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Theoretical and Experimental Investigation of the Polarization Switching Process of Ferroelectric Thin Films

by

Hongzhou Zhang

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
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ABSTRACT

Theoretical and Experimental Investigation of the Polarization Switching Process of Ferroelectric Thin Films

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Polarization switching of ferroelectric thin films is essential to the operation of ferroelectric memories. The switching process involves domain formation and development. To understand the process, domain nucleation close to a domain wall and within an unswitched domain of a ferroelectric thin film as well as heterogeneous nucleation have been analyzed theoretically in terms of the local field, from which a model of ferroelectric polarization switching is developed. The elongation of the switching current and the polarization relaxation are found to be due to the depolarization field. The asymmetricality of the hysteresis loop arises from the heterogeneous nucleation. The maximum switching current vs. the magnitude of external field shows two regimes: large field and small field, which correspond to nuclei-formation-dominant and domain-wall-motion-dominant switching, respectively. In addition, the coercive field is calculated as a function of film thickness.
The implications of the model are explored experimentally using Lithium niobate (LiNbO₃) thin films on p-type (111) oriented silicon substrates deposited by metallo-organic decomposition (MOD) process. The thicknesses of the films are controlled by both dilution of the precursor and the conventional technique of applying varying numbers of layers. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images show that the surface of the films is uniform. The relation between dynamic switching current and the magnitude of external pulse is investigated, and the total switched charges of the negative pulses are much larger than that of the positive pulses. The result is further verified by the hysteresis measurement. This effect is due to the asymmetrical structure of the samples. In addition, polarization suppression and the effects of the depolarization field are observed. The experimental results are compared with the results obtained from our proposed theoretical models.
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Chapter 1
Introduction

Ferroelectric materials have been widely used in many applications, some of which are surface acoustic wave (SAW) devices [1, 2], electro-optical devices [3], optical waveguides [4], mechanical actuators and detectors [5], and nonvolatile memory devices [6, 7]. The most distinguishing property of ferroelectric materials is their switchable electrical polarization, i.e., ferroelectric materials exhibit stable electrical polarization oriented in two or more directions and the direction of the polarization can be changed by an external field [8]. However, many devices using ferroelectrics do not require this property at all. It had been a de facto awkward situation for the ferroelectric research society that no actual device using ferroelectricity until the invention of the nonvolatile ferroelectric memory in 1980s, albeit such an idea of using ferroelectric materials for information storage is almost as old as the discovery of ferroelectricity. While the main reason for the slow realization of the great idea was the difficulties to fabricate ferroelectric materials with desirable qualities, the deficiency of the theories on polarization switching and polarization stability was a serious hindrance. The theoretical aspect of ferroelectric research can be preliminarily divided into two categories: understanding the origin of ferroelectricity and modeling the polarization switching. People have devoted much energy into solving the former
question, and some theories have been hitherto well accepted already [8]. Contrarily, the mechanism of polarization switching has also attracted much attention, but the answer is still vague especially in the thin-film regime.

For further development of ferroelectric memory technology, it is imperative to develop a theory of the polarization switching for ferroelectric thin films. This is the motivation of this thesis. Specifically, the objective of this thesis is to work out a theoretical model, which can be used to answer the following questions: How long does it take to reverse the polarization? How fast do the domain walls move? How large is the switching current? How do these properties depend on the external electrical field and the dimension of samples? In this thesis, based on the Avrami’s theory [9], a model of ferroelectric switching has been developed. The proposed model can be used not only to understand the dynamic behavior of polarization switching and the hysteresis phenomena but also to interpret the finite-size effect, the polarization relaxation and fatigue phenomena. On the other hand, in order to verify the validation of the theory, Lithium Niobate (LiNbO₃) thin films have been grown by metallo-organic deposition (MOD), and switching transient current and dielectric hysteresis have been measured and compared with the theory.

The thesis is developed as follows:

1. Chapter 2 contains an introduction of the ferroelectricity. This chapter gives a background that describes the static properties of ferroelectric materials such as
the ferroelectric phase stability and the equilibrium domain structure followed by a survey of previous theoretical works in the switching of ferroelectric polarization. In addition, the theories of reliable phenomena, i.e., retention, fatigue and imprint and the theories of the finite-size-effect are reviewed briefly.

2. Chapter 3 discusses some problems about the switching theories presented in Chapter 2 by considering some experimental results, which are culled from the literature.

3. In Chapter 4, a model of polarization switching is developed. The model is based on the analysis of the local field, domain nucleation and domain development. The effects of physical parameters are analyzed and special examples of using this theory in predicting retention and thickness effects are discussed with numerical results.

4. Chapter 5 presents the growth and switching properties of LiNbO$_3$ thin films. The growth procedure of LiNbO$_3$ thin films is presented. Some preliminary results of electrical properties are analyzed by using the model developed in Chapter 4.

5. In the final chapter, Chapter 6, suggestions for further research and conclusions are given.
Chapter 2
Review of Ferroelectricity and Polarization Switching

Up to now, more than 200 ferroelectric materials have been produced since the discovery of ferroelectricity [10]. A review of the history of ferroelectricity can be found in Lines and Glass's book [8]. There were three significant breakthroughs. First, in 1920, the discovery of Rochelle salt (NaKC₄H₄O₆·4H₂O) gave birth to the research on ferroelectricity. Next, in 1935 and 1938, Busch and Scherrer found a whole serials of isomorphous ferroelectric crystals, such as KDP (KH₂PO₄). Based on the analysis of those crystals, Slater presented the first microscopic model for ferroelectricity in 1941. Third, from 1945 to 1950, a class of ferroelectric oxides was reported, such as BaTiO₃, KNbO₃, KTaO₃, LiNbO₃, LiTaO₃, and PbTiO₃. The simplicity of the structure of the ferroelectric oxides made it easier to understand why they possessed this property. A phenomenological theory was originated by Mueller in 1940, and it was matured by Ginzburg and Devonshire around 1951. This phenomenological theory of ferroelectricity is referred to as the Ginzburg-Devonshire theory [8].

Besides the interest in the general theory of ferroelectricity, the properties of ferroelectric thin films and particles have attracted much attention as well. It is well known that as the dimensions of a ferroelectric material are reduced, its physical properties change, i.e., the surface energy and the depolarization field have to be taken into
account. This problem is identified as the polarization stability. Batra et al [11]-[17] published a series of papers on the depolarization field, and they concluded that the ferroelectric phase of 1-µm-thick TGS films with semiconductor electrodes is unstable [15]. However, recent experiments indicate that the thin films with nanometer thickness [18]-[21] can be ferroelectric. A theory has also been developed by Watanabe, Scott and Fridkin [22]-[25] to interpret the maintenance of the ferroelectricity.

The theories mentioned above assume homogeneous systems, whereas typical ferroelectric materials usually have several regions with different polarization directions. Inside each region, which is called a ferroelectric domain, the properties of the material are uniform. Therefore, the total polarization of the specimen is determined not only by the polarization of a single domain but also by the domain configuration. The equilibrium domain structure strongly depends on boundary conditions. Examples of these are passive layer (non-ferroelectric dielectrics layer between the ferroelectrics and the electrode) [26], grain size [27, 28], defects [29], and film inner stress [30] as well as the external field. For some simplified cases, the domain structure can be predicted theoretically by using the Ginzburg-Devonshire theory [26, 31, 32].

The switching of ferroelectric polarization refers to the dynamic process of the polarization changing from one configuration to another usually under the influence of an electrical field. The switching can be categorized as intrinsic and extrinsic processes. During the intrinsic switching, the whole sample remains uniform without
the appearance of multi-domains, while the extrinsic switching is directly related to the evolution of the domain structure. Several models have been proposed for the extrinsic process, whereas the mechanism of the intrinsic switching is still unknown. Besides the theories for bulk materials, researchers have also developed a few theories to interpret the size effects of the polarization switching for ferroelectric thin films. In addition, some switching-related phenomena, such as retention [33], fatigue [34], and imprint [35] have been investigated for decades.

The motivation of this chapter is to give the background of the thesis. This chapter is organized as follows: (1). Basic concepts of ferroelectricity are given. The hysteretic phenomena are described briefly. (2). The phenomenological theory of the ferroelectric phase transition (Ginzburg-Devonshire theory) is reviewed. (3). The phase stability and equilibrium domain structure are discussed. (4). Based on these static properties, a review of switching theories is presented. (5). Finally, the theories of size effects are given, and an introduction to the phenomena and theories of the reliabilities, i.e., fatigue, retention and imprint, is presented.

2.1 Dielectric Hysteresis [8]

The ferroelectric polarization depends on the history of the external field. The plot of the polarization vs. the external field is called a hysteresis loop. An ideal ferroelectric hysteresis is depicted in Figure 2.1 (a), where the abscissa and the ordinates are proportional to the external field and the electric displacement, respectively.
For simplicity, it is assumed that the ferroelectric material has only one polarization axis, and the external field is along the direction of the polarization. It can be seen that, given an external field, two polarization states are possible within a range of the external field. The history of the external field determines in which state the polarization can be, for example, if the external field runs from positive to negative, the values of the polarization stays on the upper branch. The value of the field, where a switchover between the two branches occurs, is called coercive field $E_c$. If the external field is large enough, the polarization becomes a single-valued function of the external field. The change of the polarization in this range is due to the linear dielectric response. The intercept by extrapolating the linear dielectric response onto the $P$-axis is called the saturation polarizations $P_s$. In addition, the values of the polarization at $E = 0$ are the remanent polarizations $P_r$. *

A hysteresis loop of an actual ferroelectric material is shown in Figure 2.1 (b). The loop is slanted and sheared. This is because the shape of the hysteresis is very sensitive to the composition and crystallinity of the material and the measurement procedure. Therefore, the quantities such as the coercive field $E_c$, the remanent polarization $P_r$, and the saturation polarization $P_s$ are material and procedure-dependent quantities. It is not meaningful to compare these quantities of two different materials or even of the same material without specifying the methodology of the measurement.

*In an ideal loop, $P_r = P_s$. 
Figure 2.1  Dielectric hysteresis: Polarization ($P$) vs. the external field ($E$) (a). Ideal hysteresis loop ($P_s = P_r$), (b). Hysteresis loop of an actual ferroelectric material, the squareness of the loop depends on specific materials, electrodes, external field and temperature.
2.2 Phase Transition

When a material transits from the \textit{paraelectric} phase (non-ferroelectric phase) to the ferroelectric phase, the crystal symmetry changes from that of a non-polar group to that of a polar group. \textit{Landau} theory is the macroscopic theory to analyze a phase transition that is accompanied with a change of the symmetry of the crystal structure [8, 36]. On the other hand, in a microscopic view, the spontaneous polarization of the ferroelectric phase arises from the fact that at least one set of ions in the crystal resides preferentially in one well of a double-well potential. When the transition occurs, if the shape of the double-well potential remains independent of temperature, it is an \textit{order-disorder} phase transition; if the shape of the well changes rapidly, the phase transition is \textit{displacive}. Although there is no clear-cut limit between the two types of transitions, it has well known that most ferroelectric phase transitions are of the displacive type [8, 37]. \textit{Landau} theory is essentially a \textit{mean-field} theory for displacive ferroelectrics [36]. A detailed review of the phenomenological theory can be found in Grindlay's book [38]. An outline of Ginzburg and Devonshire's work is presented below.

Herein, the Gibbs free energy $G$ is selected as the characteristic thermodynamic potential for an infinite homogenous ferroelectric crystal. Assuming a uniaxial ferroelectric material and using the polarization $P$ as the order parameter, the Gibbs free
energy density $G$ in the Ginzburg-Devonshire Taylor expansion is given by [25]

$$G = F - EP = F_0 + \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 - PE \quad ,$$  \hspace{1cm} (2.1)

where $F_0$ is the free energy density of the paraelectric phase when $E = 0$. $E$ is the electrical field, and the expansion coefficients ($\alpha$, $\beta$ and $\gamma$) are in general temperature and pressure-dependent. The equilibrium conditions correspond to the minimum of the free energy density, where

$$\frac{\partial F}{\partial P} = 0, \quad \frac{\partial^2 F}{\partial P^2} > 0 \quad .$$ \hspace{1cm} (2.2)

For a second-order transition, $\alpha = (T - T_0)/(C\epsilon_0)$, $\beta > 0$, and $\gamma = 0$, where $C$ is the Curie-Weiss constant. $\epsilon_0$ is the permittivity of the free space, and $T_0$ is the Curie temperature. When $E = 0$ and $T < T_0$, equation (2.2) gives two nonzero spontaneous polarizations

$$P_s = \pm \sqrt{-\frac{\alpha}{\beta}} \quad (E = 0 \quad \text{and} \quad T < T_0) \quad .$$ \hspace{1cm} (2.3)

For a first-order transition, $\alpha = (T - T_0)/(C\epsilon_0)$, $\beta < 0$, and $\gamma > 0$. Similarly, the values of the spontaneous polarization are given by

$$P_s = \pm \sqrt{-\beta \frac{1 + \sqrt{1 - t}}{2\gamma}} \quad (E = 0 \quad \text{and} \quad T < T_c = T_0 + \frac{3}{16} \frac{C\epsilon_0\beta^2}{\gamma}) \quad ,$$ \hspace{1cm} (2.4)

where $t = 4\alpha\gamma/\beta^2$. Equation (2.3) and (2.4) show that the stable polarizations of the ferroelectric materials are nonzero, in another word, according to the thermodynamic consideration, the ferroelectric materials exhibit stable polarizations.
2.3 Phase Stability

At the interface between a ferroelectric material and free space, the electrodynamic boundary condition for the electrical displacement is given by

\[ \mathbf{n} \cdot \mathbf{D}_f = \mathbf{n} \cdot (\varepsilon_0 \mathbf{E} + \mathbf{P}) = 0 \quad , \]

(2.5)

where \( \mathbf{D}_f \) is the electrical displacement on the surface of the ferroelectric. Without the external field, i.e., \( \mathbf{E} = 0 \), the boundary condition results in \( \mathbf{P} = 0 \) on the surface of the ferroelectric material. Therefore, the polarization is inhomogeneous near the surface, and two surface terms of the free energy arise from the inhomogeneity: a gradient term in the ferroelectric material proportional to \( |\nabla \mathbf{P}|^2 \), and a polarization discontinuity term proportional to \( |\Delta \mathbf{P}|^2 \) on the surface. The first factor is related to the surface energy, and the second factor is associated to the depolarization field [25, 39]. *

2.3.1 Depolarization Field [11]-[17]

The polarization discontinuity is equivalent to a layer of bounded charges on the surface. The bounded charges can be compensated by the flow of free carriers either in the ferroelectric material or in the electrode, or in both. Moreover, it is frequently observed that compensation is not complete. The value of the depolariza-

---

*In another word, the polarization of the free space vanishes, meanwhile the polarization inside the ferroelectric material is nonzero. At the interface between the ferroelectric material and the free space, the total free energy of the system (ferroelectric material and the free space) includes the surface energy of the interface, which arises from the discontinuity of the polarization.
tion field hereby collaterally depends on the interface charge density, the electrode
carrier density and the screening length, because the distributions of the free charges
are determined by these factors.

Next, we neglect the trap states in the bulk, the interface and the surface states,
and we assume the ferroelectric film is perfectly insulating, sandwiched between two
metallic electrodes, and that the structure is short-circuited. By solving Maxwell’s
equation, the depolarization field is given by

\[ E_d = -\frac{2\xi_f}{\frac{\xi_e}{d_s} + \frac{2\xi_f}{d_f}} \equiv -\frac{P}{\epsilon_f} (1 - \theta) \quad , \tag{2.6} \]

where \( d_s^2 = [\epsilon_e/(3q^2)][3/(8\pi)]^{2/3}[h^2/(m_{eff}n_0^{1/3})] \), \( d_s \) is the screening length that characterizes
the space-charge extent in the electrode *, \( d_f \) is the thickness of the specimen,
\( \epsilon_e \) and \( \epsilon_f \) are dielectric constants of the electrode and the ferroelectric, respectively,
\( q \) is the elementary charge, \( h \) is the Planck constant, \( m_{eff} \) is the effective mass of the
free carriers in the electrode, and \( n_0 \) is the average carrier density under conditions of
zero field. If one of the electrodes is a semiconductor, and all the other assumptions
hold, the depolarization field is given by

\[ E_d = -\frac{2k_B T}{qd} \ln \left[ \frac{2\pi \rho_0^2}{\epsilon_e n_i(T) k_B T} \right] \quad , \tag{2.7} \]

where \( n_i(T) = n_0 \exp[-E_g/(2k_B T)] \) is the intrinsic carrier concentration of the semiconduc-
tor electrode, which is determined by the semiconductor band gap \( E_g \). \( \rho_0 \) is

* \( d_s \) is calculated by using Boltzmann’s distribution.
the total charge per unit area in the electrode. \( k_B \) and \( T \) stand for Boltzmann's constant and the absolute temperature, respectively.

Fridkin calculated the critical thickness for the ferroelectricity of thin films with metallic electrode [25]. The contribution of the depolarization to the generalized free energy (2.1) in the ferroelectric film is given by an amount

\[
\Delta G_s = -\int_{-d_f/2}^{d_f/2} \left[ \frac{V}{d_f + d_e} P(z) + \frac{1}{2} E_d(z) P(z) \right] dz, \tag{2.8}
\]

where \( V \) is the external voltage. \( z \) is the direction normal to the film. \( d_e/2 \) is the thickness of the electrode. By minimizing the free energy, the critical thickness is given by

\[
L_c = \frac{2x \epsilon C}{T_0 \epsilon_0} d_s, \tag{2.9}
\]

where \( T_0 \) is the phase transition temperature of the bulk material. The numerical approximation shows that the critical thickness of ferroelectric oxides is about 1 nanometer and is physically unachievable [25]. However, for semiconducting electrodes, the ferroelectric phase is unstable as discussed in Watanabe's papers [22, 23]. On the other hand, it is also pointed out [22, 23] that this instability is overestimated by using the assumptions of Boltzmann's distribution for the free carriers and without considerations of the surface energy.

2.3.2 Surface energy [24, 25]

Assume that the surrounding material is nonpolar and the depolarization field is completely compensated, and that the polarization at \( z = \pm d_f/2 \) equal to the
spontaneous polarization $P_{s\pm}$, respectively. The Gibbs free energy per unit area has the form

$$G = F_0 + \frac{1}{d_f} \int_{-d_f/2}^{d_f/2} \left[ \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 + \frac{D}{2} \left( \frac{\partial P}{\partial z} \right)^2 \right] dz + \frac{D}{2\delta} (P_{s+}^2 + P_{s-}^2), \tag{2.10}$$

where $D$ is the correlation factor, and $\delta$ the decay length determining the strength of the coupling in the surface layer. The stable spontaneous polarization, again, is calculated by minimizing the total free energy. The results show that if $\delta > 0$, the spontaneous polarization decreases with decreasing the specimen thickness. The ferroelectric phase is completely suppressed for

$$L_c \simeq 0.85 \xi = 0.85 \sqrt{\frac{D}{|\alpha|}}. \tag{2.11}$$

Herein, it is difficult to estimate a value for $L_c$ since the parameters $D$ and $\alpha$ are unknown. If $\delta < 0$, the spontaneous polarization increases with decreasing thickness, a phenomenon known as superferroelectricity [24, 25], and the ferroelectric phase is stable.

### 2.4 Domain Statics

It is well known that the $180^0$ domains can lower the depolarization energy [8, 26, 32], and $90^0$ domains can relax the internal elastic strain [8, 10, 30] (Figure 2.2 depicts the structures of the $180^0$ and $90^0$ domains). On the other hand, adjacent to the domain walls, the gradient of polarization increases the total free energy, which is defined as the domain wall energy [8, 31, 32]. Therefore, whether a ferroelectric crystal
Figure 2.2  Schematic pictures of 90° domain and 180° domain. 90° domains can reduce the internal stress of ferroelectric films. 180° domains can assist in minimizing the depolarization field.

...has a single-domain or a multi-domain structure depends on which configuration can yield a minimum total free energy. In this thesis, only 180° domains are considered, because they are the most likely and important issue for the polarization switching in Lithium Niobate memory applications.

Figure 2.3 Periodic domain structure [32]: the domain width depends on the film thickness
Assume a periodic domain structure with domain width $w$, as shown in Figure 2.4. The domain width that minimizes the free energy at $E = 0$ is [32]

$$w = \frac{0.54}{P_s} [(\varepsilon_x \varepsilon_z)^{1/2} f_w d_j]^{1/2},$$

(2.12)

where $f_w$ is the domain wall energy per area, and $\varepsilon_x$ and $\varepsilon_z$ are the dielectric constants in $x$ and $z$ directions, respectively. It can be seen that the domain structure depends on the thickness of the ferroelectric film. In addition, the domain structure drastically depends on the thickness of the passive layer [26]-[28], which is a non-ferroelectric dielectric layer between the ferroelectric material and the electrodes. It is found that an abrupt transition from a single-domain to a multi-domain state occurs with the increase of the thickness of the passive layer [26].

2.5 Review of Theories of Polarization Switching

Polarization switching is vital to the operation of ferroelectric devices. The simplest ferroelectric device is the ferroelectric capacitor (FECAP) [7, 40, 41]. Another proposed device structure is the ferroelectric field-effect transistor (FEFET) [6, 42], which is a classical metal-oxide-semiconductor (MOS) transistor with the SiO$_2$ gate dielectric replaced by a thin ferroelectric film. The essential operation of these devices is to control and measure the polarization state. The dynamic switching process is hereby an important topic. Besides, to improve the reliability of the devices requires the knowledge of fatigue, retention, imprint and aging, which are phenomena related
to polarization switching. In this section, first the terminology of the polarization switching is defined. Then, theories of polarization switching are reviewed.

2.5.1 Terminologies of Polarization Switching Experiment [8]

Assume the ferroelectric exhibits a hysteresis loop as shown in Figure 2.4. At time \( t = 0 \), suppose \( P = P_r \) with external field \( E = 0 \). When a positive field is applied for a while, if the magnitude of the field is large enough, the polarization of the film will eventually become \( P = P_s \). The change of the polarization during this process is then given by

\[
P_{ns} = P_s - P_r,
\]

(2.13)

where \( P_{ns} \) is called the unswitched polarization (Figure 2.4).

![Figure 2.4](image)

**Figure 2.4** Terminologies of ferroelectric polarization switching: switched polarization and unswitched polarization

With the same initial condition, if a negative field is applied, the polarization of
the film will become \( P = -P_s \). Therefore, the change of the polarization during this process is given by

\[
P_{sd} = P_s + P_r,
\]

(2.14)

where \( P_{sd} \) is called the switched polarization (Figure 2.4). For a ferroelectric capacitor, a reading cycle measures the change of the polarization and distinguish the measured value between the two quantities, \( P_{sd} \) and \( P_{ns} \). Therefore, if \( P_r \) is defined as 1 and \(-P_r\) as 0, a positive read signal will result in a \( P_{sd} \) for state 0 and a \( P_{ns} \) for state 1.

![Figure 2.5](image)

Figure 2.5 Typical shape of switching current: the first peak is due to the RC circuit response.

Another important issue is the shape of the switching current. Figure 2.5 shows a typical curve of the switching current. The relation between the current and the
polarization switching is given by

\[ i(t) = -\frac{dP(t)}{dt} . \] (2.15)

The integral of the above equation gives either \( P_{sd} \) or \( P_{ns} \) depending on the process.

For the first approach, i.e., assuming \( P_r = P_s \), the maximum switching current \( i_{sm} \) (Figure 2.5) and the switching time \( t_s \) (Figure 2.5) is given by

\[ 2P_s = t_s i_{sm} f , \] (2.16)

where \( f = \int_0^\infty [i(t)/(i_{sm} t_s)] dt \) is determined by the shape of the switching current.

### 2.5.2 Theories of Polarization Switching

The Landau theory can be used to understand the intrinsic switching, whereas the theory is a static theory and is thus not capable of answering a dynamic question such as the switching process [25]. However, no other physical model is available for the intrinsic switching yet, and few experiments claimed the observation of the pure intrinsic switching. On the other hand, the extrinsic switching process has been studied since 1950 and a number of theories have been developed to describe the evolution of the domain structures, such as the Fatuzzo and Ishibashi model [43, 44], Ising Model and Monte Carlo method [45]-[47], discrete molecular model [48, 49], rate equation [50], Preisach model [51], and equivalent circuit model [52, 53]. Each of them can explain some aspects of the switching phenomena, but a general theory of ferroelectric polarization switching is still lacking.
1. Landau-Devonshire Theory [25],[54]-[56]

In the discussion of the phase transition, equation (2.1) shows the ferroelectric has two stable polarization states when \( E = 0 \) and \( T < T_0 \). Similarly, the values of the stable polarization in a finite external field \( E \) can be calculated. For instance, for a material undergoing a second-order phase transition, the electric field required for a given value of the polarization can be determined by taking the derivative of equation (2.1) with \( \partial G/\partial P = 0 \),

\[
E(P) = \frac{\partial F(P)}{\partial P} = -\alpha P + \beta P^3 .
\] (2.17)

The curve of polarization versus electric field can be derived by finding the inverse roots of equation (2.17). As expected, three solutions are found for a given \( E \). The hysteresis is determined for each value of \( E \) by selecting the real valued root, which is closest in value to the previous point.

2. Empirical Equations [57]-[67]

Based on the analysis of domain wall motion and the shape of the switching current, a few empirical equations for the switching current have been given in these papers published around 1960. For example, the relation between the maximum switching current \( i_{sm} \) and the external field \( E \) for a triglycine sulfate single crystal [57] is given by

\[
i_{sm} = \begin{cases} 
\exp \left[ -\frac{c(T)}{E} \right] & \text{low field} \\
\mu (E - E'') & \text{high field}
\end{cases},
\] (2.18)

where \( \mu \), \( E'' \) and \( c(T) \) are material-specific constant and \( T \) is the temperature. An-
other work [58] shows the relation between \( i_{sm} \) and \( E \) for BaTiO\(_3\) as
\[
i_{sm} = 2P_2c_1 \left[ 1 - \left( \frac{P}{P_s} \right)^2 \right] \exp \left( -\frac{c_2}{E} \right), \tag{2.19}\]
where \( c_1 \) and \( c_2 \) are empirical constants. Other equations can be found in the literature for different materials [59]-[67].

3. Fatuzzo and Ishibashi Theories [43, 44]

Because the nucleation, dilation, and coalescence of the ferroelectric domains during the polarization switching are analogous to the process of the new phase formation and development during a first-order phase transition, the extrinsic polarization switching can be analyzed in the framework of the Avrami theory, which is a theory for the kinetics of a first-order phase transition [9, 68, 69]. Based on the Avrami theory, Fatuzzo developed a theory for polarization switching in 1962 [43]. Later, Ishibashi generalized the theory using Kolmogorovs method [44]. In this section, first domain nucleation probabilities are discussed, and then the Fatuzzo and Ishibashi models are presented.

Landauer [70] calculated the nucleation probability inside an unswitched domain, \( R_t \), for a BaTiO\(_3\) single crystal plate, and found it to be given by:
\[
R_t \sim \exp \left( -\frac{\alpha}{EPK_BT} \right), \tag{2.20}\]
where \( \alpha \) is a constant. On the other hand, Miller and Weinreich [71] calculated the nucleation probability adjacent to the domain wall, \( R_w \), finding
\[
R_w \sim \exp \left( -\frac{\alpha'}{P_sEk_BT} \right), \tag{2.21}\]
where $\alpha'$ is a constant. Although $R_i$ and $R_w$ have the same form, it is found that $\alpha$ is much larger than $\alpha'$. Hence, nucleation adjacent to the domain wall is much easier than nucleation inside the domains.

![Diagram of nucleation and growth](image)

**Figure 2.6** Fatuzzo model: Domain nucleation adjacent to domain wall and forward growth. The time needed for nucleation is much shorter than the time for its growing through the whole thickness.

In Fatuzzo's model [43], it is assumed that the growth of the domain is via nucleation adjacent to the domain wall, and the formation time of a nucleus adjacent to a domain wall is much larger than the forward growth time (as shown in Figure 2.6). The polarization direction is perpendicular to the surface of the specimen taken to be an infinite single crystal. Nucleation inside unswitched domains occurs randomly. The nucleation probabilities ($R_w$ and $R_i$) are constants. According to the physical model, at time $t$, the radius of a domain that formed at time $t = 0$ is given by

$$r = r_c + (2r_c)R_w t,$$  \hspace{1cm} (2.22)
where \( r_c \) is the critical radius of the domain. The fractional area of the domain is then given by

\[
\sigma \equiv \frac{\pi r^2}{T} = \left( \frac{v_0^2}{T} \right) (t_0 + t)^2 ,
\]

(2.23)

where \( T \) is the total area of the sample, and \( v_0^2 \equiv 4\pi r_c^2 R_w^2 \), \( t_0 \equiv 1/(2R_w) \). The area expanded by the sidewise motion is given by

\[
\sigma_n \equiv \sigma - \sigma_c = \frac{\pi r^2}{T} - \frac{\pi r_c^2}{T} = \left( \frac{v_0^2}{T} \right) (t_0 + t)^2 - \frac{\pi r_c^2}{T} .
\]

(2.24)

If the coalescence of domains and the overlap of new nuclei within the existed domains are neglected, the switched area \( A \) is given by

\[
A = \int_0^t \left( \frac{dN}{ds} \right) \left( \sigma_n \right)_{t-s} + \frac{\pi r_c^2}{T} N(t) ,
\]

(2.25)

where \( N_0 \) is the number of the total latent nucleation sites and \( N(t) \) is the number of the existing nuclei. The switched area \( q \) with the domain coalescence can be calculated from \( A \) according to the Avrami theory

\[
\theta = 1 - \exp \left( - \left[ A + \frac{\pi r_c^2 N_0 R_w T}{T} + \frac{\pi r_c^2 N(t)}{T} \right] \right) .
\]

(2.26)

The switching current \( i(t) \) is then given by

\[
i(t) = 2P_s \frac{d\theta}{dt} .
\]

(2.27)

Ishibashi [44] developed the Fatuzzos theory by considering the dimensionality of the domain motion. Geometrically, there are three possible styles of the sidewise motion of a domain wall. Figure 2.7 (a) illustrates a one-dimensional case: the domain
boundary moves along one direction after the formation of plate-like nuclei. Figure 2.7 (b) illustrates a two-dimensional case: the domain boundary moves two dimensionally after the formation of cylindrical nuclei. Figure 2.7 (c) illustrates a three-dimensional case: the domain boundary moves three dimensions after the formation of a spherical nucleus. In addition, two categories of domain nucleation are considered in the model: constant nucleation rate during switching (Fatuzzos case) and latent nuclei of a given definite number and no further nucleation during the switching. For either case, an infinite single crystal and constant domain velocity are assumed.

4. Ising Model and Monte Carlo Simulation [45]-[47]

The Monte Carlo simulation [72] is a powerful numerical technique to elucidate the behavior of the model Hamiltonian of the Ising type. In the case of the ferroelectricity, the Ising system is a dipole lattice. The model Hamiltonian [45,46] of a ferroelectric
system can be written as
\[ H = \sum_{i,j} \left( H_{ij}^{\text{dipole}} + H_i^{\text{wall}} + H_i^{\text{field}} \right) + H^{\text{elastic}}, \tag{2.28} \]

where \( H_{ij}^{\text{dipole}} \) is the dipole-dipole interaction, \( H_i^{\text{wall}} \) is the domain wall energy, \( H_i^{\text{field}} \) is the energy related to the interaction between the field and the dipoles, and \( H^{\text{elastic}} \) is the elastic strain energy. With this model Hamiltonian, the numerical strategy is to allow the system to relax to its equilibrium state, and an equilibrium domain structure is then obtained under different constraints. Furthermore, the dynamic switching properties [47] are approximated by introducing a time scale for each relaxation step, which is given by
\[ \tau_{ij} = \tau_0 \exp \left( \frac{\Delta U_{ij}^b}{k_B T} \right), \tag{2.29} \]

where \( \Delta U_{ij}^b \) is the energy barrier. By setting the time scale into the Monte Carlo Method, the dynamic information of polarization switching, such as the hysteresis and the switching current, can be calculated.

5. Rate Equations [50]

The two stable polarization states together with the flipping process of a dipole polarization present an analogy to an electron residence problem with two energy levels, which is usually described by the rate equation, for example, the laser operation. With this similarity, for a uniaxial ferroelectric, we assume the dipoles are embedded in a local field \( E_{\text{eff}} = E + \beta P \) with the potential barrier \( \Delta U_{\text{barr}} \). The
flipping probability per dipole per unit time is given by [84]
\[
\rho_\pm = \nu \exp \left( \frac{\Delta U_{\text{bar}} \mp E_{\text{eff}} P}{k_B T} \right) = \rho_0 \exp \left( \pm \frac{E_{\text{eff}} P}{k_B T} \right) ,
\]
(2.30)
where \( \nu \) is an attempt frequency. \( p \) is the dipole moment.

In a high external field, any individual dipole can be switched disregard its loc-

ation. At a given time, assume there are \( N_\text{-} \) dipoles per unit volume pointing

opposite to the field and \( N_\text{+} \) in the direction of the field. The total dipole number is
\( N = N_\text{-} + N_\text{+} \). The rate equation is written as
\[
\begin{align*}
\left\{ \begin{array}{ll}
\frac{dN_\text{-}}{dt} &= -\rho_\mp N_\text{-} + \rho_\pm N_\text{+} \\
\frac{dN_\text{+}}{dt} &= \rho_\mp mp N_\text{-} - \rho_\pm N_\text{+} 
\end{array} \right. ,
\end{align*}
\]
(2.31)
where \( \rho_\mp = \rho_3 \exp\left[-(E - \beta_3 P)p/k_B T\right] \) and \( \rho_\pm = \rho_3 \exp\left[-(E + \beta_3 P)p/k_B T\right] \). With
the polarization \( P = (N_\text{+} - N_\text{-})p \), the switching current is then given by the solution
of the above equations:
\[
i(t) = \frac{dP}{dt} = Np(\rho_\mp - \rho_\pm) - P(\rho_\mp + \rho_\pm) .
\]
(2.32)

With small spike-shaped micro-domains, in moderate fields, forward domain wall
motion proceeds at a faster pace than sidewise motion. Assuming the micro-domains
are equidistant parallel-piped arranged periodically with an average distance between
nearest neighbors, the rate equations are then
\[
\begin{align*}
\left\{ \begin{array}{ll}
\frac{dN_\text{-}}{dt} &= -4n \left( \frac{r}{u} + 1 \right) \left( \frac{d_f}{b} \right) \rho_\mp + 4n \left( \frac{r_d}{ub} \right) \rho_\pm \\
\frac{dN_\text{+}}{dt} &= 4n \left( \frac{r}{u} + 1 \right) \left( \frac{d_f}{b} \right) \rho_\mp - 4n \left( \frac{r_d}{ub} \right) \rho_\pm 
\end{array} \right. ,
\end{align*}
\]
(2.33)
where \( n = 1/(2\pi^2) \) is the number of the micro-domains per unit surface, \( u \) is the
lateral distance between neighboring unit cells, \( d_f \) is the sample thickness, \( b \) is the
unit cell parameter along the ferroelectric axis. Using equation (2.32), the switching properties can be calculated by solving the above equation.

6. Other Models

Besides the theories described above, several models have been developed to attack the problem of ferroelectric switching. First, Bartic et al [51] proposed a model that is based on the Preisach theory of hysteresis. The model is developed to calculate the switching properties under a varying external field. Second, based on the behavior of ferroelectric switching and some physical equations, a few equivalent-circuit models [52, 53] have been developed for some ferroelectric devices. Finally, Ishibashi proposes a discrete molecular model [48, 49], which is indeed a hybrid theory of the Avrami theory and the Ising model.

2.6 Finite Grain Size Effects

The theories introduced above assume an infinite ferroelectric system. However, real ferroelectric films are usually polycrystalline with finite grain sizes. The grain boundaries limit the expansion of the domains. According to this consideration, two modifications have been proposed: Duiker's [73] and Shur's modifications [74]-[76].

1. Duiker's Modification [73]

Assume the grains are identical hypercubes with size $L^n$, where $n$ is the dimension of the grains. The nucleation rate of a domain is assumed constant and uniform around the whole grain, and periodic boundary conditions are considered. According
to these assumptions, the number of possible nucleation sites is proportional to the
volume of the grain: $V = L^n$. The probability that exactly $N$ nuclei form is the
probability that $N$ nuclei form and $V - N$ do not, multiplied by the number of ways
of distributing $N$ nuclei on $V$ nucleation sites,

$$W_N = \frac{V!}{(V - N)!N!} R^N (1 - R)^{V - N}. \quad (2.34)$$

The time step is set as $\Delta \tau$. At time $t = j\Delta \tau$, the volume of a domain forms at time
$t = i\Delta \tau$ ($i \leq j$, $i$ and $j$ are integers) is

$$V_D(j\Delta \tau, i\Delta \tau) = \begin{cases} 
C[r_c + \nu(j\Delta \tau - i\Delta \tau)]^2 & j < i + s \\
V & \text{else}
\end{cases}, \quad (2.35)$$

where $s$ is the time step required for one domain to grow to include the whole grain:

$$s = \frac{1}{\nu\Delta \tau} \left[ \left( \frac{V}{C} \right)^{\frac{1}{3}} - r_c \right]. \quad (2.36)$$

Suppose $N_i$ is the number of nuclei that form in a given grain during the $i$th time
step. At time step $j$, the probability that a given point in the grain is not inside a
switched domain is given by

$$q(j\Delta \tau) = \prod_{i=0}^{j} \left[ 1 - \frac{V_D(j\Delta \tau, i\Delta \tau)}{V} \right]^{N_i}. \quad (2.37)$$

The ensemble average $\langle q(j\Delta \tau) \rangle$ is the value of $q(j\Delta \tau)$ averaged with the probabilities
$W_n$. With $V_D(j\Delta \tau, i\Delta \tau) \ll V$, it can be written as

$$\langle q(j\Delta \tau) \rangle \approx \prod_{i=0}^{j} \left[ 1 - RV_D(j\Delta \tau, i\Delta \tau) \right]. \quad (2.38)$$
The above result is consistent with Ishibashi’s model. On the other hand, with \( j \gg s \),

\[ V(j \Delta \tau, i \Delta \tau) \gg V, \] equation (2.37) can be simplified to

\[ \langle q(j \Delta \tau) \rangle \cong \exp[-R \Delta \tau V_D(j \Delta \tau - i \Delta \tau)] \langle q(s \Delta \tau) \rangle. \] (2.39)

Combining the two cases and substituting the time step \( j \Delta \tau \) with real time \( t \), \( q(t) \) is then given by

\[ q(t) = \begin{cases} 
\exp \left\{ -\frac{CR}{\nu(n+1)} [(r_c + \nu t)^{n+1} - r_c^{n+1}] \right\} & t < t_s \\
q(t_s) \exp[-RV(t - t_s)] & t \geq t_s 
\end{cases}, \] (2.40)

where

\[ t_s = \frac{L}{\nu} \left[ \left( \frac{1}{C} \right)^{\frac{1}{n}} - \frac{r_c}{L} \right]. \] (2.41)

Hence, the switching current is given by:

\[ i(t) = 2P_s \frac{dq(t)}{dt} \]

\[ = \begin{cases} 
2P_s CR(r_c + \nu t)^{n} \exp \left\{ -\frac{CR}{\nu(n+1)} [(r_c + \nu t)^{n+1} - r_c^{n+1}] \right\} & t < t_s \\
2P_s CRV \exp \left\{ -\frac{CR}{\nu(n+1)} [(r_c + \nu t)^{n+1} - r_c^{n+1}] \right\} & t \geq t_s 
\end{cases}. \] (2.42)

The model were applied to Ising-model simulations and current transients were accurately fit by this modified model.

2. Shur's Modification [74]-[76]

Shur introduced a concept of geometrical catastrophe to describe the effect of the grain size. The geometrical catastrophe infers a suddenly change of the dimensionality of the domain wall motion. As discussed in the Ishibashi model, there are three types of domain wall motion. For a small grain, the initial stage of domain dilation is believed to be two-dimensional. When the domains penetrate the thickness of the grain, a geometrical catastrophe occurs, that is to say, the dimensionality of the
domain wall motion abruptly changes from 2 to 1. The mathematic treatment is straightforward and can be found in his papers

2.7 Film Thickness Effects

Compared to the grain size effects, where the shape of the switching current is the focus, the study of the effects of the film thickness is concentrated on the dependence of the coercive on the film thickness. It is known that an effective method to increase the coercive field is to reduce the thickness of the ferroelectric film [77]-[80]. Although there is no doubt about the tendency, i.e., the thinner the ferroelectric the higher its coercive field, the mechanism is still a controversial question. For the same reason as the discussion of the phase stability, the surface effect and the electrical field distribution are important to the polarization switching of a thin film [81, 82], whereas some authors believe that it is the passive layer and the injection charges that result in the coercive variation [83]-[87]. In addition, the domain structure is believed to be a reason for the thickness effects [27, 28], [88]-[91].

1. Built-in Electrical Field Effect [82]

Assume the electrode-film interface is a metal-semiconductor interface, and the ferroelectric is not an ideal insulator but an n-type semiconductor with donor concentration $N_D$. The Schottky barrier causes the ferroelectric film to form a depletion of electrons on its surface. Assume the width of the depletion region is $W$. If the film thickness $d_f \gg W$, in the absence of the external voltage, the field near the electrode
is given by
\[ \delta E_0 = \frac{qWN_D}{\epsilon_s} \]  
\[ (2.43) \]

If \( d_f < 2W \), the electrical field near to the surface is given by
\[ \delta E = \frac{d_f\delta E_0}{2W} \]  
\[ (2.44) \]

Hence, the coercive field can be approximated as
\[ E_c = \begin{cases} 
E_{cn} - \frac{V_0d_f}{W^2} & d_0 < d_f < 2W \\
E_{cn} - \delta E_0 & d_f \gg W < d_0 \\
E_{cm} & d_f \gg W > d_0 
\end{cases} \]  
\[ (2.45) \]

where \( d_0 = (E_{cn} - E_{cm})W^2/(2V_0) \) and \( E_{cn}, E_{cm} \) are the threshold field for domain nucleation and domain wall motion respectively. It shows a linear dependence of coercive field on the film thickness.

2. Passive Layer [85]

Assume a passive layer with thickness \( d_d \) and dielectric constant \( \epsilon_d \) exists between the ferroelectric material and the electrode. For a given external voltage, if the thickness of such a layer is fixed, the thinner the ferroelectric film the smaller fraction of the voltage dropped on the ferroelectric material. Suppose the properties of the ferroelectric material do not change with decreasing its thickness. In order to reach the same internal coercive field, the observed coercive field (external field) has to be larger than the internal coercive field, and it increases as the film thickness decreases.

According to these considerations, the observed coercive field is given by
\[ E_c = E_i \left(1 + \frac{d_d}{d_f} - \frac{d_d}{\epsilon_d d_f} \right)^{-1} \]  
\[ (2.46) \]
where $E_i$ is the field acting on the ferroelectric material when $P = 0$. It can be seen from equation (2.46) that for a given $d_d$ and $E_0$, the decrease of $d_f$ results in a large coercive field $E_c$.

3. Injection Charge Effect [83]

Suppose the charges can be injected into the interface between the dielectric layer and the ferroelectric film. The electrical field in the ferroelectric film is then given by

$$E_f = E - \frac{d_d}{d_f} \frac{P(E_f) - \sigma}{\epsilon_d} = E - \frac{d_d}{d_f} E_d$$

(2.47)

where $E$ is the total field, $E_d$ is the field in the dielectric, and $\sigma$ is the injected charge density, which depends on the field exerting on the dielectric:

$$\frac{d\sigma}{dt} = J(E_d)$$

(2.48)

Suppose a rectangular hysteresis of the ferroelectric with coercive field $E_{c0}$, and a steep $J(E_d)$ with threshold $E_{th}$, i.e. if $E_d < E_{th}$, the dielectric behave as an insulating layer; if $E_d > E_{th}$, the field in the dielectric can no longer increase due to the charge injection and hereby $E_d \cong E_{th}$. The relation between $E_d$ and $E_{th}$ depends on the saturation polarization of the ferroelectric film. The field applied on the dielectric depends on the saturation polarization of the ferroelectric material, and the coercive field is then given by

$$E_c = \begin{cases} 
E_{c0} + \frac{d_d}{\epsilon_d d_f} (P_s - \epsilon_d E_{th}) & \epsilon_d E_{th} < P_s < 2\epsilon_d E_{th} \\
E_{c0} + \frac{d_d}{d_f} E_{th} & P_s > 2\epsilon_d E_{th}
\end{cases}$$

(2.49)

This also shows the thickness dependence of the coercive field.
5. Surface Effect [81]

Using the lattice model, Baudry et al demonstrate that the size effect exists even if the surface charge is compensated at the metallic electrodes. The size-effect strongly depends on the bulk correlation length [81] and the extrapolation length [81] of the ferroelectric material.

6. Domain Structure Effect [27, 28, 88]

Ren et al [27] propose that the coercive field change with the thickness is not necessarily a thickness dependent phenomenon. They suggest that the dependence is due to the change of the domain structure, which is related to the grain size. The grain size may depend on the thickness of the film, but not necessarily. Therefore, the coercive field is determined essentially by the domain structure of the grains instead of the thickness. A few experimental results have been published to claim the transition of the domain structure, i.e., from multi-domain to a single-domain [26]. In addition, a theory of domain structure transition has been developed (section (2.4)). However, to the best of our knowledge, there is no theoretical work based on this idea. This is a topic of the present thesis and will be discussed in Chapter 4.

2.8 Reliability of Polarization Switching

Because of the material defects and the degradation of the ferroelectric properties, the difference between switched polarization and unswitched polarization may not be detected when the ferroelectric device is operated under certain conditions. The
incapability of distinguishing the two quantities results in the reliability failures. The reliability of ferroelectric devices includes retention [33], fatigue [34] and imprint [35]. In this section, these phenomena and some previous theories are discussed.

1. Retention [17, 33],[92]-[95]

Retention is the ability to retain and to be able to read-out the stored information at a certain time after programming, which is defined as the application of a certain writing voltage and is large enough to switch the polarization. Within the first second after programming, the polarization decreases rapidly. It is called polarization relaxation by some researchers, while it is in fact short-time retention. Assuming symmetry situation, i.e., $P_s^+ = P_s^- = P_s$ and $P_r^+ = P_r^- = P_r$, the difference between $P_{sd}$ and $P_{ns}$ is given by

$$\Delta P = P_{sd} - P_{ns} = 2P_r.$$ \hspace{1cm} (2.50)

If the magnitude of $P_r$ becomes too small to be measurable due to the retention degradation, retention failure occurs.

The retention process shows logarithmic time dependence, which can be described by the empirical equation [33]

$$P(t) = P_0 - m \log \left( \frac{t}{t_0} \right),$$ \hspace{1cm} (2.51)

where $t_0$, $m$ and $P_0$ are empirical constants. Using the Avrami theory, Mehta [17] et al discussed the retention with the consideration of the depolarization field. They
assume the depolarization field can be written as

\[ E_{\text{dep}} = \lambda \frac{P(t)}{P_s}, \quad (2.52) \]

where \( \lambda \) is a constant. The polarization is then given by

\[ P(t) = 2P_s[1 - (1 - \alpha_{ex})^n], \quad (2.53) \]

where \( n \) is the number of domains and \( \alpha_{ex} \) is the extended area of the domains:

\[ \alpha_{ex}(t) = \pi \left\{ \int_0^t \nu \exp \left[ -\frac{\delta}{E_{\text{dep}}(\xi)} \right] d\xi \right\}^2. \quad (2.54) \]

Equation (2.54) gives the behavior of the polarization after programming. The predicted decay of this model is more rapid than that observed.

2. Fatigue [34],[96]-[109]

Fatigue is defined as the reduction of the switchable polarization with increasing number of switching cycles. It limits the endurance of the memory, i.e. the maximum number of read/write (switching) cycles that can be applied to a memory element still allowing discrimination between the two memory states (i.e. polarization “up” or “down”).

3. Imprint [35], [110]-[116]

Imprint is the decrease of the ability to program (switch) the memory element to the opposite state when programmed for a long period in one state. This imprint failure has been correlated to the polarization-driven field-shift of the hysteresis loop. The shift is in the field direction to stabilize the present polarization direction. Failure
occurs if
\[ P_{ns} = P_s - P_r^+ \approx P_s + P_r^+ = P_{sd} \]  \hspace{1cm} (2.55)

Imprint results from charge migration. For example, the imprint of the ferroelectric potassium zirconate titanium (PZT) is due to trapping of oxygen vacancies [111]-[115]. In positive external field, the oxygen vacancies may diffuse to the interface and they can be preferentially trapped near one of the electrodes. With the accumulation of such trapped charge, an internal field is built up so that the hysteresis is biased. Robels et al [116] demonstrate that the inclusions of non-switched dielectrics can also induce an internal field and imprint.
Chapter 3
Problems with Polarization Switching Theories

The properties of polarization switching have been vastly investigated for a number of ferroelectric materials. The most popular model is the Ishibashi model. However, people are more interested in using empirical relations to interpret their data. Although many authors have suggested mechanisms for the switching phenomena observed in their research, the theoretical models have not been investigated and developed systematically.

In this chapter, with the highlights of some experimental results, the deficiencies of the previous theories of switching are discussed, and the problems for the thesis are defined.

3.1 Highlights of Experimental Results

First, the switching properties depend on the lattice parameters and stoichiometry of the ferroelectric. For example, the microstructure and the oxygen-vacancy density of PZT films can be modified by doping with La [35, 92, 93] and Nb [106, 113]. It is well known that fatigue properties can be improved dramatically by such doping [98]. On the other hand, the nonstoichiometry of Pb, Zr and Ti can influence ferroelectric properties as well. It is found that the domain reverse is much faster if the stoichiometric ratio of Zr and Ti reaches a point that turns the films to the rhombohedral
structure [117], and with excess lead, the polarization relaxation is significantly enhanced [118]. In addition, the ferroelectric properties are closely related to the defect chemistry [119].

Second, the properties of the electrode are vital to ferroelectric switching. It is found that oxide electrodes can decrease fatigue, and even make the films fatigue-free [120]-[123]. The conductance of the ferroelectric capacitor can be controlled predominantly by the characteristics of the interface between the ferroelectrics and the electrodes [124]. The interface states provide nuclei sites for heterogeneous nucleation, which can speed up the switching process [125]-[127].

Third, the velocity of the domain wall depends on mechanical constraints, materials and amplitude of the external field [61]-[67]. The field dependence of the velocity over a range of several decades in velocity is described by [67]

$$\nu = \nu_\infty \exp \left( -\frac{\delta}{E} \right)$$  \hspace{1cm} (3.1)

On the other hand, there is no evidence of a well-defined microscopic coercive field, i.e. a field $E_c$ below which the wall will not move, and the wall velocity hardly depends on the size of the domains. It is generally agreed that a $180^\circ$ domain wall does not move sidewise in a continuous manner but as a unit parallel to itself on an atomic scale. The rate controlling process is the nucleation of steps along a wall, and not the subsequent growth of the nucleated steps. Therefore, the macroscopic coercive field and other switching properties of a ferroelectric material depend on the waveform of
the external field such as the frequency and magnitude [128].

Finally, the shape of the switching current, i.e., maximum switching current, switching time, rise time, decay time, and symmetry of the curve, is a function of external field, temperature, history of the sample [8, 76]. It is found that keeps constant [57], that is to say, when the external field increases, the switching time decreases and the maximum switching current increases with their product constant. The dependence of switching time on the external field shows three regimes: (1) large curved (2) small curved (3) linear [57]. When the external field decreases, the symmetry of the switching current is reduced, which manifests itself in that the tail of the switching current is elongated [74]-[76].

3.2 Problems with the Previous Theories

Scott and Ishibashi [43, 44], [129]-[132] have used the Ishibashi model to analyze the switching properties of some materials such as KNO$_3$ and PZT. According to their work [129]-[132], there are three parameters, i.e., saturation polarization $P_s$, dimensionality of the domain wall motion $n$, and domain wall velocity $v$, which can be adjusted for fitting the experiment data. Figure 3.1 [74] shows the switching current measured in PZT/YBCO thin film heterostructure. Experimental points are fitted by different theoretical curves: (a) the Fatuzzo model, (b) the Ishibashi model, and (c) Shur's modification. It can be seen that Fatuzzo and Ishibashi's models are ineffective for describing the decaying part of the current pulses. Besides, the best fitting value
for $n$ is not an integer, which is inconsistent with the original physical model of the theory. Using the geometric catastrophe, Shur [74]-[76] solved these two problems by introducing additional fitting parameter: catastrophe time $t_c$, at which the domain changes growth dimensionality.

![Diagram](image)

**Figure 3.1** The switching current data measured in PZT/YBCO thin film heterostructure. Experimental points are fitted by theoretical curves: (a) Fatuzzo Model, (b) Ishibashi Model, and (c) Shur's modification. (From Ref. [74])

However, there are still some problems with the Fatuzzo/Ishibashi model. First, the model can only deal with constant external voltage. The writing/reading signal
for operating a ferroelectric element is usually square waveform, but the rising and falling edge cannot be neglected for a fast operation. Therefore, it is impossible to elucidate the fast switching properties by using the Ishibashi model. In addition, even with a constant voltage, the domain wall velocity is not constant as shown by experiment [57]-[67]. Second, the nucleation process described in the Ishibashi model is vague. The classification of the two categories, i.e., constant nucleation rate and fix preexisting nuclei, is somewhat arbitrary. Finally, the Fatuzzo/Ishibashi model is not a model developed for the switching of thin films. The specific characterizations of thin films such as surface energy and depolarization field are considered in this model.

The Preisach model [51] can deal with the inconstant external field. However, for establishing the Preisach ensemble, a pair of coercive field has to be set. It is not physically true, because the coercive field depends on the characteristics of the external field, and it cannot be preset as a constant value. It is a problem for several other models [81]-[83].

The Ising model and the Monte Carlo [45]-[47] simulation are good for the understanding of some basic physical phenomena. However, they are not supposed to model a real ferroelectric, because the number of dipoles in the modeled ensemble cannot be very large, usually thousands dipoles, otherwise the computing time and cost is unacceptable. In addition, it is a static model dealing with equilibrium states
instead of treating a dynamic process as the case of ferroelectric switching. Landau theory [8], [54]-[56] has the same deficiency when it is used to study the switching properties. The results predicted by static models usually can provide qualitative understandings rather than a good quantitative data fitting.

The models of the thickness effects may be tentative solutions for the thin film applications. However, as pointed out earlier, the passive layer theory appoints a fixed hysteresis loop for any situation and ignores the intrinsic properties of the ferroelectrics. Finally, because the reliability problem is directly related to the switching process, a model for the switching should be able to describe these reliability phenomena as well.

In summary, the problems for the theoretical part of the thesis are to develop a model for the polarization switching of thin films. By considering the depolarization field and surface effects, the nucleation processes should be clarified. In addition, the model can give explanations to the thickness effects and the reliability phenomena. The parameters in the model should have physical meaning, and the effects of these physical parameters should be consistent with experimental results. According to these considerations, a model is proposed in the following chapter.
Chapter 4
A Theory of Polarization Switching for Ferroelectric Thin Films

A model for polarization switching of ferroelectric thin films is proposed in this chapter. The chapter is developed as follows: first, the assumptions related to the thin films are made. Based on these assumptions, domain nucleation processes are clarified, and the nucleation probabilities are calculated. Second, the polarization switching is modeled and formulated by developing the Fatuzzo model. Numerical techniques for solving the equations are introduced. Third, the model results are presented. Hysteresis loops and switching current are calculated. Finally, the model is used to investigate the phenomena of reliability, and the thickness effects are studied as well.

4.1 Thin Film Regime

Assume the film in question is a single crystalline ferroelectric material with its uniaxial polarization perpendicular to the film surface *. Polarization switching is the process of new domain formation and dilation, i.e., the extrinsic switching process. In thin film regime, it is assumed that once a nucleus forms, it grows through the whole thickness of the film quickly, i.e., the time of forward growth can be neglected. On the other hand, due to the surface effects of thin films, surface nucleation dominates

*Assume the two surfaces of the film are parallel to each other
body nucleation [125]-[127]. According to this assumption, the switching process can be simplified to a two-dimensional problem, i.e., the polarization switching can be calculated through the fraction of the switched area on the film surface.

Besides the surface effects, the depolarization field of a thin film can be comparable to the activation field of domain nucleation, so it has to be taken into account for the switching of thin films. In addition, the varies with the domain configuration. The probabilities of the domain nucleation are determined by the local field. According to this consideration, the processes of the domain nucleation have to be clarified.

4.2 Nucleation Processes

The switching process starts with the nucleation of the domains with reversed polarization direction. It is well known that the oxygen vacancies [96]-[109] and 90° domain boundaries [125]-[127] can provide heterogeneous sites for domain nucleation. On the other hand, domain nucleation can take place homogeneously, i.e., anywhere inside domains in a large external field. The nucleation probabilities are determined by the local field, and the local field is a function of the external field, the depolarization field and the domain configuration.

The nucleation probabilities adjacent to domain walls and inside domains are different. The domain wall velocity is determined by the nucleation probability adjacent to domain walls, and the number of domains is controlled by the nucleation inside unswitched domains. Hence, the switching properties such as switching current,
switching time and coercive field depends on these nucleation processes.

Nucleation can be classified into three types: heterogeneous nucleation, nucleation inside domains and nucleation adjacent to domain walls. For simplicity, because heterogeneous nucleation is much faster than the other nucleation processes, the time of the heterogeneous nucleation is neglected and a number of preexisting nuclei is assumed, i.e., there are a number of nuclei existed at the beginning of the switching process.

1. Heterogeneous Nucleation

The preexisting nucleation sites arise from the accumulation of oxygen vacancies, the 90° domain boundaries and other crystalline defects [160]-[163]. The charges bounded by the oxygen vacancies and the stress induced by the 90° domain boundaries can decrease the barrier required by the domain nucleation. Herein, only the charged defects are modeled. For example, as shown in Figure 4.1, assume the polarization of the film has been biased in the positive state for a long time, so a large number of the oxygen vacancies (positive charged) is transported and bonded onto the upper surface compared with that accumulated on the lower surface. On the other hand, the distribution of the negative charged defects and the electrons has a inverse profile. The positive oxygen vacancies on the upper surface and the negative defects on the lower surface are the nucleation sites for the domain with positive polarization. Therefore, the number of the preexisting nuclei for the positive domains is the sum of the two
\textbf{Figure 4.1} Schematic picture of the heterogeneous nucleation: by applying a constant positive field $E$, the oxygen deficiency transport to the upper surface and oxygen excess accumulate at the lower surface. These charged defects have low mobility and cannot respond to the fast changing field during the switching process. They apply additional negative field (downward) inside the film, therefore, they can assist the nucleation process for the switching from positive polarization to negative polarization.

quantities. For instance, assume the area fractions occupied by the positive and negative trapped charges on the upper surface are $n_{upper}^+$ and $n_{upper}^-$, respectively, and the area fractions covered by the positive and negative trapped charges on the lower surface is $n_{lower}^+$ and $n_{lower}^-$, respectively. Hence, the area fraction of the nucleation sites for positive domain is then given by

$$n_s^+ = n_{upper}^+ + n_{lower}^-,$$

and for negative domain is given by

$$n_s^- = n_{upper}^- + n_{lower}^+.$$

In Figure 4.1, the circled charges stand for the nucleation sites, which have fixed polarization direction and are un-switchable during the switching process. The number
of such nucleation sites, $N_s$, is proportional to the area covered by these trapped charges, and it can be written as

$$N_s = \begin{cases} kn_s^+ r_g^2 & \text{nuclei for positive domains} \\ kn_s^- r_g^2 & \text{nuclei for negative domains} \end{cases}$$ \hspace{1cm} (4.3)

where $n_s^+$ and $n_s^-$ are given by equation (4.1) and (4.2) respectively, $r_g$ is the radius of the grain, and $k$ is a constant, which equals to the number of preexisting nuclei per unit area.

Because the trapped charges of these nucleation sites cannot be switched by the external field during a fast switching process, the amount of the un-switchable polarization of the total film is given by

$$P_s^{\text{Fixed}} = \begin{cases} -n_s^- P_s^* & \text{negatively biased} \\ n_s^+ P_s^* & \text{positively biased} \end{cases}$$ \hspace{1cm} (4.4)

where $P_s^*$ is the saturation polarization without these defects. Therefore, the saturated polarization of the film is can be written as

$$P_s^+ = (1 - 2n_s^-)P_s^*$$ \hspace{1cm} (4.5)

and

$$P_s^- = -(1 - 2n_s^+)P_s^*$$ \hspace{1cm} (4.6)

where $P_s^+$ and $P_s^-$ are the observed positive and negative saturation polarization of the film, respectively.

The error introduced by neglecting the uncharged nucleation sites exists in the approximation of the total saturation polarization, which indeed depends on many
other factors, for example, the surface morphology. In this model, this does not affect the dynamic switching properties, if the values for $n^+_s$ and $n^-_s$ are selected appropriately. It is expected that the more the preexisting nucleation sites are, the quicker and easier the switching can be. Therefore, the magnitudes of and can affect the switching process. In addition, the non-equality of the two values can lead to the imprint phenomena, which is discussed in section (4.7.1).

2. Nucleation inside Domains

If the external field is large enough to overcome the nucleation barrier, the nucleation can occur anywhere in the film. The latent number of such nucleation sites is proportional to the ratio of the area of the grain to the area of a nucleus, and it can be written as

$$N_b = k_b \left( \frac{r_g}{r_c} \right)^2 ,$$

(4.7)

where $k_b$ is a constant, which is related to the crystal structure of the material. Assume the nucleation process obeys a Gaussian distribution, i.e., the nuclei emerge randomly anywhere inside domains. If the switched volume fraction is $q(t)$ at time $t$, the variation of the existed nuclei because of the body nucleation is given by

$$dN_i = [1 - q(t)][N_b - N_i(t)]R_i(E, t)dt ,$$

(4.8)

where $R_i(E, t)$ is the nucleation probability inside domains, which is a function of the local field and time. The number of the nuclei arising from the nucleation inside domains is given by the integral of equation (4.8).
3. Nucleation Adjacent to Domain Walls

The nucleation adjacent to the domain walls results in the domain wall motion. According to the assumptions of the thin film regime, once a nucleus emerges on the domain wall, it develops itself to form the new domain boundary. For the nucleation adjacent to domain walls, it is assumed that the boundaries of any domain in a crystallite have the same environment, i.e., the nucleation probability adjacent to the domain walls is independent of the location of the domain and the size of the domain.

In addition, it is assumed that the interface between the preexisting nuclei and the other part of the film can be treated as domain boundaries. In next section, the nucleation probabilities for the different types of nucleation are calculated.

4.3 Nucleation Probabilities

In order to calculate the nucleation probabilities, the local field is considered. The local field is determined by the external field and the dipole field. The dipole field depends on the configuration of the domains. In this section, first, the dipole interaction is discussed, and the dipole field is calculated for a simple domain structure. Then, the local field is modified by considering the equilibrium state of the film. Finally, the nucleation probabilities are calculated.
4.3.1 Dipole-dipole Interaction

The electrical field at a point \( r \) due to a dipole \( p \) at the point \( r_0 \) can be written as

\[
E(r, r_0) = \frac{3n(p \cdot n) - p}{4\pi\varepsilon_0 |r - r_0|^3},
\]

(4.9)

* where, \( n = (r - r_0)/|r - r_0| \) is the unit vector. For a dipole lattice, the electric field at each lattice point is given by the superposition of the field generated by all the other dipoles except the one at the point in question, which is

\[
E(r) = \sum_{r' \neq r} E(r, (r')) = \sum_{r' \neq r} \frac{3n(p \cdot n) - p}{4\pi\varepsilon_0 |r - r_0|^3}.
\]

(4.10)

As shown in Figure 4.2 (a), a dipole lattice is built to simulate a domain boundary. The lattice is a \( L_x \times L_y \times L_z \) dipole ensemble. The polarization of the left half (\( 1 \leq x \leq L_x \), \( 1 \leq y \leq L_y/2 \), \( 1 \leq z \leq L_z \)) points up and the right side (\( 1 \leq x \leq L_x \), \( L_x/2 \leq y \leq L_y \), \( 1 \leq z \leq L_z \)) points down. Therefore, a domain boundary is defined at \( x = L_x/2 \). The dipole field is calculated using equation (4.10), and the curve depicted in Figure 4.2(b) is the electrical field along the line shown in Figure 4.2 (a) with the horizontal axis representing the horizontal position and the vertical axis standing for the electrical field. It can be seen that the electric field adjacent to the domain wall is much smaller than the field inside the domain. This field distribution gives a hint for the consideration of the local field, and it is discussed in the next section.

*The external applied field and the polarization are functions of time. In this section, for the sake of simplicity, the time variable is not written in the equations.
Figure 4.2  Dipole field adjacent to a domain wall: (a) A dipole lattice with the direction of dipole moments of the left half points up and that of the right half points down, therefore, a 180° domain boundary is defined at $y = L_y/2$, (b) The field generated by the dipole lattice. The field adjacent to the domain wall is much smaller than inside domains.
4.3.2 Local Field

By introducing mathematically a spherical cavity with appropriate radius (domain wall width) [133], the local field can be divided into macroscopic and microscopic components. The boundary condition and local structure change due to domain configuration can be investigated separately. Accordingly, the local field acting on an atom can be written as [134]

\[ E_{\text{loc}} = E_0 + E_1 + E_2 + E_3 \]

(4.11)

where \( E_0 \) is the external electric field, and \( E_1 \) is the local depolarization field. It is the average field acting on an atom because of all the other dipoles out of the cavity. Because of the cancellation of the surface equivalent polarization charge by free carriers of the electrodes, the depolarizing field \( E_1 \) is given by \( E_1 = -NP \) (\( N \) is the depolarization factor, \( P \) is the polarization density). \( E_2 \) and \( E_3 \) are the local fields and reflect the fine local field fluctuation. \( E_2 \) is the Lorentz cavity field, i.e., the field due to the surface polarization charges of the spherical cavity, equals to \( \pm p/2\varepsilon_0 \) inside a domain (where \( p \) is the polarization of a single dipole) and vanishing at a domain wall. \( E_3 \) is the dipole field inside the cavity, which vanishes under the assumption of an isotropic distribution of dipoles.

However, according to the considerations of the equilibrium state of the polarization, the local field can be modified as follows: If a ferroelectric film is biased to its positive saturated polarization and the external bias voltage is then removed, the
polarization of the film relaxes to and stays at a lower value, which is the remanent polarization. On the other hand, when the film is in its equilibrium state, the net effect of the local field (equation (4.11)) adjacent to the domain walls should be zero, so that there is no nucleation process, which is required by the maintenance of the stable polarization. That is to say, a stable polarization corresponds to an unvaried domain structure, which is a result of the null nucleation. Therefore, a driving force for the domain nucleation is needed for the relaxation process described above and the maintenance of the polarization requires a cancellation of $E_1$, when the external field equals to zero. Physically, the electrical properties of the ferroelectric film are also affected by the film stress, the interface and other confinements, which can change the equilibrium domain configuration. The equilibrium state of domain configuration can be described if the second term in equation (4.11) is of the form

$$E_1 = -\frac{\lambda}{\epsilon_0}(P - P_r),$$

(4.12)

where $P_r$ is the remanent polarization of a single grain, and $\lambda$ is a phenomenological parameter. By this modification, one achieves a phenomenological description for the relaxation of a ferroelectric film from saturation to a smaller polarization state without the assistance of an external field.

The experimental results show that the remanent polarization of a ferroelectric material depends on the history of the external field. For instance, the unsaturated loops have much smaller remanent polarizations, and it is believed that those states
are equally stable. This phenomenon indicates that the instant external field adjusts not only the momentary polarization but also the equilibrium states of the polarization, which the film will relax to when the external field has vanished. For the first approach, assume the equilibrium polarization $P_e$ corresponds to the polarization $P$, and is given by

$$P_e = \frac{P_r}{P_s} P ,$$

(4.13)

where $P_r$ and $P_s$ are the saturation value of the remanent and saturation polarization. As a special case, if the external field vanishes when the polarization equals to $P_s$, the equilibrium state of the films is given by $P_r$. On the other hand, if the external field vanishes at instant $t$ with polarization value $P < P_s$, the equilibrium polarization is then reduced to $P_e < P_r$, and the hysteresis becomes unsaturated. Hence, according to equation (4.13), $E_1$ can be rewritten as

$$E_1 = -\frac{\lambda}{\varepsilon_0} (P - P_0) = -\frac{\lambda}{\varepsilon_0} \left(1 - \frac{P_r}{P_s}\right) P \equiv -\frac{\lambda'}{\varepsilon_0} P .$$

(4.14)

Finally, the local field is given by

$$E_{loc} = \begin{cases} E_0 - \frac{\lambda'}{\varepsilon_0} P & \text{Adjacent to domain walls} \\ E_0 - \frac{\lambda'}{\varepsilon_0} P + \frac{p^2}{3k_0} & \text{Inside domain} \end{cases} ,$$

(4.15)

where the dipole polarization $p$ is replaced by the saturation polarization of the single crystal.
4.3.3 Nucleation Probabilities

According to the discussion of the nucleation probabilities in section (2.2), the above considerations give the domain nucleation probabilities:

\[ R_w(t) = \exp \left( -\frac{\alpha}{E_{\text{loc}}(t)} \right) = \exp \left( -\frac{\alpha}{E_0(t) - \frac{\lambda}{\epsilon_0} P(t)} \right), \]

\[ R_i(t) = \exp \left( -\frac{\alpha'}{E_{\text{loc}}(t)} \right) = \exp \left( -\frac{\alpha'}{E_0(t) - \frac{\lambda}{\epsilon_0} P(t) + \frac{P_s}{3\epsilon_0}} \right), \]

(4.16) (4.17)

where \( R_w \) and \( R_i \) are the nucleation probabilities adjacent to the domain walls and inside unswitched domains, respectively; \( \alpha, \alpha' \) are the activation fields, which are material-specific parameters. For simplicity, the activation field of the nucleation probability inside domains is set as

\[ \alpha' = \frac{P_s^*}{3\epsilon_0 \epsilon_f}. \]

(4.18)

Hence, the nucleation processes and the nucleation probabilities are modeled. In next section, based on the understanding of the nucleation processes, the domain development, i.e., the switching process, is discussed and formulated.

4.4 Formulation of Polarization Switching

Following the framework of the Fatuzzo’s theory, the switching process is modeled in this section. Compared with Fatuzzos original model, the nucleation probabilities are determined by the local field, so they are not necessarily constant in this model. That is to say, the velocity of the domain wall is time and field-dependent. Besides, the
nucleation processes are clarified as the heterogeneous nucleation and the nucleation inside the domains.

A method is developed to deal with the unswitchable area in this model. The total film is divided into two regions: the switchable and the unswitchable. For the switchable part, the switching process can be formulized in the Fatuzzos framework, while the unswitchable part is treated as the preexisting nucleation sites.

On the other hand, the Fatuzzo model builds up a relation between the real finite system and an imaginary infinite system. The domains in the imaginary system grow without overlap, and the nuclei emerge always in the unswitched area. In other words, the domain can dilate infinitely without encountering other expanding domains in the imaginary system. However, the overlap has to be considered in the real system, and the domain development in the real system can be extracted from the switching of the imaginary system. This method is utilized in the model proposed here.

In this section, first, the domain development for the switchable part is modeled for the imaginary system. Then, the switched area and the polarization are calculated for the whole film including the un-switchable part and the overlap effect. Finally, the relation between the proposed model and the Fatuzzos and Ishibashis model are discussed as a special case of the current model.
4.4.1 Domain Development

Without the overlap, the radius of the domain formed at instant \( \tau \) is assumed to increase with time according to the equation

\[
r(t, \tau) = r_c + (2r_c) \int_\tau^t R_w(\xi) d\xi,
\]

(4.19)

where \( r_c \) is the critical radius of the nucleus adjacent to the domain wall. \( R_w(t) \) is the nucleation probability adjacent to the domain wall, and it is given by equation (4.16). Hence, the fractional area of the developed domain is given by

\[
S(t, \tau) = \frac{\pi r^2(t, \tau)}{T}
\]

(4.20)

where \( T \) is the total area of the crystallite. The area that is the amount the domain has expanded through sidewise motion is given by

\[
S_e(t, \tau) = \frac{\pi [r^2(t, \tau) - r_c^2]}{T}.
\]

(4.21)

In the infinite imaginary system, the possibility of over-running of nucleation sites by the sidewise growth of domains is neglected, and the coalescence of the domains due to their sidewise expansions is neglected as well. Therefore, the area covered by the switched domains is given by

\[
A(t) = \int_0^t \left[ \frac{dN_1(t)}{dt} \right] \int_\xi S(t, \xi) d\xi + N_2 S_e(t, 0)
\]

(4.22)

The first term in the above equation arises from the domains that come from the nuclei formed inside unswitched domains. The second term is the dilation of the preexisting nuclei, for which, only the extended area are counted on, because the system of interest is the switchable part. The total polarization is discussed below.
4.4.2 Switching Area and Total Polarization

In order to relate the switched area \( A(t) \) in the imaginary system to its counterpart in the real finite system, let's divide the area \( A(t) \) into two parts: the developed area

\[
A_e(t) = \int_0^t \left[ \frac{dN_1(t)}{dt} \right] S_e(t, \xi) d\xi + N_s S_e(t, 0) ,
\]

and the area covered by the nuclei

\[
A_0(t) = \frac{\pi r_c^2}{T} N_1(t) .
\]

The fractional area covered by the switched domains in the real finite system without the two restrictive conditions is called \( q(t) \). It can also be divided into two parts: \( q_e(t) \) and \( q_0(t) \), where \( q_e(t) \) corresponds to \( A_e(t) \), and \( q_0(t) \) corresponds to \( A_0(t) \). In a time \( dt \), the increment of the non-overlapped volume is \( dv_{nou} \) and the increment of the extended volume is \( dv_{ext} \), where the extended area is defined as the area which domain would have if it had extended without meeting any other domains. According to the Avrami theory, we have

\[
\frac{dv_{nou}}{dv_{ext}} = 1 - q(t) .
\]

Because of \( N(t)dv_{ext} = dA_e(t) \) and \( N(t)dv_{nou} = dq_e(t) \), we obtain

\[
\frac{dq_e(t)}{dA_e(t)} = 1 - q(t) .
\]

Equation (4.8) can be rewritten as

\[
\frac{dN_1(t)}{[N_0 - N_1(t)][1 - q(t)]} = R_4(t)dt .
\]
Assume \( q_0(t) = A_0(t) \), by doing it, it is assumed that there is no overlap just after the nucleus formed. Hence,

\[
dq_0(t) = \frac{\pi r_e^2}{T} dN_1(t) ,
\]

and equation (4.28) times \( \pi r_e^2 / T \), using equation (4.27), the result is given by

\[
\frac{dq_0(t)}{[N_b - N_1(t)][1 - q(t)]} = \frac{\pi r_e^2}{T} R_i(t) dt .
\]

Combining the equation (4.29) and (4.26), it gives

\[
\frac{dq_0(t) + dq_e(t)}{1 - q(t)} = \frac{dq(t)}{1 - q(t)} = [N_b - N_1(t)] \frac{\pi r_e^2}{T} R_i(t) + dA_e(t) .
\]

From which, it follows that

\[
q(t) = 1 - \exp \left\{ - \left[ A_e(t) + \frac{\pi r_e^2}{T} \int_0^t [N_b - N_1(t)] R_i(\xi) d\xi \right] \right\}
= 1 - \exp \left[ -A(t) - \frac{\pi r_e^2}{T} \int_0^t [N_b - N_1(t)] R_i(\xi) d\xi \right]
\approx 1 - \exp [-A(t)]
\]

In the above equation, the approximation for the last step is based on the fact that

\[
A(t) \gg \frac{\pi r_e^2}{T} \int_0^t q(t) [N_b - N_1(t)] R_i(\xi) d\xi
\]

Using equation (4.32), the switched area of the switchable part can be calculated.

However, for the whole film, the preexisting nuclei have to be taken into account for the total switched area and the total polarization of the film. By the geometric consideration, the switched area of the total film is then given by

\[
Q(t) = \begin{cases} 
(1 - n_s^- - n_s^+) q(t) + n_s^- & P : \text{positive} \rightarrow \text{negative} \\
(1 - n_s^- - n_s^+) q(t) + n_s^+ & P : \text{negative} \rightarrow \text{positive} 
\end{cases}
\]
where $P$ : positive $\rightarrow$ negative means the switching is from the positive biased to the negative biased. Therefore, the total polarization due to the ferroelectric switching is given by

$$P_F(t) = \begin{cases} P_s^*[2Q(t) - 1] & P: \text{positive} \rightarrow \text{negative} \\ P_s^*[1 - 2Q(t)] & P: \text{negative} \rightarrow \text{positive} \end{cases} \quad (4.34)$$

Finally, by considering the linear response, the total polarization is given by

$$P(t, E) = P_F(t, E) + P_L \quad , (4.35)$$

where $P_L = \epsilon_f^{\text{linear}} \epsilon_0 E$.

Equation (4.35) can be used to calculate the dynamic switching of ferroelectric thin films. In addition, the proposed model is consistent with Fatuzzo's and Ishibashi's models with some additional constraints, which is discussed in next section.

4.4.3 Special Case

In this section, the relation between the new model and the Fatuzzo/Ishibashi model is discussed. It can be seen that by introducing some additional assumptions and constraints, the current model can be reduced to their models.

In the Fatuzzo model [74], it is assumed that the nucleation probability is constant, because it is determined solely by the external field, which is constant in his model. Besides, the domain nucleation probabilities are uniform around the whole film during the whole switching process and no preexisting nuclei are considered. These additional constraints requires $n_+^* = n_-^* = 0$ and $\lambda' = 0$, and equations (4.16) and (4.17) then
give constant nucleation probabilities. Equation (4.35) is reduced to equation (2.26). Therefore, the current theory is a generation of the Fatuzzo model.

On the other hand, if the field is low enough during the switching process, the nucleation inside domains is prohibited so that there is no nuclei form during the switching. Together with the assumption that the domain velocity is constant, i.e., \( \lambda' = 0 \), and there is a number of preexisting nuclei sites, i.e., \( n_0^+ = n_0^- \neq 0 \), the current theory turns out to be the first category of the Ishibashi model [75]. As pointed out in section (2.2), the second category of the Ishibashi model is the case of Fatuzzo’s model.

An analytic solution of equations (4.31)-(4.35) is not possible because of the recursion dependence of the nucleation probabilities on the polarization. A numerical approach is developed to solve this problem in next section.

### 4.5 Numerical Analysis Technique

In order to solve equations (4.31)-(4.35) numerically, first, the units of the quantities are defined. Then, the initial conditions are selected. Finally, the technique of numerical integration is introduced.

#### 4.5.1 Units

The units of the quantities are chosen as the follows: The unit of the polarization is \( \mu C/cm^2 \). The activation field and the electrical field are in the unit of \( kV/cm \).
The vacuum dielectric constant is given by
\[ \epsilon_0 = 8.85 \times 10^{-12} \frac{(\mu C)^2}{N \cdot cm^2}. \] (4.36)

Therefore, the relation between the units of the quantities is given by
\[ \frac{[P]}{[\epsilon_0]} = \frac{\frac{\mu C}{cm^2}}{\frac{N}{\mu C} \frac{cm}{cm^2}} = \frac{N}{\mu C} = 10 \frac{kV}{cm} = 10[E], \] (4.37)

where "[Q]" means take the unit of the quantity Q. For example, according to equations (4.15) and (4.37), if \( P = 40 \mu C/cm^2 \), the depolarization field is then given by
\[ E_d = \frac{\lambda'}{\epsilon_0} P = \lambda' \left( \frac{40 \frac{\mu C}{cm^2}}{8.85 \times 10^{-12} \frac{\mu C}{N \cdot cm^2}} \right) = \lambda' \times 4.52 \times 10^4 \times \left( 10 \frac{kV}{cm} \right), \] (4.38)

where \( \lambda' \) is a dimensionless constant.

**4.5.2 Initial Condition Computations**

1. First, define the constants required for the computation. These include: \( \lambda', r_0, r_g, P_s^*, \alpha, n_s^+, \) and \( n_s^- \). The values of these quantities are listed in tables (4.1) and (4.2) for the calculations discussed in the next section.

2. Second, define the initial conditions. At time \( t = 0 \), i.e., at the calculation step \( m = 1 \), assume the film is fully saturated in its positive saturation state. The initial polarization is given by equation (4.5) and it is rewritten as
\[ P(m = 1) = (1 - 2n_s^-)P_s^*, \] (4.39)

and the initial number of the nuclei is given by
\[ N(m - 1) = N_s^- = kn_s^- r_g^2. \] (4.40)
The initial nucleation probability adjacent to the domain wall is given by equations (4.16) and (4.17),

\[ R_w(m = 1) = \exp \left( -\frac{\alpha}{E_{loc}} \right) = \exp \left[ -\frac{\alpha}{E_0(1) - \frac{\lambda'}{\epsilon_0} P(1)} \right], \quad (4.41) \]

\[ R_s(m = 1) = \exp \left( -\frac{\alpha'}{E_{loc}} \right) = \exp \left[ -\frac{\alpha'}{E_0(1) - \frac{\lambda'}{\epsilon_0} P(1) + \frac{Pr}{3\epsilon_0}} \right], \quad (4.42) \]

where \( E_0(1) \) is the initial value of the external field. The initial switched area of the switchable part is given by

\[ q(m = 1) = 0 \quad , \quad (4.43) \]

and the initial switched area of the whole specimen is given by

\[ Q(m = 1) = n_s^- \quad . \quad (4.44) \]

It is consistent with the initial polarization according to equations (4.34) and (4.39).

### 4.5.3 Numerical Integration

At step \( m \), the nucleation probabilities are calculated by using the polarization at step \( m - 1 \) and the external electrical field at step \( m \):

\[ R_w(m) = \exp \left( -\frac{\alpha}{E_{loc}} \right) = \exp \left[ -\frac{\alpha}{E_0(m) - \frac{\lambda'}{\epsilon_0} P(m - 1)} \right], \quad (4.45) \]

\[ R_s(m) = \exp \left( -\frac{\alpha'}{E_{loc}} \right) = \exp \left[ -\frac{\alpha'}{E_0(m) - \frac{\lambda'}{\epsilon_0} P(m - 1) + \frac{Pr}{3\epsilon_0}} \right], \quad (4.46) \]

Then, the radius of a domain formed at step \( n \) is given by

\[ r(m, n) = r(m - 1, n) + (2r_c) R_w(m) \quad , \quad (4.47) \]
Figure 4.3  Routine of numerical calculation: using \( P(m) \) and the external field \( E(m+1) \), the local field at time \( t = m + 1 \) can be calculated, then the nucleation probabilities are calculated using \( E_{local}(m+1) \). Finally, Using equations (4.31)-(4.35), \( P(m+1) \) can be achieved.

where \( m > n \). Hence, the area covered by the domain is given by

\[
S(m, n) = \frac{\pi r^2(m, n)}{T}.
\]

(4.48)

In addition, the area that the preexisting nuclei has expanded is given by

\[
S_e(m, 1) = \frac{\pi [r^2(m, 1) - r_e^2]}{T}.
\]

(4.49)

Therefore, the switched area developed in the imaginary system at step \( m \) is given by

\[
A(m) = \sum_{l=1}^{m-1} [1 - q(t)][N_b - N_1(l)]R_1(l)S(m, l) + N_e^- S_e(m, l).
\]

(4.50)

The switched area in the real finite system at step \( m \) is then given by

\[
q(m) = 1 - \exp[-A(m)].
\]

(4.51)
Finally, the switched area of the whole specimen and the polarization is given by

\[ Q(m) = (1 - n_s^- - n_s^+) q(m) + n_s^- \]  \hspace{1cm} (4.52)

\[ P(m) = P_s^* [1 - 2Q(m)] + \epsilon_f^\text{linear} \epsilon_0 E(m) \]  \hspace{1cm} (4.53)

The calculation routine discussed above is sketched in Figure 4.3.

4.6 Model Results

The switching behavior of a ferroelectric thin film is now investigated using the equations derived above. According to these equations, nine parameters can be adjusted to perform the calculation: calculation steps \( N \), amplitude of external field \( E_m \), saturation polarization of the single crystallite \( P_s^* \), coefficient of depolarization field \( \lambda \), critical nuclei radius \( r_c \), crystallite radius \( r_g \), activation field \( \alpha \), and area fraction covered the preexisting nuclei \( n_s^+ \) and \( n_s^- \). Among them, some are determined by the external experimental routines such as \( N \), \( E_m \), and some can be computed directly from the experimental results such as \( r_g \), and \( P_s^* \). Some parameters such as \( r_c \) and \( \alpha \), can be calculated from basic thermodynamic principles as discussed in section (2.2). Given a set of experimental switching data, the parameters of a theoretical curve should be consistent with the values from these basic theories and the other related experimental results. However, the experimental data fitting is not included in the present thesis, but the way these parameters affect the hysteresis and the switching current in general will be addressed. In this section, first, the hysteresis is calculated by applying a cosinusoidal external field. Then, the dynamic switching current is
calculated.

4.6.1 Hysteresis

For the hysteresis phenomena, a cosinusoid field with amplitude $E_m$ is applied on the film and is depicted in Figure 4.4. The horizontal axis represents the calculation step, which is proportional to the time. The vertical axis stands for the external field $E_0$.

**Figure 4.4** The history of the external field used for the calculation of hysteresis loop.

For each calculation in the following sections, the parameters are defined, while only one of them is varied. The effects of the varying parameters are discussed in the
sequence of $n_s$, $\lambda$, $r_c$, $\alpha$, $P_s^*$, and the calculation steps, $N$. The parameters used to perform the analysis are listed in table 4.1.

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<td>$150$, $200$, $250$ (Figure 4.8)</td>
</tr>
<tr>
<td>$P_s^*$</td>
<td>40</td>
<td>$30$, $40$, $50$ (Figure 4.9)</td>
</tr>
</tbody>
</table>

Table 4.1 Parameters used for hysteresis calculation. Unless specified in comments, the values in second column are used.

1. Effects of Preexisting Nuclei (Heterogeneous Nucleation: $n_s^+ = n_s^- = n_s$)

The hysteresises calculated for different values of $n_s$ ($n_s^+ = n_s^- = n_s$) are plotted in Figure 4.5 (a). The saturation polarization decreases and the switching time decreases with increasing the number of the preexisting charged nuclei. The decrease of the polarization is due to the increase of the un-switchable area, and it can be understood from equation (4.5) and (4.6). The curves show that the coercive field decreases with increasing the number of preexisting nuclei. On the other hand, with $n_s = 0$, the coercive field calculated ($\sim 170 kV/cm$) is still much smaller than the intrinsic value.
Figure 4.5  Theoretical hysteresises with different numbers of the heterogeneous nuclei ($n_s$): (a) Hysteresis loops, the larger number of the heterogeneous nuclei the more slanted the hysteresis loop, which means a smaller coercive field and remanent polarization. (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
\( \sim P_s / \epsilon_0 \epsilon_f \sim 10^5 kV/cm \). This is a result of the extrinsic polarization, i.e., the sidewise motion of the domains is predominant, once the nuclei form.

The nucleation probability adjacent to domain walls \( R_w \) vs. the external field \( E \) is plotted in Figure 4.5 (b). It can be seen that under the same external field, \( R_w \) decreases with increasing preexisting charged nuclei. The low value of \( R_w \) corresponds to a small domain wall velocity. That is to say, if the number of domains is constant, the smaller the domain velocity is, the slower the switching and the more slant the hysteresises are.

However, because of the preexisting nuclei provide a large number of developing domains, it compensates the small domain velocity. Figure 4.5 (c) shows the nucleation probability inside domains. For \( n_s = 1\% \), the switching is finished before the electrical field reaches 200kV/cm, at which the nucleation inside domains is not start yet. It indicates that the switching is predominantly controlled by the preexisting nuclei development. However, with \( n_s = 0 \), the switching does not start until the nucleation probability inside domains \( R_i > 0 \). *

2. Effects of Depolarization Field \( (\lambda') \)

As shown in Figure 4.6 (a), the hysteresis loop is slanted with increasing the coefficient of the depolarization field. Physically, with the polarization \( P > 0 \), the

*At \( E_0 = 0 \), the film has a single domain configuration with \( n_s > 0 \), while it shows multi-domains with \( n_s > 0 \). Therefore, the calculation shows the effects of domain structures on the switching properties.
Figure 4.6  Theoretical hysteresis with depolarization field coefficient ($\lambda'$): (a) Hysteresis loops, the larger the depolarization field the more slanted the hysteresis loop, which means a smaller coercive field and remanent polarization, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
depolarization field assists the nucleation of the domains with reversed polarization, and the switching starts earlier with larger \( \lambda' \). On the other hand, if the polarization \( P < 0 \), the depolarization field retards the switching process. It can be seen from Figure 4.6 (b), where the nucleation probability adjacent to the domain wall is illustrated. Figure 4.6 (c) indicates that the switching for the three hysterises (in Figure 4.6 (a)) are all controlled by the development of the preexisting nuclei, because the nucleation probabilities insides domains are zero during the whole switching processes. In addition, the coercive field and the remanent polarization decrease with increasing the coefficient of depolarization field.

3. Effects of Critical Nuclear Radius \((r_c)\)

The effects of increasing the critical radius of the nuclei are shown in Figure 4.7(a). As shown in Figure 4.7(c), the nucleation inside domains is around zero until the external field reaches \(-250kV/cm\) at which the switching process is almost finished. Therefore, the switching is determined by the development of the preexisting nuclei. The shrinking of the hysteresis loop with large critical nucleation radius is due to the increase of the domain velocity. From equation (4.19), the domain velocity \( v \) is proportional to the critical nucleation radius and the nucleation probability adjacent to domain walls, i.e.,

\[
v \propto r_c R_w \quad .
\]  \hfill (4.54)

The domain velocities are shown in Figure 4.7 (b), which are corresponding to the
Figure 4.7  Theoretical hysteresis with different nuclei radius ($r_c$): (a) Hysteresis loops, the larger nuclei radius the smaller coercive field, (b) Domain wall velocity, (c) Nucleation Probability inside domains.
hysteresises shown in Figure 4.7 (a). It can be seen that the larger the size of the critical nuclei is the larger the domain wall velocity is. Therefore, with increasing the critical nuclei size, the switching terminates quickly and the coercive field decreases.

4. Effects of Activation Field ($\alpha$)

From equations (4.16) and (4.17), the larger the activation field is, the smaller the nucleation probability is and hence, the smaller the domain velocity is. This effect is depicted in Figure 4.8 (a). The nucleation probability adjacent to the domain walls, i.e., the domain velocity, is plotted in Figure 4.8 (b). The nucleation probabilities inside domains are zero for these processes (as shown in Figure 4.8 (c). From Figure 4.7 (a), a large coercive field is predicted for a material with large activation field.

5. Effects of Saturation Polarization ($P_s$)

The hysteresis, nucleation probabilities adjacent to domain wall and nucleation inside domains are shown in Figure 4.9 (a), (b) and (c) for different saturation polarization, respectively. As a reference, the relation between the saturation polarization and the coercive field can be approximated as follows: The energy density associated with the spontaneous polarization is

$$u_p = \frac{1}{2} \frac{P_s^2}{\varepsilon_f \varepsilon_0} \quad .$$

(4.55)

The external field $E$ would contribute to the energy density by

$$u_E = E \cdot P_s \quad .$$

(4.56)
Figure 4.8 Theoretical hysteresises with different activation field ($\alpha$): (a) Hysteresis loops, the larger the activation field, the larger the coercive field, (b) Nucleation probability adjacent to domain walls, (c) Nucleation probability inside domains.
By assuming \( u_E \approx u_p \), the coercive field can be estimated as

\[ E_c \approx \frac{1}{2} \frac{P_s}{\varepsilon_f \varepsilon_0} \quad (4.57) \]

Therefore, a large saturation polarization results in a large coercive field. However, the calculation results are not consistent with this physical consideration. It is because the switching process calculated in Figure 4.9 is an extrinsic process, while the above discuss is for intrinsic switching. For an extrinsic polarization switching, the determinative parameters are the domain numbers and the domain velocity. As shown in Figure 4.9 (b), the domain velocities for a material with small saturation polarization are large during most of the switching process. Figure 4.9 (c) shows that the nucleation probability inside domains is large for a material with small saturation polarization. The calculation shows the difference between the extrinsic switching and the intrinsic switching.

6. Effects of Frequency (Calculation Steps \( N \))

For the numerical calculation, the frequency of the external field is controlled by the calculation steps \( N \). Assuming the time interval for the calculation is \( N \), the period of the external field is then given by

\[ T = N \Delta t \quad (4.58) \]

Therefore, the frequency is dependent on the reciprocal of the calculation steps. Figure 4.10 (a) shows the coercive field decreases with increasing the calculation steps.

*See Appendix A for detailed descriptions of the technique of numerical calculation.
Figure 4.9  Theoretical hysteresises with different saturation polarization ($P_s$): (a) Hysteresis loops, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
Figure 4.10  Theoretical hysteresises with different frequency of the external filed (Calculation steps $N$: (a) Hysteresis loops, the larger the frequency (the smaller the calculation step), the larger the coercive field, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
i.e., decreasing the frequency of the external field. With decreasing the frequency, although the nucleation probabilities adjacent to the domain walls decrease as shown in Figure 4.10 (b), the increase of the growth times (time interval) at lower external field results in the decrease of the coercive field. Figure 4.10 (c) shows the nucleation inside domains can be neglected for this set of calculation parameters.

7. Unsaturated Hysteresis Loop

The proposed model can also be used to investigate unsaturated hysteresis loops. Figure 4.11 (a) shows the history of the applied external field, which has a sinusoidal waveform. However, at time \( t = 3T/8 \) (where \( T \) is the period of the input field), the amplitude of the external field changes from \( E_m = 350kV/cm \) to a smaller value \( (E_m = 250kV/cm) \). Figure 4.11 (b) shows the corresponding hysteresis loops. A saturated loop is also plotted in Figure 4.11 (b). The dashed line stands for the transition from a saturated loops to an unsaturated one. The calculation result shows that the coercive field, saturation polarization and remnant polarization of the unsaturated loop are smaller than the saturated one. The differences between the saturated and unsaturated loops can be understood as follows: When the amplitude of the external field decreases without saturating the film, it leaves a relative large number of domains. Because these domains have opposite polarization directions, the total polarization is smaller. In addition, with a large number of domain walls, the switching is easier and the coercive field is therefore smaller than that of a saturated
loop.

Figure 4.11 Unsaturated hysteresises: (a) The history of the external field, (b) Unsaturated loop (red line) and Saturated loop (black line) with the transition line BC.
4.6.2 Switching Current

The current response to a constant external field is discussed in this section. The external field used for calculation is a step function i.e., when time $t < 0$, $E = 0$ and the magnitude of the external field is $E_m$, when $t > 0$. The effects of the varying parameters are discussed in the sequence of $N_s$, $\lambda'$, $r_c$, $\alpha$, $P_s^*$, and $E_m$. The parameters used for calculation are listed in table 4.2.

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<td>$E$</td>
<td>300</td>
<td>$125$, $130$, $135$ (Figure 4.17)</td>
</tr>
</tbody>
</table>

Table 4.2 Parameters used for switching current calculation. Unless specified in comments, the values in second column are used.

1. Effects of Preexisting Nuclei (Heterogeneous nucleation: $n_s^+ = n_s^- = n_s$)

Figure 4.12 (a) shows that the maximum value of the switching current increases with increasing the number of the preexisting nuclei, while the switching time decreases. Although the domain nucleation adjacent to the domain walls (Figure 4.12
Figure 4.12  Theoretical switching current with different number of the preexisting nuclei $n_s$: (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
(b)) and inside domains (Figure 4.12 (c)) with large number of preexisting nuclei are smaller than these without preexisting nuclei, the slow switching of the material without the preexisting nuclei is because that it spends time for forming a number of nuclei through the nucleation inside domains

2. Effects of Depolarization Field ($\lambda'$)

The effects of the depolarization field are depicted in Figure 4.13 (a), (b) and (c). Figure 4.13 (a) is the switching current vs. time. Figure 4.13 (b) and Figure 4.13 (c) are the nucleation probabilities adjacent to domain walls and inside domains, respectively. With $\lambda'$, the nucleation probabilities keep constant during the whole switching process. Therefore, the switching current is symmetric. It is the case described in Fatuzzos model. On the other hand, because the depolarization field depends on the sign of the polarization, its contribution to the local field is non-symmetric during the switching process. As shown in Figure 4.13 (b), the larger the depolarization field is the non-symmetric the nucleation probability is, which causes that the domain velocity is large at the beginning of the switching and small at the end of the process. The result shows that the long tail of the switching current observed in the experiments can arise from the depolarization field. Compared to the explanation of the non-integer dimensionality of domain wall motion and the abruptly change of the domain growth dimensionality, the current proposed model keeps the physical meaning of the original Avrami theory.
Figure 4.13  Theoretical switching current with different depolarization field $\lambda'$: (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
3. Effects of Critical Nuclear Radius \( (r_c) \)

The switching time is determined by the domain wall velocity, and the domain wall velocity is proportional to the size of the critical nuclei (equation (4.54)). The calculated curves of the switching current are plotted in Figure 4.14 (a), and the domain wall velocity \( (\propto R_w r_c) \) is depicted in Figure 4.14 (b). Figure 4.14 (c) indicates the nucleation probabilities inside domains are in the same order for different critical nuclei size. The model results consistent with the physical analysis.

4. Effects of Activation Field \( (\alpha) \)

The switching current, the nucleation probability adjacent to domain walls and the nucleation probability inside domains are shown in Figure 4.15 (a), (b) and (c), respectively. It can be seen that the smaller the activation field is the larger the nucleation probability adjacent to the domain walls is, i.e., the larger the domain velocity (Figure 4.15 (b)). Therefore, the switching time decrease with decreasing the activation field as shown in Figure 4.15 (a). There are only slight differences between the nucleation probabilities inside domains with different activation fields (Figure 4.15 (c)), which indicate that the differences of switching speed arise from the domain wall velocity not the domain numbers.

5. Effects of Saturation Polarization \( (P_s) \)

Equations (4.17) and (4.18) show that the nucleation inside domains is determined by the magnitude of the saturation polarization. It is easier to form nuclei inside
Figure 4.14  Theoretical switching current with different nuclei radius \( r_c \): (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
Figure 4.15  Theoretical switching current with different activation field $\alpha$: (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
domains for a ferroelectric material with a smaller saturation polarization. This
effect is shown in Figure 4.16 (a)-(c), which illustrates the nucleation probabilities
inside domains. Although the nucleation probability adjacent to domain walls of a
material with small saturation polarization is slightly smaller than that with a large
saturation polarization (Figure 4.16 (b)), the large number of nuclei produced by the
nucleation inside domains speed up the switching for a ferroelectric material with a
smaller saturation polarization as shown in Figure 4.16 (a).

6. Effects of the Amplitude of External Field \(E_m\)

The dependence of the switching current on the magnitude of the external field
is shown in Figure 4.17 (a)-(c). In Figure 4.17 (a), the switching current is depicted
as a function of time. Figure 4.17 (b) and (c) shows the nucleation probabilities
adjacent to domain walls and inside domains, respectively. It can be seen that the
fast switching, i.e., the large maximum switching current, in a large external field
arises from the large nucleation probability inside domains, which results in a large
number of nuclei. Figure 4.18 is curve of the maximum of the switching current vs. the
external field. The inset in Figure 4.18 plots the same data with x-axis \(1/E\) and y-axis
\(\log(i_m)\). The linear dependence is predicted as observed in the experiments [66, 84],
and the change of the slope is because the predominant process of a switching in a
lower external field is the development of the preexisting nuclei, while the switching is
controlled by the nucleation inside domains in a high field (Figure 4.17 (b) and (c)).
Figure 4.16  Theoretical switching current with different saturation polarization $P_s$:
(a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
Figure 4.17  Theoretical switching current with different external field $E_m$: (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
Figure 4.18  Relation between the amplitude of the external field $E_m$ and the maximum switching current $i_m$: inset plots $\log(i_m)$ vs. $1/E$. It shows linear dependences at both high (III) and low field (I) ends, which correspond to the domain formation control and domain wall motion control regimes.

The above discussion assumes the external field is a perfect step wave, i.e., when time $t < 0$, $E_0 = 0$; and $t \geq 0$, $E = E_m$. In next section, the effects of the rising edge of the external field are discussed.
4.6.3 Effect of the Rising Edge of the External Field

In order to model the rising edge of the external field, assume the external field can be written as

\[ E(t) = E_m \left[ 1 - \exp \left( \frac{t}{t_s} \right) \right] , \]  

(4.59)

where \( t_s \) is a time constant. As shown in Figure 4.19, a large \( t_s \) corresponds to a slow rising edge of the external field. The effects of the rising edge are discussed for two cases: a film with preexisting nuclei \( (n_s \neq 0) \) and a film without preexisting nuclei \( (n_s = 0) \).

Figure 4.20 (a) shows the curves of switching current vs. time by given the fields
Figure 4.20  Theoretical switching current with different rising edge of the external field $t_s (n_s \neq 0)$: (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
depicted in Figure 4.19. Figure 4.20 (b) and (c) are the nucleation probabilities adjacent to domain walls and inside domains, respectively. For a sharp rising edge, for example, $t_s = 1$, the fast switching of the film is due to the large nucleation probabilities both adjacent to domain walls and inside domains.

However, an interesting result is predicted by the model for the film without preexisting nuclei, as shown in Figure 4.21. In this case, the nuclei can only arise from the nucleation inside domains. There is no switching until the local field is large enough to overcome the barrier of nucleation inside domains. Therefore, a slow rising edge can retard the forming of the nuclei as shown in Figure 4.21 (c). A direct result of this retardation is the switching current is nearly zero at the beginning of the switching, which is shown in Figure 4.21 (a), and the period without switching is called waiting time. It can be seen that the sharper the rising-edge the shorter the waiting time. This phenomenon has been observed in some experiments. Compared with the explanation proposed in their literatures, the relation between the waiting time and the rising-edge of the external field is clarified.

Hereto, it is assumed that $n_s^- = n_s^+$, so the hysteresises are symmetric. In next section, non-symmetric hysteresises will be discussed.
Figure 4.21  Theoretical switching current with different rising edge of the external field $t_s$ ($n_s = 0$): (a) Switching current, (b) Nucleation Probability adjacent to domain walls, (c) Nucleation Probability inside domains.
4.7 Applications

In this section, first, the proposed model is used to understand the phenomena of reliability, such as retention, imprint and fatigue. Then, the dependence of the coercive field on film thickness is discussed by using the model.

4.7.1 Reliability

1. Retention (Polarization Relaxation)

![Graph showing polarization decay over time](image)

**Figure 4.22** Fast decay of the polarization after programming (polarization relaxation). It is due to the depolarization field.

As discussed in section (4.2.1), if the film is biased at positive saturation, and then the external field is vanished. The equilibrium polarization of the film equals
\( P_r \). Therefore, the nucleation probabilities are given by

\[
R_w = \exp \left( -\frac{\alpha}{E_{loc}} \right) = \exp \left[ -\frac{\alpha}{\varepsilon_0 \alpha_0 (P - P_r)} \right] ,
\]

\( 4.60 \)

\[
R_i = \exp \left( -\frac{\alpha'}{E_{loc}} \right) = \exp \left[ -\frac{\alpha'}{\varepsilon_0 \alpha_0 (P - P_r) + \frac{E_s}{2\varepsilon_0}} \right] .
\]

\( 4.61 \)

The relaxation of the polarization is then calculated by using equations (4.31)-(4.35).

The result is shown in Figure 4.22. The polarization undergoes a fast decay when the field is vanished, then it relaxes to the value of the remanent polarization slowly.

The results satisfy the experimental data.

2. Imprint

If a film is biased at negative polarization for a long time, the charged defects and impurities can diffuse onto one surface preferentially. Therefore, the preexisting nuclei for the nucleation of the negative domains overwhelm that of the positive domains in quantity. The effects of the preexisting nuclei have been discussed in the previous section. The difference between \( n_s^- \) and \( n_s^+ \) results in a nonsymmetrical hysteresis, i.e., the positive coercive field does not equal to the negative one as shown in Figure 4.23.*

3. Fatigue

The increase of the un-switchable charged area decreases the total polarization of the film, and speed the switching process. Therefore, the fatigue can be interpreted by the development of the un-switchable area. However, the mechanism of the

*The hysteresis without the preexisting nuclei can be found in figure 4.5 (a).
development of the un-switchable area is out of the scope of this thesis.

![Graph showing polarization vs. external field.](image)

**Figure 4.23** Imprint of the film arises from the nonsymmetrical configuration of the preexisting nuclei.

### 4.7.2 Effects of Film Thickness

In this section, the proposed model is used to investigate the thickness effects. Because the nucleation probabilities adjacent to domain walls are much larger than those insides domains, it indicates that a multi-domain configuration can result in a fast switching and a low coercive field. It has been demonstrated that the equilibrium domain configuration depends on the grain size, and the grain size of the film is a function of its thickness. In addition, the multi-domain configuration corresponds to a small remanent polarization. Therefore, by dealing with the relation between the
remanent polarization and the film thickness, the model proposed in this chapter can be used to calculate the coercive field variation on the domain structure, which is directly related to the thickness of the film.

The remanent polarization of a single grain is determined by its equilibrium domain structure. Assuming the total switched area is $T_s$ and the total surface of the grain is $T$, the remanent polarization can be written as,

$$P_r = \frac{1}{T}[P_s T_s + (T - T_s)(-P_s)]. \quad (4.62)$$

For simplicity, consider a cylindrical configuration, i.e., $T_s$ and $T$ are proportional to the square of the domain width $w$ and the square of the grain linear size $r_g$, respectively. The above equation can then be rewritten as

$$P_r = P_s - 2n_s \left(\frac{w}{r_g}\right)^2 P_s, \quad (4.63)$$

where $n_s$ is the average number of switched domains. Using equation (4.3), the above equation can be written as:

$$P_r = P_s - 2kw^2 P_s. \quad (4.64)$$

In Ref. [26], it is argued, in accord with both intuition and results of earlier studies, that a domain-structure transition, from predominantly multi-domain to predominantly single-domain, occurs below a certain grain size. Therefore, $k$ is not a constant, but a decreasing function of grain size; we assume $k \sim r_g^n$, with $n < 0$.

According to basic thermodynamic considerations, the domain width and grain size satisfy $w \sim r_g^{1/2}$ [30]. In addition, it has been shown that the grain size has a
square root dependence on the film thickness $\tau$, i.e., $r_g \sim \tau^{1/2}$ [27]. Therefore, from (4.64), the remanent polarization of a single grain and the film thickness are related by:

$$P_r \sim \tau^m,$$

(4.65)

where $m = n + 1/2$ is a parameter that depends on the material and growth processing.

For a given equilibrium domain configuration, a hysteresis loop is calculated by the following treatment. As a start point, the film is fully biased at positive saturation state. A sinusoid-applied electric field $E(t)$ is then applied. The calculation strategy is to select appropriate values for the parameters $n_s$, $\alpha$ and $\lambda'$ in equations (4.16) and (4.17), so that the calculated remanent polarization is consistent with the preset value, which is determined by the given equilibrium domain configuration. The conceive field can be directly extracted from the calculated hysteresis loop. By varying domain configuration, i.e., the remanent polarization, a relation between coercive field and remanent polarization can be calculated. With experimental data, the value of $m$ in equation (4.65) can be fitted for different films.

Figure 4.24 shows the dependence of the coercive field on the film thickness. Equation (4.65) is used to relate the remanent polarization of a single grain to the thickness of the film. The circles in Figure 4.24 are the experimental data taken from Ref. [90]. The strongly c-axis oriented characteristics of the film analyzed in Ref. [90] validates our one-dimensional analysis (polarization along the c-axis). The coercive field is
taken from the P-E hysteresis loops, which are observed by a Sawyer-Tower circuit at 60Hz. The best fit for \( m \) in equation (4.65) is \( m = 1/3 \). However, the value for \( m \) is not universal, i.e., it differs for different materials with different thickness ranges.

![Graph](image)

**Figure 4.24** Relationship between film thickness and coercive field. The solid line is the theoretical prediction. The circles are experiment data taken from Ref. [90]

Another argument is that the remanent polarization and saturation polarization of a thin film are not a monotone function of the film thickness. Ref [90] gives an almost random relation between the remanent polarization and the film thickness. This is directly in conflict with our postulation (equation (4.65)). It can be solved by noticing that the remanent polarization and saturation polarization of the ferroelectric thin
film depends not only on the size of an individual grain, but also on the film density, 
the surface coverage and the characteristics of the interface between the ferroelectric 
film and the electrode. However, for a single grain, the polarization is only determined 
by the domain structure
Chapter 5
Growth and Polarization Switching of Lithium Niobate Thin Films

Lithium niobate (LiNbO$_3$) is a man-made ferroelectric material, which has found many applications in the fields of optics, acoustics and electronics, such as surface acoustic wave devices [135], nonlinear optic devices (photonic crystal) [136], waveguiding applications [137, 138], holographic memories [139], and ferroelectric field effect transistors [6, 140, 141]. The properties of bulk LiNbO$_3$ have been extensively studied [142]-[151]. Currently, the fabrication and characterization of LiNbO$_3$ thin films attract much attention [152]-[164], while researches are mainly focused on their optical applications. As a ferroelectric material, LiNbO$_3$ has unique electrical properties as well, however, compared with other ferroelectric materials such as PZT [92] and SBT [108], the switching properties of LiNbO$_3$ thin films are still not well understood.

In this chapter, first, a brief review of LiNbO$_3$ is presented. The structure of LiNbO$_3$ and the growth method of LiNbO$_3$ thin films are introduced. Some works on the electrical properties of LiNbO$_3$ are outlined. Then, the methodologies of our experiments are discussed, which include the growth procedure and the characterization methods. Finally, the experimental results are given and analyzed.
5.1 A brief review of LiNbO$_3$

Reference [142] gives a thorough description of the history and properties of the bulk LiNbO$_3$. A good summary of crystal structure of LiNbO$_3$ can be found in Weis and Gaylors review article [151]. In this section, first, the structure of LiNbO$_3$ is discussed. Then, a number of fabrication methods of LiNbO$_3$ thin films are introduced. Finally, the electrical properties of LiNbO$_3$ are summarized.

5.1.1 Structure of LiNbO$_3$

LiNbO$_3$ shows the highest Curie temperature ($1210^0$C) and the largest spontaneous polarization ($\sim 70\mu C/cm^2$). According to the symmetry, the paraelectric and ferroelectric phases of LiNbO$_3$ belong to $R\bar{3}c$ and $R3c$, respectively. The positions of the lithium atoms and niobium atoms with respect to the oxygen octahedral in the ferroelectric phase are shown in Figure 5.1. It can be seen that the polarization is along the direction of the three-fold rotation axis of the oxygen octahedral. Microscopically, the polarization switching of LiNbO$_3$ arises from the movement of the Li and Nb ions relative to the oxygen octahedral.

5.1.2 Growth of LiNbO$_3$ Thin Films

A number of techniques of growing LiNbO$_3$ thin films have been proposed, such as metallo-organic chemical vapor decomposition (MOCVD) [152, 153], solution gelatin (sol-gel) [154]-[157], chemical beam epitaxy [158], pulsed laser deposition [159]-[161],
Figure 5.1  Structure of LiNbO$_3$ (Ref. [151]): Polarization is along the direction of the three-fold rotation axis of the oxygen octahedral.

molecular beam epitaxy (MBE) [162], metallo-organic decomposition (MOD) [4], and radio frequency (r-f) magnetron sputtering [163, 164]. According to the requirements of the applications, different substrates are used, for example, (100)-oriented or (111)-oriented silicon [152, 154], (0001)-oriented or (1120)-oriented sapphire [153, 155], LiTaO$_3$ [156], diamond [4], and bulk LiNbO$_3$ [162]. On the other hand, highly textured stoichiometric films with crystallographic perfection and optical quality are generally desired for these applications. Besides, it is demanded that the deposition processes of the LiNbO$_3$ thin films are compatible with the other processing approaches of the whole fabrication process of the devices.

It is well accepted that sol-gel, MOD, and LPE (Liquid Phase Epitaxy) methods
are viable to grow stoichiometric films, while it is difficult to control the crystal orientation of the films. Pt [164], MgO [157], and SiO₂ [152] have been used as the buffer layer to solve this problem. Sputtering and laser ablation can easily reach oriented films, whereas the composition of the targets and the ambient are critical to the films stoichiometry, which require additional efforts to find appropriate growth parameters to control the stoichiometry. MOCVD [152, 153] and MBE [162] can take care both the stoichiometry and the orientation issues, however, because of the contamination, the MOCVD process may not be compatible with other fabrication processes, and the MBE process is not cost-efficient for industrial mass production. Although each fabrication process has its deficiencies, researchers have grown LiNbO₃ films with desirable properties. For example, stoichiometric films with (104), (006), and (001) orientations have been fabricated through these different methods [152]-[164], respectively.

5.1.3 Switching Properties of LiNbO₃

Table 5.1 lists some experimental results of the switching properties of LiNbO₃ collected from several papers. It can be seen that the data spread in a large range. As discussed in the preceding chapters, the switching properties are not only related to the crystal perfection, stoichiometry and the interface of the films but also the measurement processes such as the frequency of the external voltage and different setups of the external circuits. In addition, some measurements in Table 5.1 did
not saturate the films. Therefore, a systematic study of the switching properties of LiNbO$_3$ films is expected, which will be one of the purposes of the remaining part of this chapter.

<table>
<thead>
<tr>
<th>Author</th>
<th>$t$ (µm)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ (µC/cm$^2$)</th>
<th>$f$ (Hz)</th>
<th>Substr.</th>
<th>Growth</th>
<th>Electr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wemrile [149]</td>
<td>Bulk</td>
<td>300</td>
<td>70</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Joshi [154]</td>
<td>0.175</td>
<td>18</td>
<td>2.1</td>
<td>3.5</td>
<td>Si</td>
<td>Sol-Gel</td>
<td>Au</td>
</tr>
<tr>
<td>Xu [165]</td>
<td>0.17</td>
<td>13.5</td>
<td>4.5</td>
<td>50</td>
<td>n-Si</td>
<td>Sol-Gel</td>
<td>Au/Al</td>
</tr>
<tr>
<td>Xu [165]</td>
<td>0.17</td>
<td>3</td>
<td>0.75</td>
<td>50</td>
<td>p-Si</td>
<td>Sol-Gel</td>
<td>Au/Al</td>
</tr>
<tr>
<td>Cheng [166]</td>
<td>0.13</td>
<td>230</td>
<td>110</td>
<td>50</td>
<td>Si</td>
<td>Sol-Gel</td>
<td>Pt,Au</td>
</tr>
</tbody>
</table>

Table 5.1 Electrical properties of LiNbO$_3$. ($t$: thickness of the film, $E_c$: coercive field, $P_r$: remnant polarization, $f$:frequency of the external field, Substr.: substrate and Electr.: electrode.)

5.2 Methodologies of the Experiments

The MOD process is used to grow LiNbO$_3$ films on (111) oriented p-type silicon wafer. The crystal phase and orientation is measured by conventional X-ray diffraction. The thicknesses of the films are given by ellipsometry measurements. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to depict the film surface morphology. The hysteresis and pulse response are measured through Sawyer-Tower circuit [167]. These experimental methodologies are described below in sequence.
5.2.1 Growth of LiNbO₃ Thin Films

The MOD procedure consists of four steps: precursor and substrate preparation, spin coating, pyrolysis, and annealing, which are similar to the sol-gel except without the gelatin formation in the MOD process [168]. Following the steps mentioned above, the growth of the LiNbO₃ thin films via MOD process is discussed below.

Lithium neodecanoate (C₉H₁₉COOLi) and Niobium tri-ethoxy dineodecanoate (Nb(OC₂H₅)₃(C₉H₁₉COO)₂) are selected as the lithium and niobium precursors, respectively [168]. They are synthesized through the reactions

\[
\text{Nb(OC}_2\text{H}_5)_5 + 2\text{C}_9\text{H}_{19}\text{COOH} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{Nb(OC}_2\text{H}_5)_3(\text{C}_9\text{H}_{19}\text{COO})_2 , \quad (5.1)
\]

\[
\text{LiOCH}_3 + 2\text{C}_9\text{H}_{19}\text{COOH} \rightarrow \text{C}_9\text{H}_{19}\text{COOLi} + \text{CH}_3\text{OH} , \quad (5.2)
\]

respectively. The chemicals used are listed in Table 5.2.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(OC₂H₅)₅</td>
<td>Noah Technologies</td>
<td>99.99%</td>
</tr>
<tr>
<td>LiOCH₃</td>
<td>Noah Technologies</td>
<td>99.9%</td>
</tr>
<tr>
<td>C₉H₁₉COOH</td>
<td>Strem Chemicals</td>
<td>99.99%</td>
</tr>
</tbody>
</table>

Table 5.2 Sources of the chemicals

According to the stoichiometric ratio (LiNbO₃: \( M_{\text{Li}}/M_{\text{Nb}} = 1:1 \)), first, appropriate amount of lithium methoxide and neodecanoic acid are mixed and stirred using a magnet stirrer for about 24 hours till the white powders of lithium methoxide are totally solved into the acid, i.e., lithium neodecanoate is synthesized. Then, by mixing
and stirring the niobium ethoxide and neodecanoic acid, niobium tri-ethoxy dineodecanoate can be synthesized. Finally, by mixing the two precursors and stirring the mixture for another 24 hours, the precursor becomes uniform and transparent. The precursor is then sealed and kept in a drier. The whole synthesis can be performed at room temperature, although it is told that slightly elevated temperature can assist the reaction. In addition, the precursor is stable, and good quality films can still be deposited using the same precursor after six-month storage. (111)-oriented p-type silicon wafers are used as the substrates. They are cleaned ultrasonically in acetone and dried in air.

The precursor is dispensed onto the surface of the substrate by using an injector. The substrate is then mounted onto the spinner. The excess of the precursor is spun off because of the centrifugal force. Therefore, the thickness of the films depends on the viscosity of the precursor, the spinning speed and the spinning time. Spinning speeds used in this work vary from 1000 to 8000 rpm.

According to the thermogravimetry (TGA) analysis of these precursors (refer to Appendix B), the precursors are pyrolyzed at 500°C for 30 minutes in the ambient. After the pyrolysis, the temperature of the oven is elevated to 800°C rapidly, and the films are annealed for 15 minutes for the crystallization both in oxygen and in the ambient.
5.2.2 Characterization of LiNbO$_3$ Thin Films

Conventional X-ray diffractometry is used to analyze the phase and the orientation of the films. Cu $K_\alpha$ ($\lambda = 1.5418\text{Å}$) is excited from the copper tube by using a voltage of 20 $kV$ and a current of 1.94 $mA$. The angles scanned ($2\theta$) are from $20^0$ to $50^0$ with $0.02^0$ step size, and the count time is 3 seconds at each step. Because of the highly orientation of the silicon substrate, the Si (111) peak ($2\theta = 28.44^0$) is the highest peak of the XRD pattern, which is used to calibrate the angles, i.e., the highest peak of the XRD pattern is indexed as $28.44^0$. However, if the X-ray tube, the sample and the detector are aligned well so that the intensity of this peak reaches the highest counts, the peaks of the films can be submerged in the strong background noise. A solution is to adjust the position of the sample so that it is slightly deviated from the best reflection situation, i.e., the detector does not collect the reflected beam in the most efficient way. Because the adjustment can also reduce the intensities of the films peaks, if the signals of the film peaks are too weak, the background noise can still overwhelm the peaks of the film. Fortunately, the misalignment affects the intensities of the peaks of the silicon substrate and the noise dramatically, while it changes the film peaks slightly [169]. It is found that a good result can be got when the count rate of the Si (111) peak is around 1000 counts/sec.

The film thickness is measured by the ellipsometry. A good review of the method can be found in reference [170]. In our experiments, the incident angle of the laser
beam is 70°. The light source is a He-Ne laser with wavelength Å. The refractivity of the substrate is measured first and used to calculate the thickness of the films. A problem is that Lithium niobate is a birefringence material. The birefringence has to be considered, because the methodology depends on the measurement of the reflection beam. Because the birefractions of the LiNbO₃ are close to each other (nₒ = 2.29; nₑ = 2.20), the birefringence can be neglected. The error introduced by the neglecting is approximated as follows:

For larger thicknesses, the results of the ellipsometry measurements are periodically depends on the thickness, and the period is given by

\[ d = \frac{\lambda}{2\sqrt{n_2^2 - \sin^2 \phi_1}} \]  \hspace{1cm} (5.3)

where \( d \) is the period, \( n_2 \) is the refractivity of the film, and \( \phi_1 = 70° \) is the incident angle. We have

\[ \frac{\delta d}{d} = \frac{n_2^2}{n_2^2 - \sin^2 \phi_1} \frac{\delta n_2}{n_2} \]  \hspace{1cm} (5.4)

where \( \delta n_2 = n_e - n_o = 0.09 \) and \( n_2 \simeq (n_e + n_o)/2 = 2.25 \). According to the above equation, the error of the thickness measurement is about 5%. On the other hand, the typical thicknesses of the films are about 1000 Å, hence, the error is about 50 Å, which is in the same order of the surface non-uniformity. Therefore, the birefringence of the LiNbO₃ can be neglected. However, it should be pointed out that the birefringence makes it difficult to tell a null output, which may result in reading errors and lower the accuracy of the measurement as well.
The surface morphology of the films is checked by SEM and AFM. SEM is used to depict the surface morphology in a large scale, and AFM is to measure the grain size and the local surface uniformity. The SEM is a Philip that is working at $10 \, kV$ (electron accelerating voltage). The AFM is a MultiMode™ SPM manufactured by Digital Instruments, Inc. that is working at the tapping mode. The principles of the microscopy can be found in many textbooks [171].

Figure 5.2  Sawyer-Tower circuit for hysteresis measurement

Figure 5.2 shows the Sawyer-Tower circuit that is used to measure the polarization response to the external electrical field. The input voltage $V_i(t)$ has a sinusoid waveform that is generated by a Wavetek 178 waveform synthesizer. A transformer may be used to increase the amplitude of the $V_i(t)$, which distort the input slightly. Au electrodes with area $0.0028 \, cm^2$ are deposited on the films surface by DC sputter-
ing. The specimen is then placed onto an Au-coated platform, and connected to the circuit through two electrical probes. In Figure 5.2, the sample is represented by a capacitance $C_f$ and a resistor $R_f$, which describes the leakage of the film. $C_0 = 18nF$ is a linear capacitor, and $R_0 = R_fC_f/C_0$ is a resistor to compensate the leakage of the sample. The input and the output are measured by an oscilloscope (TDS 3054). If $C_0 \gg C_f$ and the leakage is small, the polarization is given by

$$P = \frac{C_0V_o(t)}{A},$$

(5.5)

where $A$ is the area of the electrode. The electric field applied on the sample is given by

$$E = \frac{V_i(t)}{d},$$

(5.6)

where $d$ is the thickness of the film. Hence, the dielectric hysteresis can be monitored.

![Circuit Diagram](image)

**Figure 5.3** Circuit for switching current measurement

The circuit for measuring the switching current is sketched in Figure 5.3. The pulser is an Avtech AVR-3-Ps-PN-Ru3, which can generate dual polarity four pulses
train trigged by a Stanford pulse generator. The voltage dropped on $R_e$ is then monitored by the oscilloscope, whence the switching current can be measured.

5.3 Experimental Results

The motivations of the experiments are to investigate the switching properties of the LiNbO$_3$ thin films and verify the theories developed in the previous chapters. First, the results of the film growth are presented, which include the thickness, phase and morphology control. Then, the dynamic switching currents are analyzed. Finally, the hysteresises are discussed.

5.3.1 Film Growth

1. Crack and Thickness Control

By using the original precursors, the films grown have cracks on the surface even with the highest spin speed of the spinner and a relatively slow rate ($\sim 1^\circ C/min$) of elevating the temperature from room temperature to the pyrolysis temperature. It is because the viscosity of the original precursor is so large that the films are too thick to avoid cracks. The original precursor is therefore diluted by using toluene as the solvent, and the uniform films without cracks can be synthesized. Meanwhile, the thicknesses of the films can be controlled by the concentrations of the precursors. However, a more conventional method to control the thicknesses of the films is the repetition of the spin coating and the pyrolysis processes. The results of the two
methods are compared as follows:

The films prepared by different dilution of the precursor are listed in Table 5.3, where the ratios in the precursor column means the original precursor (unit: cc) over the solvent (toluene, unit: ml), the colors are observed by optical microscopy, and $\Delta$, $\Psi$ are the average values of the ellipsometry measurement [170]. The spin speeds are about 7600 rpm, and the spin times are 40 sec for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Color</th>
<th>$\Delta$</th>
<th>$\Psi$</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1:10</td>
<td>Light yellow</td>
<td>133.36</td>
<td>13.82</td>
<td>2200</td>
</tr>
<tr>
<td>#2</td>
<td>2:10</td>
<td>Green yellow</td>
<td>99.99</td>
<td>19.81</td>
<td>2350</td>
</tr>
<tr>
<td>#3</td>
<td>3:10</td>
<td>Yellow orange</td>
<td>82.38</td>
<td>25.15</td>
<td>2500</td>
</tr>
<tr>
<td>#4</td>
<td>7.5:10</td>
<td>Blue green</td>
<td>53.44</td>
<td>35.62</td>
<td>4900</td>
</tr>
</tbody>
</table>

Table 5.3 Thickness control by the dilution of the precursor

The refractivity of the substrate is measured by the ellipsometry, which is 3.869-j0.111 ($\Psi = 10.53$, $\Delta = 175.46$). The refractivity of the films is 2.1, which is slightly smaller than the bulk value ($n_o = 2.29$; $n_e = 2.20$). This can be understood by considering the surface roughness, which can be modeled as a solid with pores. Let $V_s$ stands for the volume fraction of the solid, in our case, which is LiNbO₃, and the pores is the air. Hence, the effective refractivity of the rough surface is given by using the Lorentz-Lorenz relationship

$$\frac{n_{e_{ff}}^2 - 1}{n_{e_{ff}}^2 + 2} = V_s \frac{n_s^2 - 1}{n_s^2 + 2},$$

where $n_{e_{ff}}$ is the effective refractivity, which equals to 2.1 in our measurement, and
$n_s$ is the refractivity of bulk LiNbO$_3$. $V_s$ is then calculated to be about 84%, which is identical to the morphology observation as discussed below.

The thicknesses measured through the ellipsometry are well consistent with the color chart except for sample #4. As discussed in the methodologies, the errors introduced by neglecting the birefringence affect the period, therefore, the thicker the film, the inaccurate the data. The trajectory of the ellipsometry is plotted in Figure 5.4. Through multiple spin-pyrolysis processes, the desirable thickness can be reached as well. Table 5.4 lists the experimental data. For each spin step, the spin

![Figure 5.4](image)

**Figure 5.4** Ellipsometry trajectory of the films deposited by precursor-dilution method, the sample numbers are listed in table 5.3.
speed is about 3000 rpm, and the spin time is 60 seconds. The precursor is 2 cc original diluted by 10 ml toluene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer</th>
<th>Color</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#5</td>
<td>1</td>
<td>Green yellow</td>
<td>2350</td>
</tr>
<tr>
<td>#6</td>
<td>2</td>
<td>Pink</td>
<td>3800</td>
</tr>
<tr>
<td>#7</td>
<td>3</td>
<td>Green</td>
<td>5850</td>
</tr>
<tr>
<td>#8</td>
<td>4</td>
<td>Dark green</td>
<td>7000</td>
</tr>
</tbody>
</table>

*Table 5.4  Thickness control by the multi-layer technique*

The thicknesses are read directly from the color chart, because the ellipsometry may cause large errors for thick films. It can be found that the multi-layer technique can control the film thickness in a large range, while the precursor dilution can adjust the film thickness in a more precise manner.

2. Crystal Phase and Orientation

The crystal phase and orientation are examined by the XRD. A typical XRD pattern (sample #8) is shown in Figure 5.5. The peaks are listed in Table 5.5. Compared with the powder diffraction file (PDF) of the LiNbO₃, which is also listed in Table 5.5, the films are stoichiometric LiNbO₃ with random orientation.

3. Surface Morphology and Grain Size

Figure 5.6 is an SEM image of the sample #8, which shows the general surface morphology of the film in a large scale (the scale bar is 200 μm). The contrast of the image is uniform except that there are some bright circular spots sparsely distributed
Figure 5.5  X-ray diffraction pattern of sample #8 (Table 5.4). The sample is stoichiometric LiNbO₃ with random crystal orientation.

<table>
<thead>
<tr>
<th>Index</th>
<th>(012)</th>
<th>(104)</th>
<th>(110)</th>
<th>(006)</th>
<th>(202)</th>
<th>(024)</th>
<th>(116)</th>
<th>(122)</th>
<th>(300)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (Exp)</td>
<td>23.66</td>
<td>32.74</td>
<td>34.84</td>
<td>39.04</td>
<td>42.48</td>
<td>48.50</td>
<td>53.36</td>
<td>56.06</td>
<td>62.56</td>
</tr>
<tr>
<td>2θ (PDF)</td>
<td>23.70</td>
<td>32.69</td>
<td>34.83</td>
<td>38.97</td>
<td>42.56</td>
<td>48.53</td>
<td>53.26</td>
<td>56.15</td>
<td>62.46</td>
</tr>
<tr>
<td>Intensity (Exp)</td>
<td>145</td>
<td>62</td>
<td>56</td>
<td>25</td>
<td>17</td>
<td>19</td>
<td>14</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>Nomalized (exp)</td>
<td>100</td>
<td>43</td>
<td>37</td>
<td>17</td>
<td>11</td>
<td>13</td>
<td>10</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>intensity (PDF)</td>
<td>100</td>
<td>40</td>
<td>20</td>
<td>14</td>
<td>10</td>
<td>16</td>
<td>20</td>
<td>12</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 5.5  XRD peaks of LiNbO₃ thin film grown by MOD process
on the surface.

![SEM image of sample #8 in a large scale. The surface is uniform with bright spots.]

**Figure 5.6** SEM image of sample #8 in a large scale. The surface is uniform with bright spots.

One of the bright spots in Figure 5.6 is magnified in Figure 5.7. The diameter of the circle is about 80 \( \mu m \). Figure 5.8 is a magnified image of the area adjacent to the center of the circle, and a porous structure is observed. It is proposed that the circular spots formed during the pyrolysis process. The precursor usually contains tiny bubbles. Besides, during the pyrolysis process, the volatile gas generated by the decomposition of the precursor may form additional bubbles inside the film, and they move and aggregate to form a larger blister. After their blow-up on the surface, a circular pit forms. However, if the mobility of the matter transfer is high enough, the pit can be mend, otherwise the pits are frozen on the surface.

A zoom-in view of the uniform region in Figure 5.6 is shown in Figure 5.9, where
Figure 5.7  A zoom-in SEM image of the bright spot.

Figure 5.8  SEM image: The porous structure inside the bright spot.
the scale is 1 $\mu m$. Black stripes with irregular shapes can be observed, which is believed to be the micro-cracks and results from the tension relaxation during the crystallization.

![SEM image](image)

**Figure 5.9** SEM image: Micro-cracks on the uniform surface.

The grain size and the local surface uniformity are studied by AFM. An AFM image is shown in Figure 5.10. The contrast of the image reflects the surface height undulation, i.e., the brighter region is higher than the darker one. These brighter dots in the image depict the shape of the grains, and the grain size can be estimated as about 0.1 $\mu m$ in diameter. A large-scale view is shown in Figure 5.11. Again, the micro-cracks can be found, which are those dark stripes in the AFM image (pointed by the arrows).
Figure 5.10  AFM image shows the grain size is about 0.1 μm.

Figure 5.11  AFM image shows the micro-cracks.
5.3.2 Electrical Characterization

The switching properties are analyzed by applied dual-polarity four-pulse train. The dependence of the total switching charge on the amplitude and polarity of the pulse train are discussed. Hysteresis loops are presented and analyzed using the model proposed in the preceding chapters.

1. Switching Current

A typical pulse train is shown in Figure 5.12. In our experiment, the amplitude of the pulses is varied, and the current response is recorded.

![Graph showing voltage over time](image)

**Figure 5.12** A typical pulse train used in the switching current measurement.
5.3.3 Electrical Characterization

Figure 5.13-5.14 are the current responses to the rising edges of the pulses in sequence, respectively (sample #8). These insets are the corresponding external voltage. A large peak followed by a decaying oscillation is observed in the current responses. The circuit is a RC circuit if the ferroelectricity is ignored and the sample is assumed an ideal isolator. The output of such circuit is the differential of the input signal. The ideal response of such circuit should have only one peak. However, if the impedances of the elements in the circuit do not match each other well, the signal can be reflected inside the circuit, and the oscillation will be observed. On the other hand, according to the theory proposed in the preceding chapter, if the external voltage holds constant, there should be no back switching occurs for the ferroelectric material. Therefore, the first dominant peak is attributed to the polarization switching and the RC characteristics of the circuit, while the decaying oscillation arises solely from the reflection of the signal. In the following analysis, the first peaks are analyzed and the oscillation is ignored.

The first peaks of the current response to the four pulses are plotted together in Figure 5.15. These symbols in stands for the experimental data, and the solid curves are the results of smoothing the original data, i.e., cutting off the high frequency noise signals. It can be found that the magnitude of the current of pulse #4 is smaller than that of pulse #3. The difference can be understood by considering the
Figure 5.13  The current response to the positive pulses: (a). The response to the first pulse, (b). The response to the second pulse. The insets are the corresponding history of the applied voltage.
Figure 5.14  The current response to the negative pulses: (a). The response to the third pulse, (b). The response to the forth pulse. The insets are the corresponding history of the applied voltage.
switching processes as follows: After pulse \#2 (positive pulse), the film polarization is in positive direction. By applying pulse \#3 (negative pulse), the switching occurs, and the direction of the film polarization eventually becomes negative. Pulse \#4 (negative pulse) has the same polarity as the film polarization, so there is no switching. Figure 5.15

![Graph showing current response to pulses](image)

**Figure 5.15** The first peaks of the current response to the four pulses.

The difference between the current responses to positive pulses (pulse \#1 and pulse \#2) is not as obvious as negative pulses (pulse \#3 and pulse \#4). The sample is a nonsymmetrical structure, i.e., the structure is a metal-ferroelectric-semiconductor structure. According to the phase stability, the positive polarization of the ferroelectric film is suppressed with a p-type substrate. A schematic picture of the suppressed
hysteresis loop is drawn in Figure 5.14. The switching charge is proportional to the switched polarization $P_{sd}$. Given this nonsymmetrical hysteresis loop, it can be found that $P_{sd}^+ < P_{sd}^-$, where $P_{sd}^+$ and $P_{sd}^-$ are shown in Figure 5.16.

![Diagram of hysteresis loop](image)

**Figure 5.16** Schematic picture of an asymmetric hysteresis loop shows the negative switched polarization is much larger than the positive one, which is suggested to be the origin of the asymmetric amount of the total switched charges.

On the other hand, if the switching current is much smaller than the $RC$ circuit response, the difference between the current responses to the two pulses with same polarity is not distinct. However, the total switched charges depend on the external voltage, i.e., the higher the external voltage, the large amount of the polarization can be switched. The switched charges are calculated by integrating the currents and subtracting the $RC$ response from the total response. For example, for the positive
switching process, the charges due to the $RC$ response can be calculated by integrating the current response to Pulse #2, and assume we get $Q_{RC}^+$. By integrating the current response to Pulse #1, the total charges are given by $Q_{tot}^+$. The switched charges are then given by

$$Q_{sd}^+ = Q_{tot}^+ - Q_{RC}^+. \quad (5.8)$$

Similarly, the switched charges of the negative switching can be calculated. Figure 5.17 (a) and (b) plot the dependence of $Q_{sd}^+$ and $Q_{sd}^-$ on the magnitude of the external voltage, respectively.

The symbols in Figure 5.15 are experimental data, while the solid curves are only for reference. It can be seen that the switching process begins even with the field below the bulk coercive field (300 $kV/cm$), and the total switched charges increase with increasing the external field. Because the pulser cannot output a clean pulse train with voltage less than 2 volts, the overshooting of the pulses and the noise make the efforts of trying to measure the threshold field of switching unsuccessful. On the other hand, with the highest voltage we can get, the switching is not saturated. However, the results already show a clear tendency from the beginning of the switching to the saturation. Besides, our experiments demonstrate the LiNbO$_3$ thin films are appropriate for the memory application with the well-defined dynamic switching characteristics. This can be further demonstrated through the hysteresis measurement as discussed below.
Figure 5.17  Total switched charges (Integral of the first peak of the current response):
(a). Negative switched charges, (b). Positive switched charges.
2. Hysteresis

For the hysteresis measurement, the external voltage is a sinusoid, which is shown in Figure 5.18. The frequency is 50 Hz. The distortion of curve arises from the transformer, which is used to get large amplitude.

![Graph showing external voltage and time](image)

**Figure 5.18** The history of the external applied voltage for hysteresis measurement

The electrode area is 0.0028 cm². The polarization is calculated by equation (5.3). A typical hysteresis loop is shown in Figure 5.19 (sample #8). The remanent polarization and the coercive field can be read from the hysteresis directly: $P_r^+ = 15\mu C/cm^2$, $P_r^- = -21\mu C/cm^2$, $E_c^- = -200kV/cm$, and $E_c^+ = 286kV/cm$. According to the theory proposed in the preceding chapter, the coercive field depends on the remanent polarization, i.e., the larger the remanent polarization the larger the coercive field,
Figure 5.19  Typical hysteresis loop of sample #8.

which is an effect of the pre-existing nuclei. We believe that the interface of the p-type silicon substrate and the film contains more negatively charged defects than the positive ones, for example, the unshielded acceptors. Therefore, it is reasonable that the number of negative preexisted nuclei is larger than that of the positive nuclei. Even with the largest voltage we can get, the hysteresis loop is still not saturated. However, the well-defined loop together with the large remanent polarization demonstrates that the LiNbO₃ thin films are good for the memory application.

The suppression of the polarization mentioned in the analysis of the dynamic switching has also been observed, which is shown in Figure 5.20. The amplitude of the external voltage is 12.5 Volts. It can be seen that the positive polarization is much
Figure 5.20  Hysteresis loop of sample #8: polarization suppression.

smaller than the negative polarization. This suppression becomes significant when the voltage decreases further. This result is consistent with the four-pulse measurement.

Finally, the effect of the depolarization field is examined by comparing the hysteresis loops of the films with different thickness, because the thinner the film, the larger the depolarization field. Sample #5 and #8 are selected (Table 5.4). The hysteresis of sample #5 is plotted in Figure 5.21, and the hysteresis of sample #8 can be found in Figure 5.17. In order to compare the effects of the depolarization, the polarization of these two loops are normalized and drawn together in Figure 5.22. It can be seen that the thinner film (sample #5) has a more shrunken hysteresis loop than the thicker film, which is consistent with the theory.
Figure 5.21  Hysteresis loop of sample #5.

Figure 5.22  Normalized hysteresis loops of sample #5 and sample #8: effects of the depolarization field.
Chapter 6
Conclusions

Polarization switching of ferroelectric thin films is the essential process of the operation of ferroelectric devices. This work shows the relation between the switching properties and the physical parameters of the films such as the number of preexisted nuclei, the depolarization field, the size of the critical nuclei, the activation field, and the magnitude and the frequency of the external field. Based on the results of this research, it is possible to tailor the growth process of ferroelectric films or to build specific structures to realize properties desired. On the other hand, this research shows that LiNbO3 thin films exhibit excellent ferroelectric properties, which can be used in memory applications.

In this Chapter, the results of the thesis are summarized and the comments about future work are suggested.

6.1 Theoretical Aspect

A theory of polarization switching for ferroelectric thin films has been proposed. Different types of domain nucleation have been clarified. The hysteresis loop and dynamic switching current have been examined. The effects of the physical parameters, such as the number of preexisted nuclei, the depolarization field, the size of the critical nuclei, the activation field, and the magnitude and frequency of the external
field, have been studied by a numerical technique. The numerical results show that
the switching time depends on the number of the preexisting nuclei, the depolarization
field, and the magnitude of the external field. It is found that a large number of the
preexisting nuclei, a large external field, a large nuclei size and a small depolarization
field speed up the switching process.

The magnitude of the switching current depends on the magnitude of the exter-
nal field and the saturation polarization of the film. In a small external field, the
polarization switching is dominated by the domain wall motion, while it is controlled
by the formation of new domains in a large external field. The model predicts two
different slopes of the semi log relation of the maximum switching current vs. the
reciprocal of the external field, which is consistent with the experimental results.

The depolarization field is significant in the thin film regime. According to our
model, the elongation of the curve of the switching current is due to the depolarization
field. Besides, the depolarization field results in the polarization relaxation, i.e., the
fast retention.

The hysteresis phenomenon is also considered by using our model. It is found
that the symmetry of the hysteresis loop is strongly dependent on the number of
the preexisting nuclei. If the positive and negative numbers of the preexisting nuclei
are different, the hysteresis loop is not symmetric, i.e., the values of the positive
and negative saturation polarization, coercive field, and remanent polarization do
not equal to each other, respectively. This is referred to the imprint phenomenon. The domain structure with absence of the external field is determined by the grain size. Grain size depends on the thickness of the film. Given a domain structure, the switching process can be calculated by using the proposed model. Our model can therefore predict the film thickness effects as well.

6.2 Experimental Aspect

LiNbO$_3$ thin films have been synthesized through MOD process. The film thickness can be adjusted by either controlling the viscosity of the precursors or using multi-layer technique. The viscosity of the precursors is modified by diluting the original precursor. Using these two methods together with adjusting the spinning parameters can control the film thickness both in a large range and with a more precise.

According to the precise of our X-ray diffractometer, the films are stoichiometric LiNbO$_3$ without other Li-Nb compounds, and are randomly oriented. Microcracks are observed by SEM and AFM. The widths of the microcracks are comparative to the grain size. In this sense, the films have uniform surface except that several large spots, which are identified as the blow-up of the bubbles from the precursor during the pyrolysis process.

The switching currents of the LiNbO$_3$ thin films show extremely nonsymmetrical behavior, i.e., the total switched charge due to the positive pulses are much smaller
than that due to the negative pulses. This results from the nonsymmetrical structure of our samples (Metal-Ferroelectric-Semiconductor structure). The hysteresis measurement verified these results. A nonsymmetrical hysteresis loops are observed. It is found that the positive remanent polarization is larger than the negative remanent polarization. According to our model, the nonsymmetrical hysteresis loops arise from the difference of negative and positive preexisted nuclei. Our model predicts that a smaller positive saturation polarization corresponds to a smaller negative coercive field compared with the positive values. This is consistent with the experimental results.

6.3 Comments about Future Work

For the theoretical aspect, first the finite grain size effects are important to the polycrystalline films and can be modeled within the framework of Fatuzzos model. Next, the relation between the polarization suppression and the polarization switching is unknown. Because the polarization suppression is critical to the semiconducting electrodes, it is worth investigating its effects on the polarization switching. Third, the current model is a one-dimensional case, which means the ferroelectric material exhibits only one polarization axial. Many commercialized ferroelectric materials, such as PZT, SBT, and BST, have multi-directions of polarization. A model is expected to describe the properties of a material with multi polarization directions. Finally, the coupling between the elastic field and the electrical field has not been consid-
ered in our model. The ferroelectric material is also ferroelastic material. Therefore, the ferroelectric phenomena can be affected by the internal and external elastic field. Theoretical work on this coupling may assist the applications of ferroelectric materials in the field of the mechanical sensor and actuator.

For the experimental aspect, first the experiments to verify the theory are proposed as follows:

1. Because an n-type silicon substrate can provide the opposite symmetry compared with the p-type silicon substrate used in the thesis, it is expected that the hysteresis loops exhibit larger negative coercive fields than the positive one. Besides, by implanting different type atoms on the surface of the ferroelectric film, the number of the preexisted nuclei can be monitored so that the effects of the preexisted nuclei can be verified.

2. The depolarization field can be adjusted by using different types of electrodes, such as metallic electrode and semiconducting electrodes with different doping levels. Therefore, the effects of the depolarization field can be examined.

3. Different ferroelectric thin films can be studied for the activation field and critical nuclei size effects.

Second, the film thickness effects can be investigated by the technique of the thickness control. Using SEM and AFM, the relation between the domain structure
and the grain size can be studied. The controversy of the origin of the thickness effects can be solved. Finally, the switching properties of LiNbO$_3$ thin films can be improved by changing the qualities of the film and modifying the properties of the interface between the film and the electrodes. Commercial applicable ferroelectric memory devices can be manufactured by using LiNbO$_3$ thin films.
Appendix A
Matlab Programs and Notes on Calculation

A.0.1 Notes on calculation

In this section, some comments related to the timing analysis and units are given. Because it is the ratio of the switched area over the total area of the sample that is important to the calculation instead of the actual value of the switched area, the calculated hysteresis loop and switching transient are indeed determined by the ratio of the critical size of the nuclei $r_c$ over the size of the sample $r_s$. However, in order to analyze the real time effects, i.e., to get the relation between the calculation steps and the physical time, the unit of the critical size of the nuclei has to be specified:

Each calculation step corresponds to a instant time. For example, step $m$ corresponds to physical time $t$ and step $m + 1$ corresponds to physical time $t + dt$. In another word, the time interval $dt$ is normalized to 1 in the numerical analysis. The question is then what the unit of the time interval is. To extract the unit of the time, let us write the radius of the domain again:

$$r(m, n) = r(m - 1, n) + (2r_c) R_w(m)$$  \hspace{1cm} (A.1)

This equation means, at time $m$, the radius of a domain formed at time $n$ equals to the sum of its radius at time $m - 1$ and the increase of the radius in the time interval from time $m - 1$ to time $m$. Therefore, the domain velocity, $v(t = m)$, is given by

$$v(t = m) = \frac{dr}{dt} = \frac{\Delta r}{\Delta t} = \frac{r(m, n) - r(m - 1, n)}{\Delta t} = \frac{(2r_c R_w(m))}{\Delta t},$$  \hspace{1cm} (A.2)
where, the time interval in the numerical calculation is set to be 1. Next, let us extract the unit of the time. Define "[ ]" as a operator to take the unit of a quantity, then we have

\[ [v(t = m)] = \frac{\text{meter}}{\text{second}} = \left[ \frac{2r_c R_w(m)}{\Delta t} \right] \frac{\text{meter}}{[\Delta t]} \]  \hspace{1cm} (A.3)

Hence, the unit of the time interval is given by

\[ [\Delta t] = [2r_c R_w(m)] \frac{\text{second}}{\text{meter}} \]  \hspace{1cm} (A.4)

where we know that \( R_w \) is a dimensionless quantity. The unit of the time interval is directly related to the unit of the critical size of the nucleus.

As an example, let us relate the calculation steps to the real physical time in the analysis of the effects of the frequency of the external field. The period of the external field \((T)\) is given by

\[ T = N \Delta t \]  \hspace{1cm} (A.5)

where \( N \) is the number of the total calculation steps. Assume the unit of the critical radius of the nucleus is \( \mu m \). According to equation \((A.4)\), the unit of \( \Delta \) is \( \mu s \). Hence, the frequency of the external field is given by

\[ f = \frac{1}{T} = \frac{10^6}{N} \text{Hz} \]  \hspace{1cm} (A.6)

For example, if \( N = 200 \), the frequency of the external field is \( 50kHz \). On the other hand, the frequency of the external field is usually determined by the experimental setup and the critical size of the nucleus is determined by the local field and the
properties of the material. These are two independent quantities. However, According to the above argument, it seems that they are related to each other. This paradox arises from the fact that there is an arbitrary parameter in the nucleation probability, i.e., the nucleation probability $R_w$ should be written as

$$R_w(t) = k_w \exp(-\frac{\alpha}{E_{loc}}),$$  \hspace{1cm} (A.7)

where $k_w$ is the arbitrary parameter. In this thesis, we set $k_w = 1$. The calculation of this parameter requires detailed knowledge of the nucleation probability, i.e., the relation between the nucleation probability and the properties of the specific material, which is out of the scope of this thesis.
A.0.2 Matlab program

The variables used in these programs are defined in the following table C.1:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part I</strong></td>
<td>Physical parameters</td>
</tr>
<tr>
<td>$A_w$</td>
<td>Activation field for nucleation besides domain wall</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Activation field for nucleation inside domain</td>
</tr>
<tr>
<td>$r_c$</td>
<td>The radius of the nucleus at its birth</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Saturation polarization of the material</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Possible nucleation sites for surface nucleation: $N_0$, $N(1) = N_0$</td>
</tr>
<tr>
<td>$N$</td>
<td>Possible nucleation sites for body nucleation: $N = T/r_c^2/\pi$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>The concentration of the surface latent nucleation sites: $N_0 = C_0 * d^n$</td>
</tr>
<tr>
<td>$dt$</td>
<td>Time step for calculation $\sim dt$</td>
</tr>
<tr>
<td>$T$</td>
<td>Total surface area of the film</td>
</tr>
<tr>
<td>$E$</td>
<td>Applied electric field</td>
</tr>
<tr>
<td>$P_r$</td>
<td>Remanent polarization</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Parameter for depolarization field: $E_f = E - \lambda * (P - P_r)$</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Linear dielectric constant</td>
</tr>
<tr>
<td>$rg$</td>
<td>Size of the crystallite</td>
</tr>
<tr>
<td><strong>Part II</strong></td>
<td>Variables</td>
</tr>
<tr>
<td>$D$</td>
<td>Calculation Steps</td>
</tr>
<tr>
<td>$P$</td>
<td>Total Polarization: $P(t)$</td>
</tr>
<tr>
<td>$sA$</td>
<td>Switched Area: $\theta(t)$</td>
</tr>
<tr>
<td>$R_w$</td>
<td>Nucleation Probability besides domain wall: $R_w(t)$</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Nucleation Probability inside domain wall: $R_s(t)$</td>
</tr>
<tr>
<td>$N_t$</td>
<td>Developed nucleation sites: $N(t)$</td>
</tr>
<tr>
<td>$A$</td>
<td>Switched area with overlap: $A$</td>
</tr>
<tr>
<td>$rA$</td>
<td>Switched area without overlap (specific area)</td>
</tr>
</tbody>
</table>

Table A.1 Variables used in these programs

% This function is to calculate the switching by using the
% theory developed in this thesis.
function out = Transient(input)
global As Aw lamda rc Pr Ps N dt T Chi d P D CO C0m NO N0m;

D = input.D;
rc = input.rc;  % unit: nm
rg = input.rg;  % unit: nm
Ps = input.Ps;  % unit: uC/cm^2
k = input.k;  % unit: uC/cm^2
Aw = input.Aw;
As = Ps/8.85*10^-3/2;
lamda = input.Lamda;
Chi = input.Chi;
T = pi*rg^2;
Eamp = input.Eamp;

% Initialize the variables
N = 10^-6*(rg/rc)^2;
Rw = zeros(D,1);
Rs = zeros(D,1);
P = zeros(D+1,1);
Nt = zeros(D,1);
A = zeros(D,1);
rA = zeros(D,1);
E = zeros(D,1);
dNdt = zeros(D,1);

dt = 1;

% Set up the initial value for variables
CO = input.CO;  % ns+
C0m = input.C0m;  % ns-
NO = CO*k*rg^2;
N0m = C0m*k*rg^2

Nt = NOm;  % this is NO
P(1) = Ps-2*Ps*C0m+AppliedField(1,Eamp,D)*8.85*10^-5;

h = waitbar(0,'Please wait...');
for i=1:D
    waitbar(i/D)
% Calculate the applied field E(t)^ Ea
E(i) = AppliedField(i,Eamp,D);
% Calculate the nucleation probability inside a domain
Rs(i) = NucleationProbabilityOS(E(i),P(i));
% Calculate the number of developed nuclei
Nt(i) = ExistedNucleaNum(Rs(i),Nt, rA(i),i);
% Calculate the nucleation probability besides a domain wall
Rw(i) = NucleationProbabilityBW(E(i),P(i));
% Calculate the switched area without consider overlap...
A(i) = OverlappedArea(A,Nt,Rs,Rw,rA(i),i);
% Calculate the total "real" switched area
rA(i) = TotalSwitchedArea(A(i),Rs,Nt,i);
% Calculate the total polarization
P(i+1) = TotalPolarization(rA(i),E(i),i)+E(i)*8.85*10^-3;
end
close(h);
I = -diff(P);

g ={'E','P','Rs','Rw','Nt','A','rA','I'};
for i=1:8
    cmd = ['out.' g{i} ' = ' g{i} ' ; '];
    eval(cmd);
end

% This function is to simulate the input Electric filed
function out = AppliedField(t,Amp,w)
out = Amp*cos(t/w*pi);

% This function is to calculate the nucleation probability
% inside domains
function out = NucleationProbabilityOS(E,P)
global lamda As Pr Ps;
Ef = E-lamda*(P-Ps)*1/8.85*10^-5;
if Ef >= 0
    out = 0;
else
    out = exp(As/Ef);
end
% This function is to calculate the number of developed nuclei
function out = ExistedNucleaNum(Rs,Nt,q,t)
global N;
if t == 1
    out = Nt(1); % this can be set to other values instead of zero
else
    out = Nt(t-1)+(N-Nt(t-1))*(1-q)*Rs;
end

% This function is to calculate the nucleation probability
% adjacent to a domain wall
function out = NucleationProbabilityBW(E,P)
global lamda Aw Pr Ps;

Ef = E- lamda*P/8.85*10^-5;
if Ef >= 0
    out = 0;
else
    out = exp(Aw/Ef);
end

% This function is to calculate the switched area without
% considering domain overlap and other fake effects
% introduced by the model.
function out = OverlappedArea(cA, Nt,Rs,Rw,q,t)
global N NOm dNdt T rc;
dNdt = zeros(t,1);
A = zeros(t,1);
dNdt(1) = N*Rs(1);
A(1) = DevelopedArea(t-1,0,Rw)*NOm;
for i = 2:t
    dNdt(i) = Nt(i)-Nt(i-1);
    A(i) = A(i-1) + dNdt(i)*DevelopedAreab(t,i,Rw);
end
out = A(t);

% This function is to calculate the total switched area by
% considering the overlap and other phenomena
function out = TotalSwitchedArea(A,Rs,Nt,t)
global rc NO NOm;
out = 1 - exp(-A);

% This function is to calculate the total polarization
function out = TotalPolarization(rA,E,t)
global Chi Ps C0m C0;
out = Ps*(1-2*(((1-C0m-C0)*rA+C0m));

% This function is to calculate the switched area of a domain
% i.e., S(t)=(rc+Rw*rc*dt)^2
% this function is only used by function "overlap"
function out = DevelopedArea(t,s,Rw)
global rc T;
R = zeros(t-s+1,1);
R(1) = rc;
% Calculate the extended radius since its birth
for i = 2:t-s+1
   R(i) = R(i-1)+2*rc*Rw(i-1);
end
out = pi*(R(t-s+1)^2-rc^2)/T;
Appendix B
Thermogram of Precursors

**Figure B.1** Thermogram: (a). Lithium Neodecanoate (b). Niobium Tri-ethoxy-di-neodecanoate (From Ref [168])
# Appendix C

## Color Chart for LiNbO$_3$ Films

<table>
<thead>
<tr>
<th>$t$ (Å)</th>
<th>Color</th>
<th>$t$ (Å)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>Tan</td>
<td>4000</td>
<td>Violet-red</td>
</tr>
<tr>
<td>400</td>
<td>Brown</td>
<td>4350</td>
<td>Bluish (Not blue but borderline violet and blue-green it appears more like a mixture between violet-red and blue green and looks grayish)</td>
</tr>
<tr>
<td>600</td>
<td>Dark violet to red violet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>Royal Blue</td>
<td>4600</td>
<td>Blue-green to green (quite broad)</td>
</tr>
<tr>
<td>1000</td>
<td>Light Blue to metallic blue</td>
<td>4900</td>
<td>&quot;Yellowish&quot;</td>
</tr>
<tr>
<td>1100</td>
<td>Metallic to very light yellow green (slightly metallic)</td>
<td>5100</td>
<td>Orange (rather broad for orange)</td>
</tr>
<tr>
<td>1400</td>
<td>Gold with slight yellow orange</td>
<td>5200</td>
<td>Salmon</td>
</tr>
<tr>
<td>1600</td>
<td>Orange to Mellon</td>
<td>5400</td>
<td>Dull, light red-violet</td>
</tr>
<tr>
<td>1700</td>
<td>Red-Violet</td>
<td>5500</td>
<td>Blue</td>
</tr>
<tr>
<td>1900</td>
<td>Blue to violet-blue</td>
<td>5550</td>
<td>Blue-Violet</td>
</tr>
<tr>
<td>1950</td>
<td>Blue</td>
<td>5700</td>
<td>Blue</td>
</tr>
<tr>
<td>2000</td>
<td>Blue to blue-green</td>
<td>5850</td>
<td>Blue green</td>
</tr>
<tr>
<td>2150</td>
<td>Light green</td>
<td>6050</td>
<td>Dull yellow-green</td>
</tr>
<tr>
<td>2200</td>
<td>Green to yellow-green</td>
<td>6200</td>
<td>Yellow to &quot;yellowish&quot;</td>
</tr>
<tr>
<td>2300</td>
<td>Yellow green</td>
<td>6300</td>
<td>Orange</td>
</tr>
<tr>
<td>2500</td>
<td>Yellow</td>
<td>6400</td>
<td>Carnation Pink</td>
</tr>
<tr>
<td>2600</td>
<td>Light orange</td>
<td>6500</td>
<td>Violet</td>
</tr>
<tr>
<td>2700</td>
<td>Carnation pink</td>
<td>6700</td>
<td>Red-violet</td>
</tr>
<tr>
<td>2800</td>
<td>Violet-red</td>
<td>6750</td>
<td>Blue</td>
</tr>
<tr>
<td>2900</td>
<td>Red-violet</td>
<td>6800</td>
<td>Blue-violet</td>
</tr>
<tr>
<td>3000</td>
<td>Violet</td>
<td>7000</td>
<td>Green</td>
</tr>
<tr>
<td>3050</td>
<td>Blue-violet</td>
<td>7100</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>3100</td>
<td>Blue</td>
<td>7150</td>
<td>Green</td>
</tr>
<tr>
<td>3200</td>
<td>Blue-green</td>
<td>7500</td>
<td>Violet</td>
</tr>
<tr>
<td>3300</td>
<td>Green (broad)</td>
<td>7600</td>
<td>Red-violet</td>
</tr>
<tr>
<td>3450</td>
<td>Yellow-green</td>
<td>7700</td>
<td>Violet-red</td>
</tr>
<tr>
<td>3550</td>
<td>Green-yellow</td>
<td>7900</td>
<td>Carnation pink to salmon</td>
</tr>
<tr>
<td>3600</td>
<td>Yellow to &quot;yellowish&quot; (not yellow but in the position where yellow is to be expected. At times it appears to be light creamy grey or metallic)</td>
<td>8120</td>
<td>Orange</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8400</td>
<td>Sky blue to green-blue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8900</td>
<td>Orange</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9200</td>
<td>Violet</td>
</tr>
<tr>
<td>3700</td>
<td>Light orange or yellow to pink</td>
<td>9300</td>
<td>Blue-violet</td>
</tr>
<tr>
<td></td>
<td>borderline</td>
<td>9600</td>
<td>Blue</td>
</tr>
<tr>
<td>3800</td>
<td>Carnation pink</td>
<td>9800</td>
<td>Dull yellow-green</td>
</tr>
</tbody>
</table>

**Table C.1** Color Chart for LiNbO$_3$ Films: Observed perpendicularly under daylight fluorescent lightning. $t$: film thickness. (Taken from Ref [168])
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