows from Eq. (5) that the product $P_2^2P_1^2$ has the same sign as $G$ and it will be seen that while $P_2^2$ is always positive for both signs of $\delta$, in the case of $\delta > 0$, there is a temperature interval in which $G$ and therefore $P_2^2$ are negative.

The $P$ integral resulting from Eq. (4) can be expressed by inverse elliptic functions so that ultimately $P(z)$ is expressed in terms of an elliptic function. The detailed forms depend on the sign of $\delta$.

In the case of $\delta > 0$, it can be shown that $0 < G < a_0^2/4\beta$ so that, $P_1^2$ and $P_2^2$ are both positive. Since positive $\delta$ leads to a decrease of $P(z)$ at the surface of the film we have the inequalities $0 < P(z) < P_1 < P_2$. The central value $P(0)$ is the maximum value of $P(z)$ and is in fact equal to $P_1$. The expression for $P(z)$ is

\[ P(z) = P_1 \operatorname{sn}(K - z / \xi, \lambda), \quad (6) \]

in standard notation for elliptic functions. The modulus $\lambda$ is given by $\lambda = P_1 / P_2$; $K = K(\lambda)$ is the complete elliptical modulus and the scale length $\xi$ is

\[ \xi = \sqrt{2e_0^2\kappa / (\beta^{1/2}P_2^2)}. \quad (7) \]

In the case of $\delta < 0$, the analytical work is complicated because the expression for polarization profile depends on temperature range. In the temperature interval $T_0 < T < T_c$ in which $G < 0$ and $P_1^2 < P_2^2 < P_2^2(z)$. In the interval where $G$ is negative, $P(z)$ takes the form,

\[ P(z) = \frac{P_2}{\operatorname{cn}(z / \xi, \lambda_1)} \quad (8) \]

where $\lambda_1 = -P_1^2 / (P_2^2 - P_1^2)$ is the modulus, and the scaling length is given by

\[ \xi^2 = \frac{2e_0^2\kappa}{\beta(P_2^2 - P_1^2)}. \quad (9) \]

While for the temperature interval $T < T_0$, the parameters satisfy the inequalities $G > 0$, $0 < P_1^2 < P_2^2 < P_2^2(z) 0$, and the polarization profile is found to be

\[ P(z) = \frac{P_2}{\operatorname{sn}(K - z / \xi, \lambda)}. \quad (10) \]

Similarly, the modulus $\lambda$ is given by $\lambda = P_1 / P_2$; $K = K(\lambda)$ is the complete elliptical modulus. These simpler analytical expressions, describing the polarization profile of a
ferroelectric film with either positive or negative $\delta$, are important in helping the study of switching properties of ferroelectric film as well as size and surface effects on properties of phase transition. In the case of negative $\delta$, there is no size induced phase transition; but for positive $\delta$ we have found an expression for the minimum thickness $L_C$ of ferroelectric film to maintain ferroelectric properties. This minimum thickness is a function of $\delta$ and temperature $T$ as shown below:

$$L_C(T) = 2\frac{\xi_C}{\delta} \tan^{-1}\left(\frac{\xi_C}{\delta}\right).$$

(11)

$\xi_C$ is the correlation length at critical temperature given by $\xi_C = \xi_0 / \sqrt{T_{C \parallel} - T_C}$ and $\xi_0$ is the zero temperature of correlation length. $T_C$ and $T_{C \parallel}$ are the critical temperatures of the film and bulk, respectively. Eq. (11) provides hints to the experimentalists that minimum thickness of ferroelectric film is dependent on the critical temperature, as well as $\delta$; hence these values are material dependent.

We have also presented new thermodynamic functions, the entropy and specific heat capacity, for ferroelectric films with both cases of $\pm \delta$. These thermodynamic functions provide useful information that the phase transitions in both cases of $\pm \delta$ are stable (Ong et al., 2001). The reports in the literature on the claims of possible surface state in the case of negative $\delta$ (Tilley and Zeks, 1984) and film transition can be first order even if its bulk is second order (Qu et al., 1997) had caught our attentions and after careful investigation, we found that there is no surface state in the negative $\delta$ case and the film transition is always second order as in the bulk transition.

4. Formalism for switching in ferroelectric thin films

Theoretical and experimental work on switching phenomena of bulk ferroelectric began about half a century ago. The interest in this research area has further been extended to ferroelectric thin films; and the interest has not waned even up to these days because of the advancement in thin film fabrication technology, where higher quality and more reliable ferroelectric thin films can be fabricated; thus making the applications of ferroelectric thin films in microelectronic devices and memories (Uchida et al., 1977; Ganpule et al., 2000) more reliable. Current theoretical and experimental researches in polarization reversal in ferroelectric thin films are focused on phenomena related to effects of size and surface in thin films on switching time and coercive field (Ishibashi and Orihara, 1992; Wang and Smith, 1996; Chew et al., 2003).

From the literature, several theoretical models based on a Landau-typed phase transition have given good explanations on switching behaviours of mesoscopic ferroelectric structures (Ishibashi and Orihara, 1992; Wang and Smith, 1996); and some of the predictions concerning size on switching behaviours by Landau-typed models agree well with experimental observations. However, the detailed understanding of surface effect on ferroelectric films under the applied electric field is still inadequate, but understanding of surface effect is important for the overall understanding on the switching behaviours of ferroelectric films. Thus, we extended the TZ model for ferroelectric thin films given in Eq. (1) by adding in the energy expression a term due to electric field ($-EP$)
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\[ F = \frac{L}{2} \int_{-L/2}^{L/2} \left[ \frac{\alpha}{2\epsilon_0} p^2 + \frac{\beta}{4\epsilon_0^2} p^4 + \frac{\kappa}{2\epsilon_0} \left( \frac{dp}{dz} \right)^2 - EP \right] dz + \frac{\kappa}{2\epsilon_0} \left( \frac{p^2 + p^2}{\delta^2} \right) \]

(12)

and minimization of Eq. (12) by variational method shows that the polarization satisfies the Euler Lagrange (EL) equation

\[ \frac{\alpha}{\epsilon_0} p + \frac{\beta}{\epsilon_0^2} p^3 - E = \frac{\kappa}{\epsilon_0} \frac{d^2 p}{dz^2} = 0, \]

(13)

with the following boundary conditions:

\[ \frac{dp}{dz} = \pm \frac{p}{\delta} \quad \text{at} \quad z = \pm L/2. \]

(14)

The Landau-Khalatnikov dynamic equation is used to study switching behaviours in ferroelectric thin films (Ahmad et al., 2009; Ong et al., 2008a; 2008b; 2009; Ahmad and Ong, 2011b), and it is simplified to the form as follow:

\[ \gamma \frac{\partial P}{\partial \tau} = -\frac{\delta \left( F / S \right)}{\delta P} = -\frac{\alpha_0 (T - T_{c0})}{\epsilon_0} p + \frac{\beta}{\epsilon_0^2} p^3 + \frac{\kappa}{\epsilon_0} \frac{d^2 P}{dz^2} + E, \]

(15)

where \( \gamma \) is the coefficient of viscosity which causes a delay in domain motion and \( \tau \) is the time. In this equation, the kinetic energy term \( m \partial^2 P / \partial \tau^2 \) is ignored, since it only contributes to phenomenon in the higher frequency range. The applied electric field \( E \) can be a static step field or a dynamic field. We obtained the equilibrium polarization profile \( P(z) \) from the elliptic function derived Eq. (1), and this profile is symmetric about the film centre \( z = 0 \). The initial polarization profile of the ferroelectric film at \( t = 0 \) is obtained from solving Eq. (4) for the elliptic functions derived by Ong et al. (2001). In all our simulations, the initial polarization in the film is switched from its negative value. By solving Eq. (15) using the Runge-Kutta integration by finite difference technique, we obtained the reversal of polarization. The reversal of polarization is studied by applying a stepped electric field and the hysteresis loops are obtained by sinusoidal field respectively, as these fields are usually used in experiments. The applied stepped field is of the form

\[ E = E_0 f(\tau), \]

(16)

where \( f(\tau) \) is a usual step-function defined as

\[ f(\tau) = \begin{cases} 1 & \text{for } 0 \leq \tau < \tau_0, \\ 0 & \text{for } \tau_0. \end{cases} \]

(17)

\( \tau_0 \) is the time taken when the field is switched off and \( E_0 \) is the maximum applied electric field. The sinusoidal field in the reduced form is
$e = e_0 \sin(\omega \tau_e)$, \hspace{1cm} (18)

where $e_0$ is the amplitude and $\omega$ is the angular frequency. The dimensionless formulations used in the calculations are obtained by scaling Eqs. (12) to (16) according to the way discussed in our articles. All parameters listed in the equations above are scaled to dimensionless quantities.

We let $\xi = z / \xi_0$ with $\xi_0^2 = \kappa / \alpha_0 T_{C0}$ and $\xi_0$ corresponds to the characteristic length of the material. Normally, $\xi_0$ is comparable to the thickness of a domain wall. $I$ is the dimensionless form of thickness $L$ scaled to $\xi_0$. We have temperature $T$ scaled as $t = T / T_{C0}$, $p = P / P_0$ with $P_0^2 = \rho_0 \kappa T_{C0} / \beta$ and $e = E / E_C$ with $E_C^2 = 4\alpha_0^2 T_{C0}^3 / (27 \kappa_0 \beta)$. The global order parameter is the average polarization of the film defined as

$$\bar{p} = \frac{1}{l} \int_{-l/2}^{l/2} p(\xi) \, d\xi.$$ \hspace{1cm} (19)

### 5. Polarization evolution in ferroelectric films

Surface condition due to $\delta$ and size of ferroelectric films affect the switching profiles of ferroelectric films. A ferroelectric film with zero $\delta$ means the surface polarization is zero at both surfaces of the film. When a positive electric field $E$ is applied on ferroelectric films with zero and non-zero $\delta$, various stages of switching profiles are shown in Fig. 1 and Fig. 2, respectively, for temperature $T = 0.6 T_{C0}$. The starting equilibrium polarization profile is set at negative at time $t = 0$; and the profile is switched over to positive state by the applied electric field $E$ until it is completely saturated. In a thin ferroelectric film (Fig. 1), switching at the surface and at the centre is almost the same irrespective of either zero or non-zero $\delta$.

![Polarization profiles](image)

Fig. 1. Polarization profiles during switching, at various time in term of fraction of the total time $\tau_S$ to reversed the profile, at temperature $T = 0.6 T_{C0}$, applied field $E = 0.83 E_C$, for thickness $\zeta = 3.3$: (a) $\delta = 0$; (b) $\delta = 2.0$. The number at each curve represents time taken to reach the stage in term of fraction of $\tau_S$. (Ong et al., 2008b)

For thick films, surface switching takes place relatively faster than the interior of the films (Fig. 2); the reversal of polarization begins near the surfaces first, and then goes on to the
centre, as shown in Figs. 2(a) and (b). This indicates that the domain wall is formed near the surfaces, followed by a domain wall movement towards the centre. Hence, when the film becomes thicker, the delay in switching at the centre of the film is more distinct compared with the delay nearer the film surfaces. In term of domain wall movement in the film, it obviously takes a longer time for a domain wall to move from the surface to the centre for a thick film than a thin film. However, the delay in switching at the centre is more remarkable in the zero-δ film as the film thickness increases. (Ong et al., 2008a; 2008b).

Fig. 2. Polarization profiles during switching, at various time in term of fraction of the total time $\tau_5$ to reversed the profile, at temperature $T = 0.6T_c$, applied field $E = 0.83E_c$, thickness $\zeta = 7.0$ for (a) $\delta = 0$; (b) $\delta = 2.0$. The number at each curve represents time taken to reach the stage in term of fraction of $\tau_5$. (Ong et al., 2008b)

Fig. 3. Polarization profile during switching at various time in term of fraction of the total time $\tau_5$ to reversed the profile, for film thickness $\zeta = 5.4$, $\delta = -2$, $E = 1.50E_c$, $T = 0.0$. The number at each curve represents time taken to reach the stage in term of fraction of $\tau_5$. (Ong et al., 2008b)
The general trend in polarization reversal of a film, irrespective of value of \( \delta \), shows clearly that total time \( \tau_s \) to reverse the profile is longer as the film gets thicker. In the case of negative \( \delta \) for thick film, switching of dipole moments at the film centre takes place before that at the film surface, which is obviously shown in Fig. 3. This phenomenon is contrary to what we observed in a ferroelectric film with positive \( \delta \) (Fig. 1 and Fig. 2); that is switching happens at surface before the film centre. For a ferroelectric film with negative \( \delta \) the polarization at the surfaces are greater than that at the centre.

6. Coercive field and switching time in ferroelectric films

The basic understanding of properties of thickness and surface dependence of switching time and coercive field in switching of ferroelectric materials is of great importance to the application of FE thin-films in non-volatile memories, for example the ferroelectric random access memory (FERAM). From the results of earlier work on switching behaviour of single crystal barium titanate (BaTiO\(_3\)) (Merz, 1954; 1956; Miller and Savage, 1958; Stadler, 1958; Fatuzzo, 1962), a few empirical formulations which illustrate the dependence of switching time on applied electric field in switching of ferroelectric crystals are cited. For instance, in 1954 Merz reported that switching time \( \tau_s \) is proportional to \( \frac{1}{E} \), where \( E \) is an applied electric field and \( E_c \) is the coercive field strength. A couple of years later, Merz (1956) showed that switching time \( \tau_s \) versus applied electric field \( E \) for low electric field (<10 kV/cm) in single crystal BaTiO\(_3\) is an exponential function \( \tau_s = \tau_\infty \exp(\alpha / E) \), where \( \tau_\infty \) is the switching time for an infinite field strength and \( \alpha \) is the activation field. This empirical formulation does not imply a definite coercive field in the switching of a single crystal BaTiO\(_3\).

A similar empirical formulation for domain wall velocity as an exponential function of applied electric field \( E \) was proposed by Miller and Savage (1958); and their formulation also does not imply a definite coercive field in the switching of ferroelectric crystals. From their formulations, we can deduced that when an electric field \( E \), however small is applied to a sample, it is just a matter of time; the dipole moments in the sample will ultimately be switched. Around the same period of time, Stadler (1958) extended Merz’s work on a single crystal BaTiO\(_3\) for high applied field, ranging from 10 kV/cm to 100 kV/cm; and he found that switching time \( \tau_s \) is related to an applied electric field \( E \) according to a power law: \( \tau_s = kE^n \), where \( k \) is a constant and \( n \) is equal to about 1.5. Later, Fatuzzo (1962) proposed a combination of the power law and the exponential relation between switching time and applied electric field in his analytical calculations based on the assumption of sideways movement of the domain wall. Again, this new formulation shows that there is no definite coercive field in the switching of FE materials. Lately, Kliem and Tadros-Morgane (2005) have shown that their experimental data on extrinsic switching time \( \tau_{ex} \) (time taken when the polarization has reached 90% of its maximum value) versus applied electric field \( E \) for various thicknesses of ultra-thin PVDF Langmuir-Blodgett films do not fit the formula \( \tau_s = \tau_\infty \exp(\alpha / E) \) or the intrinsic switching formula \( 1/ \tau_{in} = (E / E_c - 1)^2 (1 - (T - T_0) / (T_1 - T_0))^2 \) derived by Vizdrik et al. (2003). In the later formula, \( \tau_{in} \) is the switching time, \( T_0 \) is the phase transition temperature and \( T_1 = T_0 + 3B^2 / (4\gamma \chi) \), where \( B \), \( \gamma \) and \( \chi \) are the Landau parameters. This formula indicates
that there is a definite coercive field for PVDF material in the intrinsic homogeneous switching. Finally Kliem and Tadros-Morgane (2005) showed a best fit of their experimental data by a formulation \( \tau_0 = \tau_{00} \exp(-\eta E / E_c) \) with \( \tau_{00} \) and \( \eta \) depending on sample thickness and \( E_c \), the coercive field obtained from the hysteresis loop. On the other hand, evidence of a definite coercive field in the switching of FE materials are reported from experimental results, for example in sodium nobate (NaNbO\(_3\)) (Pulvari, 1960; Miller et al., 1962). Another example is from Fousek and Brezina (1960; 1964), who reported that when the applied voltage on BaTiO\(_3\) is below a certain threshold value, no domain wall movement has been observed; but when the applied field is above a threshold field, domain wall movement is detected to be out of phase with the applied voltage. Further more, Fang and Fatuzzo (1962) also reported the occurrence of coercive field on bismuth titanate (Bi\(_4\)TiO\(_{12}\)). In later measurements on good single crystals by Pulvari (1962, 1964 cited in Fatuzzo and Merz, 1967) also indicated there was definite coercive field in the switching and it was confirmed by Cummins (1965). More recent evidence of definite coercive field observed experimentally was reported in the switching kinetics of ferroelectric Langmuir-Blodgett films of 70% vinylidenefluoride and 30% trifluoroethylene copolymer with thickness up to 15 nm (Vizdrik et al., 2003).

There are a couple of theoretical models proposed to study the switching behaviours of FE films; the Kolmogorov-Avrami-Ishibashi theory (Ishibashi and Orihara, 1992a; 1992b; Ishibashi, 1993) which is originated from a model of crystal growth (Kolmogorov, 1937; Avrami, 1939, 1940, 1941) and the Landau-typed model (Ishibashi, 1990; 1992; Wang and Smith, 1996). In the later model, one of the authors (Ishibashi, 1992) fitted his numerical data by the formula \( \tau_\infty = \tau_{\infty 0} \exp(\alpha E / E_c) \). While the other authors (Ishibashi, 1990; Nagaya and Ishibashi, 1991) fitted their numerical data by the empirical formulations of Merz (1954, 1956) and Stadler (1958) mentioned above. However, they have not mentioned which formulation gives the best fit. With these developments in the area of research in switching phenomena of FE materials especially in FE thin films, we are motivated to use Landau Devonshire (L-D) free energy of a FE film proposed by Tilley and Zeks (T-Z) (1984) and Landau Khalatnikov equation of motion to look into the dependence of switching time on applied electric field. We have also investigated the effects of thickness on coercive field and switching time and made comparisons with some experimental findings. From the literature, some experimental results (Hase and Shiosaki, 1991; Fujisawa et al., 1999) show that coercive field increases with decreasing film thickness while others (Wang et al., 2002; Yanase et al., 1999) claim the reversed; and these contradictions are explained by the effects of negative and positive values of extrapolation length, \( \delta \) in the TZ model (Tilley and Zeks, 1984; Ong et al., 2001; Ahmad and Ong, 2009).

There are several definitions of switching time in the literature (Fatuzzo and Merz, 1967; Ishibashi, 1990; 1992; Nagaya and Ishibashi, 1991; Omura and Ishibashi, 1992; Katayama et al., 1993); however, in our case, the switching time \( \tau_\infty \) is taken as the time taken when the current has reached 10% of its maximum value (Ahmad and Ong, 2009, Omura and Ishibashi, 1992; Katayama et al., 1993) similar to what we have done in our previous work\(^{32}\). The variation of switching time \( \tau_\infty \) in a film of thickness \( l = 2.0 \) and extrapolation length \( \delta = 3.0 \) at temperature \( t = 0.0 \), with applied field \( e \) is shown in Fig. 4. The triangular markers indicated in Fig. 4 represent the numerical data obtained from our calculations. To investigate whether coercive field truly exists in ferroelectric thin films, curves based on
three chosen formulations are drawn to fit the data. The solid-line is drawn based on the formulation by Merz (1954)

\[
\tau_s = \frac{k}{(e - \alpha)} ,
\]

where \( e \) is the applied field and \( k \) and \( \alpha \) are constants. From this solid-line curve, the switching time diverges at \( e = \alpha \) where \( \alpha \) is the sort of coercive field; and the FE film can not be switched for field lower than the coercive field \( \alpha \). Secondly, we have used the empirical formulation (Merz, 1956; Miller and Savage, 1958),

\[
\tau_s = \tau_0 \exp(\beta / e)
\]

where \( \tau_0 \) and \( \beta \) are constants, to fit our calculated data; and the dashed line in Fig. 4 represents this formulation. Finally, we fit our data by the following formulation:

\[
\tau_s = \tau_0 \exp[a / (e - b)]
\]

where \( \tau_0 \), \( a \) and \( b \) are constants. The dotted-line curve in Fig. 4 is drawn from Eq. (22) and it shows that switching time \( \tau_s \) diverges when the applied electric field \( e \) approaches \( b \). In order to determine the best fit to our calculated data among the three formulations plotted in Fig. 4, a regression analysis, tabulated in Table I, was carried out for each fitting.
Table I. Regression analysis of curve fittings for the numerical data shown in Fig. 4

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Regression factor, $R$</th>
<th>$\sqrt{R}$</th>
<th>Standard error</th>
<th>Values of coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_s = k / (e - \alpha)$</td>
<td>0.9550</td>
<td>0.9119</td>
<td>1.5573</td>
<td>$k = 0.433$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\alpha = 0.579$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\tau_0 = 6.278$</td>
</tr>
<tr>
<td>$\tau_s = \tau_0 \exp[a / (e - b)]$</td>
<td>0.9891</td>
<td>0.9783</td>
<td>0.7753</td>
<td>$a = 0.014$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$b = 0.577$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\tau_0 = 0.793$</td>
</tr>
<tr>
<td>$\tau_s = \tau_0 \exp(\beta / e)$</td>
<td>0.9305</td>
<td>0.8658</td>
<td>1.9225</td>
<td>$\beta = 2.067$</td>
</tr>
</tbody>
</table>

Based on the regression factors obtained, we find that our simulated data are best fitted by Eq. (22) with the highest regression factor of 0.99. To ascertain this fact, a plot of $\ln \tau_s$ versus $1/e$ from our data is shown as the inset (a) of Fig. 4, where $\tau_s$ diverges at the value corresponds to $b$ in the equation which is the presumed coercive field. While inset (b) of Fig. 4, which is also plotted from our data, shows the reciprocal switching time $1/\tau_s$ versus electric field $e$, where the reciprocal switching time decreases precipitously towards zero when the field decreases towards the presumed coercive field $b$. The same trend of $1/\tau_s$ versus electric field $e$ for PVDF Langmuir-Blodgett films is shown by Vizdrik et al. (2003).

Figs. 5 (a), (b) and (c) show the plots of calculated data for switching time $\tau_s$ versus applied field $e$ in triangular markers when the film has negative extrapolation length $\delta$. In each of these plots, a lined curve is drawn to represent the three formulations we have discussed in the previous paragraph, respectively. The electric field dependence of switching time is analyzed statistically and the regression factors for the curves to fit the data are compared as shown in Table II. From the analysis, it has again shown that switching time versus applied field for a film with negative extrapolation length $\delta$ follows the same formulation given by Eq. (22). Other than the two examples given in Figs. 4 and 5 and Tables I and II, we have also fitted other calculated data for various thicknesses and values of $\delta$ by the formulations mentioned above; and we have found that the formulation given in Eq. (22) gives consistently the highest regression factor for various film thicknesses and extrapolation lengths compared with the other two formulations. Hence, a thin ferroelectric film has a definite coercive field and the switching time is an exponential function of electric field $e$, which may be in the form suggested by Eq. (22).

In order to illustrate how switching time $\tau_s$ of a ferroelectric film depends on film thickness and surface order parameter more explicitly, graphs of $\tau_s$ versus thicknesses $l$ for films with positive $\delta$ and negative $\delta$ are plotted respectively in Figs. 6 and 7. Fig. 6 shows that switching time increases monotonically with increasing film thickness for films with positive $\delta$’s. The increased in switching time from thickness close to critical thickness is steep and as the film becomes thicker, the increased in switching time becomes gradual. Indication of critical thickness in Fig. 6 corresponds with the fact that a ferroelectric film of positive $\delta$ surface property, ceases to behave as ferroelectric when the film thickness falls below the critical thickness. For thin films, Fig. 6 also shows that surface parameter
significantly increases with increasing positive $\delta$, but this increasing trend becomes less significant when film becomes thick; and it approaches the limit of a bulk case when the film is thick enough.

Fig. 5. Switching time $\tau_s$ versus applied electric field $e$ for film thickness $l = 2.0$, extrapolation length $\delta = -3$, and $t = 0.0$. The triangular markings in (a), (b), and (c) represent the numerical data. The data are fitted by $\tau_s = \tau_0 \exp(a/(c-b))$ in (a), $\tau_s = k/(e-\alpha)$ in (b) and $\tau_s = \tau_0 \exp(\beta/e)$ in (c). (Ahmad and Ong, 2011b)

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Regression factor, $R$</th>
<th>$\sqrt{R}$</th>
<th>Standard error</th>
<th>Values of coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_s = k/(e-\alpha)$</td>
<td>0.9711</td>
<td>0.9430</td>
<td>1.9225</td>
<td>$k = 1.9439$; $\alpha = 1.5643$</td>
</tr>
<tr>
<td>$\tau_s = \tau_0 \exp[a/(c-b)]$</td>
<td>0.9931</td>
<td>0.9863</td>
<td>0.9458</td>
<td>$\tau_0 = 3.3300$; $a = 0.1883$; $b = 1.5405$</td>
</tr>
<tr>
<td>$\tau_s = \tau_0 \exp(\beta/e)$</td>
<td>0.8947</td>
<td>0.8005</td>
<td>3.5973</td>
<td>$\tau_0 = 0.0011$; $\beta = 16.5115$</td>
</tr>
</tbody>
</table>

Table II. Regression analysis of curve fittings for the numerical data shown in Fig. 5
In negative $\delta$ case, Fig. 7 shows that $\tau_s$ becomes infinitely large for ultra-thin films. Switching time decreases significantly as film thickness increases from ultra-thin state; subsequently, the decrease in $\tau_s$ becomes gradual and approaches the limiting value when the film thickness reaches the bulk thickness. In general, a strong surface effect in film with positive of negative $\delta$ corresponds to small magnitude of surface parameter $|\delta|$. Hence, in the case of negative $\delta$, switching time decreases with increasing magnitude of surface parameter $|\delta|$ (Fig. 7) and this surface effect in film with negative $\delta$ on switching time tones down when film becomes thick.

Figs. 8 and 9 show the thickness dependence of coercive field for positive $\delta$ and negative $\delta$ respectively. In Fig. 8 we find that for positive $\delta$, the coercive field decreases with decreasing film thickness; and it is consistent with the experimental results of Wang et al. (2002). Deduction from Eq. (13) and Eq. (14) shows that the initial remnant polarization decreases with decreasing thickness when the extrapolation length $\delta$ is positive; and this phenomenon agrees with the results obtained from the lattice model (Ricinschi et al., 1998). While for negative $\delta$ (Fig. 9), coercive field $e_{CF}$ increases with decreasing film thickness and the values of $e_{CF}$ are above $e_C$ of the bulk. This result is also consistent with the experimental results reported (Hase and Shiosaki, 1991; Fujisawa et al., 1999). The semi-empirical scaling law of Janovec-Kay-Dunn (JKD) on the thickness dependence of coercive field $E_c$ predicts that $E_c(d) \propto d^{-2/3}$, where $d$ is the film thickness (Dawber et al., 2003). This implies that the negative $\delta$ case of our theoretical prediction, where coercive field increases with decreasing thickness, follows the same trend as the JKD law. However, our data on coercive field versus thickness follow the exponential relationship rather than the negative power law.
It is worth giving some comments on Figs. 8 and 9. For positive $\delta$ given in Fig. 8, it is interesting to see that the coercive field has finite size behaviour similar to that of the Curie temperature (Zhong, 1994; Wang et al., 1994; Wang and Smith, 1995; Mitoseriu et al., 1996) where FE phase vanishes at certain critical thickness (Ishibashi et al., 1998). Extrapolating the three curves in Fig. 8 to meet the horizontal axis gives the critical thickness of 0.68, 0.24 and 0.04 for $\delta = 3.0$, 10.0 and 50.0 respectively. While for negative $\delta$ (Fig. 9), it is clear that there is no size-driven phase transition. For a film of given thickness, increasing value of positive $\delta$ increases the coercive field of the film. From Fig. 8, it is obvious that for a FE film of large values of positive $\delta$ and $l$ (thicker film), the coercive field approaches $1 \left( \epsilon_{CF} \rightarrow \epsilon_C = 1 \right)$, where $\epsilon_C = 1$ is the dimensionless coercive field of the bulk at temperature $t = 0.0$.

In contrary to a film with surface effect of positive $\delta$, it is clearly shown in Fig. 9 that in a thin film of small $l$ with surface effect of negative $\delta$, the coercive field of the film increases with increasing surface effect (smaller $|\delta|$). However, the influence of surface effect becomes weaker as the film becomes thicker as illustrated in Fig. 9, where the coercive fields of thick films, irrespective of magnitudes of negative $\delta$, approach the bulk coercive field. It is interesting to see that surface effect, which is parameterized by the extrapolation length $\pm \delta$ in this model, is more significant for thin films (small values of $l$); but for thick films, surface effect is weak and less significant.

Fig. 7. Switching time $\tau_s$ versus film thickness $l$ for various negative $\delta$, applied electric field $e = 25.0$, and temperature $t = 0.0$. Symbols: Triangle for $\delta = -3.0$, circle for $\delta = -10.0$ and square for $\delta = -50.0$. (Ahmad and Ong, 2011b)
Fig. 8. Coercive field $e_{CF}$ versus film thickness $l$ for various positive $\delta$, and temperature $t = 0.0$. Symbols: Triangle for $\delta = 3$, circle for $\delta = 10$ and square for $\delta = 50$. (Ahmad and Ong, 2011b)

Fig. 9. Coercive field $e_{CF}$ versus film thickness $l$ for various negative $\delta$, and temperature $t = 0.0$. Symbols: Triangle for $\delta = -3$, circle for $\delta = -10$ and square for $\delta = -50$. The dashed line is bulk coercive field $e_c = 1.0$. The inset shows the zoom in view for $l \leq 3$. (Ahmad and Ong, 2011b)
7. Hysteresis loops of ferroelectric films

Another experimental method in the elucidation of switching behaviours of a ferroelectric film is by applying a sinusoidal electric field to the film and observing the hysteresis loops. From the hysteresis loop obtained, one can find out the coercive field and the remnant polarization; hence the switching characteristics of the film. We use the TZ model, which is described in Section 2, to simulate the hysteresis loops of a ferroelectric film in the application of sinusoidal electric field. The influence of the sinusoidal electric field strength $e_0$ on the ferroelectric hysteresis loop for a ferroelectric film with positive $\delta$, at constant temperature, shows that the average remnant polarization $\bar{p}_r$ and coercive field increase with increasing $e_0$ (Fig. 10 (a)); but for thick film, only the coercive field is increased (Fig. 10(b)). This result is consistent with the experimental result (Tokumitsu et al., 1994) and the theoretical result of lattice model given by Omura et al. (1991).

The effect of the temperature $t$ on the hysteresis loop for positive and negative $\delta$’s can be observed from the curves in Figs. 11 (a) and (b). It can be seen that the system at higher temperature needs lower applied electric field $e$ to switch; and the average polarization $\bar{p}_r$ is lower at higher temperature as the system is at a state which is nearer to the phase transition. These results are consistent with experimental results given by Yuan et al. (2005); and from their studies on strontium Bismuth Titanate $Sr_2Bi0.5Ti_2O_{12}$ (SBT) which has lower density of oxygen vacancies, so the pinning of domain wall is weak. However our result is not consistent with the experimental results given by Zhang et al. (2004) on $\bar{p}_r$ where they used $Ba_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) that has high density of oxygen vacancies which tends to be trapped at the domain boundaries. The oxygen vacancies formed the domain walls pinning centres and hence reduce the number of switchable dipoles. Nevertheless, our study is consistent with the theoretical results of lattice model reported by Tura et al. (1997). Similar features of decreasing size of hysteresis loops with increasing temperature for both positive and negative signs of $\delta$ given in their results are found in Figs. 11 (a) and (b).

![Fig. 10. Hysteresis loops at $t = 0.0, \delta = 3$, $\omega = 0.08$ for various values of field strength $e_0$ : (a) 0.6, 1.0, 2.0 and $l = 1.35$; (b) 0.91, 1.0, 1.5, 2.0 and $l = 5.0$. (Ong and Ahmad, 2009)](www.intechopen.com)
The effects of thickness $l$ on hysteresis loops are illustrated in Figs. 12 (a) and (b) for positive and negative $\delta$, respectively. Fig. 12 (a) reveals that for a given positive $\delta$, coercive field $e_{CF}$ and remnant polarization $\overline{p}_r$ increases with increasing thickness and it is consistent with the experimental results by Wang et al. (2002) and Yanase et al. (1999), and also in agreement with the results obtained from the lattice model (Ricinschi et al., 1998). On the contrary, Hase et al. (1991) and Fujisawa et al. (1999) in their hysteresis loops measurements found that $e_{CF}$ decreases with increasing film thickness; and this trend of thickness dependence of $e_{CF}$ is found in Fig. 12 (b). In Fig. 12 (b), it reveals that for negative $\delta$, both $e_{CF}$ and $\overline{p}_r$ decrease with increasing thickness and these values of $e_{CF}$ are above $e_{C0}$ of the bulk. However, $\overline{p}_r$ is reported to increase with increasing thickness by Hase et al. (1991); but Fujisawa et al. (1999) reported that $\overline{p}_r$ is almost unchanged with thickness.
Surface effects of FE films are represented via the effects of positive and negative extrapolation lengths on hysteresis loop are shown in Figs. 13 (a) and (b) for positive and negative $\delta$, respectively. Both values of $c_{CF}$ and $p_r$ increase with increasing values of positive $\delta$ (Fig. 13 (a)). This effect can be explained by the increase of initial polarization profile with increasing values of positive $\delta$. It is obvious from Fig. 13 (b) that increasing $|\delta|$, which leads to decreasing surface polarization, tends to decrease $c_{CF}$ and $p_r$.

Fig. 13. Hysteresis loops for various values of $\delta$: (a) $\delta = 3.0, 10.0$ and $50.0$; (b) $\delta = -3.0, -10.0$ and $-50.0$; for $t = 0.0$, $e_0 = 3.0$, and $\omega = 0.1$. (Ong and Ahmad, 2009)

8. Summary and future work

From the analytical calculations using the TZ model for ferroelectric films, we discovered that the minimum thickness of a ferroelectric film is dependent on critical temperature and surface parameter $\delta$ and these parameters are material dependent. In our study of the intrinsic switching phenomena of a ferroelectric film, an exponential function, proposed in Eq. (22), for switching time dependence of applied electric field reveals that a ferroelectric film has an intrinsic coercive field $c_{CF}$; and this may provide a technical reference to device designers. We have also found that by increasing the film thickness, switching time $\tau_s$ and coercive field $c_{CF}$ of a film will increase for film with positive $\delta$; but these intrinsic values will decrease for film with negative $\delta$. The surface effect ($\pm \delta$) on switching time and coercive field of a film is more spectacular for thinner films. The dependence of coercive field and switching time on surface parameter $\delta$, discovered from our theory, indicates that when negative-$\delta$ materials are used in fabricating memory devices, switching time $\tau_s$ and coercive field $c_{CF}$ will increase when film thicknesses are reduced. Since nano-sized ferroelectric film is currently used in fabricating ferroelectric RAMs, the use of this type of materials, interpreted by theory as negative-$\delta$ material, in memory fabrication will be problematic. Hence, we should avoid using materials with negative $\delta$ such as triglycerine sulfate (Hadni et al., 1983) and potassium nitrate (Scott et al., 1988). Ferroelectric materials with position $\delta$ are favourable for finite-sized memory device applications; and an example of such materials is lead zirconium titanate.

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On the whole, surface parameter $\delta$ is a crucial parameter to consider when making the choice of material for thin film fabrication in memory devices. However, it is beyond the scope of a phenomenological model to predict the value of $\delta$ from material properties; the type of surface parameter $\delta$ in a material could be determined theoretically, for example, by comparison of the film critical temperature with the bulk value. When the film critical temperature is lower than the bulk critical temperature, then the material is said to be of positive-$\delta$ material; and for the negative-$\delta$ material, the opposite is true.

In our current work, we have restricted attention to materials in which the bulk phase transition is second order and the extension of our analysis to first-order materials is straightforward. The model presented here is concerned with single domain switching, as might occur in a sample of small lateral dimension. Lastly, since in reality, ferroelectric thin films are fabricated on conductive materials (such as SrRuO$_3$) as electrodes, we have included the effects of misfit strain in the study of phase transition of epitaxial film of BaTiO$_3$ (Ahmad and Ong, 2011a). The results showed that the order of transition is modified and the transition temperature has also been increased when the misfit strain is high. The extension of the model to the study of strain effect on switching phenomena is in our immediate plan and we anticipate the results from this study will provide more hints to resolve the current problems in memory device application.

9. Acknowledgments

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10. Keywords

ferroelectric, thin films, surface effect, switching properties

11. References


Ahmad M. and Ong L. H., Phase Transitions of Strained Barium Titanate Epitaxial Films, unpublished (2011a)


Avrami M., Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III, Journal of Chemical Physics, Vol 9, (1941) pp. 177-84, ISSN: 1089-7690


Fang P. H. and Fatuzzo E., Switching Properties in Ferroelectrics of the Family Bi$_4$Ba$_{m-2}$Ti$_m$O$_{3(m+2)}$, Journal of the Physical Society Japan, Vol 17, (1962) pp. 238-238, ISSN: 1347-4073


Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the characterization of ferroelectric materials, including structural, electrical and multiphysic aspects, as well as innovative techniques for modeling and predicting the performance of these devices using phenomenological approaches and nonlinear methods. Hence, the aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric system characterization and modeling, allowing a deep understanding of ferroelectricity.

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