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DOMAIN SWITCHING AND SPATIAL DEPENDENCE OF PERMITTIVITY IN
FERROELECTRIC THIN FILMS

by

Francis Kang-liang Chai

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in ferroelectric thin films

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To my parents

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Abstract

A domain model consistent with the measured capacitance-voltage (*CV*) characteristic of *PZT* ($Pb(Zr,Ti)O_3$) capacitors is proposed. The model is introduced using a macroscopic electric field that is spatially uniform through the depth of the film. Then this multiple-domain model is generalized, and a spatially varying electric field model with a domain structure varying through the depth of the film is proposed. The spatial variation of the electric field is caused by dopant-ion charges in this work. A position-dependent permittivity is then deduced. Based upon this permittivity, the extraction of doping profiles in ferroelectric thin film capacitors using ferroelectric capacitance-voltage (*CV*) measurements is studied. The doping profile relation to measured *CV* curves for ferroelectric thin film capacitors is found to be analogous to the well-known result of metal-semiconductor Schottky junctions with an easily determined effective dielectric constant. Computer simulation shows the electrical doping concentration of ferroelectric thin film capacitors can be profiled accurately with the proposed model. The profiling shows compensation of the p-type *PZT* samples by the n-type niobium doping. Limitations of the Schottky profiling on ferroelectrics are investigated. Based on the approximate doping profiles extracted from *CV* measurement and the deduced permittivity, the measured *CV* characteristics are reconstructed through computer simulations. It is found that there is a minimum doping level below which it is not possible to obtain the doping profile from *CV* measurements. This minimum level depends on the shape of the *CV* curve, and a method to determine this minimum level from the *CV* curve is presented. For the films measured in this work, the minimum level is about 10^{18} cm^{-3} . It is also found using the model that niobium doping slightly slows the volume growth of polarization with the electric field and has a tendency to increase the coercive field.

Chapter I Background

In this chapter, the background of ferroelectricity is covered. The definition and characteristics of ferroelectricity are presented. The origin of the ferroelectricity is explained followed by the memory application of ferroelectric thin films. Representative types of ferroelectric materials and sample preparation of this work are introduced. Finally, the motivation, goal and scope of this work are discussed.

§I.I Definition of ferroelectricity and the hysteresis characteristic [1, 2]

Simply put, a ferroelectric material retains polarization in the absence of an externally applied electric field, a polarization that can be reversed by an externally applied field.

In 1920, Valasek discovered that the polarization of sodium potassium tartrate tetrahydrate ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), better known as Rochelle salt, could be reversed by application of an external electric field [3]. Valasek recognized ferroelectricity by experiments which showed that the dielectric properties of this crystal were in many respects similar in nature to the ferromagnetic properties of iron in that there was a hysteresis effect in the field-polarization curve [3, 4].

The hysteresis loop illustrated in Fig. 1 is a representative characteristic of ferroelectrics. The measurement of the ferroelectric hysteresis characteristic is discussed

further in §II.II. At large applied biases in Fig. 1, the measured polarization (P_{total}) exhibits a linear asymptotic characteristic. The measured polarization, P_{total} , hence can be expressed as the sum of two polarization components, that is, the linear polarization, P_{linear} ; and the switching polarization, $P_{switching}$, where $P_{total} = P_{linear} + P_{switching}$. P_{linear} is proportional to the applied bias and is a straight line going through the origin. In other words, when the applied bias is removed, no linear polarization remains. Therefore, P_{linear} is a common characteristic to all dielectric materials, both paraelectric (linear dielectric, for instance, silicon dioxide) and ferroelectric. The switching polarization ($P_{switching}$), on the other hand, is a unique property of ferroelectrics. When there is no applied bias, there are two stable polarization states (P_r and $-P_r$) arising from the switching polarization. This is the nonvolatility of ferroelectrics that makes the material a candidate for nonvolatile memory capacitors. The nonvolatile memory application of ferroelectric thin films is discussed more in §I.IV.

Besides nonvolatility, the linear polarization also is an attractive property of ferroelectrics. Suppose the polarization of silicon dioxide is plotted together with the P_{linear} of a ferroelectric material in Fig. 1; it will be a straight line going through the origin. However, the straight line will appear to be almost horizontal since the linear dielectric constant of a ferroelectric material is much larger than that of silicon dioxide. In other words, the charge storage capability of ferroelectrics is much better than that of silicon dioxide. Therefore, the area consumption of capacitors can be significantly improved if high dielectric constant materials such as the ferroelectrics replace silicon dioxide. Driven by the development of Giga-bit DRAMs (Dynamic Random Access Memories), $SrTiO_3$, $(Ba,Sr)TiO_3$ and PZT have been widely investigated for their applications in storage capacitors [5, 6].

Parameters that quantify the hysteresis loop are now introduced. The saturation or spontaneous polarization, P_s , is the polarization due to maximum domain growth. P_s is extrapolated to zero field to remove the polarization that is not due to domain switching. The remanent polarization, P_r , is the polarization that remains upon actual field removal. The critical or coercive voltage V_c marks the bias level required to achieve a polarization reversal. The figures of merit for ferroelectric thin film devices are P_r and V_c . P_r is regarded as the charge that a ferroelectric capacitor can retain after the removal of the electric field. V_c is considered as a threshold voltage that can switch the polarization from one state to the other.

Instead of the *bias* axis in the hysteresis loop shown in Fig. 1, the x -axis in a hysteresis characteristic is also often seen presented as the *applied* electric field. This electric field is a macroscopic quantity and is equal to the applied bias divided by the thickness of the capacitor. The applied electric field is assumed to be uniform through the depth of the capacitor. In our earlier work [7], the hysteresis characteristic in Fig. 1 was applied at a microscopic level and was incorporated into the solution of Poisson's equation. It is then explicitly assumed that the applied field in a macroscopic hysteresis characteristic can be replaced by the microscopic local field.

§I.II Ferroelectric capacitance-voltage (CV) characteristic

A typical ferroelectric CV characteristic is illustrated in Fig. 2. The measurement setup is identical to the MOS (Metal-Oxide-Semiconductor) capacitor CV characterization. CV characterization and results of ferroelectric thin film capacitors are presented later in

§II.III. The qualitative behavior of the capacitance curve can be understood from the hysteresis loop (inset in Fig. 2). The polarization (P) in a hysteresis characteristic is the charge per unit area on a ferroelectric capacitor. Capacitance at bias V_a is defined as

$$C(V_a) = \left. \frac{dQ}{dV} \right|_{V_a} = \left. \frac{dP}{dV} \right|_{V_a} \quad (1)$$

That is, the CV characteristic is *qualitatively* the derivative (slope) of a hysteresis loop.

This work relates a field-dependent permittivity based upon a microscopic domain picture to measured ferroelectric CV characteristics. The measured CV curves serve as a standard for evaluating the proposed field-dependent permittivity model and the microscopic domain structure. In the computer simulation of this work, Poisson's equation is solved taking into account the proposed form of field dependence of the permittivity. Then the computer simulated CV characteristics are fitted to the measured CV curves to examine the consistency between the model and the measurable macroscopic behavior.

§I.III The physical origin of ferroelectricity [1, 2]

The physical origin of ferroelectricity is now explained using a representative material, barium titanate ($BaTiO_3$). For $BaTiO_3$, the cubic structure shown in Fig. 3 is found above 120°C (the Curie temperature, $T_C = 120^\circ\text{C}$, marks the onset of ferroelectric behavior for $BaTiO_3$ when cooled from a temperature above T_C). When cooled below

120°C, $BaTiO_3$ undergoes a phase transformation to a tetragonal modification, as shown in Fig. 4. The structure shown in Fig. 4 is not symmetrical. Thus, the overall center of positive charge for the distribution of cations within the unit cell is separate from the overall center of negative charge for the anion distribution. Equivalently, there is a permanent electrical dipole in the tetragonal $BaTiO_3$ unit cell, as illustrated in Fig. 5. In Fig. 6 it is shown that unlike the cubic structure shown in Fig. 3, the permanent electric dipoles of the tetragonal unit cell allow for a large polarization of the material in response to an applied electric field. Fig. 7 summarizes the hysteresis loop that results when the electric field is repeatedly cycled.

Even though permanent electric dipoles exist in a ferroelectric material, the ferroelectric material can have zero average polarization under zero applied field due to a random orientation of microscopic scale *domains*, regions where electric dipoles are aligned in a common direction. This zero polarization case usually occurs when a ferroelectric material has never been biased, for what is called a virgin sample. Under an applied field, unit cell dipole orientations roughly parallel to the applied field direction are favored. Domains with such orientations grow at the expense of other, less favorably oriented ones. On the other hand, the symmetrical unit cell shown in Fig. 3 is *paraelectric*, and only a small polarization is produced as the applied electric field causes a small amount of induced dipoles (cations drawn slightly toward the negative electrode and anions toward the positive electrode).

§I.IV Nonvolatile memory application of ferroelectric thin films

Besides the application to DRAM storage capacitors, ferroelectric materials have been investigated extensively for their nonvolatile memory applications. Ferroelectric nonvolatile memories offer the potential for large capacity chips (256 K-bit to 1 M-bit) [8, 9]. For aerospace applications, ferroelectric nonvolatile memories give a significant improvement in radiation hardness [10, 11]. Ferroelectric nonvolatile memories also provide the advantages of low power and high speed operation over EEPROM (Electrically Erasable Programmable Read Only Memory) [12]. Further, the deposition technique of ferroelectric thin films has been demonstrated to be compatible with CMOS (Complementary Metal Oxide Semiconductor) integrated circuit processes [13].

Fig. 8(a) shows an example of the destructive readout (DRO) nonvolatile memory unit cell [14]. The operation of this example is based on the hysteresis characteristic illustrated in Fig. 8(b). If the ferroelectric capacitor stored a "1", when the capacitor is read, the word line transistor is turned on, a large read bias (V_{rb}) is applied on the capacitor by grounding the bit line and raising the drive line voltage to V_{rb} . The polarization then varies by following the arrow on the right branch of the hysteresis loops (Fig. 8(b)) to P_{max} and a current corresponding to the polarization change $\Delta P(1)$ charges up the bit-line capacitance. After V_{rb} is removed, the polarization varies by tracking the left branch of the hysteresis loops to "0". Hence, the information stored in the ferroelectric capacitor changes from "1" to "0" after the read operation and needs to be refreshed. Therefore, the unit cell shown in Fig. 8(a) is called a destructive read-out scheme.

On the other hand, if a "0" was stored in the ferroelectric capacitor shown in Fig. 8(a), during a read operation, the polarization increases to P_{max} and a current corresponding to $\Delta P(0)$ charges up the bit-line node. After V_{rb} is removed, the polarization relaxes back to "0". Thus, destructive readout only occurs if a "1" is stored in the ferroelectric capacitor.

Since $\Delta P(0) < \Delta P(1)$, the bit-line node is charged to different voltage levels for "0" and "1", the stored information can be verified by comparing the bit-line node voltage with a reference level. For the example discussed above, ΔP is the difference between the polarization states "0" and "1".

An example of a nondestructive readout memory scheme (NDRO) has been reported [15, 16] based on the ferroelectric CV characteristic discussed in §I.II. The principle of operation is illustrated in Fig. 9. The readout is nondestructive since the read bias V_{rb} does not exceed the coercive bias V_c ; thus, no polarization reversal occurs due to V_{rb} . If a "1" is stored in the ferroelectric capacitor, the capacitance increases from C_0 to C_h when V_{rb} is applied during the read operation. On the other hand, if a "0" is stored, the capacitance reduces from C_0 to C_l at the read bias V_{rb} . The capacitance difference ΔC at V_{rb} allows a sense amplifier to distinguish "0" and "1".

It is found in our earlier work [7] that the high electrical doping level tends to degrade ΔP , resulting in confusion between "0" and "1" states in the DRO memory scheme. A result from Ref. [7] illustrating this ΔP degradation at high electrical doping level is shown in Fig. 10. Similar degradation occurs in ΔC as the electrical doping increases, leading to confusion between "0" and "1" in NDRO scheme. This is illustrated in Fig. 11 [17]. Both Figs. 10 and 11 are generated using computer simulations with a fixed

film thickness ($0.75 \mu\text{m}$) and the electrical doping level as a variable. It can be seen from Figs. 10 and 11 that significant reductions in ΔP and ΔC is observed as the electrical doping level of the film increases. Degradation in both ΔP and ΔC are caused by the saturation of ferroelectric switching behavior at large surface electric fields due to high electrical doping levels. In other words, heavily doped ferroelectric thin films behave like linear dielectrics, and collapses in hysteresis loops and CV characteristics may be observed.

The degradations discussed above motivate the study of electrical doping profiling for ferroelectric thin film capacitors. Our current work will propose a basis for applying the Schottky doping profiling technique on ferroelectric thin film capacitors. Further, this work may be a basis for a more complex model which enables simulations for device CV characteristics.

§I.V Representative types of ferroelectric materials

The PZT ($Pb(Zr,Ti)O_3$) samples studied in this work have the basic ABO_3 structure illustrated in Fig. 3 with Zr^{4+}/Ti^{4+} at the center of the cube, Pb^{2+} ions at the corners and O^{2-} at the face centers. PZT has a Curie point of $\sim 269^\circ\text{C}$ and thus is in stable ferroelectric phase at room temperature. When cooled below its Curie point, the transition from cubic to tetragonal phase is similar to what has been discussed above for $BaTiO_3$.

An interesting "fatigue free" (fatigue is the degradation in polarization of ferroelectric materials due to repeated polarization reversals caused by externally applied field) material reported in the 1995 7th International Symposium on Integrated Ferroelectrics by Symetrix Corporation is the *Y-1* family. Among them, $SrBi_2Ta_2O_9$ is found to be the best candidate for ferroelectric nonvolatile memories [18]. The material has a complex bi-layered perovskite structure consisting of a hypothetical perovskite layer ($SrTaO$) sandwiched between two bismuth layers ($(Bi_2O_2)^{2+}$). The ferroelectricity originates from the perovskite layer. The "fatigue free" feature may arise from coherent domain motion.

Ferroelectrics are often categorized as being of either displacive or order-disorder character [2, 19]. In permanent-dipole materials, transition to and from the ferroelectric state at the Curie temperature occurs through ordering and disordering of these permanent dipoles. An example of the order-disorder type ferroelectric material is triglycine sulphate $((NH_2CH_2COOH)_3 \cdot H_2SO_4)$, also known as "TGS". For induced-dipole materials, the microscopic dipole moments are able to take values in a range around zero ("displaced" from zero) and the phase transition is referred to as displacive. Barium titanate ($BaTiO_3$, the material used earlier to illustrate the origin of ferroelectricity) belongs to the displacive category.

Most early theoretical work and experimental studies of fundamental ferroelectric properties were carried out on large single crystals, however, the use of polycrystalline materials or ceramics is of particular importance because of the possibilities of preparing a wide range of compositions in order to obtain different properties for various applications and because the presence of grain boundaries gives rise to effects which have important practical implications. Besides, ferroelectric ceramics have the

advantage of being a great deal easier to prepare than their single-crystal counterparts. A ferroelectric ceramic is an aggregate of ferroelectric single-crystal grains (or crystallites) with dimensions typically between 0.5 and 50 μm . Due to the imperfect alignment of the crystallographic axes of the grains within the aggregate, the macroscopic properties of a ceramic in general differ significantly from those of a single crystal. Ferroelectric ceramics are generally prepared by reacting well-mixed constituent powders at a relatively low temperature. It is then formed into some shape and fired at a higher temperature where sintering occurs. The various procedures for mixing, forming, and firing ceramics are reviewed by Jaffe et al. [20].

Motivated by special applications such as memory capacitors and optical waveguides for the large polarizability of ferroelectrics, extensive research efforts have been focused on the development of ferroelectric thin films. Ferroelectric thin films can be deposited using evaporation, sol-gel, MOCVD (Metallo-Organic Chemical Vapor Deposition), PLD (Pulsed Excimer Laser Deposition), sputtering, laser ablation, etc. The *PZT* ($Pb(Zr,Ti)O_3$) samples used in this work were processed by the sol-gel method and will be discussed in detail in §II.I later. The ferroelectric behavior of thin films is complicated by space charge fields arising from energy-band bending and the condition at metal-ferroelectric interfaces (for ferroelectric capacitors). Defect structure in films sensitive to processing techniques further increases the difficulty of analyzing the ferroelectric behavior of thin films. A more detailed overview of ferroelectric ceramics and thin films can be found in [2].

§I.VI Motivation and goal

It is shown in §I.IV that the NDRO memory operation depends on resolving the capacitance difference ΔC between the "0" and "1" states, and ΔC degrades at high electrical doping levels, leading to confusion between the states [17]. Possibly due to the contamination in the processing chemicals, *PZT* is inherently heavily doped and has an electrical doping level typically above 10^{18} cm^{-3} . This motivates the investigation of electrical doping profiling for ferroelectric *PZT* thin film capacitors and the search for a physical model accounting for ferroelectric *CV* characteristics. The goal of this work is not a Spice-level circuit model; instead, it is hoped that this study will provide some microscopic understanding of the physical behavior leading to the macroscopically measurable ferroelectric *CV* characteristic. Further, through the microscopic understanding obtained from this study, correlation with processing parameters to allow control of the macroscopic *CV* characteristic on which memory operation is based becomes possible. The current work is a first-order, time-independent model; however, it is hoped that this study provides a foundation for a more powerful model which could be used in a commercial device-simulation tool and will shed light on ferroelectric memory design. This work relates a position-dependent dielectric constant to a microscopic domain structure. It is demonstrated that the simple model presented in this study fits measured ferroelectric *CV* characteristic very well. The basis for applying the Schottky doping profiling technique on ferroelectric thin film capacitors is proposed based on a position-dependent permittivity model.

§I.VII Scope of this work

This work investigates a form of field-dependent permittivity related to measured ferroelectric *CV* characteristics and a consistent microscopic domain structure. Beginning with a simple case by assuming that the electric field is spatially uniform, a multiple-domain model is introduced and a field-dependent permittivity is deduced based upon the domain structure. Only two domain orientations are considered in this model, namely, parallel and antiparallel to the applied field. A function is proposed describing the growth of the volume fraction of domains oriented to the direction of the applied field. No time dependence is considered for domain nucleation and domains are assumed to penetrate through the depth of the film, that is, domain wall motion is assumed to require no energy. It is demonstrated that the multiple-domain model assuming a spatially uniform field fits measured *CV* characteristics reasonably well.

The multiple-domain structure is then generalized to the case when the electric field is spatially varying, specifically, due to the presence of dopant-ion charge. The field-dependent permittivity deduced assuming a spatially uniform field becomes position dependent. The multiple-domain structure is shown to evolve into a different structure with a saw-toothed interface between domains oriented oppositely. The application of the Schottky electrical doping profiling technique to ferroelectric thin films is studied based on the position-dependent permittivity. Basis, limitations, and complications of applying the Schottky profiling technique to ferroelectric thin films are investigated. The profiling technique is then applied to measured *CV* characteristics of *PZT* capacitors with various levels of niobium doping and the result shows compensation of the p-type *PZT* by the n-type niobium content. The position-dependent permittivity

model assuming a spatially varying field is shown to fit measured *CV* characteristics extremely well.

The last part of this study tackles the reliability of the electrical doping level extracted from measured *CV* characteristics. As mentioned, two models have been presented in this work. The first model describes a field-dependent permittivity and a consistent multiple-domain structure assuming a spatially uniform electric field, i.e., a case of zero electrical doping level. The second model generalizes the first model for the case of a spatially varying electric field due to the presence of dopant ion charge. The field-dependent permittivity maps into a position-dependent permittivity and the domain structure has a saw-toothed interface between domains with opposite polarities. Both models are demonstrated to be able to fit measured *CV* curves well. Therefore, the issue regarding the existence of the electrical doping level is raised.

It is concluded that due to the switching behavior of ferroelectric materials, the electrical doping level has to be high enough in order to show an effect on the ferroelectric *CV* characteristics, in order for doping to be measurable. The concept of the background doping level is introduced and this level marks the lower bound of measurable electrical doping. It will be shown that if the actual doping level is smaller than the background doping level, false doping information may be obtained due to the nonideal structure in the field-dependent permittivity. A rule of thumb is provided to estimate the background doping level for the nonideal field-dependent permittivity. Based on the proposed rule, it is found that the spatially varying electric field in ferroelectric thin films is likely.

This work provides a simple first-order model which relates a microscopic domain structure to measured *CV* characteristics. It is hoped that this work will initiate interest

in: 1.) Understanding the more complex behavior of domain switching. For example, the current model can be expanded to account for the dependence of domain growth on the frequency of the applied field in order to obtain a more advanced model with the capability of describing the frequency dependence of ferroelectric *CV* measurements.

2.) Correlation of this type of microscopic-level model to macroscopic device-level characteristics and, the development of a ferroelectric device simulation tool benefiting nonvolatile memory design.

Chapter II Experiments

In this chapter, the experiments performed in this work are presented. *PZT* and *Y-I* thin film capacitors are the samples characterized in this work. Sample preparation is described. Measured hysteresis characteristics are discussed. Measured *CV* characteristics are later compared to results of computer simulations based on the proposed model.

§II.I Sample preparation

The *PZT* samples studied in this work were fabricated using the inverted mixing order (IMO) sol-gel route to *PZT* [21]. The *PZT* composition was 50:50 *Zr:Ti* with 10% *Pb* excess and with niobium concentrations of 0, 1, 3, and 5 mole%. Monolithic sputtered platinum back electrodes were deposited on thermally oxidized silicon wafers using a thin *Ti* adhesion layer [22]. Devices were made with 3 layers of the *PZT* precursor which were separately dried before the final 650°C oxygen-ambient firing. This resulted in coatings that were approximately 0.25 μm thick. Platinum top electrodes were patterned using a lift-off process. Each discrete capacitor has dimensions of $150 \times 150 \mu\text{m}^2$. After top electrode deposition, an oxidizing heat treatment was performed to improve the capacitor symmetry. A cross section of the *PZT* capacitor samples is illustrated in Fig. 12.

The *Y-I* thin film capacitors characterized in this work were provided by Hughes Aircraft Company. The measurements were performed on $100 \times 100 \mu m^2$ discrete capacitors with a film thickness of 2000 Å.

In the next section, the measurement of the hysteresis and *CV* characteristics is described for *PZT* and *Y-I* capacitors. The device-to-device variations of the hysteresis and *CV* characteristics for capacitors on a single wafer were not significant for either *Y-I* or *PZT* samples.

§II.II Measured hysteresis characteristics

The ferroelectric hysteresis characteristic discussed in §I.I is typically measured using a Sawyer-Tower circuit [23], as shown in Fig. 13. The measurement setup is now discussed. In the Sawyer-Tower circuit shown in Fig. 13, C_f is the ferroelectric capacitor, C_n is a linear capacitor and R_n is a linear resistor. R_n is used to bypass the leakage current through C_f in order for V_o to follow V_i ; thus, R_n does not have to be very conductive if the leakage of C_f is not serious. The input V_i is a large ac signal. Ferroelectric hysteresis characteristics can be obtained by plotting V_o versus V_i on an oscilloscope. V_o can be translated into charge (polarization) by assuming that the charge on the bias-dependent C_f is reflected entirely by the linear capacitor C_n . That is, the charge on C_f can be expressed as $C_n V_o$. In the Sawyer-Tower circuit setup, the linear capacitor C_n typically is chosen to be larger than C_f so that most of the input signal V_i drops across the ferroelectric capacitor C_f . However, C_n cannot be so large that V_o becomes shorted to ground.

Measured hysteresis loops of *PZT* capacitors with various levels of niobium content are shown in Fig. 14. In this example, V_i is a $30 V_{p-p}$, $100 kHz$ sinusoidal signal, $R_n = 1.5 M\Omega$, and $C_n = 470 pF$. V_o versus V_i data were taken using a Tektronix TDS 420 digitizing oscilloscope. It can be observed from Fig. 14 that niobium doping has the tendency of reducing the remanent polarization (ΔP in Fig. 8(b)). As mentioned in §I.IV, degradation in ΔP is not desirable for DRO memories; however, niobium doping reduces the leakage current of *PZT* capacitors [24]. Thus, tradeoffs in memory design between leakage current reduction and ΔP degradation should be made with caution [6].

A measured hysteresis loop of a *Y-I* capacitor is shown in Fig. 15. In this example, V_i is a $14 V_{p-p}$, $100 kHz$ sinusoidal signal, $R_n = 1.5 M\Omega$, and $C_n = 470 pF$. The hysteresis loop of the *Y-I* capacitor shown in Fig. 15 exhibits significantly superior characteristics to the results shown in Fig. 14 for *PZT* capacitors. The hysteresis loop of the *Y-I* capacitor saturates at a much lower applied bias when compared with the characteristics of the *PZT* capacitors. Furthermore, the polarization reversal at the coercive voltage is much more rapid for *Y-I* than for *PZT* capacitors and the ramp-ups of polarization at the coercive voltages are almost vertical. This is a desired characteristic for DRO memory applications (§I.IV) because the rapid polarization reversal with the applied bias and a smaller bias to saturate the polarization suggest possible low-voltage operation.

Sawyer-Tower measurements are commonly used for measuring the figure-of-merit parameters (e.g., P_r and V_c as discussed in §I.I) and are based on a continuous wave method. However, discontinuous pulses, rather than continuous waves, are used when operating memories. Thus, pulse polarization characterization techniques were reported

to simulate the memory operation conditions [25, 26]. In this method, the input signal is a pulse train with adjustable delay time between each pulse. It was reported by Benedetto et al. [27] that the remanent polarization is a function of both the delay time between write-read pulses and the duration of the write pulse. A worst case of 70% remanent polarization decay was found from 30 μs to 100 ms after the initial write. Hence, P_r characterized by Sawyer-Tower hysteresis measurement may overestimate the available polarization in realistic memory operation.

§II.III Measured CV characteristics

In this work, the CV characteristics of PZT ($Pb(Zr,Ti)O_3$) capacitors are studied. Measured CV characteristics of ferroelectric PZT capacitors with various levels of niobium doping are shown in Fig. 16. The setup is identical to an MOS (Metal-Oxide-Semiconductor) capacitor measurement. In this work, CV measurements were performed on 150 μm square capacitors with a 100 kHz small-signal superimposed upon a slow dc bias. An HP 4192A LF impedance analyzer was used for the characterization. The measurement starts with a -7 V dc bias, steps to 7 V and then back to -7 V at an increment of 0.1 V .

It is obvious from Fig. 16 that niobium modifies the CV characteristics of PZT capacitors. This work provides a model that accounts for these modifications from a microscopic perspective. It will be demonstrated that niobium weakens the dependence of domain growth with the applied field, reduces the remanent polarization, and increase the coercive voltage of PZT capacitors. Also, niobium compensates the p-type

electrical doping level of *PZT*. The variations of the hysteresis characteristics due to the added niobium shown in Fig. 14 (§II.II) may be attributed to the same mechanisms.

A measured *CV* characteristic of a *Y-I* capacitor is shown in Fig. 17. The *CV* characteristic of the *Y-I* capacitor exhibits much sharper peaks at the coercive voltages due to the rapid polarization reversal in the neighborhood of the coercive voltage discussed in §II.II. An interesting characteristic of the *CV* curves of the *Y-I* capacitor is the Ramer-Drab effect [28]. The effect describes two distinct capacitance states at zero dc bias, as shown in Fig. 17. It was observed that ΔC does not drift with time and an NDRO memory scheme was proposed based on this ΔC at zero bias [28].

As discussed in §I.II, the *CV* characteristic is *qualitatively* the derivative (slope) of a hysteresis loop. However, the result of differentiating a Sawyer-Tower hysteresis loop does not yield the measured *CV* characteristic. As mentioned, the Sawyer-Tower characterization is a continuous measurement and the *CV* measurement is closer to the pulse measurement (dc steps with small-signal superimposed). The fast-decaying polarization discussed in Ref. [27] may be responsible for the difference between the measured *CV* curves and the derivative of a hysteresis loop obtained from a Sawyer-Tower setup.

Chapter III Theory and review

In this chapter, the customary thermodynamic phenomenological theory of ferroelectricity is reviewed including treatments of phase transitions and ferroelectric hysteresis characteristics. A review of relevant research work to this study is presented.

§III.I Thermodynamic phenomenological treatment of modeling phase transition

Landau free energy theory is used extensively to treat ferroelectric phase transitions [2, 19, 29-32]. In this approach, the free energy (F) can be expressed in terms of spontaneous polarization (P) with the absolute temperature (T) as a parameter, namely,

$$F(T, P) = F(P=0) + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 + \dots \quad (2)$$

where α , β and γ are coefficients of the expansion and the first term, $F(P=0)$, contains information associated with the nonferroelectric aspects of the material. In the treatment of phase transition, β and γ are temperature independent. Conventional phenomenological theory (known as Devonshire theory [33-35]) assumes that near the Curie point T_C , the parameter α is proportional to temperature, i.e., $\alpha \propto (T - T_C)$, with a positive coefficient. Thus, when $T > T_C$, $\alpha > 0$, the free energy (F) versus P has one minimum at $P = 0$ and when $T < T_C$, the material is in the paraelectric phase.

However, when $T < T_C$, $\alpha < 0$, F versus P has two stable minima corresponding to two stable polarization states for temperatures lower than the Curie point. When $T < T_C$, the material is in the ferroelectric phase. Phase transition, i.e., the change of the spontaneous polarization (P) behavior in response to the electric field (E) from $T < T_C$ to $T > T_C$, can be described by the Landau-Devonshire polynomial, i.e.,

$$E = \left(\frac{\partial F}{\partial P} \right)_T = \alpha'(T - T_C)P + \beta P^3 + \gamma P^5 + \dots \quad (3)$$

where E is the macroscopic electric field and $\alpha' = \alpha/(T - T_C)$. The Curie point, T_C , marks the temperature below which ferroelectric characteristics can be observed. Details of this treatment can be found in Ref. [2]. The phase transition is not a concern of this work. Instead, the behavior of polarization and permittivity in the ferroelectric phase is the focus. The thermodynamic treatment discussed above assumes that the polarization P is spatially uniform, namely, the approach applies to bulk samples with a single domain.

§III.II Thermodynamic phenomenological treatment of modeling behavior in ferroelectric phase

Landau's phenomenological approach described above also is used for the treatment of behavior in the ferroelectric phase. Ishibashi et al. studied the phenomenology of domain walls (boundaries separating domains) using a Landau-type thermodynamic potential. Based on this potential, he derived the total energy needed to form a domain

wall and a characteristic function describing the motions of domain walls. Detailed review of this analysis can be found in Ref. [36]. Ref. [36] describes how polarization $P(x)$ varies with position x in the region between two domains, and finds estimates for the domain wall thickness. Because polarization P varies with position x , terms in the polarization gradient $\partial P/\partial x$ contribute to the free energy. For one particular case, Ishibashi finds

$$P(x) = P_0 \tanh(Kx) \quad (4)$$

where P_0 is the polarization of a fully polarized domain and K^{-1} is a measure of the domain wall thickness. Both the local free energy $V(P)$ due to the displacement of atoms and the polarization gradient dP/dx contribute to the system free energy. The system is at a stable state when both the local free energy $V(P)$ is minimal and the polarization is not varying too fast with position, that is, dP/dx is small. Ishibashi also discussed ferroelectric hysteresis loops in terms of the free energy expansion in a qualitative sense without the presence of domains in ferroelectric switching [37].

In §III.I, the Landau free energy expansion (Eq. (2)) is related to electric field E through the Landau-Devonshire polynomial (Eq. (3)). Because $F(P)$ in Eq. (2) is based on a single and spatially uniform domain, the corresponding E is also spatially uniform.

A description of hysteresis based upon Eqs. (2) and (3) necessarily neglects any dependence of ferroelectric hysteresis characteristic upon domain wall motion and nucleation, because the terms in $\partial P/\partial x$ due to domain interaction (as described by Ishibashi in Ref. [36]) are neglected. Brennan [38] has described the ferroelectric hysteresis characteristic using this approach. In our work, the thermodynamic

phenomenological approach is not used and, instead the hysteresis characteristic is formulated based on the volume fractions of domains oriented in each direction. These volume fractions are assumed to incorporate domain wall and nucleation effects empirically.

The case where electric field varies with position also is considered in our work, where the position dependence is due to dopant ion charge. Because $D = \epsilon_0 E + P$ and from Poisson's equation

$$\frac{\partial D}{\partial x} = \rho \quad (5)$$

it follows that the dopant ion charge density ρ leads to spatial variation in $P(x)$. The position dependence of the dielectric constant also arises from the spatially varying field due to the presence of dopant ion charge.

Brennan [39, 40] has pointed out these facts. In Ref. [39], he combined these observations with his formulation based on a Landau-Devonshire polynomial of E using Eq. (3) to third order. That is, the single-domain origin of his $E(P)$ relation does not include nucleation and domain interaction effects. In our work, we use the volume fraction approach already mentioned, and so incorporate these effects empirically.

For ferroelectric materials with a moderately-wide bandgap ($E_g \leq \sim 3 \text{ eV}$), e.g., BaTiO_3 , $A^V B^V I C^{VII}$ type of compounds, these materials are treated as nonlinear semiconductors with thermodynamic approaches in Ref. [41]. Fridkin focused mainly on the effects of the electron subsystem on the generation of ferroelectricity and the

ferroelectric properties. Further, the effects of the dielectric nonlinearity, and the effects of screening and phase transitions on electron processes in ferroelectrics are also considered in Ref. [41].

Again, the thermodynamic approach reviewed above is not used in our work. A semiconductor-device-physics approach, instead, is taken to relate a microscopic picture of domain structure to the measurable macroscopic ferroelectric behavior, especially, the capacitance-voltage (CV) characteristic. In the next section, relevant work will be reviewed.

§III.III Review of relevant work

Kahng et al. [42] studied the effects produced by a field-dependent permittivity on capacitance measurements. Ref. [42] noted substantial deviations of measured $1/C^2$ versus bias behavior from the ideal Schottky theory for large reverse bias voltages of gold- $KTaO_3$ surface barrier Schottky diodes. The CV measurements in Ref. [42] were performed above the Curie temperature of $KTaO_3$, that is, the $KTaO_3$ samples were in the paraelectric phase. Further, the curvature in the $1/C^2$ versus bias plot was attributed to a field-dependent permittivity. Even though in the ferroelectric phase, this nonlinear dielectric constant was observed by Ref. [43] in analyzing the CV characteristic measured at room temperature of the perovskite family barium titanate Schottky barrier diodes (i.e., barium titanate $T_C = 120^\circ\text{C}$). The well-known Schottky theory [44] that describes the dependence of diode capacitance per unit area C on applied bias voltage V_B is

$$(1/C^2) = 2(V_D + V_B)/qN\varepsilon \quad (6)$$

where ε is the assumed field-*independent* permittivity of the semiconductor, qN is the assumed uniform charge density in the depletion layer, V_D is the diffusion potential, and q is the electronic charge. The analysis presented by Kahng et al. provided a generalization of Eq. (6) when ε is field *dependent*, as now to be described.

In Kahng et al.'s. analysis, Poisson's equation is solved within the depletion region of the diode. The electric field is nonuniform in the depletion region due to the presence of dopant-ion charge. The field dependent permittivity becomes *position* dependent within the depletion region due to the spatially varying electric field. The capacitance of the Schottky diode was calculated using

$$\frac{1}{C} = \int_0^\lambda \frac{dx}{\varepsilon_{x,\lambda}} \quad (7)$$

where λ is the width of the depletion region and x is the distance from the $Au-KTaO_3$ interface. $\varepsilon_{x,\lambda}$ is the permittivity at depth x from the interface. The expression in Eq. (7) is the series capacitance of the diode depletion region composed of layers with various values of permittivity. The treatment in our work takes a similar approach to calculate the film capacitance.

Assuming that the charge density is uniform in the depletion region, Kahng et al. related the diode depletion capacitance to the permittivity at the $Au-KTaO_3$ interface, namely,

$$\left| \frac{\partial}{\partial V_T} \left(\frac{1}{C^2} \right) \right| = \frac{2}{qN\epsilon_{0,\lambda}} \quad (8)$$

where V_T is the total voltage drop across the depletion layer, i.e., $V_T = V_D + V_B$. $\epsilon_{0,\lambda}$ is the permittivity at $Au-KTaO_3$ interface. Eq. (8) is identical to the Schottky theory (Eq. (6)) with a replacement of the field-independent permittivity, ϵ , by the surface permittivity $\epsilon_{0,\lambda}$. However, since a uniform doping level was assumed in Kahng et al's. analysis, Eq. (8) does not include the *profiling* capability. Besides, the sample $KTaO_3$ remains paraelectric to at least 4.2°K [45]; thus, because the measurements were performed at room temperature in Ref. [42], no domain structure was present in their sample. The proposed polarization and permittivity versus electric field relations were not related to any microscopic physical model, although the proposed form of field dependence of the permittivity is later supported by the form reported in Ref. [46] for $SrTiO_3$ Schottky diodes at room temperature ($T_C = 30^\circ\text{K}$ for $SrTiO_3$).

Bar-Chaim et al. [47] studied the bias dependence of and the contributions of 180° and 90° domains to the dielectric constant of PZT ferroelectric ceramics. In Ref. [47], the sample dielectric constant is calculated by summing up the relative volume fractions of domains of various orientations with different dielectric constants, i.e.,

$$\epsilon = v_1\epsilon_1 + v_2\epsilon_2 \quad (9)$$

where ϵ_1 , ϵ_2 , and ϵ are the dielectric constants of domains of various orientations and their mixture, respectively, and v_1 and v_2 are the relative volume fractions of these

domains. This concept is used in our work to calculate the sample polarization with both positively- and negatively-polarized domains present.

Miller et al. [48] adopted a $\tanh$ function to describe the field-dependent polarization of ferroelectric capacitors, namely,

$$P_d^\pm(E) = P_s \tanh[(E \mp E_c)/2\delta] \quad (10)$$

where P_d is the contribution to the polarization due to switching dipoles. The electric field E is treated as a macroscopic field in Ref. [48]. The $\tanh$ function is chosen for its convenient mathematical properties. The superscript "+" indicates the branch of the polarization for the positive-going field ramp and "-" the branch for the negative-going field ramp in a hysteresis measurement. In Ref. [48], it was demonstrated that the $\tanh$ polarization function describes accurately the distortions of hysteresis loops measured using a modified Sawyer-Tower circuit due to resistive losses (modeled by various values for the linear resistor R_n in Fig. 13) as a function of input signal frequency. Also, the effect of signal amplitude variations on the measured hysteresis loops was predicted by the model. In Ref. [49], Miller et al. applied the $\tanh$ polarization model further to describe the IV and CV behavior of ferroelectric transistors.

The $\tanh$ polarization model proposed by Miller et al. can be categorized as a macroscopic circuit level model. The electric field dependence of the polarization is not microscopically modeled, but is treated as a dependence on the applied field, i.e., applied bias divided by the capacitor thickness. Though modeling the circuit level

behavior of ferroelectric capacitors well, the model provides no connection to the microscopic information.

Tagantsev et al. [50] treated *PZT* thin films as semiconducting and studied the switching behavior of the samples for both partially and fully depleted cases. In Ref. [50], a switching model was proposed to explain the film thickness dependence of the coercive field and found to be in qualitative agreement with their experimental results. Though the surface dielectric layer proposed in Ref. [50] was later discarded by the analysis in Ref. [51], one major concept in their switching model that is especially enlightening for this work is the proposed threshold electric fields required for domain wall motion and reverse domain nucleation. Two important threshold electric fields were defined: the nucleation critical field, E_{cn} ; and the domain wall motion critical field, E_{cm} . It is assumed in their switching model that once nucleation of domains of opposite polarity begins, the domains propagate through the depth of the film rapidly. In other words, $E_{cn} \gg E_{cm}$.

In Ref. [50], it is assumed that the electric field in the film is strongly inhomogeneous due to the metal-semiconductor contact phenomena. Fig. 18 illustrates a fully depleted film at two different biases. In Fig. 18(a), the film is not biased and the sample has been poled negatively. No positive domains exist in the sample because the electric field is below the nucleation critical field, E_{cn} . However, in the bias condition shown in Fig. 18(b), the electric field is larger than E_{cn} in the surface portion of the film, $x > x_n$; therefore, nucleation of positive domains occurs in the region $x > x_n$. Now note that the electric field across the depth of the film is larger than the domain wall motion critical field, E_{cm} ; hence, positive domains propagate through the depth of the film rapidly, resulting in the polarization shown in Fig. 18(c). The above illustration of switching

assumes that $E_{cn} \gg E_{cm}$. In our analysis of the multiple-domain model (§IV.III), a similar assumption is made implicitly, namely, $E_{cm} = 0$.

Another situation explained in Ref. [50] is similar to the concept of a high dielectric constant switching region in our work and is illustrated in Fig. 19. Notice that in Fig. 19, $E_{cn} \approx E_{cm}$. Thus, even though nucleation occurs in the region $x > x_n$ (Fig. 19(a)), positive domains do not propagate through the depth of the sample but stop at $x = x_m$ (Fig. 19(b)) because the electric field in the region $x < x_m$ is smaller than E_{cm} . From x_m to x_n in the film, the electric field is very close to E_{cm} and domains of both polarities may exist simultaneously. This region is similar to the switching region discussed in §V.II of our work. The switching concept proposed by Tagantsev is found to be pertinent to the domain switching model in this work.

Blom et al. [52] studied the effect of polarization on gold- $PbTiO_3$ Schottky diodes. The study was performed at room temperature; thus, $PbTiO_3$ was in the ferroelectric phase with domains present in the sample. They adopted the tanh polarization model used by Miller et al. [48] and solved Gauss's law with the field-dependent polarization taken into account. That is, Miller et al.'s. formulation was extended to a position-dependent $E(x)$. Blom et al. pointed out an important concept that such a spatially varying electric field in the space-charge region of a Schottky diode leads to a position dependence of the dielectric constant and of the polarization. In our work, it will be shown that the application of the Schottky profiling equation to ferroelectrics relies on a particular form for the position dependence of the permittivity.

Van der Berg et al. [46] derived a field-dependent permittivity from measured CV characteristics of $SrTiO_3$ Schottky diodes at room temperature ($T_C = 30^\circ\text{K}$ for $SrTiO_3$).

In their analysis, the Schottky profiling equation was applied empirically to $SrTiO_3$ samples with no domains present and the profiling location was assumed to be at the depletion region edge. Their result is in agreement with the proposed form of field-dependent permittivity in Ref. [42] and the spatial dependence of the position-dependent permittivity is found in our work to result in ideal profiling. It will be demonstrated in our work that the Schottky profiling equation applies to ferroelectrics when there exists a sharp spatial transition in the permittivity, and that the profile is found at the location of this sharp transition in the permittivity.

In our earlier work [7], the tanh polarization model of Miller et al. was applied at a microscopic level and Poisson's equation was solved (using an approach similar to Ref. [42]) by assuming the ferroelectric capacitor to be a back-to-back Schottky barrier system. The effects of the electrical doping level on ferroelectric hysteresis loops was demonstrated and related to a microscopic physical model. The electric field distribution has been shown to be highly nonuniform due to the presence of dopant-ion charge.

In our present work, an approach similar to Ref. [42] is taken to study a special form of field-dependent permittivity and its relation to measured CV characteristics below the Curie point. This special form of field-dependent permittivity will be shown to agree with a simple microscopic domain structure. Based on the proposed field-dependent permittivity, the Schottky doping *profiling* technique is rigorously shown to be applicable to ferroelectric thin films for specific physical situations.

Chapter IV A multiple-domain model for ferroelectric films with uniform electric fields

In this chapter, *CV* characteristics of a ferroelectric thin film capacitor below the Curie point are related to the domain populations oriented variously with the applied field. A multiple-domain model is introduced for the case of a spatially uniform electric field, and shown to be capable of fitting measured *CV* curves. Based on the model, it is found that niobium slows the volume growth of domains with the applied electric field in *PZT* capacitors, reduces the maximum switching polarization of *PZT* and increases the electric field required for domain switching.

§IV.I Introduction

This work draws upon Ref. [42, 46, 52] where a field-dependent permittivity was used to model *CV* characteristics of *PbTiO₃*, *SrTiO₃* and *KTaO₃*. Kahng et al. [42] and van der Berg et al. [46] related field-dependent permittivity models to measured *CV* characteristics in *KTaO₃* and *SrTiO₃* Schottky diodes respectively. However, domain structure did not cause the field-dependence of the permittivity in their work, which applies only above the Curie temperatures of the materials studied. Blom et al. [52] introduced a position-dependent permittivity for *PbTiO₃* Schottky diodes based on a field-dependent polarization and a spatially varying electric field. However, even though domains were present in the material under study, the field-dependence of the polarization was postulated with no explanation of the role of domain structure.

In this chapter, a basic microscopic domain picture is related to a consistent field-dependent permittivity model. The domain picture presented provides a basis for the analysis of more complex models.

§IV.II **A multiple-domain model for ferroelectric films with uniform electric fields**

Consider the domain structure of a ferroelectric film as illustrated in Fig. 20(a). The sample is fully polarized in the negative x -direction by a large negative applied electric field. The electric field, E , in this section is defined as the applied bias divided by the film thickness, namely, $E = V / t$, and E is uniform through the depth of the film. As the electric field increases, domains polarized in the positive x -direction begin to emerge. In the example shown in Fig. 20(b), the polarization states consist of two types of domain, one type polarized in the positive x -direction and the other type polarized in the negative x -direction (shaded). Domains of both polarizations penetrate throughout the depth of the film. If the electric field increases further, the sample will be poled entirely in the positive x -direction as seen in Fig. 20(c). Let $\hat{P}$ be the maximum polarization when the film is poled entirely in the positive x -direction, then $-\hat{P}$ is the polarization when the film is poled entirely in the negative x -direction. Suppose that the polarization of the sample is simply given by the volume fractions (cf. Bar-Chaim et al. [47]) α and $1 - \alpha$ that are oriented in the positive and negative x -directions respectively (as shown in Fig. 20(b)). The switching polarization of the sample at field E can then be expressed as

$$P(E) = \alpha(E)\hat{P} + (1 - \alpha(E))(-\hat{P}) \quad (11)$$

where $P(E)$ excludes the non-ferroelectric background polarization that varies linearly with the electric field, which is common to all dielectric materials. For $\alpha = 0$, $P = -\hat{P}$ and the sample is polarized entirely in the negative x -direction (Fig. 20(a)); on the other hand, when $\alpha = 1$, $P = \hat{P}$ and the sample is polarized entirely in the positive x -direction (Fig. 20(c)).

To construct a P versus E curve based upon Eq. (11) as illustrated in Fig. 21, assume that nucleation of aligned domains does not occur until $E \geq E_a$ (or equivalently, $V \geq V_a$ where $V_a = E_a \times t$). Also, for the sake of simplicity, assume that α increases linearly with E once $E \geq E_a$ and aligned domain growth begins. Finally, for E greater than some single domain value E_d , $\alpha = 1$ and the sample is a single domain oriented in the positive x -direction. If now the applied bias is reversed, hysteresis results (dashed lines) because the negatively oriented electric field cannot generate negatively oriented domains until $E \leq -E_a$, assuming a symmetric contact and interface structure. Note that α increases from 0 to 1 when the electric field increases, and α can take any functional form without being restricted to a linear function of E as assumed for Fig. 21. Evidently, the above picture of domain switching ignores any dynamics of domain wall motion, nucleation, and penetration of nucleated domains. These effects require further study.

It is shown next how $\alpha(E)$ can be determined from a measured CV curve. A field-dependent permittivity model also will be derived based on Eq. (11). The relation between the displacement and the polarization is

$$D(E) = \kappa \epsilon_0 E + P(E) \quad (12)$$

where κ is the background dielectric constant that includes non-ferroelectric processes (processes not included in the ferroelectric $P(E)$). Using the usual small-signal definition of the dielectric constant

$$\epsilon(E) = \frac{\partial D}{\partial E}, \quad (13)$$

together with Eqs. (11) and (12), the field-dependent permittivity can be expressed in terms of α , i.e.,

$$\epsilon(E) = \kappa \epsilon_0 + 2\hat{P} \frac{d\alpha}{dE} \quad (14)$$

The capacitance can then be expressed as

$$C(V) = \left. \frac{\epsilon(E)}{t} \right|_{E=V/\ell} = \frac{\kappa \epsilon_0}{t} + \frac{2\hat{P}}{t} \left(\frac{d\alpha}{dE} \right) \quad (15)$$

Therefore, based on the multiple-domain picture illustrated in Fig. 20(b), the volume growth of domains in response to electric field $\alpha(E)$ and a field-dependent permittivity model $\epsilon(E)$ can be deduced from a ferroelectric CV characteristic. Namely, from Eqs. (14) and (15),

$$\frac{d\alpha}{dE} = \frac{\epsilon(E) - \kappa \epsilon_0}{2\hat{P}} = \frac{C(V)t - \kappa \epsilon_0}{2\hat{P}} \quad (16)$$

Integrating Eq. (16) using $\alpha(E = -\infty) = 0$ and $V = Et$ yields

$$\alpha(E) = \frac{1}{2\hat{P}} \int_{-\infty}^V \left[C(V') - \frac{\kappa\epsilon_0}{t} \right] dV' \quad (17)$$

and because $\alpha(E = \infty) = 1$,

$$\hat{P} = \frac{1}{2} \int_{-\infty}^{\infty} \left[C(V') - \frac{\kappa\epsilon_0}{t} \right] dV' \quad (18)$$

In other words, $\alpha(E)$ is the fraction of the total area between the CV curve and its asymptote $\kappa\epsilon_0 / t$ contained in the range of voltage up to $V = E \times t$. It is found that $\alpha(E)$ can be extracted based on Eq. (17) from measured CV curves. By using the extracted $\alpha(E)$ in Eqs. (14) and (15), the measured CV characteristic can then be reproduced. From Eq. (15) and the asymptotes of a CV characteristic, the minimum of the permittivity can be calculated, i.e., $\epsilon_l = \kappa\epsilon_0$. Similarly, the maximum in the permittivity can be calculated using Eq. (15) with the maximum in $d\alpha/dE$, namely,

$$\epsilon_h = \epsilon_l + 2\hat{P} \left(\frac{d\alpha}{dE} \right)_{\max} \quad (19)$$

As an example, $\alpha(E)$ extracted from a measured CV curve (the branch with negative coercive voltage, $V_c < 0$) of the PZT capacitor with 0% niobium is shown in Fig. 22. The parameters obtained are: $\kappa = 250$ and $\hat{P} = 4.69 \mu C/cm^2$. Also shown in Fig. 22 is a mathematical form fitted to the $\alpha(E)$ extracted from the CV measurement using

$$\alpha(E) = 0.5 + \tanh\left[\left(E - E_{half}\right)/\eta\right]/2 \quad (20)$$

where $\alpha(E_{half}) = 0.5$ (in this example, $E_{half} = -20 \text{ kV/cm}$) and $\eta = 120.5 \text{ kV/cm}$ in the example shown in Fig. 22. The choice of a $\tanh$ function for $\alpha(E)$ is motivated by its mathematical convenience [7, 48]. Other functional forms of $\alpha(E)$ may be used.

With Eq. (20), the capacitance can be expressed based on Eqs. (14) and (15) as

$$C(V = Et) = \left(\kappa \epsilon_0 + \frac{2\hat{P}}{\eta} \text{sech}^2\left[\left(E - E_{half}\right)/\eta\right] \right) / t \quad (21)$$

Using Eq. (21) and the parameters given above for κ , $\hat{P}$, E_{half} , and η , a C V characteristic is produced and is plotted in Fig. 23 with the measured curve for the PZT capacitor with 0% niobium. The fit is reasonable. The procedure described above is now applied to PZT capacitors with various levels of niobium doping to examine the effect of niobium doping on the behavior of $\alpha(E)$.

§IV.III Application of the multiple-domain model to PZT capacitors with various niobium doping levels

As discussed above, the growth of the volume fraction $\alpha(E)$ of the positively polarized domains with the electric field E , can be deduced from a ferroelectric CV characteristic according to Eq. (17). As shown in Fig. 16, niobium doping modifies the CV characteristic of PZT capacitors. This implies that modifications in $\alpha(E)$ can occur due to niobium doping.

By following the procedure described in §IV.II for a *PZT* capacitor with 0% niobium, $\alpha(E)$ can be extracted from measured *CV* curves for *PZT* capacitors with various niobium doping levels and the result is shown in Fig. 24. Eq. (20) is fitted to the $\alpha(E)$ shown in Fig. 24 and the values of the parameters are summarized in Tab. I. The capacitance calculated using Eq. (21) is plotted in Fig. 25 based on the parameters summarized in Tab. I. The $C(V)$ fits the measured curves reasonably well. Within this model, it appears from Tab. I that the maximum polarization $\hat{P}$ is strongly reduced by increasing niobium content, and the field E_{half} is significantly increased.

The model discussed above assumes a uniform electric field. If the ferroelectric film contains ionized dopant atoms (or other charges), then the field cannot be spatially uniform. Next, a generalization of this model is presented for the case when the electric field becomes spatially varying through the depth of the film, for example, due to the dopant-ion charge.

§IV.IV Application of the multiple-domain model to the *Y-I* capacitor

Following the procedure described in §IV.II, $\alpha(E)$ may be deduced for *Y-I* capacitors from the measured *CV* characteristic in Fig. 17 using Eq. (17). The $\alpha(E)$ for *Y-I* is shown, together with the $\alpha(E)$ for *PZT* in Fig. 26. The parameters used for the *Y-I* sample are: $\epsilon_l/\epsilon_0 = 147$ and $\hat{P} = 1.46 \mu\text{C}/\text{cm}^2$.

As $\alpha(E)$ of *Y-I* starts to increase from zero, $d\alpha/dE$ starts to ramp up significantly around the electric field $E = -20 \text{ kV}/\text{cm}$. After passing the electric field $E = 40 \text{ kV}/\text{cm}$,

$\alpha(E)$ of *Y-I* becomes almost parallel to the $\alpha(E)$ of *PZT*. It is obvious from Fig. 26 that $\alpha(E)$ of *Y-I* spans a larger range of electric field than that of *PZT*. However, because of the large $d\alpha/dE$ around $E = 200 \text{ kV/cm}$ and because $d\alpha/dE$ is related to the *CV* characteristic by Eq. (15), the peaks of the *CV* characteristic of *Y-I* are much sharper than the *CV* curves of *PZT*. The characteristic of $\alpha(E)$ around $E = 200 \text{ kV/cm}$ suggests that the domain nucleation of *Y-I* occurs intensely around $E = 200 \text{ kV/cm}$ unlike *PZT*, in which on the other hand, nucleation of domains occurs more uniformly, leading to rounded *CV* curves. Hence, the macroscopic *CV* curves have been related to the microscopic-level domain growth with the electric field.

Due to the significant asymmetry in the $\alpha(E)$ of *Y-I* shown in Fig. 26, the tanh function used in Eq. (20), and as a result, the sech function in Eq. (21), do not fit the $\alpha(E)$ and *CV* characteristics of *Y-I* capacitors very well. However, the discussion in §IV.II of the relation between the microscopic level growth of the volume fraction of domains and the macroscopic *CV* curves is still applicable to *Y-I*. In order to produce a mathematical model for the *CV* characteristic of *Y-I* such as Eq. (21) for *PZT*, a more complex piecewise fit is required for $\alpha(E)$ of *Y-I* due to the asymmetrical nature of the behavior.

Chapter V A spatially varying domain structure for ferroelectric films subject to nonuniform electric field

In this chapter, the volume growth function of positively-polarized domains ($\alpha(E)$) introduced in **Chapter IV** is applied to a generalized case when the electric field is spatially varying, specifically, due to the presence of dopant-ion charge. In **Chapter IV**, $\alpha(E)$ has been introduced under the assumption that the electric field is spatially uniform through the depth of the film. For the uniform field case, both the positively- and the negatively-polarized domains penetrate through the depth of the film. Because of the spatially-varying electric field, however, a nonuniform interface between the positively- and negatively-polarized domains exists and a position-dependent permittivity is deduced. With the position-dependent permittivity and a spatially-varying electric field, the application of the Schottky doping profiling technique to ferroelectrics is studied and details are presented in **Chapter VI**. The profiling shows compensation of the p-type *PZT* samples by the n-type niobium doping. Based on the approximate doping profiles extracted from *CV* measurement and the deduced permittivity, the measured *CV* characteristics are reconstructed through computer simulations.

§V.I Introduction

In **Chapter IV**, a consistent physical picture is presented to explain capacitance measurements on *PZT* capacitors with various niobium doping levels. The assumption that the electric field is uniform through the depth of the film leads to the suggestion that

niobium modifies the domain growth rate with the electric field. However, evidence supporting the existence of Schottky barriers at the ferroelectric-metal electrode interfaces of ferroelectric capacitors has been reported [53-56]. Besides, it has been reported that *PZT* has p-type conductivity [46] and niobium is an n-type dopant for *PZT* [47] that compensates the p-type doping of *PZT*. The presence of dopant-ion charge implies that the electric field is not uniform through the depth of the film. Therefore, a generalization of the physical picture in **Chapter IV** consistent with the measured ferroelectric *CV* characteristic is needed for cases where the electric field is spatially varying through the depth of the film. A generalization of the uniform field model now is presented that fits the measured ferroelectric *CV* characteristics.

§V.II A spatially varying domain structure for ferroelectric films subject to nonuniform electric field

Based upon the uniform field model in **Chapter IV**, a spatially varying electric field model can be constructed by stacking films with uniform field on top of one another, each with a different value of field and each film layer of a thickness δt . As an idealization of such a stacked film, let δt become very small. An important assumption will be made for the spatially varying field model: each film layer has a uniform electric field and has a domain structure that behaves according to the P versus E relation shown in Fig. 21. The question of physically how small δt can be made is beyond the scope of this work.

In the limit of small layer thicknesses, i.e., $\delta t \rightarrow 0$, the stacked films lead to a case where the field is not spatially uniform through the depth of the sample, that is, the electric field at a selected atomic site in the unit cell varies from one layer to another. This variation can occur, for instance, if the presence of dopant-ion charge makes the field spatially nonuniform. Due to the spatially nonuniform electric field $E(x)$, the $\alpha(E)$ introduced in **Chapter IV** becomes position-dependent, i.e., $\alpha(x) = \alpha(E(x))$. Similarly, the field-dependent polarization $P(E)$ in Eq. (11) maps into a position-dependent polarization $P(x)$. Also, the field-dependent permittivity $\varepsilon(E)$ shown in Fig. 27 becomes position-dependent, namely, $\varepsilon(E) = \varepsilon(E(x))$. To be concrete, a possible schematic domain structure for the sample is shown in Fig. 28 at some applied bias. For positions $x \leq x_\lambda$, the field $E \geq E_d$ and the material is entirely polarized in the positive x -direction. For positions $x \geq x_\rho$, $E \leq E_a$, and the sample is entirely polarized in the negative x -direction. Domains of both orientations exist where $E_a \leq E \leq E_d$, corresponding to a layer in the sample with $x_\lambda \leq x \leq x_\rho$. In this *switching region* $x_\lambda \leq x \leq x_\rho$, the polarization varies with x according to the relation

$$P(x) = \alpha(x)\hat{P} + (1 - \alpha(x))(-\hat{P}) \quad (22)$$

where $P(x)$ = polarization in the interval between x and $x + dx$, and where $\alpha(x)$ is the volume fraction of positively oriented domains in this interval. Evidently, $\alpha(x_\lambda) = 1$ and $\alpha(x_\rho) = 0$. More complicated statistical transition regions consistent with a monotonic $\alpha(E)$ could be constructed, but Fig. 28 illustrates the features of interest.

To build a schematic domain picture for the case of a spatially nonuniform electric field, consider the P versus E relation shown in Fig. 21 assuming a simple linear $\alpha(E)$. With this assumption,

$$\frac{\partial P}{\partial E} = \begin{cases} 0 & E \leq E_a \text{ or } E \geq E_d \\ 2\hat{P}/(E_d - E_a) & E_a \leq E \leq E_d \end{cases} \quad (23)$$

In the range of fields $E_a \leq E \leq E_d$, domains exist in both the positive and negative x -directions. With Eq. (23) substituted in Eqs. (12) and (13), a simple field-dependent permittivity in Fig. 27 (curve (a)) results with

$$\varepsilon_l = \kappa \varepsilon_0 \quad (24)$$

and

$$\varepsilon_h = \kappa \varepsilon_0 + \frac{2\hat{P}}{E_d - E_a} \quad (25)$$

A more realistic $\varepsilon(E)$ is also shown in Fig. 27 (curve (b)) with gradual transitions between ε_h and ε_l . The gradual transitions will be approximated later by ramps connecting ε_h and ε_l for the convenience of computer simulations.

Suppose that for any x inside the switching region there is an electric field value $E(x)$ such that $\alpha(x)$ is given by $\alpha(x) = \alpha(E(x))$. That is, each section of width dx within the transition layer behaves like a slice of the spatially uniform ferroelectric considered in **Chapter IV**. Then based on the simple schematic domain structure shown in Fig.

28, a *position*-dependent permittivity $\epsilon(x)$ is proposed and is shown in Fig. 29. The position-dependent permittivity which results from a nonuniform electric field and a field-dependent permittivity, i.e., $\epsilon(x) = \epsilon(E(x))$ has been noted by Blom et al. [52]. ϵ_h now can be expressed in terms of the dopant-ion charge. Poisson's equation for a fully-depleted film is,

$$\frac{\partial D}{\partial x} = \frac{\partial D}{\partial E} \frac{\partial E}{\partial x} = \epsilon(E) \frac{\partial E}{\partial x} = \rho(x) \quad (26)$$

where the space charge density, $\rho(x) = -qN(x)$ for p-type samples (e.g., *PZT* films). With the definition of $\epsilon(E)$ in Eq. (13),

$$\frac{\partial D}{\partial E} = \epsilon = \kappa\epsilon_0 + \frac{\partial P}{\partial x} \frac{\partial x}{\partial E} = \kappa\epsilon_0 + \frac{\partial P}{\partial x} \frac{\epsilon}{\rho} \quad (27)$$

Solving for ϵ yields

$$\epsilon = \frac{\kappa\epsilon_0}{1 - \frac{1}{\rho} \frac{\partial P}{\partial x}} \quad (28)$$

According to Eq. (28), outside the switching layer where $\partial P / \partial x = 0$, $\epsilon = \epsilon_l = \kappa\epsilon_0$. Inside the switching layer, $\partial P / \partial x$ can be approximated by the change in $P(x)$ across the switching layer

$$\frac{\partial P}{\partial x} \approx 2\hat{P}/\Delta_s, \quad x_\lambda \leq x \leq x_\rho \quad (29)$$

with $\Delta_s = x_p - x_\lambda$ the thickness of the switching layer, and $2\hat{P}$ the change in polarization from one side of the switching layer to the other. Using Eq. (29) in (28) gives

$$\begin{cases} \varepsilon_h = \frac{\kappa\varepsilon_0}{1 - \frac{2\hat{P}}{|\rho|\Delta_s}} & x_\lambda < x < x_p \\ \varepsilon_l = \kappa\varepsilon_0 & x < x_\lambda \text{ or } x > x_p \end{cases} \quad (30)$$

The position-dependent permittivity $\varepsilon(x)$ described by Eq. (30) is illustrated in Fig. 29.

In summary, due to the spatially nonuniform electric field, the field-dependent $\alpha(E)$, $P(E)$ and $\varepsilon(E)$ map into the position-dependent $\alpha(x)$, $P(x)$, and $\varepsilon(x)$. Next, it will be demonstrated through computer simulations that the nonuniform electric field model is able to predict the measured *CV* characteristic of *PZT* capacitors with various niobium doping levels.

§V.III Computer Simulations

It will now be demonstrated through computer simulations that the proposed field-dependent permittivity $\varepsilon(E)$ has excellent consistency with the measured *CV* characteristic taking into account the nonuniform electric field, and assuming a fully-depleted sample.

Integrating both sides of Poisson's equation for a fully-depleted film (Eq. (26)) from a position $x' = 0$ to a point, $x' = x$, in the depth of the film gives

$$\int_{E(0)}^{E(x)} \epsilon(E) dE = \int_0^x \rho(x') dx' \quad (31)$$

where the electric field is spatially-varying and the surface field $E(0) = E(x = 0)$. The electric field at the depth x is $E(x)$. $\rho(x)$ is the distribution of dopant-ion charge as a function of position x , that is, $\rho(x) = qN(x)$, where $N(x)$ is the doping profile. For given functions $N(x)$ and $\epsilon(E)$, there exists a distribution of electric field $E(x)$ for a surface field $E(0)$, as suggested by Eq. (31). The applied bias, V , is equal to the integral of $-E(x)$ over the thickness of the film, and so V is a function of $E(0)$. $E(0)$, therefore, is determined by V , the bias across the film. Thus, the distribution of electric field $E(x)$ at a given bias is completely determined, given a particular form of $\epsilon(E)$ and a particular $N(x)$. Due to the spatial variation of the electric field $E(x)$, for any given $\epsilon(E)$, there is a distribution of dielectric constant $\epsilon(x)$ through the depth of the film at the given bias. The capacitance at a chosen bias can be related to the spatially-varying permittivity by (see, for example, Ref. [42, 46, 52])

$$1/C = \int_0^t \frac{dx}{\epsilon(x)} \quad (32)$$

where t is the film thickness. Therefore, a characteristic ferroelectric CV behavior is associated with any particular forms of $\epsilon(E)$ and the doping profile $N(x)$. In other words, the measured CV characteristic may be predicted based on the proposed form of $\epsilon(E)$ shown in Fig. 27 and a given form of doping profile $N(x)$. The calculation of a

CV curve will be presented once the doping profile $N(x)$ is determined, as discussed next.

§V.IV Doping profiling with CV characteristic

Within the framework of the field-dependent permittivity model for ferroelectrics subject to spatially nonuniform electric field, it is possible to extract the doping profile in ferroelectric thin films using an analog of the usual formula for doping profiling in Schottky barriers. A derivation of the relation between the dopant-ion charge profile, $\rho(x)$, and CV measurements for ferroelectrics is presented in **Chapter VI**. The profile is found from

$$\rho(x_j) = \frac{2}{\epsilon_{eff} d (1/C^2) / dV_a} \quad (33)$$

where the effective dielectric constant, ϵ_{eff} , is defined as

$$\frac{1}{\epsilon_{eff}} \equiv \frac{1}{\epsilon_l} - \frac{1}{\epsilon_h}. \quad (34)$$

$\rho(x_j)$ is the charge density of the ferroelectric film at $x = x_j$. ϵ_l is the saturated (low) dielectric constant, and ϵ_h is the nonsaturated (high) dielectric constant. The profiling location, x_j , is at the position where the dielectric constant changes from ϵ_l to ϵ_h . It will be shown in **Chapter VI** that a good approximation to x_j that is directly measurable is given by

$$x_j = \varepsilon_{eff} \left(\frac{1}{C} - \frac{t}{\varepsilon_h} \right) \quad (35)$$

Practically, $\varepsilon_{l,h}$ can be estimated using the measured maximum and minimum capacitance values per unit area, $C_{max,min}$, as follows:

$$\varepsilon_{h,l} \approx C_{max,min} \times t \quad (36)$$

where t is the film thickness. Note that ε_h and ε_l calculated from Eq. (36) will be adjusted slightly in later computer simulations in order to obtain a good fit to the measured CV characteristic. Strictly speaking, the estimated ε_h from Eq. (36) is a lower bound upon the possible values of the high dielectric constant since it is assumed implicitly in Eq. (36) that the switching layer penetrates through the depth of the film at the peak capacitance, C_{max} . However, if the switching layer is narrower than the film thickness, then the actual high dielectric constant is larger than the estimate of ε_h in Eq. (36). Also, the measured CV characteristic never reaches its large field asymptotes because high voltages cause breakdown of the samples. Hence, the estimated ε_l from Eq. (36) is an upper limit for the actual low dielectric constant. In short, Eq. (36) provides some "initial guesses" of ε_h and ε_l for computer simulations, but ε_h is then slightly increased and ε_l is slightly reduced in order to obtain a good fit to the measured CV characteristic. The values of ε_l summarized in Tab. I are obtained with the approach described above and will be used shortly in doping profiling.

Eqs. (33) and (35) apply provided (i) the ferroelectric film is fully depleted, and (ii) that there is only one transition between ε_h and ε_l within the film (i.e., film thickness $< \Delta$).

It is found in our prior work¹² that the first condition is likely to be satisfied for ferroelectric thin films. The second condition corresponds to the physical picture of the distribution of the permittivity through the depth of the film reported by van der Berg et al. in Ref. [46].

§V.V Application of the nonuniform electric field model to *PZT* capacitors with various niobium doping levels

Doping profile results obtained from the measured *CV* characteristic of *PZT* (Fig. 16) using Eqs. (33) and (35) are shown in Fig. 30. $x = 0$ corresponds to the top electrode. The straight lines shown in Fig. 30 are the approximate doping profiles (later used in computer simulations) based on the profiles extracted from an overall best-fit to both the right and left legs of the $V_c < 0$ branch of the measured *CV* characteristic for each sample. Error bars are shown for the *PZT* samples with 0% and 5% niobium to indicate the range of the doping concentrations obtained from separate fits to the two legs of the $V_c < 0$ branch of the measured *CV* characteristic. The error becomes larger close to the surfaces of the film because the extracted doping concentrations close to the surfaces involve fitting around the peak of the measured *CV* characteristic. A gradual reduction in the average doping level is observed as more niobium is added to the samples. It has been reported that *PZT* has p-type conductivity [57] and niobium is an n-type dopant for *PZT*[24]. The compensation of p-type *PZT* doping by the n-type niobium is supported by the result shown in Fig. 30.

Based on the approximate doping profiles shown in Fig. 30 and the form of $\varepsilon(E)$ illustrated in Fig. 27 (for convenience, with ramps connecting ε_h and ε_l to approximate the more realistic transitions), computer simulations were performed to generate ferroelectric CV characteristics based on Eqs. (31) and (32). The parameters used in computer simulations are summarized in Tab. II. Tab. II shows that both low and high dielectric constants decrease with niobium content. The coercive field also tends to increase with niobium content. These trends are similar to those of the uniform field model. The simulated and measured CV characteristics are compared in Fig. 31 and the correspondence is found to be excellent. This indicates the consistency of the proposed $\varepsilon(E)$ under the assumption that the electric field is spatially nonuniform due to the dopant-ion charge.

In summary, based on the proposed $\varepsilon(E)$ model, doping profiles $N(x)$ have been extracted from the measured CV characteristic of PZT capacitors with various niobium doping levels. Computer simulations have reconstructed the measured CV characteristics based on the proposed $\varepsilon(E)$ and the approximate $N(x)$ extracted from measurement. Thus, a consistent formulation of $\varepsilon(E)$, $\varepsilon(x)$, $\rho(x)$ and measured CV characteristic within the framework of the nonuniform electric field assumption has been demonstrated.

§V.VI Application of the nonuniform electric field model to *Y-I* capacitors

Using Eqs. (33) and (35) in §V.IV, the electrical doping profile of the *Y-I* capacitor is obtained based on the measured *CV* characteristic (Fig. 17) and is shown in Fig. 32. Again, $x = 0$ corresponds to the top electrode and the straight line shown in Fig. 32 is the approximate doping profiles later used in the computer simulation to fit the measured *CV* curves. Error bars indicate the fluctuations of the doping concentration obtained from separate fits to the two legs of the $V_c < 0$ branch of the measured *CV* characteristic shown in Fig. 17. Fig. 32 shows that the electrical doping level of the *Y-I* samples is approximately $1.8 \times 10^{18} \text{ cm}^{-3}$ and is in the range of doping concentrations of *PZT*.

Following the procedure described in §V.V with the approximate doping profile in Fig. 32, computer simulations were performed to generate *CV* curves to fit the measured *CV* characteristic in Fig. 17. It is found that the simple trapezoidal $\epsilon(E)$ used to fit the measured *CV* curves of *PZT* capacitors could not yield a good fit to the measured *CV* characteristic of the *Y-I* capacitor. The simulation result is shown in Fig. 33 with various values of δ_l . Recall that δ_l is the width (in electric field) of the nonideal transition region where $\epsilon(E)$ changes from ϵ_l to ϵ_h , as illustrated in Fig. 27. The parameters used in the computer simulation are: $\epsilon_l/\epsilon_0 = 147$, $\epsilon_h/\epsilon_0 = 280.8$, $\eta_0 = 40 \text{ kV/cm}$, $N(x) = 3.15 \times 10^{22} x (\text{cm}) + 1.48 \times 10^{18} \text{ cm}^{-3}$, $\delta_r = 0$ and $\delta_l = 0 - 50 \text{ kV/cm}$ with an increment of 10 kV/cm .

It is obvious from Fig. 33 that as δ_l increases, the simulated CV curve broadens. For a δ_l between 0 and 10 kV/cm (curves (a) and (b)), the left leg of the simulated CV curve fits the measured CV characteristic well around the peak (from ~ -1.25 to -0.8 V). However, both curves (a) and (b) drop too quickly away from the peak region. On the other hand, when δ_l is increased to 20 kV/cm , the simulated CV curve becomes parallel to the measured CV characteristic from ~ -2 to -1.25 V. Clearly, increasing δ_l from 0 to 50 kV/cm makes the curvature of the simulated CV curves become similar to the measured CV characteristic in different bias regimes. According to the above discussion, a more complex $\varepsilon(E)$ may be proposed in order to generate a good fit to the measured CV curves. This $\varepsilon(E)$ is shown in Fig. 34. Piecewise linear structures are used in the transition regions where $\varepsilon(E)$ changes between ε_h and ε_l . This piecewise linear structure will allow the desired curvatures in the measured CV curve in various bias regimes. However, computer simulations become more complex for this structure since more parameters are involved in the fit; for instance, the slopes in various regions and the width of each region.

Chapter VI Profiling of electrical doping concentration in ferroelectrics

In this chapter, the extraction of doping profiles in ferroelectric thin film capacitors using ferroelectric capacitance-voltage (*CV*) measurements is studied. The Schottky electrical doping profiling equation will be derived for ferroelectrics based upon the spatially varying permittivity $\epsilon(x)$ introduced in §V.II. Also, it will be demonstrated that the resolution of profiling is determined by the abruptness of the transition in $\epsilon(x)$. For a ferroelectric field-dependent permittivity model assuming a spatially-varying electric field due to the presence of dopant-ion charge, the doping profile relation to measured *CV* curves for ferroelectric thin film capacitors is found to be analogous to the well-known result of metal-semiconductor Schottky junctions with an easily determined effective dielectric constant. Computer simulation shows the electrical doping concentration of ferroelectric thin film capacitors can be profiled accurately with the proposed model. Limitations of Schottky profiling in ferroelectrics are investigated.

§VI.I Introduction

It is well known that the doping concentration of semiconductors can be profiled from *CV* measurements of a Schottky junction using

$$N(W) = \frac{2}{q\epsilon_s} \left[\frac{1}{d(1/C^2)/dV_a} \right], \quad (37)$$

where N is the doping concentration at depth, W , in the semiconductor. ϵ_s is the dielectric constant of the semiconductor and C is the capacitance per unit area of the Schottky capacitor. V_a is the applied bias. Note that ϵ_s of a semiconductor is a well-known constant, however, for ferroelectrics, permittivity can be a field-dependent quantity; this complicates the application of Eq. (37) to ferroelectrics. The profiling depth, W , for a material with field-independent ϵ_s can be expressed as

$$W = \frac{\epsilon_s}{C} \quad (38)$$

Researchers suggested that the electrical doping concentration of semiconducting ferroelectric thin films can be profiled in the same way using ferroelectric CV characteristics [46, 58]. However, for ferroelectric materials, the physical basis and limitations of Eq. (37) are not well understood.

A field-dependent permittivity in materials with the perovskite crystal structure, such as $SrTiO_3$ and $KTaO_3$, has been reported [42, 46]. Kahng et al. [42] reported a field-dependent permittivity at the metal-semiconductor interface and solved Poisson's equation, calculating the surface electric field based on the doping concentration extracted from CV measurements made on $KTaO_3$ Schottky diodes. A field-dependent permittivity extracted from CV measurements on $SrTiO_3$ Schottky diodes was also reported by van der Berg et al. [46]. These materials were measured and analyzed at temperatures above their Curie points where no domain structure is present. Blom et al. [52] applied Schottky barrier analysis to $PbTiO_3$ where domains were present, but did not attempt profiling. Brennan [58] used Schottky theory to derive CV curves when domains are present and suggested that a constant doping could be deduced from his

capacitance expression. However, he did not examine use of the Schottky profiling Eq. (37). This paper is different from earlier work, then, in combining the effects of (i) a field and spatially dependent permittivity, and (ii) domains and domain switching in an analysis of the Schottky profiling Eq. (37), as applied to not only partially but also *fully* depleted ferroelectric films.

In this chapter, the use of Eq. (37) for doping profiling in ferroelectric films is studied. A simple field-dependent permittivity model is introduced and a more general numerical approach follows. It will be demonstrated that the doping profiling in ferroelectrics is given by

$$\rho(x_j) = \frac{2}{\epsilon_{eff} d (1/C^2) / dV_a} \quad (39)$$

where the effective dielectric constant, ϵ_{eff} , is defined as

$$\frac{1}{\epsilon_{eff}} \equiv \frac{1}{\epsilon_l} - \frac{1}{\epsilon_h}, \quad (40)$$

$\rho(x_j)$ is the charge density of the ferroelectric film at $x = x_j$, ϵ_l is the saturated dielectric constant, ϵ_h is the nonsaturated dielectric constant and $\epsilon_h > \epsilon_l$. The profiling location, x_j , is expressed as

$$x_j = \epsilon_{eff} \left(\frac{1}{C} - \frac{t}{\epsilon_h} \right) \quad (41)$$

Eqs. (39) and (41) are shown to apply provided (i) the ferroelectric film is fully depleted, (ii) that there is only one transition between ϵ_h and ϵ_l within the film, and (iii) there is a switching layer in the ferroelectric, as discussed shortly.

However, it will also be shown that more complicated cases can occur in ferroelectric films. In particular, doping profiling can occur simultaneously at more than one location in ferroelectrics.

§VI.II Review of a simple model

In **Chapter IV**, a simple field-dependent permittivity model is proposed. The field-dependent permittivity becomes position dependent in the presence of dopant ion charge, as discussed in **Chapter V**. As mentioned in **Chapter V**, curve (b) in Fig. 35 accounts for the possibly more gradual nature of the response of the permittivity with the electric field around E_a and E_d . First, the idealized form of the dielectric constant is used with abrupt transitions at E_a and E_d , as illustrated by curve (a) in Fig. 35.

The idealized model gives insight for studying the doping profiling in ferroelectric films, as will be discussed shortly. Then a more realistic $\epsilon(E)$ is used in a computer analysis. Based on this idealized model, a high-dielectric constant switching region is present for ferroelectric films subject to a nonuniform electric field. Consistency between our model and the measured *CV* characteristic shown in **Chapter V** provides evidence for a high-dielectric constant switching region in ferroelectric films subject to a spatially varying electric field.

To introduce doping profiling, the idealized dielectric constant-electric field relation is adopted, as illustrated by curve (a) in Fig. 35,

$$\epsilon(E) = \begin{cases} \epsilon_h & E < E_a \text{ or } E > E_d \\ \epsilon_l & E_a \leq E \leq E_d \end{cases} \quad (42)$$

where ϵ_h and ϵ_l are the nonsaturated and the saturated dielectric constants and $\epsilon_h > \epsilon_l$. E_a and E_d are fields that mark the beginning and completion of domain nucleation when the field increases toward the positive direction. It is assumed, as discussed in **Chapter IV**, that nucleation of aligned domains does not occur until $E \geq E_a$, and for values of E greater than some "single-domain" value E_d , alignment is complete and a single domain results. E_c is the coercive field and can be expressed as $E_c = (E_a + E_d)/2$. The following analysis is based on the idealized $\epsilon(E)$ of Eq. (42), as illustrated by curve (a) in Fig. 35. Later, computer simulations are used to show the impact of relaxing the idealized dielectric constant into a more realistic form, as shown by curve (b) in Fig. 35, upon doping profiling.

§VI.III Analysis

§VI.III.A Doping profiling in fully-depleted ferroelectric films

The electrical doping concentration of ferroelectric films is now related to the CV characteristic through the idealized field-dependent permittivity of Eq. (42). As

mentioned in **Chapter V**, due to the spatially-varying electric field caused by dopant-ion charge in the ferroelectric film, the dielectric constant is position-dependent. At a given bias, the position-dependent dielectric constant can be idealized as shown in Fig. 36, assuming the width of the switching layer is larger than the film thickness. Namely,

$$\varepsilon(x) = \begin{cases} \varepsilon_l & 0 < x < x_j \\ \varepsilon_h & x_j < x < t \end{cases} \quad (43)$$

where t is the film thickness. x_j is the location where the dielectric constant changes its value, i.e., $E(x = x_j) = E_a$, according to the field-dependent dielectric constant model shown in Fig. 35. The low permittivity regions where, $\varepsilon = \varepsilon_l$, correspond to fully polarized regions of the film, while the high permittivity region where $\varepsilon = \varepsilon_h$, corresponds to the region in the film where domain switching occurs and E is near the coercive field. The idealized $\varepsilon(E)$ shown in Fig. 35 and the $\varepsilon(x)$ in Fig. 36 are equivalent. For the purpose of doping profiling, the simplest situation is one where the position-dependent dielectric constant changes value only once (as illustrated in Fig. 36) and it will be shown for this case that doping profiling occurs at the "junction" where the dielectric constant changes its value. The case when the dielectric constant changes value twice in the film corresponds to profiling at two locations and will be discussed later. Also, the idealization of an abrupt transition in $\varepsilon(E)$ will be relaxed, and doping profiling for more gradual changes in $\varepsilon(E)$ will be examined.

Poisson's equation then can be written, for the ferroelectric film in Fig. 36, as

$$\frac{dE}{dx} = \frac{\rho(x)}{\varepsilon(x)} = \begin{cases} \frac{\rho(x)}{\varepsilon_l} & 0 \leq x < x_j \\ \frac{\rho(x)}{\varepsilon_h} & x_j < x \leq t \end{cases} \quad (44)$$

On the other hand, for a metal-semiconductor Schottky junction, Poisson's equation is

$$\frac{dE}{dx} = \begin{cases} \frac{\rho(x)}{\varepsilon_s} & 0 \leq x < W \\ 0 & W \leq x \leq t \end{cases} \quad (45)$$

Thus, for a metal-semiconductor Schottky junction, Eq. (45) can be viewed as

$$\frac{1}{\varepsilon(x)} = \begin{cases} \frac{1}{\varepsilon_s} & 0 < x < W \\ 0 & W \leq x < t \end{cases} \quad (46)$$

The function $1/\varepsilon(x)$ for ferroelectric films and the artificial $1/\varepsilon(x)$ for Schottky junctions are illustrated together in Fig. 37 for comparison. Within the proposed approach, the Schottky junction becomes a special case of Eq. (44) when $\varepsilon_h \gg \varepsilon_l$. Fig. 37 shows that the location $x = x_j$ in ferroelectric films, where the dielectric constant switches, can be viewed as an analog of the depletion region edge in Schottky junctions. As will be demonstrated next, just as doping profiling in Schottky junctions occurs at the depletion region edge, doping profiling in ferroelectric films occurs at the "junction" where the dielectric constant changes. Most importantly, the capability for doping profiling stems from the fact that $d(1/\varepsilon)/dx$ assumes an abrupt transition at the profiling location in both cases, as illustrated in Fig. 37. More generally, the derivative of the dielectric constant with respect to position has to be a function sharply peaked at

the doping profiling location to yield an accurate doping profile. Further, the width of this peak determines the resolution of the extracted profile.

Eq. (39) will now be derived. Define

$$Q(x) \equiv \int_0^x dx' \rho(x') \quad (47)$$

Note $Q(x=0) = 0$. Integrate Eq. (44) and get

$$E(x) - E_0 = \int_0^x dx' \frac{\rho(x')}{\varepsilon(x')} = \int_0^x dx' \frac{dQ/dx'}{\varepsilon(x')} \quad (48)$$

where $E_0 = E(x=0)$. By applying the chain rule to Eq. (48),

$$\int_0^x \frac{dQ}{\varepsilon} = \int_0^{Q(x)/\varepsilon(x)} d\left(\frac{Q}{\varepsilon}\right) - \int_{1/\varepsilon(0)}^{1/\varepsilon(x)} Q d\left(\frac{1}{\varepsilon}\right) \quad (49)$$

As shown in Fig. 37,

$$\frac{d}{dx}\left(\frac{1}{\varepsilon}\right) = -\frac{\delta(x-x_j)}{\varepsilon_{eff}} \quad (50)$$

where $\delta(x-x_j)$ is a delta function centered at $x = x_j$. ε_{eff} is defined by Eq. (40). Eq. (49) then becomes

$$\int_0^x \frac{dQ}{\varepsilon} = \frac{Q(x)}{\varepsilon(x)} + \frac{1}{\varepsilon_{eff}} \int_0^x dx' Q(x') \delta(x' - x_j) \quad (51)$$

Thus, Eq. (48) can be reduced to

$$E(x) = -\frac{d\phi}{dx} = E_0 + \frac{Q(x)}{\varepsilon(x)} + \frac{Q(x_j)}{\varepsilon_{eff}} u(x - x_j) \quad (52)$$

where ϕ is the potential distribution and the unit step function, $u(x - x_j)$, is defined as

$$u(x - x_j) = \begin{cases} 0 & x < x_j \\ 1 & x \geq x_j \end{cases} \quad (53)$$

Integration of Eq. (52) gives

$$-\left[\phi(x) - \phi(0)\right] = E_0 x + \int_0^x dx' \frac{Q(x')}{\varepsilon(x')} + \frac{Q(x_j)}{\varepsilon_{eff}} \int_0^x dx' u(x' - x_j) \quad (54)$$

An expression for the applied bias, V_a , can be obtained from Eq. (54) when $x = t$, the film thickness,

$$-V_a = -\left[\phi(t) - \phi(0)\right] = E_0 t + \int_0^t dx' \frac{Q(x')}{\varepsilon(x')} + \frac{Q(x_j)}{\varepsilon_{eff}} (t - x_j) \quad (55)$$

Next a small variation in the applied bias (small-signal) can be expressed by differencing Eq. (55).

$$-\Delta V_a = \Delta E_0 t + \int_0^t dx' Q(x') \Delta(1/\varepsilon) + \frac{\Delta Q(x_j)}{\varepsilon_{eff}} (t - x_j) - \frac{Q(x_j)}{\varepsilon_{eff}} \Delta x_j \quad (56)$$

Note that the small-signal (ΔV_a) results in a small variation in the surface electric field (ΔE_0) and a small shift in the position (Δx_j) where the dielectric constant switches from ϵ_l to ϵ_h . Eq. (56) can be greatly simplified if $\Delta E_0/\Delta x_j$ and $\Delta(1/\epsilon)/\Delta x_j$ are known, and next these quantities are evaluated.

To find $\Delta E_0/\Delta x_j$, consider Poisson's equation at $x = x_j^-$ (in the neighborhood of x_j , but for $x < x_j$)

$$E(x_j) - E_0 = -\frac{d\phi}{dx} - E_0 = \int_0^{x_j} dx \frac{\rho(x)}{\epsilon_l} \quad (57)$$

It is clear from Eq. (57) that

$$\Delta E_0 = -\frac{\rho(x_j)}{\epsilon_l} \Delta x_j \quad (58)$$

An assumption of the model is that the magnitude of electric field where the dielectric constant switches ($E_j = E(x = x_j) = E_a$) does not change with ΔV_a , i.e., $\Delta E_j/\Delta V_a = 0$. In other words, the electric field that marks the transition from ferroelectric to linear behavior, E_j , is treated as a characteristic of the material itself.

With the relation

$$\Delta(1/\epsilon) = \frac{\delta(x - x_j)}{\epsilon_{eff}} \Delta x_j \quad (59)$$

and

$$\Delta Q(x_j) = \rho(x_j) \Delta x_j \quad (60)$$

Eq. (56) then reduces to

$$\Delta V_a = \rho(x_j) \left(\frac{x_j}{\varepsilon_l} + \frac{t - x_j}{\varepsilon_h} \right) \Delta x_j \quad (61)$$

The capacitance of the film can be expressed as the series capacitance of the two layers with different dielectric constants, as illustrated in Fig. 36, namely,

$$\frac{1}{C} = \frac{x_j}{\varepsilon_l} + \frac{t - x_j}{\varepsilon_h} \quad (62)$$

With Eq. (62), Eq.(61) is further simplified to

$$\Delta V_a = \frac{\rho(x_j)}{C} \Delta x_j \quad (63)$$

From Eq. (62), Δx_j can be expressed in terms of $\Delta(1/C)$

$$\Delta x_j = \varepsilon_{eff} \Delta \left(\frac{1}{C} \right) \quad (64)$$

Recall the definition of the effective dielectric constant, ε_{eff} in Eq. (40). Substituting Eq. (64) into Eq. (63) and rearranging terms yields the ferroelectric doping profiling equation,

$$\rho(x_j) = \frac{2}{\varepsilon_{eff} d (1/C^2) / dV_a} \quad (65)$$

The profiling depth, x_j , can be derived from Eq. (62).

$$x_j = \epsilon_{eff} \left(\frac{1}{C} - \frac{t}{\epsilon_h} \right) \quad (66)$$

Comparison between Eqs. (37) and (65) shows that within the approximation of a step-like change in $1/\epsilon$, the equation of ferroelectric doping profiling is identical to the well-known result of Schottky junction doping profiling with the defined effective dielectric constant, ϵ_{eff} , replacing the semiconductor dielectric constant, ϵ_s . As mentioned, a Schottky junction can be arranged to be a special case of this model for a ferroelectric film that results when $\epsilon_h \gg \epsilon_l$. At this extreme, it is easy to see that the ferroelectric doping profiling equation (Eq. (65)) reduces to the Schottky junction doping profiling result (Eq. (37)). According to Eq. (65), the doping profile of ferroelectric films is found at $x = x_j$, or the "junction" where the dielectric constant changes. Eq. (59) is a key relation leading to Eq. (65) for doping profiling. That is, doping profiling capability relies strongly on the existence of an abrupt step in $1/\epsilon$ at the profiling location, as illustrated in Fig. 37.

§VI.III.B Doping profiling in partially-depleted ferroelectric films

The partially-depleted case provides an interesting combination of Eqs. (37) and (39). As shown in Eq. (46), the depletion region edge can be viewed as a sharp change in effective dielectric constant. Thus, doping profiling occurs at *two locations* for partially-depleted ferroelectric films. As shown in Fig. 38, there are two abrupt

transitions in the dielectric constant when the film is partially-depleted; therefore, Eqs. (65) - (66) are no longer valid.

To study the partially-depleted case, consider the more general dielectric constant model with three steps, as shown in Fig. 39. As $1/\epsilon_w \rightarrow 0$, the case illustrated in Fig. 39 becomes a partially-depleted film.

For the model shown in Fig. 39, Poisson's equation is identical to the previous case; thus,

$$E(x) - E_0 = \int_0^x dx' \frac{\rho(x')}{\epsilon(x')} = \int_0^x dx' \frac{dQ/dx'}{\epsilon(x')} \quad (67)$$

where Q is defined in Eq. (47). By applying the chain rule to Eq. (67) we get

$$\int_0^x \frac{dQ}{\epsilon} = \int_0^{Q(x)/\epsilon(x)} d\left(\frac{Q}{\epsilon}\right) - \int_{1/\epsilon(0)}^{1/\epsilon(x)} Q d\left(\frac{1}{\epsilon}\right) \quad (68)$$

Due to the existence of the "depletion edge" at $x = W$ and the actual dielectric constant transition from ϵ_i to ϵ_h at $x = x_j$,

$$\frac{d}{dx} \left(\frac{1}{\epsilon} \right) = - \frac{\delta(x - x_j)}{\epsilon_{eff}} - \left(\frac{1}{\epsilon_h} - \frac{1}{\epsilon_w} \right) \delta(x - W) \quad (69)$$

Eq. (68) then becomes

$$\begin{aligned} \int_0^x \frac{dQ}{\varepsilon} &= \frac{Q(x)}{\varepsilon(x)} + \frac{1}{\varepsilon_{eff}} \int_0^x dx' Q(x') \delta(x - x_j) \\ &+ \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_w} \right) \int_0^x dx' Q(x') \delta(x - W) \end{aligned} \quad (70)$$

Note that the last term in Eq. (70) is a result of the second step in $1/\varepsilon$. Otherwise, Eqs. (70) and (51) are identical. Eq. (67) can now be reduced to

$$E(x) = -\frac{d\phi}{dx} = E_0 + \frac{Q(x)}{\varepsilon(x)} + \frac{Q(x_j)}{\varepsilon_{eff}} u(x - x_j) + \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_w} \right) Q(W) u(x - W) \quad (71)$$

where u is the unit step function defined in Eq. (53). Integration of Eq. (71) gives

$$\begin{aligned} -[\phi(x) - \phi(0)] &= E_0 x + \int_0^x dx' \frac{Q(x')}{\varepsilon(x')} + \frac{Q(x_j)}{\varepsilon_{eff}} \int_0^x dx' u(x' - x_j) \\ &+ \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_w} \right) Q(W) \int_0^x dx' u(x' - W) \end{aligned} \quad (72)$$

An expression for the applied bias, V_a , can be obtained from Eq. (72) when $x = t$,

$$-V_a = -[\phi(t) - \phi(0)] = E_0 t + \int_0^t dx' \frac{Q(x')}{\varepsilon(x')} + \frac{Q(x_j)}{\varepsilon_{eff}} (t - x_j) + \left(\frac{1}{\varepsilon_h} - \frac{1}{\varepsilon_w} \right) Q(W) (t - W) \quad (73)$$

Next a small variation in the applied bias (small-signal) can be expressed by differencing Eq. (73).

$$-\Delta V_a = \Delta E_0 t + \int_0^t dx' Q(x') \Delta(1/\varepsilon) + \frac{\Delta Q(x_j)}{\varepsilon_{eff}} (t - x_j) - \frac{Q(x_j)}{\varepsilon_{eff}} \Delta x_j$$

$$+\left(\frac{1}{\varepsilon_h}-\frac{1}{\varepsilon_w}\right)\Delta Q(W)(t-W)-\left(\frac{1}{\varepsilon_h}-\frac{1}{\varepsilon_w}\right)Q(W)\Delta W \quad (74)$$

Note that the small-signal (ΔV_a) results in a small variation in the surface electric field (ΔE_0) and a small shift in the position (Δx_j) where the dielectric constant switches from ε_l to ε_h and, in addition, a shift in the depletion region edge (ΔW).

However, $\Delta(1/\varepsilon)$ now becomes

$$\Delta(1/\varepsilon) = \frac{\delta(x-x_j)}{\varepsilon_{eff}}\Delta x_j + \left(\frac{1}{\varepsilon_h}-\frac{1}{\varepsilon_w}\right)\delta(x-W)\Delta W \quad (75)$$

$\Delta E_0/\Delta x_j$ found in Eq. (58) still holds. Eq. (74) then reduces to

$$-\Delta V_a = -\rho(x_j)\left(\frac{x_j}{\varepsilon_l} + \frac{t-x_j}{\varepsilon_h}\right)\Delta x_j + \rho(W)\left(\frac{1}{\varepsilon_h}-\frac{1}{\varepsilon_w}\right)(t-W)\Delta W \quad (76)$$

To further simplify Eq. (76), Δx_j needs to be related to ΔW . To do so, let $\varepsilon_h = \varepsilon_l = \varepsilon$ and $1/\varepsilon_w \rightarrow 0$. Eq. (76) becomes

$$-\Delta V_a = -\rho(x_j)\left(\frac{t}{\varepsilon}\right)\Delta x_j + \rho(W)\frac{(t-W)}{\varepsilon}\Delta W \quad (77)$$

However, when $\varepsilon_h = \varepsilon_l = \varepsilon$ and $1/\varepsilon_w \rightarrow 0$, the case of Eq. (77) approaches Eq. (61) with $\varepsilon_h \rightarrow \infty$, and $x_j = W$. Namely,

$$-\Delta V_a = -\rho(W)\frac{W}{\varepsilon}\Delta W \quad (78)$$

Comparison of Eqs. (77) and (78) gives the relation between Δx_j and ΔW ,

$$\rho(x_j)\Delta x_j = \rho(W)\Delta W \quad (79)$$

For partial depletion, let $1/\varepsilon_w \rightarrow 0$. With Eq. (79), Eq. (76) is greatly simplified,

$$\Delta V_a = \rho(W) \left(\frac{x_j}{\varepsilon_l} + \frac{W - x_j}{\varepsilon_h} \right) \Delta W \quad (80)$$

Notice that when $W \rightarrow t$, Eq. (80) becomes Eq. (61) as expected. For partially-depleted films, the capacitance can be expressed as

$$\frac{1}{C} = \frac{x_j}{\varepsilon_l} + \frac{W - x_j}{\varepsilon_h} \quad (81)$$

The neutral region does not contribute to the film capacitance due to charge neutrality (thus, no voltage drop) through the region, $x = W$ to $x = t$. From Eqs. (80) and (81),

$$\Delta V_a = \frac{\rho(W)}{C} \Delta W \quad (82)$$

Eq. (82) can be compared to Eq. (63). However, because both x_j and W exhibit variations Δx_j and ΔW , the simple relation between $\Delta(1/C)$ and Δx_j (Eq. (64)) is lost, and instead, with Eqs. (79) and (81), ΔW can be expressed in terms of $\Delta(1/C)$,

$$\Delta W = \Delta \left(\frac{1}{C} \right) \bigg/ \left(\frac{\rho(W)}{\rho(x_j)\varepsilon_{eff}} + \frac{1}{\varepsilon_h} \right) \quad (83)$$

The doping profiling equation in partially-depleted films is obtained by substituting Eq. (83) into Eq. (80), i.e.,

$$\frac{1}{\rho(x_j)\epsilon_{eff}} + \frac{1}{\rho(W)\epsilon_h} = \frac{d(1/C^2)/dV_a}{2} \quad (84)$$

Eq. (84) is the doping profiling equation for partially-depleted ferroelectric films. Evidently, the derivative of $d(1/C^2)/dV_a$ involves the doping concentrations at both $x = x_j$ and $x = W$ due to the simultaneous profiling of the two locations. Note that Eq. (83) reduces to Eq. (64) as $\epsilon_h \rightarrow \infty$ since there is only one doping profiling location at $x = x_j$ when $\epsilon_h \rightarrow \infty$. Likewise, when $\epsilon_h = \epsilon_l$, Eq. (84) reduces to the Schottky junction doping profiling result (Eq. (37)). According to Eq. (84), doping profiling may not be simply related to $d(1/C^2)/dV_a$ when ferroelectric films become partially depleted. Hence, a more complex strategy will be needed to find the profile than simple evaluation of this derivative.

§VI.III.C Multiple doping profiling in fully-depleted ferroelectric films

There may be situations when the width of the high-dielectric constant switching layer is narrower than the film thickness, as illustrated in Fig. 40. Then there are two locations profiling two different doping concentrations at once. The simultaneous doping profiling of two locations is analogous to the previous partially-depleted case.

When this occurs, the doping profiling equations (Eqs. (65) - (66)) are no longer valid.

Using an analysis parallel to that of the last section it is found that

$$\frac{1}{\rho(x_{j1})} - \frac{1}{\rho(x_{j2})} = \frac{\epsilon_{eff}}{2} \frac{d(1/C^2)}{dV_a} \quad (85)$$

Notice that when $\rho(x_{j1}) = \rho(x_{j2})$, $d(1/C^2)/dV_a = 0$ which corresponds to a peak in the ferroelectric CV characteristic. When $\rho(x_{j1}) > \rho(x_{j2})$ and the switching region is fully contained in the film, $d(1/C^2)/dV_a < 0$ according to Eq. (85), or equivalently, $dC/dV_a > 0$. The branch with positive coercive voltage, $V_c > 0$, of a CV characteristic resulted from this situation is illustrated with a computer simulation result shown in Fig. 41. The computer simulated characteristic in Fig. 41 is obtained with $\epsilon_h = 300\epsilon_0$, $\epsilon_l = 150\epsilon_0$, $E_d - E_a = 150 \text{ kV/cm}$, and a linear doping profile $N(x) = 10^{23}x + 10^{18} \text{ cm}^{-3}$ with x in cm and $t = 0.3 \mu\text{m}$. A similar situation results when $\rho(x_{j1}) < \rho(x_{j2})$. The voltage dependence of capacitance does not vanish because $\rho(x_{j1}) \neq \rho(x_{j2})$. One can easily verify the relation

$$\rho(x_{j1})\Delta x_{j1} = \rho(x_{j2})\Delta x_{j2} \quad (86)$$

analogous to Eq. (79) where $\Delta x_{j1,2}$ are the changes in the switching region edges due to the variation in the applied bias. It is clear from Eq. (86) that the edge located at the higher doping moves more slowly with voltage than the edge at the lower doping. Therefore, the progressions of x_{j1} and x_{j2} with applied bias are not identical, leading to a change in the switching region width as the region translates through the film. This change in turn causes the variation in the capacitance with the applied bias. One should note that multiple profiling in a fully-depleted film always occurs around the peak

capacitance of the CV characteristic since the high dielectric constant switching region is completely contained in the film. Therefore, the neighborhood of CV peaks should be treated with caution when profiling.

Even though the multiple doping profiling complicates doping profiling, it is found that the situation illustrated in Fig. 40 may be useful to estimate the width of the switching region. Suppose the width of the switching region is Δ_s and the point x_j is at the middle of $x_{j1,2}$, i.e., $\Delta_s = x_{j2} - x_{j1}$ and $x_j = (x_{j1} + x_{j2})/2$, then by Taylor series expansion,

$$\frac{1}{\rho(x_{j1})} - \frac{1}{\rho(x_{j2})} = \frac{1}{\rho(x_j - \Delta_s/2)} - \frac{1}{\rho(x_j + \Delta_s/2)} \approx \frac{\Delta_s}{\rho(x_j)^2} \frac{d\rho}{dx} \Big|_{x_j} \quad (87)$$

with the assumption that the higher order variations of charge with position can be ignored, i.e., $\Delta_s d^2\rho/dx^2 \ll d\rho/dx$. Substitution of Eq. (87) into Eq. (85) yields

$$\Delta_s = \frac{\epsilon_{eff}}{2} \frac{\rho(x_j)^2}{[d\rho/dx]_{x_j}} \frac{d(1/C^2)}{dV_a} \quad (88)$$

As mentioned, Δ_s may vary due to the nonuniform charge density as the switching region progresses through the film. If the charge density does not change too much through the film (this is partially contained in our assumption in obtaining Eq. (87)), then the width of the switching region can be estimated, for example, by setting x_j to be at the middle of the film. $\rho(x_j)$ and $d\rho/dx$ at $x = x_j$ can be measured from the portion of the CV curves away from the peaks using Eqs. (65) and (66). Finally, by taking $d(1/C^2)/dV_a$ in the neighborhood of the CV peak (the portion where the

switching layer is fully contained as shown in Fig. 41), one can estimate the switching region width Δ_s using Eq. (88). However, it should be noted that Eq. (88) holds only when Δ_s is smaller than the film thickness and $\Delta_s d^2\rho/dx^2 \ll d\rho/dx$ must be satisfied. Since one does not have any information about the thickness of the switching layer, a possible indication of a narrower switching layer than the film thickness is an observation of a *CV* characteristic similar to the one shown in Fig. 41. Another caution is that Eq. (88) involves curve fitting close to the peaks of the *CV* curves, so the sensitivity may be an issue.

§VI.IV Computer simulations

The analysis of §VI.III involves complex algebra and some special assumptions, e.g., Eqs. (50) and (69) contain delta functions. To provide a check on the algebra and to replace the delta function idealizations with more realistic, broadly peaked functions, now computer simulations are used to illustrate the ferroelectric doping profiling for dielectric constants with a variety of spatial transitions. The approach is to use simulations to generate *CV* characteristics with a given doping profile and a given form of field-dependent permittivity. Details of computer simulations can be found in §V.III. With the simulated *CV* characteristics, Eq. (65) is used to extract the doping concentration and Eq. (66) is used to find the profiling location.

§VI.V Results and discussion

As mentioned, the doping profiling capability in both ferroelectric films and metal-semiconductor Schottky junctions relies on the fact that $1/\epsilon$ exhibits an abrupt transition at the profiling location. Even though the dielectric constant of ferroelectric materials is field-dependent, in reality the transition from high to low dielectric constant may not be as abrupt as the idealization described by Eq. (42), i.e., Eq. (59) may not be a true delta function, affecting the accuracy of the doping profiling using Eq. (65). A more realistic $1/\epsilon(x)$ may be as illustrated in Fig. 42. In this case, $d(1/\epsilon)/dx$ is not a delta function but the derivative is still peaked. The profile that results for a dielectric constant transition such as Fig. 42 is a local average of the actual doping profile between x_1 and x_2 .

To explore this possibly more realistic case, computer simulation was exercised with the procedures described in §V.III using the dielectric constant model shown in Fig. 43(a) with a variety of abruptness of transition in $\epsilon(E)$. The high-to-low transition in the dielectric constant is adopted and the results do not change if the low-high transition is used. A form of $\epsilon(E)$ is chosen,

$$\epsilon(E) = 510 - 490 \tanh[(E + 1.956\delta)/\eta] \quad (89)$$

The coefficients are chosen in Eq. (59) so that $\epsilon_h/\epsilon_0 = 1000$, $\epsilon_l/\epsilon_0 = 20$ and $1/\epsilon(E)$ is centered at a fixed electric field when η changes. The values chosen do not correspond to any actual sample and were made based solely on convenience. As the parameter η in the $\epsilon(E)$ increases, the transition becomes more gradual. The equivalent position-

dependent $\varepsilon(x)$ is shown in Fig. 43(b). Likewise, the larger η is, the more gradual $\varepsilon(x)$ transition becomes. Also, a step doping distribution is used as input to the computer simulation,

$$N(x) = \begin{cases} N_1, & 0 \leq x \leq t/2 \\ N_2, & t/2 \leq x \leq t \end{cases} \quad (90)$$

where t is the film thickness and $t = 0.3\mu m$ in the following example. The step doping profile described by Eq. (90) will demonstrate the worst-case smearing effect when the transition in $\varepsilon(x)$ is not abrupt. Again Eqs. (65) and (66) are used for doping profiling in the computer simulations. The results are shown in Fig. 43(c).

As expected, the step doping profile is accurately reproduced using Eqs. (65) and (66) when the dielectric constant exhibits an abrupt (idealized) transition. Fig. 43(b) shows that the transition of $1/\varepsilon(x)$ is close to the idealized dielectric constant model when $\eta = 10\text{ kV/cm}$; thus, the profiling result does not deviate from the actual step doping profile significantly. However, when the abruptness of the $1/\varepsilon(x)$ transition is reduced, $d(1/\varepsilon)/dx$ broadens from a delta function into a broadly peaked function that leads to a smearing of the profile near the sharp corners of the actual doping profile. This smearing of the profile can be viewed as a local averaging of the actual doping profile.

To describe the progression of the profiling location with bias, a ferroelectric CV characteristic is plotted in Fig. 44 with illustrations of the corresponding translation of the high-dielectric constant layer with the applied bias. For instance, when the applied bias changes such that the CV traces from leg A to B , the right edge of the high-dielectric constant layer profiles the film, moves out of the film at some bias, then the

left edge enters and profiles the film. The high-dielectric constant layer moves in and out of the film under a change in the applied bias. This progression is now examined using computer simulated electric field for the idealized dielectric constant at three biases: 2.1 V (corresponding profiling location, $x = 0.01\mu\text{m}$), -0.7 V (corresponding profiling location, $x = 0.29\mu\text{m}$), and -11.4 V (corresponding profiling location, $x = 0.15\mu\text{m}$). The electric field together with the dielectric constant as functions of depth position are shown in Fig. 45. For a uniform doping profile, according to Eq. (26), the region with larger slope for the electric field has a lower dielectric constant. Similarly, in a region with a given dielectric constant, a higher doping concentration results in a larger slope for the electric field. Therefore, the electric field distribution can be translated into a dielectric constant distribution through the depth of the film, as shown in Fig. 45. By comparing the $\epsilon(x)$ with the input step profile as shown in Fig. 45, it is apparent that doping profiling occurs at the location where the dielectric constant changes. Furthermore, as the applied bias increases, the high dielectric constant portion in the film translates in the direction of positive x . In this way, the progression under bias of the dielectric constant transition point, x_j , profiles the doping concentration at larger and larger values of x_j .

As mentioned, the doping profiling Eqs. (65) and (66) are valid when there is only one region in the film where polarization is fully saturated. It is found through computer simulations that the width of the high-dielectric constant switching layer is comparable to film thickness for *PZT* capacitors with various niobium doping levels. Besides, it is concluded in our prior work that ferroelectric thin films are likely to be fully depleted [7]. Thus, it is postulated that the complicated multiple profiling cases are not probable. The case of one-edge doping profiling ordinarily applies.

Chapter VII Comparison of the uniform and the nonuniform field models

In this chapter, the reliability of the extracted information on doping profile assuming that the electric field is spatially varying is studied. It has been demonstrated in **Chapter IV** that when the electric field is spatially uniform through the depth of the film, the domain growth function, $\alpha(E)$, fits the measured *CV* characteristic reasonably well if an appropriate form of $\alpha(E)$ is chosen. In **Chapter V**, $\alpha(E)$ is applied to a generalized case when the electric field is spatially varying due to the presence of dopant-ion charge and is found to be consistent with the measured *CV* characteristic. That is, either model fits measurement well, but one model has zero doping and the other has a doping profile. The extracted information on doping profile thus could be the result of inadvisably applying the Schottky profiling technique to undoped ferroelectric. A rule of thumb will be provided in this chapter to evaluate the accuracy of the extracted information on doping profile.

§VII.I Introduction

It has been shown that the uniform field model of **Chapter IV** and the spatially varying field model of **Chapter V** are both consistent with measured *CV* characteristics of *PZT* capacitors shown in **Chapter II**. Based on the analysis in **Chapter VI**, the presence of dopant-ion charge can be deduced from *CV* measurements. A possible confusion arises: if a *CV* curve of an undoped sample is

measured, where the electric field is uniform, but the Schottky profiling formula Eq. (33) is inadvisably applied, an apparent doping profile will be extracted, even though the dopant concentration actually is zero.

In order to illustrate the issue regarding the *false* doping information, the trapezoidal $\epsilon(E)$ is shown in Fig. 46. For the case when there is no electrical doping, capacitance can be calculated using $C = \epsilon / t$. The electric field is spatially uniform without dopant ion charge, the electric field $E = V / t$, where V is the applied bias. Therefore, the CV characteristic at zero doping resembles the $\epsilon(E)$ illustrated in Fig. 46.

However, due to the nonideal transitions in $\epsilon(E)$ between ϵ_l and ϵ_h , some doping information can be extracted from the slopes of the CV characteristic, that is, $N \propto 1/(d(1/C^2)/dV)$. Since the actual electrical doping level is zero, this apparent doping level extracted from the CV characteristic is then false information. On the other hand, if the transitions in $\epsilon(E)$ are ideal, i.e., abrupt steps, then $d(1/C^2)/dV = \infty$ at zero doping and the extracted doping level is zero. It is now apparent that the nonideal structure in $\epsilon(E)$ may lead to a false extracted doping.

In this chapter, it will be shown that for each proposed form of $\epsilon(E)$, there is a "background" level of doping, N_{bg} , below which the electrical doping concentration cannot be measured. If $\epsilon(E)$ is parameterized as illustrated in Fig. 27, it will be shown shortly that for an $\epsilon(E)$ such as curve (a) (abrupt transitions), $N_{bg} = 0$. However, as the shape of $\epsilon(E)$ becomes rounded, leading to non-zero values of δ_l and δ_r , N_{bg} increases, becoming about 10^{18} cm^{-3} for parameters appropriate to the films measured in this work.

§VII.II Comparison of the uniform and the nonuniform field models

In order to establish an approach for evaluating the accuracy of the extracted electrical doping level, the effect of the electrical doping concentration on ferroelectric CV characteristic is examined. The effects of doping on CV curves are explored in Fig. 47. To obtain this figure, the first column of Tab. II (0% niobium) was used. For simplicity, a symmetrical trapezoid for $\varepsilon(E)$ was chosen with $\delta_r = \delta_l = \eta = 135 \text{ kV/cm}$. Using Eq. (31), with $\rho = 0$, $E(x)$ is found. Then Eq. (32) with $\varepsilon(x) = \varepsilon(E(x))$ produces the solid-line CV curve as the capacitance that corresponds to $\rho = 0$ (we do not have measured CV curves for $\rho = 0$). A uniform doping of several values of ρ is then substituted in Eq. (31) and CV curves are found from Eq. (32) as just described produce the remaining curves of Fig. 47. As Fig. 47 shows, even at $N = 10^{18} \text{ cm}^{-3}$, there is little change in the simulated CV curve. In other words, for the assumed form of $\varepsilon(E)$, there is no practical difference in CV curves for any doping in the range $0 \leq N \leq N_{bg} = 10^{18} \text{ cm}^{-3}$. For heavier electrical doping, however, there is a clear doping dependence of the simulated CV curves.

When the electrical doping is lighter than $2 \times 10^{18} \text{ cm}^{-3}$, a plateau appears at the peak of the CV curve, as shown in Fig. 47. The peak is independent of the doping level for light doping. When the electrical doping is reduced, the spatially varying field model approaches the uniform electric field case where, according to Eq. (15), the CV curve resembles $\varepsilon(E)$. On the other hand, when the electrical doping becomes heavier than $3 \times 10^{18} \text{ cm}^{-3}$, the plateau on top of the CV curve disappears and the peak lowers. The

effect of the electrical doping on the ferroelectric CV characteristic can be explained as follows.

Equating the value of ϵ_h from Eq. (30) to that from Eq. (25) yields

$$\kappa\epsilon_0(E_a - E_d) = |\rho| \cdot \Delta_s - 2\hat{P} \quad (91)$$

which is Gauss' law for the switching region. The tendency for the polarization charge and the "free" charge to compensate was noted by Blom et al. [52] The parameters $\hat{P}$, E_a , E_d , and κ are held constant in the example shown in Fig. 47. Consequently, Eq. (91) suggests that the net dopant-ion charge per unit area in the switching region $\rho \cdot \Delta_s$ is an invariant. When the electrical doping is very light, the thickness of the switching layer increases to the point $\Delta_s > t$. Then there exists a wide voltage range for which the switching region extends the full depth of the film, leading to a plateau in the CV curve given by $C = \epsilon_h / t$, independent of the electrical doping level. On the other hand, if the electrical doping level is increased, the thickness of the switching region must decrease. When the electrical doping is so heavy that $\Delta_s < t$, the capacitance of the film can be expressed as the series combination

$$\frac{1}{C} = \frac{t - \Delta_s}{\epsilon_l} + \frac{\Delta_s}{\epsilon_h} \quad (92)$$

Due to the reduction in the thickness of the switching layer, the contribution of the layer with permittivity ϵ_h to the peak capacitance is reduced, leading to a reduced peak value in the CV curve.

The doping dependence of the CV characteristics shown in Fig. 47 suggests the electrical doping level extracted using the Schottky formula Eq. (33) might deviate from the actual doping level that was input into the simulation. A plot of the extracted electrical doping level (N_{ext}) versus the actual doping level (N_{act}) is shown in Fig. 48. Clearly, the extracted doping is meaningful provided the extracted doping N_{ext} is sufficiently above the background doping N_{bg} . This background level could be set as the doping level that results in a 10% error in extracted doping, for instance.

Fig. 48 is not a universal curve, because it depends on the form of the assumed $\varepsilon(E)$. Therefore, a variety of forms for $\varepsilon(E)$ based on the notation of Fig. 27 are examined. If N_{bg} is defined such that when $N_{act} = N_{bg}$,

$$\frac{N_{ext} - N_{bg}}{N_{bg}} \equiv 10\%, \quad (93)$$

and if for simplicity, it is chosen that $\delta_l = \delta_r = \delta_0$, then Fig. 49 is a plot of N_{bg} versus maximum $d\alpha/dE$ with various values for δ_0 . The maximum $d\alpha/dE$ is the maximum slope of the $\alpha(E)$ relation that occurs approximately at $E = E_c$ given by Eq. (19), that is,

$$\left(\frac{d\alpha}{dE} \right)_{\max} \approx \frac{\varepsilon_h - \varepsilon_l}{2\hat{P}} \quad (94)$$

with $\hat{P}$ the area under the CV curve from Eq. (18). That is, maximum $d\alpha/dE$ is directly determined from a measured CV characteristic. It has been assumed that the electrical doping will not seriously affect the estimation. In other words, it is assumed that the direct effect of the electrical doping on $\alpha(E)$ through domain wall pinning or other mechanisms not included in this work is negligible. From the solid curve in Fig. 49, it can be observed that the narrower the nonideal transition region (smaller δ_0 -values), the lower the background doping level becomes. Likewise, the larger $d\alpha/dE$ (the larger the peak capacitance and the smaller the area under the entire CV curve), the lower the value of N_{bg} . The best case ($N_{bg} = 0$) is the idealized step transition with $\delta_0 = 0$, as has been demonstrated by the illustration in Fig. 46. Also shown in Fig. 49 as dotted lines is the extracted doping N_{ext} when $N_{act} = N_{bg}$, which is 10% higher than the actual electrical doping level.

Now the dependence of N_{bg} on $d\alpha/dE$ is explained. The relation between $\alpha(E)$ and the trapezoidal $\epsilon(E)$ is illustrated in Fig. 50. The ferroelectric switching characteristic is contained within the trapezoidal switching region of width $\eta_0 + 2\delta_0$ (in electric field) and this switching region in $\epsilon(E)$ corresponds to the region where the function of domain volume fraction is in the process of growing from zero to unity, i.e., $0 < \alpha(E) < 1$. When $\eta_0 + 2\delta_0$ is large ($d\alpha/dE$ is small), the ferroelectric switching behavior spans a large range of electric field. Hence, the electrical doping must increase in order to overcome the masking effect of the ferroelectric switching behavior on the CV characteristic, namely, the background doping N_{bg} , above which the CV characteristic begins to depend strongly on the electrical doping level, is high. However, $\eta_0 + 2\delta_0$ is not directly measurable and it is apparent from Fig. 50 that the slope of $\alpha(E)$ is a

measurement of $\eta_0 + 2 \delta_0$. Based on Eqs. (16) and (18), $d\alpha/dE$ can be calculated easily from the measured CV characteristic.

In short, Fig. 49 shows that when δ_0 becomes larger, N_{bg} must increase in order for N_{ext} to remain accurate within the 10% error. As $d\alpha/dE$ decreases, the width of the switching region increases, and a larger N_{bg} is required to overcome the masking effect of the ferroelectric switching and yield reliable extracted doping information. Fig. 49 provides a rule of thumb to evaluate the accuracy of the extracted electrical doping information. Note that values for parameters η_0 , δ_0 and $d\alpha/dE$ covered in Fig. 49 are pertinent to thin films measured in this work.

With Fig. 49, the error of the profiling result for PZT capacitors shown in Fig. 30 is examined. Based on the $\epsilon(E)$ described by the parameters in Tab. II, the corresponding $\alpha(E)$ is calculated using Eqs. (15) and (17), and is shown in Fig. 51 with the parameters: $d\alpha/dE = 43.14 - 54.06 (\times 10^6 \epsilon_0 \text{ cm} / \text{V})$, and $\delta_0 = 0 - 1.56 \eta_0$ for various levels of niobium doping. It is found from Fig. 49 in this range of $d\alpha/dE$ and δ_0 that a background doping of $N_{bg} \approx 9 \times 10^{17} \text{ cm}^{-3}$ yields an extracted doping $N_{ext} \approx 10^{18} \text{ cm}^{-3}$. The extracted doping concentrations shown in Fig. 30 are above 10^{18} cm^{-3} which indicates that these extracted values are within the 10% error defined. Therefore, Fig. 30 presents reliable doping information.

Summary

A domain model has been proposed and related to the measured *CV* characteristic of *PZT* capacitors with various niobium doping levels. For zero dopant-ion charge, the model has a spatially uniform electric field and a simple multiple-domain structure with two domain orientations (parallel and antiparallel to the applied field). For the switching range of fields, domains of both orientations are assumed to penetrate throughout the depth of the film. A novel formulation for the growth of polarization as a function of electric field $\alpha(E)$ has been expressed in terms of a field-dependent volume fraction of aligned domains. This fraction has been extracted from the measured *CV* characteristic.

The zero-dopant model then was generalized for the case of a spatially-varying electric field. The extended model accounts for a nonuniform electric field caused by dopant-ion charges. Based on the nonuniform electric fields, a position-dependent permittivity has been deduced. The field dependence on position results in a switching region where $\alpha[E(x)]$ undergoes a transition from zero to unity. A complex domain structure is postulated in this region and approximated by a saw-toothed domain structure. This region is shown to lead to a step in the permittivity that is of the form shown later to be necessary for profiling. Doping profiling has been performed based on the permittivity model.

Furthermore, the interaction between the electrical doping and the switching behavior of ferroelectric domains has been demonstrated. The concept of the background doping concentration has been introduced. The actual electrical doping level has to be higher

than the background doping concentration in order to be measurable by Schottky profiling.

The profiling supports the reported compensation of the p-type *PZT* samples by the n-type niobium doping. Based on the proposed permittivity model and the approximate doping profiles extracted from *CV* measurement, the measured *CV* characteristics of *PZT* capacitors with various niobium doping levels have been predicted.

Comparison of *CV* measurements made on samples with various niobium content suggests that niobium doping slightly slows the volume growth of polarization (as shown by the decrease in $d\alpha/dE$ and ε_h in Tabs. I and II) with the electric field and that niobium is a compensating donor dopant in *PZT* (as shown in Fig. 30). Further, a methodology is proposed to identify the minimum electrical doping level above which doping profile information can be reliably extracted. This minimum doping level can be estimated using the measured *CV* curve and is approximately 10^{18} cm^{-3} for measurements in this work.

Practical applications and future work

As demonstrated, the model presented in this work has the capability of reproducing the results of electrical measurements. This suggests that the presented model may serve as a tool for ferroelectric device simulations if it is correlated with practical materials. On the other hand, microscopic level ferroelectric behavior may be inferred by fitting the model to measurement results. The applications of this model are discussed in four aspects including material characterization, process and fabrication monitoring, device and materials design and implications for specific research. Further research is proposed to extend the understanding of the proposed model.

1. Material characterization

This model has the capability of tracking the differences in the electrical behavior of different materials and relating them to microscopic properties such as domain structure and nucleation critical fields. Specifically, the function $\alpha(E)$ describing the growth of volume fraction of domains may be correlated with various materials. Model parameters such as the critical nucleation fields E_a and E_d , $[d\alpha/dE]_{\max}$ (describing the dependence of domain growth on the electric field), and the electrical doping level can be easily obtained by fitting the proposed model to electrical measurements. As a result, the model can benefit the characterization of various materials through linking electrical measurements and device simulations, furthermore, improving the understanding of underlying microscopic phenomena.

2. Process and fabrication monitoring

The model proposed in this work is useful in monitoring an actual manufacturing operation. The objective is to track unintended changes of the device behavior over the course of a production run and to identify the cause of drift with enough detail to know what particular process is out of specifications. Particularly, the parameters of interests are ε_h , ε_l , η_0 (the width of the switching region in electric field), E_a and E_d (nucleation critical fields), and the electrical doping level, etc. Once the processing parameters are correlated with the model parameters, the proposed model has the potential of becoming a useful computer simulation tool.

3. Device and materials design

Through computer simulations, the proposed model is capable of identifying the important material properties for a specific device or circuit function, for instance, the storage capacitors and circuits for ferroelectric nonvolatile memory applications. The model provides the utility of bracketing ranges of parameters that result in acceptable operation, and of relating these parameters to specific materials and process control issues.

As an example, high electrical doping levels have been shown (§I.IV) to degrade ΔP and ΔC in DRO and NDRO memories. As a result, the high electrical doping level causes confusion of "0" and "1" states in DRO and NDRO memories. Besides,

ferroelectric materials are fabricated with an inherent electrical doping level. Approaches for controlling the electrical doping level thus are important and this model suggests that a doping concentration below 10^{18} cm^{-3} is desired for well-behaved ferroelectric characteristics that are important for nonvolatile memory applications.

Another example is now discussed. Eq. (91) provides information for designing material parameters such as film thickness and the electrical doping level in order to produce well-behaved *CV* characteristics. Based on the progression of $\varepsilon(x)$ with bias illustrated in Fig. 44 and the discussion in §VII.II, collapse in ferroelectric *CV* characteristics occurs when the switching region width Δ_s is much smaller or much larger than the film thickness t (the cases when $\Delta_s \ll t$ and $\Delta_s \gg t$ can be viewed as the linear dielectric extremes of the ferroelectric model proposed in this work. That is, the cases when $\Delta_s \ll t$ and $\Delta_s \gg t$ approach the case of a uniform permittivity through the depth of the film). As shown in Fig. 11, degradation in ΔC is not desired for NDRO memory. Thus, $\Delta_s \approx t$ is a desired condition for well-behaved ferroelectric *CV* characteristics assuming fully-depleted thin films. Therefore, as the film thickness is reduced for low-power applications, the switching region width Δ_s should be reduced in order to maintain the quality of the *CV* characteristics. According to Eq. (91), the switching region width is reduced as the electrical doping level increases if $E_a - E_d$ does not vary significantly. On the other hand, reduction in $E_a - E_d$ yields a narrower switching region if the electrical doping level can be held constant. This points out directions in the search for both new materials and techniques to control parameters such as the electrical doping level and $E_a - E_d$ as the film thickness is reduced for low-power applications.

4. Implications for specific research

There are uncertainties and limitations of the proposed model that require further exploration from a materials and physics standpoint, such as the frequency dependence and also from a materials preparation perspective, for example, the relations between stress, film thickness, and defects to nucleation energy and field dependence of domain growth, etc. Specifically, the nature of the relation between the domain structure and the field-dependent permittivity proposed in this work needs to be explored further both experimentally and theoretically. Though it agrees well with measurement, the domain structure presented in this work is simplified. For example, only two domain orientations are considered, the critical electric field for domain wall motion is neglected and there is no time dependence for domain nucleation and growth. Generalization of the current model may add more realistic physical pictures and lead to a more powerful model, for instance, the frequency dependence of this model.

Further, though the Schottky profiling equation has been used widely to profile the doping concentration in ferroelectrics, the physical basis and the limitations were not understood. This work provides a more general treatment and the derivation applies to many materials with an abrupt feature in a physical parameter, for instance, spatially varying space charge density for silicon and position-dependent permittivity for ferroelectrics. The presented derivation is based on a quasi-static treatment of ferroelectrics. The dynamics of domain growth and nucleation are not included. Additional work is needed to explore the frequency range over which the model applies.

This work assumes a back-to-back Schottky barrier system with fully-depleted ferroelectric thin films, then it is demonstrated that the assumption is consistent with the measured CV characteristic. That is, the model builds upon a consistent framework. Therefore, independent approaches are required to demonstrate the effects due to, for example, the switching region and the electrical doping level.

Experiments such as the following can be proposed. The electrical doping level can be measured for temperatures above T_C (the Curie point), using a partially-depleted sample and the approach proposed by Kahng et al [42]. Then the electrical doping level can be remeasured at temperatures below T_C where domains form. Based on the theory discussed in §VI.III.B, multiple profiling occurs for partially-depleted ferroelectric thin films. Comparison between the electrical doping profiles measured above and below T_C may identify the ferroelectric switching region and the complications of profiling in ferroelectrics such as profiling at multiple positions.

It is hoped that this work will invite interest in exploring the interaction between domain switching and the electrical doping level, especially, independent approaches to verify the validity of the model.

Appendix: Figures

[†] P_{total} can be measured from a Sawyer-Tower circuit.

Fig. 1 A typical hysteresis loop measured by a Sawyer-Tower circuit. P_{total} is the measured characteristic. Due to the linear asymptotic behavior of P_{total} at large biases, $P_{total} = P_{linear} + P_{switching}$. P_{linear} is a common characteristic to all dielectric materials. $P_{switching}$ is a unique feature to the ferroelectrics. Saturation or spontaneous polarization (P_s) is the result of maximum domain growth. When the external field is removed, some remanent polarization (P_r) remains. V_c is the critical or coercive bias required to initiate polarization reversal.

Fig. 2 A typical ferroelectric CV characteristic measured using an MOS capacitor CV characterization setup. The measuring signal is a dc bias with a small signal (typically ~ 100 kHz) superimposed.

(a)

Structure: perovskite

Bravais lattice: simple cubic

Ions/unit cell: $1Ba^{2+} + 1Ti^{4+} + 3O^{2-}$ Fig. 3(a) Perovskite ($BaTiO_3$) unit cell showing the ion positions.

Fig. 3(b) Perovskite ($BaTiO_3$) unit cell showing front view of the structure in Fig. 3(a).

† Scale of ion shifts exaggerated

Fig. 4 Below 120°C , a tetragonal modification of the symmetrical structure shown in Fig. 3 occurs. The net result is an upward shift of cations and a downward shift of anions.

Fig. 5 The tetragonal unit cell shown in Fig. 4 is equivalent to an electrical dipole.

Fig. 6 An illustration of polarization (P) versus applied electric field (E) of a virgin ferroelectric sample. A *paraelectric* material exhibits only a modest level of polarization with applied fields. In contrast, a *ferroelectric* material exhibits spontaneous polarization in which domains of similarly oriented unit cells “grow” under increasing fields of similar orientation.

Fig. 7 A ferroelectric hysteresis loop is the result of an alternating electric field. Saturation or spontaneous polarization (P_s) is the result of maximum domain growth. When the external field is removed, some remanent polarization (P_r) remains. A coercive field (E_c) is required to initiate polarization reversal.

Fig. 8(a) An example of the destructive readout (DRO) nonvolatile memory unit cell. (b) The operation of the DRO cell shown in (a) is based on the ferroelectric hysteresis characteristic.

Fig. 9 Illustration of the operation of an NDRO memory scheme. V_c is the coercive bias and V_{rb} is the read bias. The readout is nondestructive because $V_{rb} < V_c$. The zero bias capacitance is C_0 . C_h and C_l are the capacitances of "1" and "0" at V_{rb} , respectively. The capacitance difference ΔC at V_{rb} allows a sense amplifier to distinguish "0" and "1".

Fig. 10 Degradation of ΔP at high electrical doping level leads to confusion of "0" and "1" for DRO memory.

Fig. 11 Degradation of ΔC at high electrical doping level leads to confusion of "0" and "1" for NDRO memory.

Fig. 12 Illustration of a cross section of the *PZT* capacitor sample.

Fig. 13 The Sawyer-Tower circuit used to characterize the ferroelectric hysteresis characteristic. C_f is the ferroelectric capacitor. C_n is a linear capacitor and R_n is a linear resistor. The input signal V_i is a large signal. Ferroelectric hysteresis characteristics can be observed by plotting V_o versus V_i on an oscilloscope. For the hysteresis measurements performed in this work, $R_n = 1.5\text{ M}\Omega$, and $C_n = 470\text{ pF}$.

Fig. 14 Measured hysteresis loops of *PZT* capacitors with various levels of niobium content.

Fig. 15 A measured hysteresis loop of the *Y-I* capacitor.

Fig. 16 *CV* measurements on *PZT* capacitors with various levels of niobium doping. *CV* measurements were performed on $150\ \mu\text{m}$ square capacitors with a $100\ \text{kHz}$ small-signal superimposed upon a slow dc bias. The measurement starts with a $-7\ \text{V}$ dc bias, steps to $7\ \text{V}$ and then back to $-7\ \text{V}$ at an increment of $0.1\ \text{V}$.

Fig. 17 A measured CV characteristic of the $Y-I$ capacitor. ΔC is the capacitance difference between the two distinct capacitance states at zero dc bias and is known as the Ramer-Duab effect of the $Y-I$ capacitor.

Fig. 18 Illustration of the switching model proposed by Tagantsev et al. E_{cn} is the nucleation critical field and E_{cm} is the domain wall motion critical field. $E_{cn} \gg E_{cm}$ for the switching illustrated in this figure. (a) The film is not biased and the sample has been poled negatively. (b) At a given bias, the electric field is larger than E_{cn} in the surface portion of the film, $x > x_n$; therefore, nucleation of positive domains occurs in the region $x > x_n$. (c) At the same bias as in (b), the electric field across the depth of the film is larger than E_{cm} ; hence, positive domains propagate through the depth of the film rapidly.

Fig. 19 The switching model of Tagantsev et al. when $E_{cn} \approx E_{cm}$. Positive domains do not propagate through the depth of the sample but stop at $x = x_m$ because the electric field in the region $x < x_m$ is smaller than E_{cm} .

Fig. 20 A schematic multiple-domain model for ferroelectric films with uniform electric fields. Two domain orientations (parallel and antiparallel to the applied field) are considered for simplicity. $\alpha(E)$ is the volume fraction of the positively polarized domains. (a) The sample is fully polarized in the negative x -direction by a large negative applied electric field ($E \leq E_a$). $\alpha = 0$. (b) As the electric field increases to a point when $E_a \leq E \leq E_d$, domains polarized in the positive x -direction begin to emerge. Domains of both polarizations penetrate throughout the depth of the film, and $0 < \alpha < 1$. (c) If the electric field increases further to a point when $E \geq E_d$, the sample will be poled entirely in the positive x -direction, and $\alpha = 1$.

Fig. 21 A plot of the hysteresis curve P versus E . $P(E)$ excludes the non-ferroelectric background polarization that varies linearly with the electric field, which is common to all dielectric materials. Nucleation of aligned domains begins when E reaches E_a and a single domain results for values of E greater than E_d . E_c is the coercive field.

Fig. 22 $\alpha(E)$ extracted from a measured CV curve (the branch with negative coercive voltage, $V_c < 0$) of the PZT capacitor with 0% niobium compared to the $\alpha(E)$ fitted by Eq. (20) (squares). The result of fitting Eq. (20) to the extracted $\alpha(E)$ is also shown with $E_{half} = -20$ kV/cm and $\eta = 120.5$ kV/cm.

Fig. 23 The result of fitting Eq. (21) to measured CV characteristic of the PZT capacitor with 0% niobium. The values of parameters used are: $\kappa = 250$ and $\hat{P} = 4.69 \mu\text{C}/\text{cm}^2$, $E_{\text{half}} = -20 \text{ kV}/\text{cm}$, $\eta = 120.5 \text{ kV}/\text{cm}$ and $t = 0.25 \mu\text{m}$.

Fig. 24 $\alpha(E)$ extracted from measured CV curves using Eq. (17) for PZT capacitors with various niobium doping levels.

Fig. 25 The result of fitting Eq. (21) to measured *CV* characteristics of *PZT* capacitors with various niobium doping levels. The parameters used are summarized in Tab. I.

Tab. I Parameters used to fit Eq. (21) to the measured CV characteristics for the case when the electric field is uniform.

	<i>PZT w/ 0% Nb</i>	<i>1% Nb</i>	<i>3% Nb</i>	<i>5% Nb</i>
$E_{half}(kV/cm)$	-20	-36	-44	-44
$^{\dagger}\epsilon_h / \epsilon_0$	743	425	351	284
$\kappa = \epsilon_l / \epsilon_0$	250	204	180	170
η (kV/cm)	120.5	124.5	124.5	126.5
$\hat{P}$ ($\mu C/cm^2$)	4.69	2.54	2.12	1.49

† From Eq. (19).

Fig. 26 $\alpha(E)$ extracted from the measured CV curve using Eq. (17) for the Y-1 capacitor. Also shown are the $\alpha(E)$ curves of PZT capacitors.

Fig. 27 The idealized (curve (a)) and the more realistic (curve (b)) form of field-dependent dielectric constant $\epsilon(E)$. δ_l and δ_r mark the range of fields where the realistic forms of $\epsilon(E)$ changes its value between ϵ_l and ϵ_h . For the idealized $\epsilon(E)$, $\delta_l = \delta_r = 0$. The gradual transitions will be approximated later by ramps connecting ϵ_h and ϵ_l for the convenience of computer simulations.

Fig. 28 A schematic view of the interface between parallel and antiparallel domains at some applied voltage in the presence of a spatially varying electric field. The expanded view is an idealized representation of the domains corresponding to different values of $\alpha(x)$ at different locations x in the switching region.

Fig. 29 The position-dependent permittivity $\varepsilon(x)$ deduced from $\varepsilon(E)$ when the electric field is spatially varying due to the presence of dopant-ion charges. Δ_s : the width of the switching layer.

Fig. 30 Doping profile results obtained from the measured CV characteristics from Fig. 16 using Eqs. (33) and (35). $x = 0$ corresponds to the top electrode. The straight lines are the approximate doping profiles (later used in computer simulations) based on the profiles extracted from an overall best-fit to both the right and left legs of the $V_c < 0$ branch of the measured CV characteristic for each sample. Compensation of p-type PZT doping by the n-type niobium is supported. Error bars are shown for the 0% and 5% niobium doped PZT samples to indicate the range of the doping concentrations obtained from separate fits to the two legs of the $V_c < 0$ branch of the measured CV characteristic.

Tab. II Parameters used in the CV characteristic simulations for the spatially varying electric field model.

	<i>PZT w/ 0% Nb</i>	<i>1% Nb</i>	<i>3% Nb</i>	<i>5% Nb</i>
E_c (kV/cm)	-56	-70	-64	-85
ϵ_h / ϵ_0	766	445	368	300
$\epsilon_l / \epsilon_0 = \kappa$	250	204	180	170
δ_r (kV/cm)	13.5	0	79.8	46.8
δ_l (kV/cm)	135	119.5	163.8	202.8
η_0 (kV/cm)	135	181	140	130
$^\dagger a$ ($\times 10^{22} \text{ cm}^{-4}$)	-1.28	-1.27	-0.02	-0.28
$^\dagger b$ ($\times 10^{18} \text{ cm}^{-3}$)	2.67	1.91	1.45	1.24

† Approximate doping profile: $N(x) = a x + b$ with x in *cm*.

Fig. 31 The simulated and measured CV characteristics. Computer simulations are performed based on Eqs. (31) and (32) using the parameters in Tab. II. The electric field is spatially varying.

Fig. 32 The approximate electrical doping profile of the *Y-I* capacitor obtained based on the measured *CV* characteristic using Eqs. (33) and (35). Error bars indicate the fluctuations of the doping concentration obtained from separate fits to the two legs of the $V_C < 0$ branch of the measured *CV* characteristic shown in Fig. 17.

Fig. 33 The simulated CV curves ($V_c < 0$) with various values of δ_l . δ_l is the width (in electric field) of the nonideal transition region where $\epsilon(E)$ changes from ϵ_l to ϵ_h , as illustrated in Fig. 27. The parameters used in the computer simulation are: $\epsilon_l/\epsilon_0 = 147$, $\epsilon_h/\epsilon_0 = 280.8$, $\eta_0 = 40 \text{ kV/cm}$, $N(x) = 3.15 \times 10^{22} x (\mu\text{m}) + 1.48 \times 10^{18} \text{ cm}^{-3}$, $\delta_r = 0$ and $\delta_l = 0 - 50 \text{ kV/cm}$ with an increment of 10 kV/cm . Curve (a): $\delta_l = 0$. Curve (b): $\delta_l = 10 \text{ kV/cm}$. Curve (c): $\delta_l = 20 \text{ kV/cm}$.

Fig. 34 A proposed $\epsilon(E)$ to fit the measured CV characteristic of the $Y-I$ capacitor.

Fig. 35 The idealized field-dependent permittivity $\varepsilon(E)$ and a possibly more realistic form. The idealized form has abrupt transitions at E_a and E_d . E_c is the coercive field.

Fig. 36 The permittivity as a function of position when the profiling Eqs. (39) and (41) are valid. Note that there is only one transition between ϵ_h and ϵ_l within the film.

Fig. 37 The function $1/\epsilon(x)$ for ferroelectric films and the artificial $1/\epsilon(x)$ for Schottky junctions. Also shown is the derivative $d(1/\epsilon)/dx$. The Schottky junction becomes a special case of Eq. (44) when $\epsilon_h \gg \epsilon_i$. The location $x = x_j$ in ferroelectric films, where the dielectric constant switches, can be viewed as an analog of the depletion region edge in Schottky junctions.

Fig. 38 Doping profiling occurs at two locations for partially depleted ferroelectric films. Profiling Eqs. (65) and (66) are no longer valid.

Fig. 39 A general dielectric constant model with three steps used in studying the partial-depletion case. Note that as $1/\epsilon_i \rightarrow 0$, the three-step case becomes the partially depleted case illustrated in Fig. 38.

Fig. 40 When the width of the high-dielectric constant switching layer is smaller than the film thickness, there are two locations profiling two different doping concentrations at once.

Fig. 41 The $V_c > 0$ branch of a CV characteristic from computer simulation when the switching region is narrower than the film thickness. The portion of the CV curve from -2 V to 1 V is a result of the full containment of the switching region in the film and $\rho(x_{j1}) > \rho(x_{j2})$. The computer simulated characteristic is obtained with $\epsilon_h = 300\epsilon_0$, $\epsilon_i = 150\epsilon_0$, $E_d - E_a = 150 \text{ kV}/\text{cm}$, and a linear doping profile $N(x) = 10^{23}x + 10^{18} \text{ cm}^{-3}$ with x in cm and film thickness $t = 0.3 \mu\text{m}$.

Fig. 42 When $1/\epsilon(x)$ does not have an abrupt transition, the derivative $d(1/\epsilon)/dx$ becomes broadly peaked. The profile that results is a local average of the actual doping profile between x_1 and x_2 .

Fig. 43(a) $\epsilon(E)$ with a variety of transitions and $\epsilon(E) = 510 - 490 \tanh[(E + 1.956\delta)/\eta]$. As the parameter δ increases, the transition in $\epsilon(E)$ becomes more gradual.

Fig. 43(b) The equivalent position-dependent $\epsilon(x)$ to the $\epsilon(E)$ shown in Fig. 43(a).

Fig. 43(c) The doping profiling results with various transitions in $\epsilon(E, x)$, as shown in Figs. 43(a) and (b).

Fig. 44 Illustration of a ferroelectric CV characteristic with the corresponding translation of the high-dielectric constant layer with the applied bias.

Fig. 45(a) The electric field together with the dielectric constant as functions of depth position from computer simulations at $V_a = 2.1$ V (corresponding profiling location, $x = 0.01 \mu\text{m}$). The high-dielectric constant switching layer propagates toward the negative x -direction as V_a decreases. This corresponds to the CV curves in Fig. 37 tracing from leg C to D. .

Fig. 45(b) The electric field together with the dielectric constant as functions of depth position from computer simulations. $V_a = -0.7 \text{ V}$ (corresponding profiling location, $x = 0.29 \mu\text{m}$).

Fig. 45(c) The electric field together with the dielectric constant as functions of depth position from computer simulations. $V_a = -11.4 \text{ V}$ (corresponding profiling location, $x = 0.15 \mu\text{m}$).

Fig. 46 Nonideal structure in $\epsilon(E)$ may lead to a false extracted doping. At zero doping, the ferroelectric CV characteristic resembles the $\epsilon(E)$.

Fig. 47 The simulated CV characteristics of the undoped PZT capacitor at various electrical doping levels.

Fig. 48 The extracted electrical doping level (N_{ext}) versus the actual doping level (N_{act}) input to the simulation. N_{ext} is calculated using Eqs. (33) and (35) based on the simulated CV characteristics in Fig. 47.

Fig. 49 The electrical doping level versus $d\alpha/dE$ with various values for δ_0 . The inset shows relevant parameters describing $\epsilon(E)$. The parameter $d\alpha/dE$ is the maximum slope of the $\alpha(E)$ relation that occurs approximately at $E = E_c$. $d\alpha/dE$ is calculated using Eqs. (16) and (18) based on the measured CV characteristic. The dotted lines are the extracted doping N_{ext} when $N_{act} = N_{bg}$. N_{ext} is 10% higher than the actual electrical doping level. Fig. 49 provides a rule of thumb based only on measured information from CV curves to evaluate the accuracy of the extracted electrical doping information.

Fig. 50 Illustration of the relation between $\alpha(E)$ and the trapezoidal $\epsilon(E)$.

Fig. 51 $\alpha(E)$ extracted using Eq. (17) with $C(V)$ calculated from Eq. (15) with a trapezoidal $\epsilon(E)$ described by parameters summarized in Tab. II.

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