CHARACTERIZATION OF LEAD ZIRCONATE-TITANATE (PZT) THIN FILMS FOR FERROELECTRIC MEMORY APPLICATIONS

by

Sungchul Lee

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A Dissertation Submitted to the Faculty of the
DEPARTMENT OF ELECTRICAL AND COMPUTER ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
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In the Graduate College
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Characterization of lead zirconate-titanate (PZT) thin films for ferroelectric memory applications

Lee, Sungchul, Ph.D.
The University of Arizona, 1993

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ABSTRACT

Recently, significant progress has been made in integrating ferroelectric materials and semiconductor technology to achieve high density, semiconductor memories. The hysteresis behavior of the polarization versus the electric field and high dielectric constant of ferroelectric materials are useful for non-volatile and dynamic random access memories (DRAMs), respectively. Lead Zirconate-Titanate (Pb(Zr,Ti)O₃), commonly called PZT, is considered to be potentially important in memory applications. PZT is the ferroelectric material studied here.

In this dissertation, the measurement methods for polarization and current-voltage characteristics of ferroelectric thin films are investigated. A new method for measuring current-voltage characteristics of ferroelectric materials is developed to distinguish the leakage current from the switching current. Further, the reliability concerns for ferroelectric memories, such as fatigue, retention, and temperature effect, are discussed based on the polarization and leakage-current characteristics of sol-gel derived PZT thin films.

In addition to the studies on the charge storage capability, a model of the ferroelectric thin films is presented. Considering the spontaneous polarization of the ferroelectric film, a back-to-back Schottky barrier system having asymmetric barriers is proposed as a model for the platinum-PZT-platinum capacitor. The potential and electric field distributions in PZT thin films are calculated by solving Poisson’s equation numerically for different doping concentrations. In this analysis, the permittivity variation with respect to the electric field is considered. Based on these numerical results, capacitance-voltage characteristics of the PZT thin film capacitor are predicted. For a doping concentration of 1x10¹⁸ cm⁻³ and the maximum relative permittivity of ~8000, the calculated C-V curve fits well with the experimental result.
CHAPTER 1

INTRODUCTION

Recently, a lot of progress has been made in integrating ferroelectric materials and semiconductor technology to achieve high-density, semiconductor memories [1,2,3]. Because of their hysteresis property, ferroelectric materials have been considered for applications to non-volatile memory elements since the 1950s [4]. In those days, the lack of suitable thin-film technology made it difficult to realize ferroelectric memories. Along with this technological barrier, unprecedented improvements in silicon-based memory during the 1970s decreased the interest in other materials because no material could compete with the thermally grown silicon dioxide as a charge storage element. With the silicon-based technologies, various non-volatile memories such as PROM (Programmable Read Only Memory), EPROM (Erasable and Programmable ROM) and EEPROM (Electrically Erasable Programmable ROM) have already been commercialized. However, these devices are inconvenient and slow when writing data, so they are still far from being ideal memories. The ideal memory is defined as a memory which would be as accessible for data changes as a RAM (Random Access Memory) and retain data indefinitely with the power off [5]. In this context of developing ideal memories, the non-volatility of ferroelectric materials has regained attention since the mid-1980s. Further, the radiation-hardness of ferroelectric materials has provided another strong motivation for developing ferroelectric memories for aerospace and military applications [6]. Owing to these demands for new memory devices and the remarkable advances in thin-film technology, high quality sub-micron ferroelectric films have become compatible with the standard semiconductor processes [7]. From these trends, the appearance of commercial ferroelectric memories is expected in the near future.
Since the first discovery of the ferroelectricity from a Rochelle salt in 1920 by Valasek, a graduate student at the University of Minnesota [8], about 150 ferroelectric materials were discovered by the beginning of the 1970s [9]. Among them, Lead Zirconate-Titanate (Pb(Zr,Ti)O₃), commonly called PZT, is considered to be potentially important in memory applications. Besides the non-volatility, PZT can store more charge per unit area than silicon-dioxide. PZT films with a thickness of 4000 Å can store 7.5 μC/cm² at 4 V [10]. In contrast, even state-of-art 50 Å silicon-dioxide can store only 3.5 μC/cm² at 5 V operation. Further, PZT shows stable characteristics over the normal operating temperature range of memory devices, typically 0 ~ 100 °C on chip. Therefore, PZT can be a good alternative to silicon-dioxide in future memory technologies.

In this chapter, the definition and basic properties of the ferroelectricity are presented first. Later, the Sawyer-Tower method is introduced to explain how the hysteresis loops of ferroelectric materials have been measured traditionally. Finally, the goal and scope of this work are specified.

1.1 Definition and Basic Properties of Ferroelectric Materials

Ferroelectric materials have a finite value of polarization after the application and subsequent removal of an external electric field [11]. Further, the polarization at zero electric field depends on the polarity of the previous electric field. Therefore, a response of the polarization to an external electric field results in a hysteresis loop as shown in Fig. 1.1. Since the hysteresis loop is a feature common to all ferroelectrics, a description on this loop is given first.

Suppose that a ferroelectric crystal consists of many regions of uniform polarization, generally called domains, and the crystal has never experienced any electric field. Therefore, the crystal has no net polarization initially because the polarization of each
domain is randomly oriented. Further, assume that the magnitude of the electric field should be larger than a certain value (coercive field) in order to switch the polarization of a domain from one direction to the other.

![Polarization vs Electric Field](image)

**Fig. 1.1.** Schematic representation of a ferroelectric hysteresis loop [12].

Now, apply an electric field in the positive direction and increase its magnitude. If the electric field is not large enough to switch any of the domains, the crystal will behave like a normal dielectric (portion OA in Fig. 1.1). As the electric field becomes larger than the coercive field, more domains with a negative polarization will switch over in the positive direction and the polarization will increase rapidly (portion AB). If the field is increased further, the crystal reaches a state of saturation (portion BC) in which all the domains are aligned in the positive direction to become a single-domain crystal. The curve OABC is called the initial or fundamental branch of the hysteresis loop.

If the field strength is decreased after reaching saturation, the polarization of the crystal will change in a manner corresponding to the curve CBD, rather than to the initial
curve. When the field is reduced to zero, some of domains will remain aligned in the positive direction and the crystal will exhibit a remanent, or residual, polarization $P_r$ (OD). The extrapolation of the linear portion BC to the polarization axis is defined as a spontaneous polarization $P_s$ (OE).

In order to annihilate the overall polarization of the crystal, it is necessary to apply an electric field in the opposite (negative) direction. The value of the field required to reduce polarization to zero (OF) is called a coercive field $E_c$. Further increase of the field in the negative direction will again reach saturation (FG). In this way, a hysteresis loop CDGHC is obtained.

In the hysteresis curve, the key parameters are spontaneous polarization $P_s$, remanent polarization $P_r$, and coercive field $E_c$. Both $P_s$ and $P_r$ are the polarization values defined at zero electric field. As might be expected in Fig. 1.1, $P_s$ is the magnitude of the polarization if a ferroelectric crystal remains in the single-domain state in the absence of an external electric field. However, because of the domain relaxation when decreasing the electric field, $P_r$ is obtained at zero electric field.

The hysteresis behavior is used for non-volatile memory applications. Two different stable states at zero electric field can be regarded as either "0" or "1". This can be used to store data that will remain after the removal of the electric power.

Another important property of ferroelectricity is the existence of a Curie point, $T_c$, at which a ferroelectric material undergoes a structural phase transition to a state where spontaneous polarization vanishes [13]. Above the Curie point, the small-signal permittivity $\varepsilon$ is of the Curie-Weiss form

$$\varepsilon = \frac{C}{T - \theta}.$$  \hspace{1cm} (1.1.1)

where $C$ is Curie constant, $T$ is absolute temperature in °K, and $\theta$ is the Curie-Weiss temperature in °K.
The Curie-Weiss temperature $\theta$ is always less than or equal to the Curie point $T_c$ and generally within a few degrees of $T_c$.

At the Curie point, the small signal permittivity usually exhibits a peak. The small-signal relative permittivity, or dielectric constant, ranges from $10^2 \sim 10^5$ in the vicinity of the Curie point [14]. Further, most ferroelectrics have high permittivity values even in temperature regions not close to $T_c$. This is a useful property for the DRAM (Dynamic Random Access Memory) applications. If high permittivity ferroelectric thin films can replace silicon dioxide in a one-transistor/one-capacitor DRAM cell, ULSI, such as 256 mega- or 1 giga-bit, DRAMs can be realized without employing a sophisticated three dimensional trench- or stack-capacitor technique to expand the charge storage area.

1.2 Traditional Hysteresis Measurement: Sawyer-Tower Circuit

Using the hysteresis curve, some key parameters for memory operation such as the remanent polarization ($P_r$) and the coercive field ($E_c$) can be found. Fig. 1.2 shows the Sawyer-Tower circuit for observing a hysteresis loop on an oscilloscope [15].

In the Sawyer-Tower circuit, an integrating linear capacitor $C_0$ is placed in series with a ferroelectric capacitor $C_f$. Assume that a voltage source $V$ supplies an ac signal, usually with a low frequency of $50 \sim 60$ Hz, to the Sawyer-Tower circuit. If $C_0$ is much larger than $C_f$, then the voltage drop across the ferroelectric capacitor is approximately equal to the input voltage $V_x$. Thus, if the electric field $E$ across the ferroelectric capacitor is constant, it will be

$$E = \frac{V_x}{d} \quad (1.2.1)$$

where $d$ is the thickness of the ferroelectric capacitor.
Fig. 1.2. Sawyer-Tower circuit for the hysteresis loop observation.

Because \( C_f \) and \( C_o \) are connected in series, electric charge \( Q \) stored in each capacitor is

\[
C_f V_x = C_o V_y = Q. \tag{1.2.2}
\]

If a displacement-flux density \( D \) exists in the ferroelectric capacitor in a direction normal to the electrode, then the surface charge density is the same as \( D \) and the electric charge \( Q \) is

\[
Q = AD \tag{1.2.3}
\]

where \( A \) is the electrode area of the ferroelectric capacitor. In this way, displacement-flux density and \( V_y \) are related to each other as follows;

\[
V_y = \frac{Q}{C_o} = \frac{AD}{C_o}, \tag{1.2.4}
\]

and

\[
D = \frac{C_o V_y}{A}. \tag{1.2.5}
\]

Therefore, from the plot of \( V_y \) vs. \( V_x \), the relationship between the displacement-flux density and the electric field can be found.

For a linear dielectric material such as silicon dioxide, \( D \) is linearly proportional to \( E \), so the plot of \( V_y \) vs. \( V_x \) is nothing but a straight line. In the case of ferroelectricity, the
non-linearity between $D$ and $E$ generates a hysteresis loop. Further, $D$ can be regarded as polarization in ferroelectric materials. In other words, if the polarization is the major contribution to the displacement-flux density, $D$ is approximately the same as the polarization $P$

$$D = \varepsilon_0 E + P \approx P.$$  \hspace{1cm} (1.2.6)

Therefore, polarization can be measured from the hysteresis loop using

$$P = \frac{C_0 V_Y}{A}.$$  \hspace{1cm} (1.2.7)

### 1.3 Goal and Scope the Work

The goal of this work is the electrical characterization of ferroelectric materials, especially PZT thin films, as a charge-storage element in memory devices. In spite of the significant progress in ferroelectric memories, no standard electrical characterization method has been established yet. Therefore, investigation of the electrical characterization method is the main focus of this work.

As a background, the general properties and fabrication of PZT thin film capacitors are explained in Chapter 2. In Chapter 3, the operational principles and the representative structures of ferroelectric memories are presented. Further, reliability concerns for ferroelectric memories are discussed.

The electrical characterization methods and characteristics of PZT thin films obtained using these methods are presented in the next two chapters. In Chapter 4, another polarization measurement method, commonly called a pulse polarization, is introduced. The relationship between the pulse polarization and the traditional Sawyer-Tower method is examined. Later, experiments on polarization characteristics in conjunction with the
ferroelectric memory operation are discussed. In Chapter 5, a new current vs. voltage measurement method for ferroelectric thin films is discussed in detail. This I-V measurement method is developed to distinguish the leakage current from the switching current. Further, this I-V measurement method is applied to characterizing PZT thin films. In Chapter 6, modeling of a PZT capacitor is discussed in order to develop an energy-band diagram for a metal-ferroelectric-metal structure. A back-to-back Schottky barrier system is introduced to explain the experimentally observed I-V and C-V characteristics. Numerical analysis for this system is performed to find potential and electric field distributions in ferroelectric films. Finally, conclusions and areas for further studies are presented in Chapter 7.
CHAPTER 2

FERROELECTRIC PZT THIN FILMS

2.1 PZT as a Ferroelectric Material

Fig. 2.1 shows a crystal structure of Lead Zirconate-Titanate, or PZT, at higher temperature than the Curie point ($T_C$). In this structure, a titanium or zirconium atom is located at the center of each octahedron whose vertices are occupied by oxygen atoms. At the center of the corner-linked eight octahedrons, a lead atom is located. Because this is the same structure as the mineral calcium titanate CaTiO$_3$, which is called perovskite [16], PZT is classified as a perovskite-type ferroelectric.

![Perovskite structure of PZT](image)

Fig. 2.1. Perovskite structure of PZT [17].
Fig. 2.2. ABO₃ structure in the unit cell of PZT. Pb atoms at the corners correspond to the A cations. The Zr or Ti atom in the center is the B cation. Oxygen atoms in the faces are the O anions. On the right side is the definition of the crystallographic coordinates.

From the perovskite structure, a unit cell of a cubic structure can be drawn as shown in Fig. 2.2. This unit cell contains one cation, commonly referred to as a B cation, in the cubic center; eight one-eighth cations, A cations, at the corners; and six half anions, O anions, at the cubic faces. Therefore, this is also called an ABO₃ structure.

In order to explain the occurrence of the ferroelectricity, imagine a specific crystal in the ABO₃ structure array. The specific crystal can receive the local electric field caused by the instantaneous mutual displacements of cations and anions in other crystals. In the specific crystal, at high temperature above the Curie point, the thermal energy of the crystal lattice is so high that the local electric field can be ignored. Therefore, the lattice vibrations are equally distributed along all directions so that no dipole moment exists on average and the crystal maintains the paraelectric cubic structure [18].

However, when the temperature cools down below the Curie point, the thermal energy is no longer high enough to overcome the local electric field. Therefore, the local electric field deforms the cubic structure. As shown in Fig. 2.3, this deformation depends
on the zirconium to titanium ratio in the PZT. For lead titanate, the new phase is tetragonal \((a=b\neq c, \alpha=\beta=\gamma=90^\circ)\). A larger zirconate content exhibits a rhombohedral (or trigonal, \(a=b=c, \alpha=\beta=\gamma<120^\circ\neq 90^\circ\)) structure after phase transition. In tetragonal structure, the cations, \(\text{Zr}^{4+}\) or \(\text{Ti}^{4+}\) and \(\text{Pb}^{2+}\) ions, are displaced slightly relative to the \(\text{O}^{2-}\) anions as shown in Fig. 2.4 [19]. This deformation develops a dipole moment and the PZT remains in the ferroelectric state. Because the phase transition in PZT induces a dipole moment by displacing ions in the crystal, this transition is generally referred to as a displacive one.

![Phase diagram of PZT](image)

Fig. 2.3. Phase diagram of PZT. F, P, and A stand for ferroelectric, paraelectric, and antiferroelectric phases, respectively. The subscript T denotes a tetragonal phase; C a cubic phase; R a rhombohedral phase, of which there are high temperature (HT) and low temperature (LT) forms. MPB refers to the morphotropic phase boundaries [19].
Fig. 2.4. Deformation from cubic to tetragonal phase. The phase transition displaces Ti$^{4+}$ (or Zr$^{4+}$) and Pb$^{2+}$ relative to the O$^{2-}$ ions, thereby developing a dipole moment [19].

In contrast to the displacive type ferroelectrics, which have no dipole in the paraelectric phase, the order-disorder type ferroelectric materials such as Rochelle salts (specific chemical formula is potassium sodium tartrate, $\text{C}_4\text{H}_4\text{O}_6\text{NaK} \cdot 4\text{H}_2\text{O}$) or Potassium dihydrogen phosphate (KH$_2$PO$_4$, commonly KDP) already have permanent dipoles in the paraelectric phase. In the paraelectric phase, the permanent dipoles are arranged so randomly that no net polarization exists. However, the ferroelectric transition accompanies the ordering of the permanent dipoles to give rise to a spontaneous polarization [20].

Here, the magnitude of the displacement in PZT will be estimated roughly. The typical spontaneous polarization $P_5$ of PZT at room temperature is 20 $\mu$C/cm$^2$ and the lattice constant of PZT is about 4 Å [21], so that the dipole moment of a cell $p$ is

$$p = 20 \ \mu\text{C} \ \text{cm}^{-2} \times (4 \times 10^{-8} \ \text{cm})^3 = 1.28 \times 10^{-27} \ \text{Coulomb cm}. \quad (2.1.1)$$
If a PZT unit cell is considered as a dipole of six electronic charges separated by $\delta$, the dipole moment will be $6e\delta$, where $e$ is the electronic charge of $1.6 \times 10^{-19}$ Coulomb. Therefore, displacement $\delta$ is approximately given by

$$\delta = \frac{p}{6e} = \frac{1.28 \times 10^{-27} \text{Coulomb} \cdot \text{cm}}{6 \times 1.6 \times 10^{-19} \text{Coulomb}} = 0.13 \text{Å} \quad (2.1.2)$$

This indicates that only a slight displacement can induce the spontaneous polarization.

In the phase diagram shown in Fig. 2.3, the tetragonal phase is separated from the rhombohedral phase by a nearly vertical boundary located at 53% Zr to 47% Ti (Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$). This boundary is generally called morphotropic phase boundary (MPB). At the MPB, the dielectric constant passes through a maximum, whereas the coercive field passes through a minimum [22]. Therefore, most experiments here focus on the characteristics of PZT thin films with an MPB composition.

### 2.2 Fabrication of a Ferroelectric PZT Thin Film Capacitor

The PZT thin film capacitors used in this study were fabricated in the Arizona Materials Laboratories. Numerous deposition techniques for PZT films are available. A sol-gel method was used in this work [23].

Fig. 2.5 shows the cross section of the PZT capacitor used in this experiment. As the bottom electrode of the PZT capacitor, a platinum layer of 1500 Å was sputtered on an oxidized 2” silicon wafer. On the bottom electrode, a PZT solution, commonly called a precursor in sol-gel terminology, with a zirconium to titanium ratio of 53/47 was spin-coated. The precursor solutions were prepared using lead acetate and Ti/Zr alkoxides [24]. In this way, three-layer PZT thin films were spin-coated with intermediate densification at 500 °C. The films were then annealed at 700 °C for 30 min. in oxygen. Top electrodes
were formed by either sputtering platinum through a shadow mask or using a lift-off process.

In the early stages of the study, the shadow mask method was used to define the top electrode. For these capacitors, due to the large area of the shadow mask (larger than $1.0 \times 10^{-2} \text{ cm}^2$), electrical characterization was limited to frequencies less than 20 kHz. Further, the capacitors defined with the shadow mask had neither uniform area nor sharp edges, so the actual area of each capacitor had to be measured by a microscope. To overcome this limitation, a lift-off process was employed to obtain small- and uniform-area capacitors. With the lift-off process, a platinum top electrode with dimensions of 120 $\mu$m x 200 $\mu$m ($2.4 \times 10^{-4} \text{ cm}^2$) was defined. To make electrical contact to the bottom electrode, a small portion of the PZT thin film was etched off in an acid solution by masking the majority of the wafer with an organic wax. Later, the organic wax was removed with toluene. At this point, the film thickness was measured from the step of PZT and the exposed bottom electrode with a profilometer such as a Sloan Dektak or an Alpha Step.

Some samples, especially at the early stage of study, underwent electrical tests immediately after the bottom electrode exposure. However, it was found that an additional heat-treatment after top electrode formation changed the electrical characteristics considerably.

Fig. 2.5. Cross section of the ferroelectric PZT capacitor.
Fig. 2.6 shows the typical hysteresis curves before and after the post-metallization anneal. Before the post-metallization anneal, the hysteresis curve has a large distortion in the positive voltage portion and has a small polarization. The post-metallization anneal at 700 °C for 5 min. makes the hysteresis curve symmetric and increases the polarization. This result indicates that the additional heat-treatment after top electrode formation not only makes the electrodes symmetric but also improves the charge storage capability of the film.

Based on these results, patterning the top electrode with lift-off and using a post-metallization anneal was selected as the standard procedure. In this study, unless otherwise specified, the experimental results are obtained from capacitors prepared with this standard procedure.
CHAPTER 3
FERROELECTRIC MEMORIES

The first application of ferroelectric materials in memory devices was for non-volatile memories based on the hysteresis property of the ferroelectric in the 1950s [4]. Most of the work since the mid-1980s also focused on non-volatile memories [25,26]. However, since the late 1980s, some work has been performed to develop ULSI (Ultra-Large Scale Integration) DRAMs using a high dielectric constant, ranging from a few hundred to a few thousand, of ferroelectric materials [27,28].

In this chapter, the operation principles and the representative cell structures of the non-volatile memories are explained first. Next, application of ferroelectric materials to DRAMs is mentioned. Finally, requirements for ferroelectric memories are discussed.

3.1 Ferroelectric Non-volatile Memories

3.1.1 Basic Concept of Non-volatile Memory Operation

The basic concept of the ferroelectric non-volatile memory operation can be explained using Fig. 3.1. For convenience, voltage, instead of electric field, is chosen as a horizontal axis in this hysteresis curve. As shown in this figure, two stable states exist at zero electric field. Arbitrarily, the positive remanent polarization is defined as the zero (0) state and the negative remanent polarization as the one (1) state. If a positive voltage greater than the positive coercive voltage (+\(V_c\)) is applied and then removed, the polarization remains in the zero state. Similarly, the one state can be obtained by applying a negative voltage. The voltage applied when writing the zero or one state is represented as \(V_{\text{write}(0)}\) or \(V_{\text{write}(1)}\), respectively.
To read the stored information, a positive voltage labeled $V_{\text{read}}$ is applied to the capacitor. If a zero is stored, polarization will change from $+P_r$ to $+P_{\text{max}}$ and current corresponding to $\Delta P(0)$, the same as $+P_{\text{max}} - (+P_r)$, will flow through the capacitor. If a one is stored, polarization will switch from $-P_r$ to $+P_{\text{max}}$. This polarization change, $\Delta P(1)$ in Fig. 3.1, is larger than $\Delta P(0)$ and is accompanied by larger current through the capacitor than for $\Delta P(0)$. Therefore, if the displacement current through a capacitor can be monitored during the read operation, the state of the previously stored information can be recognized.

After reading the data, the capacitor remains in the zero state regardless of the previous state because the application and subsequent removal of the positive read voltage will locate the capacitor in the positive remanent polarization. This memory operation, which alters the original data after a read, is called Destructive Read Out (DRO). In the DRO scheme, the data must be restored to their correct states after each read operation. One of the drawbacks of DRO mode is the loss of the data if some event, such as a power
failure or a radiation exposure to a high ionizing dose-rate event, disrupts the memory operation during the read cycle [29]. Further, the restore cycle after each read operation inevitably decreases the life-time of the ferroelectric memories by increasing the fatigue effect, which is defined as the reduction of the polarization due to repetitive switching [1].

Recently, some work has been performed to develop Non-Destructive Read Out (NDRO) ferroelectric memories [30,31]. However, most of the ferroelectric non-volatile memories proposed to date have employed DRO schemes. In the next section, the structure of a representative ferroelectric non-volatile memory with a DRO scheme is introduced.

3.1.2 Primitive Memory Cell

Fig. 3.2 shows a prototypical ferroelectric memory using a cross-point matrix architecture proposed in 1952 [4]. Orthogonal row and column electrodes are fabricated on the opposite surfaces of the ferroelectric material.

To write information in a particular cell, half of the switching voltage (+0.5Vs), where Vs is defined as a product of nominal coercive field Ec and a film thickness d, is applied to the appropriate row. At the same time, another half of the switching voltage but of opposite sign (-0.5Vs) is applied to the appropriate column to produce a total of Vs to the selected cell. Thus, the full polarizing voltage will appear across the cell, which is the cross-point of these row and column, but only one-half of the polarizing voltage will appear across all other cells in the array. However, such a simple row-and-column address scheme is impractical for ferroelectric memories. One reason is that the real ferroelectrics do not exhibit well-defined coercive fields or switching voltages. In other words, the coercive field depends on the duration of the applied field and on the history of the cell. Therefore, electric fields much smaller than Ec can switch the crystal [32]. This problem is referred to as a "half-select disturb pulse threshold," which means that half the Vs could
unintentionally disturb, or switch, stored data in a cell [1]. Besides this problem, large operating voltages (10-100 volts) due to thick films were unacceptable for practical commercial devices.

Fig. 3.2. The prototypical row and column address scheme ferroelectric memory.

3.1.3 Typical Non-volatile Memory Cells

In 1987, a non-volatile memory cell based on ferroelectric storage capacitors as shown in Fig 3.3 (a) was proposed [33]. A conceptual cross section of the memory cell is also illustrated in Fig. 3.3 (b). The top electrode of a parallel plate ferroelectric capacitor fabricated on top of the interlayer glass, Dielectric 1 in Fig. 3.3 (b), is connected to the source of the underlying silicon-based transistor. A high-density memory with a one-transistor/one-capacitor cell can be realized in this way. In this circuit schematic, the bit-line capacitance is a parasitic capacitance of the bit line and not a discrete element.
Fig. 3.4 shows the logic pulses for operations of write, read and restore of this memory cell [34]. The transistor pertaining to the memory cell is turned on if a particular memory cell is selected for write, read and restore. For the rest of operation, the ferroelectric capacitor is isolated from other circuitry by turning the transistor off.

Fig. 3.3. Ferroelectric non-volatile memory. (a) Schematic of memory cell with a single-capacitor architecture. (b) Conceptual cross section of a memory cell [33].
One state is written in the cell by holding the drive line low while pulsing the bit line high. This puts negative voltage across the capacitor. In read operation, the bit line floats while the drive line is taken high. The voltage level in the bit line is compared to a reference voltage by an external circuit which is generally called a sense amplifier. If a one is stored, due to the large switching current, the bit line voltage becomes higher than the reference voltage and the sense amplifier outputs a high state. Because read operation switches the polarization state from one to zero, the original state must be restored. Once the sense amplifier detects the one state, it automatically raises a voltage level of the bit line to a high state after the drive line returns to the low state. In this way, the ferroelectric capacitor once again remains in the one state.

To write the zero state, a high voltage pulse is applied to the drive line with the bit line low. During read, the bit line voltage does not increase if a zero is stored because the drive line voltage does not change the polarity of the ferroelectric capacitor. The sense amplifier detects a low level and forces the bit line to remain in the low state. This does not
change the state of the ferroelectric capacitor and no restore operation is necessary if the original state is zero.

The major problem of this single-capacitor memory cell is the fatigue effect. The repeated read/write cycles gradually decrease $\Delta P(1)$, in Fig. 3.2. Eventually, the bit line voltage is no longer high enough to be regarded as a one state.

To improve the life-time, another memory cell structure was developed by combining two single capacitor cells as shown in Fig. 3.5 [26]. One single-capacitor remains in the positive remanent polarization state and the other in the negative remanent polarization state. In this scheme, instead of using a reference voltage, the sense amplifier compares the voltages of the bit line and the bit-bar line. This memory cell can work as long as the sense amplifier can detect the difference of the positive and the negative remanent polarization. Therefore, at the cost of larger cell area, longer life time will be achieved.

![Schematic of a dual-capacitor ferroelectric non-volatile memory cell](image)

Fig. 3.5. Schematic of a dual-capacitor ferroelectric non-volatile memory cell [26].
3.2 Ferroelectric Dynamic Memories

Fig. 3.6 shows the conceptual operation principle of ferroelectric dynamic memories. Only the first quadrant of the hysteresis loop is used for DRAM operation. The maximum polarization is defined as the one state and the positive remanent polarization as the zero state.

Fig. 3.6. Operation of a ferroelectric DRAM cell.

Logic signals for writing zero or one states to the cell are shown in Fig. 3.7. In contrast to non-volatile memories, the plate line always has the same voltage level. For convenience, suppose that the plate voltage level is ground here. During the write interval, the signal level of the word line becomes high enough to turn on the transistor. If the voltage of the bit line is zero, then the ferroelectric capacitor stores charges amounting to the remanent polarization. If the bit line is connected to \( V_{DD} \) during the write interval, the voltage across the ferroelectric capacitor is \( V_{DD} \) and charges corresponding to the
maximum polarization are stored in the capacitor. After writing data, the capacitor is isolated from the external circuitry by turning off the transistor and it stores the information.

The data read can be explained in the same way as non-volatile memory operation. Here, the read-out disturbs the stored data also. Therefore, a restore cycle is needed after the read cycle. Aside from the data loss after read-out, leakage current can change the charges stored in the capacitor. Therefore, the data stored in each memory cell should be periodically restored. This periodic data-restore process is commonly called a refresh cycle.

Figure 3.7. Logic signals for writing zero (left side) or one state (right side) in ferroelectric DRAM cells.

### 3.3 Requirements for the Ferroelectric Memories

In the last two sub-sections, the principles of ferroelectric memories, both non-volatile and dynamic, were explained. In these two memories, when reading data, charges stored in the ferroelectric capacitor are converted to a voltage change. This voltage change must be large enough to be detected by the sense amplifier. In this section, how many
charges the ferroelectric capacitor must store in order that ferroelectric materials may be
used for future memory devices will be discussed.

For convenience, charge-storage requirements for DRAM cells will be discussed
first. In Fig. 3.8 (a), the one-capacitor/one-transistor DRAM cell is shown once again. The
ferroelectric storage-capacitor $C_s$ and the bit line capacitor $C_{bit}$ are analogized to two
reservoirs. Because bit line capacitance is generally 10 times as large as the storage
capacitor [35], the bit line capacitor is represented as the bigger reservoir. When a one is
stored in the cell, the ferroelectric capacitor has a charge of

$$Q_s = P_{\text{max}} \cdot A_s,$$  \hspace{1cm} (3.3.1)

where $A_s$ is the area of the ferroelectric capacitor.

Because the ferroelectric capacitor can store a charge of $P_r \cdot A_s$ at 0 V, the stored charge in
the cell $Q_s$ can be split into two charges, $(P_{\text{max}} - P_r) \cdot A_s$ and $P_r \cdot A_s$, as shown in Fig. 3.8
(b). The bit line capacitor is pictured as an empty reservoir isolated from a small reservoir
in this figure. During the read cycle, isolation valve between the two reservoirs opens and
charges flow from the ferroelectric capacitor to the bit line capacitor. The charge flow
increases the bit line voltage by

$$\Delta V = \frac{(P_{\text{max}} - P_r) \cdot A_s}{C_{bit} + C_c}.$$  \hspace{1cm} (3.3.2)

Because bit-line capacitance is much larger than the storage capacitance, it is simplified as

$$\Delta V = \frac{(P_{\text{max}} - P_r) \cdot A_s}{C_{bit}}.$$  \hspace{1cm} (3.3.3)

If a data zero is stored in the ferroelectric capacitor, bit line voltage remains zero
during the read cycle. Therefore, if the reference voltage of a sense amplifier is zero and
this amplifier can detect $\Delta V$, the voltage increment can be recognized as a data one.
Now, using Eq. (3.3.3), the minimum value of $P_{\text{max}} - P_r$ for a ferroelectric DRAM will be estimated. Fig. 3.9 is a plot of the cell area vs. DRAM density. In this figure, memories from the same manufacturer are represented using the same symbol. From this trend, it can be expected that 64 and 256 mega-bit (Mb) DRAMs will have cell areas of 1.5 and 0.6 $\mu$m$^2$, respectively. Up to the 1Mb DRAM, the storage capacitor has been fabricated simply on a plane, which is generally called a planar capacitor. In this case, the ratio of storage-capacitor area to cell area is about 0.5. For a 1Mb DRAM, this ratio ranges from 0.3 to 0.5 [36]. To make higher density DRAMs using conventional dielectrics such as
silicon-dioxide or silicon-nitride, a planar capacitor is no longer used because it can not store charges large enough to be detected by the sense amplifier. In order for ferroelectric materials to replace the conventional dielectrics, a ferroelectric memory cell must be realized with the planar technology. Therefore, based on 50% storage-area to cell-area ratio, estimated storage capacitor areas for 64 and 256 Mb DRAMs are 0.75 and 0.3 \( \mu \text{m}^2 \), respectively.

Fig. 3.10 shows the typical bit-line capacitance for each DRAM integration level. Owing to the improvements in memory design, bit-line capacitance has decreased below 500 fF for 1 Mb or higher density DRAMs. However, due to the increase in the integration level, the bit-line capacitance will range from 250 to 500 fF for 64 and 256 Mb DRAMs [36].

![Graph showing cell area vs. DRAM density](image)

Fig. 3.9. Cell area vs. DRAM density. The same symbol is used for the same manufacturer's product [37].
Further, the sensitivity of the sense amplifier has been improved continuously from the early stage of the DRAM technology. In the new memory devices, the sense amplifier can detect a voltage difference of 50 mV ~ 150 mV [36].

From these numbers, the minimum charge required for a ferroelectric DRAM in the best and the worst cases can be estimated as

$$P_{\text{max}} - P_r = \frac{\Delta V \times C_{\text{bit}}}{A_s} = \frac{50 \text{mV} \times 250 \text{fF}}{A_s} = \frac{12.5 \text{fC}}{A_s} \text{ in the best case, (3.3.4)}$$

and

$$P_{\text{max}} - P_r = \frac{\Delta V \times C_{\text{bit}}}{A_s} = \frac{150 \text{mV} \times 500 \text{fF}}{A_s} = \frac{75 \text{fC}}{A_s} \text{ in the worst case. (3.3.5)}$$

Thus, for 64 Mb DRAM with a storage-capacitor area of 0.75 µm², the minimum charge will be 1.6 ~ 10.0 µC/cm². For 256 Mb DRAM with a 0.3 µm² storage-capacitor, the minimum charge will be 4.2 ~ 25.0 µC/cm².

Fig. 3.10. Typical bit-line capacitance for each DRAM generation [38].
Even though these estimates have been made based on the trend in DRAM technology, the same parameters for cell area, storage-capacitor area, bit-line capacitance and sensitivity of the sense amplifier can be used for non-volatile memories. For non-volatile memories, the charge-storage requirements can be easily obtained by replacing $P_{\text{max}} - P_{r}$ in the previous analyses by $\Delta P_{r}$, the difference between the positive and the negative remanent polarizations. Whatever memory scheme, either single- or dual-capacitor, is used, the high and low states will produce the bit-line voltage difference corresponding to $\Delta P_{r}$.

Besides these charge-storage requirements, each memory technology has its own reliability concerns. For non-volatile memories, fatigue and data retention are the important concerns. Fatigue effects are also called endurance. Data retention refers to the loss of stored charges under static conditions. Even though the typical current EEPROMs can endure only $10^5$ erase-write cycles [39], they permit $10^{15}$ read operations and retain data for 10 years [1]. To be competitive with EEPROMs, the fatigue endurance and data retention of ferroelectric memories are required to be longer than $10^{12}$ cycles and 10 years, respectively. In other words, after $10^{12}$ polarization reversals, $\Delta P_{r}$ must be larger than the minimum charge-storage requirement. Similarly, charge loss should be small enough for $\Delta P_{r}$ to be larger than the minimum charge-storage requirement after 10 years. Sometimes life-time is defined as the number of cycles, for fatigue, or time, for retention, at which the stored charge is degraded to 50% of the initial value.

In DRAM operation, because of the periodic data refresh, long-term data retention is not so important as in non-volatile memories. Rather, leakage current should be low enough for a memory cell to maintain the data level between refresh intervals. Refresh intervals for 64 and 256 Mb DRAMs are targeting 64 and 128 ms, respectively [36]. Based on the assumption that at least 80% of the charges must remain in the cell between refresh
intervals, the maximum level of the leakage current can be calculated using the relation of

\[ I_L \cdot \tau_R = 0.2 \cdot Q_s \]  \hspace{1cm} (3.3.6)

where \( I_L \) is leakage current, \( \tau_R \) the refresh interval, and \( Q_s \) the stored charge.

For a 64 Mb DRAM, the leakage-current density is

\[ J_L \cdot 64 \text{ ms} = 0.2 \cdot 1.6 \mu \text{C/cm}^2 \text{ in the worst case}, \]  \hspace{1cm} (3.3.7)

or

\[ J_L \cdot 64 \text{ ms} = 0.2 \cdot 10 \mu \text{C/cm}^2 \text{ in the best case.} \]  \hspace{1cm} (3.3.8)

Therefore, the leakage-current density for 64 Mb DRAM must range from 5 to 31.3 \( \mu \text{A/cm}^2 \). Similarly, 256 Mb DRAMs must have a leakage-current density from 6.5 to 39 \( \mu \text{A/cm}^2 \).

In Table 3.1, the requirements for ferroelectric memories discussed so far are summarized. In the next two chapters, polarization and leakage-current characteristics of ferroelectric PZT thin films will be presented, along with discussions of characterization methods.

Table 3.1. Requirements of ferroelectric materials for memory applications.

<table>
<thead>
<tr>
<th>Application</th>
<th>Reliability Concerns</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-volatile Memory</td>
<td>Charge-storage</td>
<td>Refer to DRAM</td>
</tr>
<tr>
<td></td>
<td>Fatigue</td>
<td>( &gt; 10^{12} ) cycles for single cell</td>
</tr>
<tr>
<td></td>
<td>Retention</td>
<td>( &gt; 10 ) years ( \text{3.2x10}^8 ) s)</td>
</tr>
<tr>
<td>64 Mb DRAM</td>
<td>Charge-storage ( (A_s:0.75 \mu \text{m}^2) )</td>
<td>( 1.6 \sim 10 \mu \text{C/cm}^2 )</td>
</tr>
<tr>
<td></td>
<td>Leakage ( (\tau_R:64 \text{ ms}) )</td>
<td>( 5 \sim 31.3 \mu \text{A/cm}^2 )</td>
</tr>
<tr>
<td>256 Mb DRAM</td>
<td>Charge-storage ( (A_s:0.3 \mu \text{m}^2) )</td>
<td>( 4.2 \sim 25 \mu \text{C/cm}^2 )</td>
</tr>
<tr>
<td></td>
<td>Leakage ( (\tau_R:128 \text{ ms}) )</td>
<td>( 6.5 \sim 39 \mu \text{A/cm}^2 )</td>
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CHAPTER 4

POLARIZATION CHARACTERISTICS OF PZT THIN FILMS

In the last chapter, the requirements for ferroelectric memories were discussed. Large charge storage capability is one of the most important requirements for ferroelectric memories. In this chapter, first of all, polarization measurement methods are explained. Later, experimental results regarding the polarization characteristics of PZT thin films are discussed.

4.1 Polarization Measurement Methods

4.1.1 Review of the Traditional Sawyer-Tower Method

A typical Sawyer-Tower circuit set-up is shown again in Fig. 4.1. Because of its simplicity, the Sawyer-Tower method has been used widely for characterizing ferroelectric materials. As mentioned earlier, the integrating linear capacitor must be much larger than a ferroelectric capacitor to make the voltage drop across the linear capacitor, $V_y$, negligible. However, contrary to this requirement, voltage $V_y$ should be large enough to be detected by the oscilloscope. Therefore, this voltage drop, typically a few tens of mV, must be considered when an accurate electric field across the ferroelectric capacitor is required.

Further, the frequency of the input signal should be carefully selected. In this circuit, the output resistance of a function generator, typically $50 \, \Omega$, and capacitance can form a low-pass filter. If the ferroelectric capacitor is much smaller than the linear capacitor, the total capacitance is approximately equal to that of the ferroelectric capacitor. If the ferroelectric capacitor is $\sim 2 \, \text{nF}$, the time constant of the low-pass filter is $100 \, \text{ns}$. 
Therefore, to prevent distortion of the input signal, the input frequency must be much lower than 10 MHz. In addition to a limitation at high frequencies, an input signal with too low frequencies is not appropriate, either. If the input signal is too slow, charges in the linear capacitor may discharge through the input resistor of the oscilloscope. If a 100 nF linear capacitor is used and an oscilloscope has 1 MΩ input resistance, the input signal should be much faster than 10 Hz. The recommended input frequency range is

\[
\frac{10}{C_o \cdot R_{in}} < \text{Input frequency} < \frac{10}{C_f \cdot R_{out}} \quad (4.1.1)
\]

where \(C_o\) is the capacitance of the integrating linear capacitor, \(R_{in}\) is the input resistance of the oscilloscope, \(C_f\) is the capacitance of a ferroelectric capacitor, and \(R_{out}\) is the output resistance of a function generator [40].

Therefore, with a 2 nF ferroelectric capacitor and a 100 nF linear capacitor, the input signal must be between 100 Hz and 2 MHz.
Fig. 4.2. Total remanent polarization ($\Delta P_r$) for different input frequencies to the Sawyer-Tower circuit.

Fig. 4.2 shows a total remanent polarization $\Delta P_r$ (difference between positive and negative remanent polarizations) for different input frequencies. In this figure, both samples show polarization reduction from $10 \text{ kHz}$. This reduction may be due to a parasitic capacitance of the measurement system. Parasitic capacitance in the measurement system causes the low-pass filter problem earlier than the estimated value of $2 \text{ MHz}$. If there is a low-pass filter effect, the actual voltage delivered to the ferroelectric capacitor is smaller than the input voltage, resulting in smaller polarizations. However, the input wave-form observed using an oscilloscope did not show significant distortion up to $1 \text{ MHz}$. Therefore, the parasitic capacitance effect can not be considered as a main factor for the polarization reduction. Even though it can be explained by the less polarizability at the higher frequency, fatigue effects during measurements can not be excluded. In these measurements, all the data of the same group, annealed or unannealed, were obtained from
the same capacitor by increasing frequency. When measuring a hysteresis loop at each frequency, the ferroelectric capacitor inevitably receives many fatigue cycles. For instance, suppose that it takes 2 min. to obtain a hysteresis loop at a certain frequency. With an input frequency of 100 Hz, the ferroelectric capacitor receives 12,000 polarization reversals. While with a 100 kHz input, it will be $12 \times 10^6$. Low frequency input may only reorganize and activate the domains, resulting in an increase of polarization. However, as frequency increases, the cumulative number of electrical cycles during hysteresis loop measurements may be already large enough to cause fatigue effects. The fatigue effect during a hysteresis measurement can be avoided by applying a single-period wave as an input signal.

4.1.2 Hysteresis Measurement Using an RT66A Ferroelectric Tester

In this section, a commercial ferroelectric tester called an RT66A system will be introduced [41]. In the RT66A system, as well as the Sawyer-Tower circuit, a virtual ground circuit is also provided as shown in Fig. 4.3. If the Sawyer-Tower mode is selected, the ferroelectric capacitor is connected to the external linear capacitor. If the virtual ground mode is selected, one terminal of the ferroelectric capacitor is connected to the input of the current amplifier. Because the input of the current amplifier is virtually grounded, the whole input signal will be transferred to the ferroelectric capacitor. A pulser in Fig. 4.3 is used for a different polarization measurement technique called pulse polarization. The pulse polarization method will be discussed in the next two sub-sections.

The computer-controlled voltage driver generates a voltage wave for hysteresis measurement as shown in Fig. 4.4. In order not to cause fatigue effects during measurement, this wave has only two periods. Before obtaining the hysteresis loop, the polarization state of the ferroelectric capacitor is initialized by a single period wave. This presets the capacitor in the negative remanent polarization ($-P_r$) state.
From PC

Ferroelectric\[\text{capacitor}\]

"A"

To PC

Fig. 4.3. RT66A ferroelectric tester [41].

Virtual Ground Mode

Sawyer-Tower Mode

Current integrator

Current amplifier

4.7 nF

x 0.005

x 100

Pulser

To PC

Linear capacitor

Fig. 4.4. Voltage waveform used in RT 66A system for measuring hysteresis loop. This voltage is applied at "A" in Fig. 4.3 [42].

After 100 ms, another single period wave, identical to the previous pre-setting wave, is applied and data for a hysteresis loop are obtained at each voltage step specified by the user. Two sweep rates, fast and slow mode, of the input signal are available. If the fast mode is selected, the hysteresis measurement is made as fast as the host personal computer allows. In slow mode, it takes approximately 1 ms to acquire data at each voltage step. In
this experiment, if one hysteresis loop consists of 200 data points, it takes ~ 60 ms in fast mode and ~ 200 ms in slow mode. Because both modes show almost identical results, the fast mode is generally used in this experiment.

The raw data after data collection can produce a hysteresis loop. In Fig. 4.5, hysteresis loops for a typical PZT capacitor are shown. The hysteresis loop labeled as "Before offsetting" is obtained using raw data. However, here, the fundamental difference between this method and the traditional Sawyer-Tower method must be considered. The traditional Sawyer-Tower method uses a multiple-period wave, more appropriately uncountable-period wave, whereas the RT66A system uses a one-period wave. As described earlier, the first wave in Fig. 4.4 presets the capacitor in a state of negative remanent polarization. This polarization state is a reference during the following hysteresis measurement. Therefore, the "Before offsetting" hysteresis starts from zero polarization. However, after completing data collection, the actual value of the reference should be considered.

In the RT66A system, the original hysteresis loop shifts based on the assumption that $|I_P_{max}| = |I_{-P_{max}}|$. A new hysteresis loop after shifting, labeled as "After offsetting", is also shown in Fig. 4.5. The traditional Sawyer-Tower hysteresis loop for another capacitor having the same process conditions is shown in Fig. 4.6. This hysteresis curve is similar to the hysteresis curve after data offsetting. Therefore, the assumption of $|I_P_{max}| = |I_{-P_{max}}|$ is reasonable in this case. Key parameters of these two hysteresis loops are listed in Table 4.1 and they agree well with each other. The hysteresis loop measured with the RT66A system has a discontinuity at 0 V. This results from the rapid decay of the transient remanent polarization during the 100 ms interval between the pre-set and measurement cycles. In the traditional measurement, the linear capacitor can smooth the output during multiple periods.
Fig. 4.5 Symmetric hysteresis loop measured by RT66A ferroelectric tester.

Fig. 4.6 Symmetric hysteresis curve measured by the traditional Sawyer-Tower method. Integrating capacitor is 100 nF. Input signal is a 1 kHz, triangle wave. One scale in x-axis is 2 V and in y-axis is 8.3 μC/cm².
Table 4.1. Comparison between the RT66A and traditional Sawyer-Tower method from the symmetric hysteresis loops in Fig. 4.5 and Fig. 4.6.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>RT66A</th>
<th>Traditional Sawyer-Tower</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+P_{\text{max}}$ ($\mu$C/cm$^2$)</td>
<td>27.850</td>
<td>26.6</td>
</tr>
<tr>
<td>$-P_{\text{max}}$ ($\mu$C/cm$^2$)</td>
<td>-27.850</td>
<td>-26.6</td>
</tr>
<tr>
<td>$+P_r$ ($\mu$C/cm$^2$)</td>
<td>12.216</td>
<td>8.3</td>
</tr>
<tr>
<td>$-P_r$ ($\mu$C/cm$^2$)</td>
<td>-10.973</td>
<td>-8.3</td>
</tr>
<tr>
<td>$+V_c$ (V)</td>
<td>0.925</td>
<td>1.0</td>
</tr>
<tr>
<td>$-V_c$ (V)</td>
<td>-1.043</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

However, the $|+P_{\text{max}}| = |-P_{\text{max}}|$ assumption should be carefully considered if the two electrodes have different properties. As explained in Chapter 2, the capacitors without top-electrode annealing have an asymmetric hysteresis loop as shown in Fig. 4.7. The offsetting process makes the hysteresis loop even worse, resulting in a negative value for the positive coercive field and a zero in the negative remanent polarization near zero. In contrast to this, the traditional Sawyer-Tower hysteresis curve, measured from the same sort of capacitor, has reasonable values for positive coercive voltage and negative remanent polarization as shown in Fig. 4.8. Key parameters of the offset and the traditional hysteresis loops are compared in Table 4.2. The different absolute values of $+P_{\text{max}}$ and $-P_{\text{max}}$ in the traditional hysteresis curve suggests that the $|+P_{\text{max}}| = |-P_{\text{max}}|$ assumption is no longer valid if the capacitor has asymmetric electrodes. This further suggests that preparing symmetric electrodes is necessary to correlate one measurement method to another.
Fig. 4.7. Asymmetric hysteresis curve measured by RT66A tester.

Fig. 4.8. Asymmetric traditional Sawyer-Tower hysteresis loop for the same sample as Fig. 4.7. $+E_c$ has a positive value. Measurement conditions are the same as Fig. 4.6.
Table 5.2. Comparison between the RT66A and traditional Sawyer-Tower method from the asymmetric hysteresis loops in Fig. 4.7 and Fig. 4.8.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>RT66A</th>
<th>Traditional Sawyer-Tower</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+P_{\text{max}}$ ($\mu$C/cm$^2$)</td>
<td>21.515</td>
<td>18.3</td>
</tr>
<tr>
<td>$-P_{\text{max}}$ ($\mu$C/cm$^2$)</td>
<td>-21.515</td>
<td>-24.9</td>
</tr>
<tr>
<td>$+P_r$ ($\mu$C/cm$^2$)</td>
<td>10.088</td>
<td>5.3</td>
</tr>
<tr>
<td>$-P_r$ ($\mu$C/cm$^2$)</td>
<td>-0.096</td>
<td>-5.3</td>
</tr>
<tr>
<td>$+V_c$ (V)</td>
<td>0.925</td>
<td>0.6</td>
</tr>
<tr>
<td>$-V_c$ (V)</td>
<td>-1.043</td>
<td>-1.3</td>
</tr>
</tbody>
</table>

4.1.3 Pulse Polarization Measurement

When observing a hysteresis loop, a continuous wave equal to or longer than a single period is used as an input signal. Since this input generates a continuous hysteresis loop, this method is commonly called a continuous hysteresis. When ferroelectric thin films are characterized using this continuous hysteresis, the remanent polarization ($P_r$) and the coercive field ($E_c$) are chosen as evaluation parameters. Remanent polarization is regarded as the charge that a ferroelectric capacitor can retain after the removal of the electric field. Coercive field is considered as a threshold voltage that can switch the polarization from one state to the other. However, discontinuous pulses, rather than continuous waves, are used when operating memories. Therefore, the continuous hysteresis may not be an adequate tool for characterizing ferroelectric thin films as a memory element. For that reason, pulse polarization measurement techniques were proposed to test the ferroelectric thin films under
the more closely simulated circuit operation conditions [34,43]. In this section, a basic idea of the pulse polarization measurement method is presented.

Assume that a sequence of pulses as shown in Fig. 4.9 is applied as an input signal to the Sawyer-Tower circuit or the virtual ground circuit. This pulse train consists of one negative, two positive, and two negative pulses. Sometimes, this is referred to as a 'PUND (Positive-Up-Negative-Down)' pulse train [43].

In the pulse polarization method shown in Fig. 4.9, the first pulse sets the ferroelectric capacitor in a state of having negative polarization. In the memory operation, this can be regarded as writing one state. After a delay time, a positive pulse, labeled \( P \), is applied to the capacitor to read the charges stored in the one state. At the same time, it will write the zero state to the capacitor. The next positive pulse, labeled \( U \), will read the charges stored in the zero state. After the removal of this pulse, the capacitor will remain in the zero state again. In the same fashion, the following two negative pulses can simulate the symmetry of the memory operation.

\[
\begin{align*}
\text{Voltage} & \\
\uparrow & \\
+V & \\
\downarrow & \\
-V & \\
\end{align*}
\]

Fig. 4.9. A sequence of 'PUND' pulses for pulse polarization measurement and the definition of pulse polarizations [43,44].
For each pulse of the PUND pulse train, two different polarizations are defined; one is at the leading edge and the other is at the trailing edge of the pulse. If the charges are measured at the leading edge, memory operation can be faster. However, reading error can be reduced by detecting the signal at the trailing edge. If a pulse is applied to the ferroelectric capacitor, an initial current due to charging the linear dielectric component of the capacitor will precede the switching current. This initial current is large even if no switching process happens, for example, when a positive pulse is applied to positively polarized state. In contrast, the switching current is significantly different for different initial polarization states. Therefore, if the polarization is detected after the decay of this initial linear displacement current, it is easier to distinguish the one state from the zero state. From this view-point, both polarizations measured at the leading and trailing edges are necessary for ferroelectric memory design. In Fig. 4.9, eight different polarizations are defined and their typical notations are also shown.

To visualize the pulse polarization method, these eight polarizations are projected on the polarization vs. electric field plane as shown in Fig. 4.10. At the end of the first negative pulse, the polarization is assumed to stay at the negative remanent polarization labeled 1 in Fig. 4.10. Because the continuous hysteresis and pulse polarization are completely different measurement methods, it should be noted that the negative remanent polarization here may be quite different from that of the continuous hysteresis curve. During the delay time prior to the first positive pulse, some of the remanent polarization relaxes and the polarization will be located at position 2. Most of the decay of polarization happens very rapidly, typically within the order of a microsecond [45] after the removal of the pulse. The polarization loss due to this rapid decay is referred to as transient remanent polarization or volatile remanent polarization. For the first positive pulse, a charge of $P^*$, the difference between the maximum polarization and the initial polarization is detected at the leading edge of the pulse (position 3).
Fig. 4.10. Conceptual projection of pulse polarization on a polarization vs. electric field (P-E) plane [43].

At the end of the first positive pulse, polarization remains at the positive remanent polarization, position 4, and charge of $P^r_+$, equal to $P^*$ - (nonremanent polarization), is measured. Once again, the positive remanent polarization here may be different from that of the continuous hysteresis. After experiencing another rapid decay of the transient remanent component, polarization will stay at position 5 at the beginning of the second positive pulse. For the second positive pulse, a charge of $P^\wedge$, the sum of the non-remenant polarization and the transient remanent polarization, is measured at the leading edge (position 6). A charge of $P^\wedge_r$, which is the same as the transient remanent polarization, is measured at the trailing edge of the pulse (position 7). Later, polarization relaxation brings
the capacitor back to the position 8. In this way, for the next two negative pulses, the negative counterparts of these four charges, $-P^*, -P^*_r, -P^w, \text{ and } -P^w_r$ are measured. The trajectories of these polarizations are from 9 to 13 in Fig. 4.10.

### 4.1.4 Pulse Polarization Using an RT66A Ferroelectric Tester

In the RT66A system, pulse polarization is measured by applying pulse train as shown in Fig. 4.11. This pulse train has the same sequence as the PUND pulse train shown in Fig. 4.9. Here, the pulse width is 2 ms and the interval between the pulses is 100 ms.

For the capacitor with the continuous hysteresis shown in Fig. 4.5, the pulse polarization has been measured. Eight different pulse polarization values are listed in Table 4.3 along with the key parameters of the continuous hysteresis curve. From Fig. 4.10, $P^* - P^w$ and $P^*_r - P^w_r$ are expected to equal to each other. However, using the polarization values in Table 4.3, $P^* - P^w$ is 15.873 $\mu$C/cm$^2$ and $P^*_r - P^w_r$ is 15.634 $\mu$C/cm$^2$. This indicates that the first and second positive pulses have different trajectories. Here, trajectories of the pulse polarizations in the polarization vs. electric field will be attempted using the experimental data listed in Table 4.3.

![Voltage waveform for pulse polarization](image.png)

**Fig. 4.11.** Voltage waveform for pulse polarization [44].
Table 4.3. Comparison of the continuous hysteresis and pulse polarization of the capacitor having hysteresis loop as shown in Fig. 4.5.

<table>
<thead>
<tr>
<th>Continuous hysteresis</th>
<th>Pulse polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Polarization</td>
</tr>
<tr>
<td>+P_{max}</td>
<td>27.850</td>
</tr>
<tr>
<td>+P_r</td>
<td>12.216</td>
</tr>
<tr>
<td>-P_r</td>
<td>-10.973</td>
</tr>
<tr>
<td>+V_c</td>
<td>0.925 V</td>
</tr>
<tr>
<td>-V_c</td>
<td>-1.043 V</td>
</tr>
</tbody>
</table>

* Unit of charges: µC/cm².

In Fig. 4.12, the pulse polarization is projected on a polarization vs. electric field plane. The initializing negative pulse followed by a decay during a 100 ms interval will locate the polarization at the B position when applying the first positive pulse. During the rise-time of this positive pulse, polarization increases by 33.372 µC/cm² and reaches the C position. During the fall-time, polarization decreases and stays at the D position at the end of this positive pulse. Up to this point, trajectories are the same as shown in Fig. 4.10. However, the second positive pulse must have different paths from those of the first positive pulse.

From Table 4.3, it can be found that P^*-P^*_r=14.391 µC/cm² and P^\wedge-P^\wedge_r=14.152 µC/cm². These results indicate that discharge during the first pulse's fall-time is larger than that during the second one's. This can be explained by assuming that the second positive pulse switches some of the domains that relaxed during the interval between the first and the second pulses, and some of these re-switched domains become so stable that they do not relax when the second pulse is removed.
Fig. 4.12. Projection of pulse polarization into a polarization vs. electric field plane using experimental data.

If the second pulse reaches the same polarization state as the first one did, the trajectories of the second positive pulse are E, F, and G as shown in Fig. 4.12. Because G is located at a higher position than D, $P^*-P^r$ is larger than $P^*-P^r$. The second pulse may reach a higher polarization state than the first one did. This is commonly referred to as the pump-up of polarization [43]. If a pulse is so short that it can not switch all of domains,
repetitive pulses will keep on switching until polarization reaches the saturation state. However, a 2 ms pulse to a 120 μm x 200 μm capacitor is not so short. If this capacitor is 2 nF and output resistance of the RT66A system is 1620 Ω [46], the RC time constant is 3.24 μs and a 2 ms pulse is 620 times longer than the time constant. Further, 2 ms is much longer than the typical switching time of the ferroelectric materials, which is at most microsecond order. Based on these considerations, trajectories of the second positive pulse are drawn to make the peak polarization state of the second pulse coincide with the first one's.

Next, the polarization state at the beginning of the third pulse, H position, is located higher than that at the beginning of the second pulse E, simply assuming that polarization decays during 100 ms intervals are the same. Polarization state H is the starting point of the next negative pulse. In the same way, trajectories of the two negative pulses, I, J, K, L, and M are drawn as shown in Fig. 4.12. Finally, polarization state M will decay to the initial state B and this completes one loop. However, as shown in Fig. 4.12, the final point is 0.574 μC/cm² lower than the starting point B. This difference in the initial and the final points can be explained also based on the previous discussion. Two consecutive negative pulses cause slower decay than a single negative pulse and locate the final point lower than the initial point.

Trajectories of the pulse polarization are overlaid on the continuous hysteresis curve as shown in Fig. 4.13. Because of the different natures of the pulse polarization and the continuous hysteresis, an exact match between these two methods can not be expected. As shown in this figure, the continuous hysteresis has a wider range of polarization values than the pulse polarization. Trajectories of the pulse polarization are simply placed in the middle of the continuous hysteresis loop considering that if the two methods have some differences in one polarity, the same differences must happen in the other direction.
From Fig. 4.12 and 4.13, several obvious differences between the pulse polarization and the continuous hysteresis can be found as follows.

1) The retained charge, the sum of the positive and the negative long-term remanent polarization, necessary for non-volatile memory operation can be found by \( P^* - P^r \). This retained charge is much smaller than the \( \Delta P_r \), the conventional definition of the total remanent polarization obtained from the continuous hysteresis. In this experiment, \( P^* - P^r \) is 15.873 \( \mu \text{C/cm}^2 \) and \( \Delta P_r \) is 23.189 \( \mu \text{C/cm}^2 \).
2) Another definition of the retained charge can be \( P^*-P^r \). This is useful if the trailing edge detection is employed. However, the charge of \( P^*-P^r \), here 15.634 \( \mu C/cm^2 \), is smaller than that of \( P^*-P^r \), 15.873 \( \mu C/cm^2 \).

3) The non-remanent polarization useful for DRAM operation can be defined by either \( P^*-P^r \) or \( P^r-P^\Delta \). Among these two charges, \( P^r-P^\Delta \) is appropriate to define a charge-storage capability of the dynamic memory because the memory operation takes place only in the first quadrant of the polarization-voltage plane. The non-remanent polarization in pulse polarization is also smaller than that in the continuous hysteresis measurement. In this experiment, \( P^r-P^\Delta \) is 14.152 \( \mu C/cm^2 \) and \( P_{nr} \) in the hysteresis curve is 15.634 \( \mu C/cm^2 \).

4) In Fig. 4.13, the transient, or volatile remanent polarization is smaller than \( P^\Delta \). The transient polarization is 3.108 \( \mu C/cm^2 \) and smaller than \( P^\Delta \), 3.347 \( \mu C/cm^2 \) by 0.239 \( \mu C/cm^2 \). Interestingly, the same difference is obtained from the negative counterparts of these polarizations. The negative transient polarization and \( -P^\Delta \) are -3.634 \( \mu C/cm^2 \) and -3.873 \( \mu C/cm^2 \), respectively, and their difference is also 0.239 \( \mu C/cm^2 \). In Fig. 4.13, the transient remanent polarization \( P_{tran} \) can be calculated from the relation of

\[
P_{tran} = P^\Delta - (P^* - P^r).
\]

Fig. 4.14 shows the pulse polarization for different voltages. Both remanent and non-remanent polarization increase as the voltage increases. The transient polarization does not increase as much as the other polarization. Further, both remanent and non-remanent polarization are larger than 10 \( \mu C/cm^2 \) in the observed low electric field ranges less than
0.2 MV/cm. Considering that even 50 Å silicon-dioxide can store only 0.07 μC/cm² at 0.2 MV/cm (0.1 V), the prospect for ferroelectric PZT thin films as a memory element is quite promising.

Fig. 4.14. Pulse polarization for different voltages.
4.2 Polarization Characteristics for Memory Operations

In this section, the polarization characteristics of the ferroelectric PZT thin films are presented. Polarization characteristics at different temperatures are investigated first. Later, experimental results on fatigue and retention will be shown. Radiation effects on ferroelectric thin films are discussed separately in Appendix A.

4.2.1 Polarization vs. Temperature

One of the requirements for memory applications is that ferroelectric materials must be stable over the normal operating temperature ranges. In the case of CMOS logic circuits, the standard temperature range is from -40 to +85 °C. However, the standard operating temperature range for NMOS memories, 0 to 70 °C, is more frequently used in industry [47]. In order to endure this ambient temperature, ferroelectric materials should maintain stable characteristics for on-chip level temperatures ranging from 0 to 100 °C [48].

Fig. 4.15 shows hysteresis loops at room temperature and 125 °C. Hysteresis loop still shows a good shape at 125 °C. After cool-down, hysteresis curve returns to its original room-temperature shape for this sample, Sample 1 here. For some samples such as Sample 2, hysteresis after cool-down does not return to its original shape as shown in Fig. 4.16. Except for using different precursors, two samples were fabricated with the same procedures, including the top electrode annealing at 700 °C for 5 min. Wide discontinuities at 0 V in the hysteresis loops of Sample 2 indicate that large transient remanent polarization components exist in this film. These transient remanent polarizations relax at high temperature, so that hysteresis curve after cool-down does not coincide with the original shape. The annealing effects are more significant for samples without top electrode annealing. For these samples, hysteresis after cool-down remains the same as that at high temperature.
Fig. 4.15. Hysteresis loops for different temperatures (Sample 1). Hysteresis returns to the original room temperature shape after cool-down.

Fig. 4.16. Hysteresis vs. temperature (Sample 2). Hysteresis does not return to the original curve after cool-down.
In Fig. 4.17, pulse polarizations for different temperatures are illustrated. The results obtained from the previous two samples were used in these plots. As temperature increases, non-remanent polarization increases, whereas the remanent polarization decreases. In Chapter 2, the origin of the spontaneous polarization is explained by a small, about 1 Å, displacement of positive and negative atoms. At high temperature, thermal vibration becomes larger. Therefore, the dipoles are more equally distributed at high temperature, resulting in decrease in the spontaneous, or remanent, polarization. However, these loosely bounded atoms can react more easily to an external field and the linear dielectric component, non-remanent polarization, increases.

For Sample 1, at 100 °C, remanent polarization falls to 65% of the room-temperature value. This is similar to other reported results [49]. For Sample 2, because of the relaxation at high temperature, remanent polarization at 100 °C is only 35% of the
room-temperature value. Considering that the Curie point is higher than 300 °C at the
morphotropic phase boundaries, these results are much worse than expected and indicate
that there is still a lot of room for improvements in film preparation.

4.2.2 Fatigue

Fatigue behaviors were studied by applying either bipolar, shown in Fig. 4.18 (a),
or unipolar, shown in Fig. 4.18 (b), square waves to ferroelectric PZT capacitors. In non-
volatile memory operations, the ferroelectric capacitor will be exposed to both bipolar and
unipolar stresses. In contrast, DRAM operation creates only the unipolar stress.

Most of the fatigue tests were performed using the external mode of the RT66A
ferroelectric tester. In this set-up, the bipolar or the unipolar square waves from an external
function generator were supplied to the capacitor by way of the RT66A system. The
RT66A system automatically interrupted the electrical cycling at the pre-selected periods
and measured pulse polarization. Pulse polarization was measured at the same magnitude of
voltage as the stress signal. Sometimes, in order to keep track of changes in the hysteresis
loop, continuous hysteresis was measured after interrupting the fatigue cycle manually.

![Waveforms for (a) the bipolar and (b) the unipolar electrical stresses.](image)

Fig. 4.18.
The definition of fatigue, the loss of polarization due to the repeated polarization reversals, implies that fatigue may happen more easily with the bipolar stress than with the unipolar stress. Further, this suggests that the number of polarization reversals should be the most important factor causing fatigue. The experiments regarding these implications were performed.

Fig. 4.19 shows typical changes in hysteresis curves due to bipolar ±8 V (148 kV/cm) or unipolar (0 to 8 V) electrical cycling at 100 kHz. Bipolar cycling decreases the polarization significantly. In contrast to bipolar stress, the hysteresis curve maintains its original shape after unipolar stress of 6.4x10⁹ cycles.

Fig. 4.20 and Fig. 4.21 show the changes in remanent polarization (P* - P⁰) as a function of the number of switching cycles and the stress time for different stress frequencies (20kHz and 100kHz). In these plots, remanent polarization is normalized with respect to the pre-stress value. As shown in Fig. 4.20, after a lot of switching cycles, almost the same trend in the normalized remanent polarization has been observed for both frequencies. However, low frequency stress increases the remanent polarization more than high frequency stress at the initial switching cycles. This can be explained by the domain reorganization [49]. At the initial phase of the fatigue process, domains will establish a new equilibrium state and it will increase the polarization. Low frequency signals may activate more domains and increase polarization more than high frequency stress does.

Fig. 4.21 clearly shows that, at the same stress duration, higher frequency stress causes more polarization reduction because the ferroelectric capacitor receives more switching cycles. This proves that the number of switching cycles, rather than the total stress time, is the main factor causing fatigue in these samples.

From the previous experimental results, it is found that fatigue is more serious in non-volatile memories than in DRAM operation. Therefore, in the next experiment, only the bipolar stress effects are discussed.
Fig. 4.19. Changes in hysteresis curves after $6.4 \times 10^9$ fatigue cycles due to (a) $\pm 8$V (148kV/cm) bipolar, and (b) 0 to 8V, unipolar, 100kHz, square waves.
Fig. 4.20. Remanent polarization ($P^*-P^*$) vs. number of switching cycles for different frequencies (20kHz and 100kHz). Remanent polarization is normalized with respect to the pre-stress value.

Fig. 4.21. Remanent polarization ($P^*-P^*$) vs. stress time for different frequencies (20kHz and 100kHz). Normalized remanent polarization is used.
Fig. 4.22 shows fatigue effects for different stress voltages. If a life-time is defined as the number of read/write cycles at which the charge-storage capability decreases to 50% of the initial value, it will be 1x10^9 cycles at 6 V and 8 V operation. At 4 V operation, from the extrapolation of the data curve, a life-time longer than 1x10^{10} read/write cycles will be obtained. These values are not sufficient to meet the endurance requirement of 1x10^{12} cycles. However, judging from the absolute polarization, 4 μC/cm^2 after 10^{10} cycles at 8 V (150 kV/cm) is still much larger than the charge stored in a 50 Å oxide, which is only 0.7 μC/cm^2. Further, a charge-storage density of 4 μC/cm^2 is sufficient to achieve 64 Mb DRAM level integration, i.e. the same cell area as a 64 Mb DRAM, if the advanced memory design technology increases the sensitivity of the sense amplifier and reduces the bit-line capacitance. Therefore, the life-time of the ferroelectric non-volatile memory can be expected to be longer than 1x10^{10} cycles for entire voltage ranges used in this experiment.

Fig. 4.22. Fatigue effects for different stress voltages using 100 kHz, bipolar stresses.
In Fig. 4.23, as well as remanent polarization, non-remanent and transient remanent polarization changes due to ±8 V, 100 kHz, bipolar stresses are shown. Before electrical stress, remanent polarization is larger than non-remanent polarization. During the electrical cycling, remanent polarization decreases more rapidly and it becomes smaller than non-remanent polarization after 5x10^8 cycles. Transient remanent polarization, calculated from $P^\wedge - (P^* - P^r)$, shows a small decrease up to 1x10^7 cycles followed by an increase afterwards.

In Table 4.4, pulse polarization values for fresh and fatigued PZT thin films are compared. For fresh samples, polarization $P^* - P^r$ is greater than polarization $P^\wedge - P^r$ for both ± 6 V and ± 8 V stress conditions. In section 4.1.4, it was explained by the slower discharge during the fall-time of the second positive pulse than during the first one's. However, for ± 8 V stress, polarization $P^* - P^r$ becomes smaller than polarization $P^\wedge - P^r$ after stress. Even for ± 6 V stress, the two non-remanent polarization values become closer each other after stress.

![Graph showing changes in pulse polarization](image.png)
The faster discharge during the fall-time of the second pulse can be explained using an equivalent circuit of the ferroelectric capacitor as shown in Fig. 4.24 [50]. A ferroelectric capacitor can be modeled as a parallel combination of a remanent ferroelectric capacitor ($C_r$), a non-remanent ferroelectric capacitor ($C_{nr}$), a parasitic linear capacitor ($C_p$) and a resistor ($R_{leak}$). For fresh samples, the remanent capacitor is larger than the non-remanent capacitor. If some of the relaxed domains during the interval between the first and second pulses are switched once again, and become so stable not to relax when the second pulse is removed, it can be modeled by increasing remanent polarization and decreasing non-remanent polarization. However, as shown in Fig. 4.23, the remanent capacitor is fatigued more rapidly than the non-remanent capacitor. Finally, more non-remanent capacitance exists in a ferroelectric capacitor than remanent capacitance. Therefore, for the fatigued samples, the possibility that the domains that relax during the interval between the first and second pulses switch during the rise-time of the second positive pulse is almost

<table>
<thead>
<tr>
<th></th>
<th>Before stress</th>
<th>After 6.4x10^9 cycles</th>
</tr>
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<tbody>
<tr>
<td>± 6 V stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P^*$</td>
<td>33.754</td>
<td>15.825</td>
</tr>
<tr>
<td>$P_r$</td>
<td>19.268</td>
<td>8.271</td>
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<tr>
<td>$P^\wedge$</td>
<td>17.068</td>
<td>10.997</td>
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<td>$P_r^\wedge$</td>
<td>2.821</td>
<td>3.490</td>
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<tr>
<td>$P^<em>-P_r^</em>$</td>
<td>14.486</td>
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</tr>
<tr>
<td>$P^\wedge-P_r^\wedge$</td>
<td>14.247</td>
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<tr>
<td>± 8 V stress</td>
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<tr>
<td>$P^*$</td>
<td>38.201</td>
<td>15.969</td>
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<tr>
<td>$P_r$</td>
<td>21.706</td>
<td>8.223</td>
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<tr>
<td>$P^\wedge$</td>
<td>19.411</td>
<td>10.997</td>
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<tr>
<td>$P_r^\wedge$</td>
<td>3.108</td>
<td>3.060</td>
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<tr>
<td>$P^<em>-P_r^</em>$</td>
<td>16.495</td>
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<tr>
<td>$P^\wedge-P_r^\wedge$</td>
<td>16.303</td>
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</table>
negligible and only the non-remanent capacitor can store the charges. Later, the charges stored in the non-remanent capacitor decay faster during the fall-time of the second pulse.

Based on these observations, the pulse polarization for a fatigued sample is drawn on the polarization vs. voltage plane as shown in Fig. 4.25. Continuous hysteresis after stress is also illustrated in this figure. Most of the trajectories are the same as those explained in Fig. 4.12. However, discharge during the second positive pulse's fall-time, portion FG, is greater than that during the first one's, portion CD. The final position, 100 ms after M, is slightly lower, 0.287 \( \mu \text{C/cm}^2 \), than the starting point B. This mismatch can be explained in the same way as in Fig. 4.12. Two consecutive negative pulses cause more negative polarization than a single negative pulse. However, the mismatch here, 0.287 \( \mu \text{C/cm}^2 \), is smaller than that of the fresh sample, 0.574 \( \mu \text{C/cm}^2 \) in Fig. 4.12. This supports the assumption that the switching process due to the second pulse can be ignored in the fatigued sample.

Fig. 4.24. Equivalent circuit model for a ferroelectric capacitor [50].
4.2.3 Retention

As defined earlier, retention refers to the loss of switchable charges under static conditions [48]. In this experiment, a retention test was conducted using the RT66A system with pulse sequences as shown in Fig. 4.26 [51].

At the beginning of the retention period, the RT66A system applies an 8.6 µs pulse with an amplitude of $V_{\text{write}}$ to a ferroelectric capacitor. Subsequently, the capacitor will remain shorted or open for a specified retention period ($T_{\text{retain}}$) depending on the user's selection. In most of the experiments here, a negative pulse was used for writing and the capacitor was left shorted during the retention period. At the end of the retention period, the test unit applies two read pulses of $V_{\text{read}}$ and $-V_{\text{read}}$. These pulses have the same shape as the pulses used in the pulse polarization measurement. At the top and bottom of the first pulse, charges $P^*$ and $P^*_r$ will be measured. If $V_{\text{write}}$ is a positive pulse, then these charges...
will be defined as $P^a$ and $P^r$. In the same fashion, the second read pulse will measure charges $-P^*$ and $-P^r$. By repeating the above procedures, the retention characteristics as a function of retention time can be obtained.

This test is limited to a 1nF capacitor due to use of an 8.6 $\mu$s writing pulse and the 1620 $\Omega$ output resistance of the RT66A system; a 1 nF capacitor has an RC time constant of 1.62 $\mu$s. Because the sample with top electrode annealing has a capacitance slightly larger than 1 nF, typically 1.5 nF, the retention test is performed on a capacitors without top electrode annealing, whose typical capacitance is 0.6 nF.

![Signal plot of retention test](image)

**Fig. 4.26.** Signal plot of retention test [51].

Fig. 4.27 shows the typical room-temperature retention of a ferroelectric capacitor without top-electrode annealing. The magnitude of write and read pulses is 6 V. The elapsed time means the absolute time from the beginning of each retention test in the consecutive retention tests.

Even though an experiment was made only up to 30,000 s, the life time can be expected from this results. In Fig. 4.27, polarization decays linearly with respect to the
logarithm of time. Therefore, decay rate of the polarization can be estimated using the relation of

$$P(t) = P_0 - R \log t,$$

where $P_0$ is the initial polarization and $R$ is the decay rate.

Because polarization decreases $\sim 0.5 \, \mu\text{C/cm}^2$ during 10,000 s, decay rate $R$ is 0.125 $\mu\text{C/cm}^2$/decade. From this result, the charge loss for 10 years, $3.2 \times 10^8$ s, can be estimated as only $1\mu\text{C/cm}^2$. Therefore, room-temperature retention is not a concern for ferroelectric memories.

Fig. 4.27. Room-temperature retention of unannealed top-electrode samples. Magnitude of write and read pulses is 6 V. Elapsed time is the absolute time from the beginning of each retention test.
CHAPTER 5

CURRENT VS. VOLTAGE CHARACTERISTICS OF A PZT THIN FILM CAPACITOR

In the last section, polarization measurement methods were explained. Polarization is one of the most important parameters for the ferroelectric memories. Most of the reliability concerns of the ferroelectric memories are related to the degradation of the polarization. Besides polarization, as a charge storage element in the memory cell, the leakage-current characteristics of the ferroelectric thin films are also important. However, only a few studies have been performed on the leakage-current characteristics [10, 27]. Further, these studies have not explained explicitly how to measure the leakage current. Because of the domain movement, the switching process should be considered in the current measurement. Therefore, it is necessary to establish a current measurement technique which can distinguish the leakage current from the switching current. In this chapter, a new method for measuring current-voltage characteristics of ferroelectric materials is introduced. For the development of this technique, the factors that affect the switching process of ferroelectric thin films are to be examined. Later, this static current measurement method is applied to characterizing ferroelectric thin films. Fatigue effects on PZT thin films are analyzed in terms of the changes in the static currents.

5.1 Review of the Switching Current

When an electric field is applied to ferroelectric thin films, a displacement current flows. From the relation of
\[ \varepsilon_0 F(t) + P(t) = D(t) \] \hspace{1cm} (5.1.1)

where \( F(t) \) is electric field, \( P(t) \) polarization, and \( D(t) \) displacement flux density, the displacement current density will be expressed as

\[ j(t) = \frac{dD(t)}{dt} = \varepsilon_0 \frac{dF(t)}{dt} + \frac{dP(t)}{dt}. \] \hspace{1cm} (5.1.2)

The first term on the right hand side is displacement current density due to charging the linear dielectric component of the ferroelectric materials. The second term is the current density due to the polarization reversal. If the direction of the applied electric field is the opposite to that of the initial polarization, the second term is generally much larger than the first term.

In general, the displacement current density due to the polarization reversal has an exponential shape with respect to time as [52]

\[ j(t) = 2P_s \frac{n+1}{t_0} \left( \frac{t}{t_0} \right)^n \exp \left[ -\left( \frac{t}{t_0} \right)^{n+1} \right]. \] \hspace{1cm} (5.1.3)

In this equation, \( t_0 \) is a time that a domain switches its direction and \( n \) is the dimensional constant. When the domain grows in three dimension, \( n \) will be 3. The detailed discussion on the switching process is given in Appendix B.

The displacement current of a ferroelectric capacitor is generally measured by means of a modified Sawyer-Tower circuit using a small (typically 10 ~ 10,000 \( \Omega \)) resistor in place of a linear capacitor as shown in Fig. 5.1 (a) [53]. The voltage across the resistor is proportional to the displacement current. Because of the hysteresis behavior, the transient responses to the same input signal are different for the different initial
polarization states. For the positive step voltage, the response of the initially negatively poled capacitor is defined as a full-switching current, while that of the initially positively poled capacitor is defined as a non-switching current as shown in Fig. 5.1 (b) [53].

Fig. 5.1. Switching current measurement method. (a) A modified Sawyer-Tower circuit. (b) A hysteresis curve and the definition of a full-switching and a non-switching current.

Fig. 5.2 shows the traditional full-switching and non-switching currents. The full-switching process occurs if a voltage applied to a ferroelectric capacitor reverses the polarization state. As the first or third pulse in the current-time plot in Fig. 5.2, the full-switching current consists of an initial spike due to charging the linear dielectric and a following humped curve due to switching the non-linear dielectric [53]. If no polarization reversal occurs during the second or the fourth pulse, only the transient current due to charging the linear dielectric flows.

Full-switching behaviors are generally characterized by a peak current $I_{\text{max}}$, the time $t_m$ at which $I_{\text{max}}$ occurs and a switching time $t_s$. The switching time $t_s$ is conveniently defined as the time when current has fallen to 1% of $I_{\text{max}}$. Most ferroelectric materials show less peak current and longer switching time as the switching field becomes smaller.
Fig. 5.2. Applied voltage (top) and resultant switching current (bottom) observed using a modified Sawyer-Tower circuit [53].

Fig. 5.3 shows the experimental full-switching and non-switching currents. These currents were measured using large capacitors without a heat-treatment after top electrode formation. Large capacitors are needed in order that the voltage across the small resistor (100 Ω in this experimental set-up) can be detectable. For this reason, the top electrodes of the capacitors were formed by sputtering platinum through a large area, 1.0x10^{-2} cm², shadow mask. After forming the top electrode, no heat-treatment was made for this sample. In spite of the asymmetric electrodes, the qualitative behaviors of the full- and the non-switching current are unaffected by this asymmetry. Process conditions will change the current density levels. However, because both the full- and non-switching
currents are measured by applying a positive voltage step to the top electrode with the bottom electrode grounded, they are dependent only on the polarization state, not on the process conditions.

To measure the full- or the non-switching current, a ± 6 V bipolar or a 0 to 6 V unipolar, 50 Hz, square wave was applied to the modified Sawyer-Tower circuit, respectively. In this experiment, because the bipolar square wave switches the capacitor immediately from \(-P_{\text{max}}\) (negative maximum polarization) to \(+P_{\text{max}}\), instead of from \(-P_{\text{r}}\) to \(+P_{\text{max}}\), the full-switching curve obtained here shows a larger initial spike than that seen in the traditional measurement [53]. The comparison of the experimental full-switching and non-switching current shows that switching with the complete polarization reversal takes longer than that with the partial polarization reversal. Both switching currents decay exponentially at the end of the switching process. Therefore, the initial polarization state and the exponential decay behavior of the switching current should be considered in the static current measurement.

![Graphs showing switching currents](image)

Fig. 5.3. Experimental switching currents of a PZT capacitor using a modified Sawyer-Tower circuit with a 100 Ω resistor. (a) Full-switching current obtained by a ± 6 V bipolar, 50 Hz, square wave. (b) Non-switching current obtained by a 0 to 6 V unipolar, 50 Hz, square wave.
5.2 Static I-V Measurement Method Set-Up

The waveforms for a static current measurement method using an HP4145A Semiconductor Parameter Analyzer are as shown in Fig. 5.4. The static current is defined as either the full-switching or non-switching static current, depending on the initial polarization state. Initializing the polarization state of a ferroelectric capacitor precedes the measurement of the static current. As shown in Fig. 5.4 (a), the full-switching static current is measured after setting the ferroelectric capacitor in a state of negative polarization. On the other hand, the capacitor remains in a state of positive polarization prior to a non-switching static current measurement, as shown in Fig. 5.4 (b). After initializing the polarization state, followed by a 22 s wait time, the static current is measured by applying a DC bias from 0 V to 6 V, increasing in 0.1 V steps. In this static current measurement set-up, the following parameters are important:

1) magnitude and duration of the poling voltage;
2) wait time, from the end of the poling voltage to the beginning of the current measurement;
3) delay time, between the application of each voltage step and the current measurement; and
4) integration mode of the measurement equipment.

The magnitude and the duration of the poling voltage determines the number of domains with a preferred orientation. In order to align the domains along a preferred orientation, a larger poling voltage (-6 V for full-switching and +6 V for non-switching) than the coercive voltage (1V) was applied for 10 s. During the wait time, some of the domains relax, or lock, into favorable energy configurations [53] and lose their initial orientations.
Fig. 5.4. Static current measurement method. (a) Full-switching static current measurement. (b) Non-switching static current measurement.
To stabilize the initial polarization state, a relatively long wait time (22 s) was used. At each voltage step, a delay time is inserted before measuring current in order to examine the exponential decay behavior of the switching current. After the delay time, current is measured in a long integration mode rather than a short integration mode. In the long integration mode, the current is the average value of 256 measurements over 267 ms. The short integration mode, which measures current directly without integration, usually results in an unstable I-V curve.

Fig. 5.5 shows the static current density vs. voltage curves for different delay times. In these I-V curves, at low voltage range, the full-switching static current is larger than the non-switching static current approximately by an order of magnitude for the same delay time. The difference between the full- and the non-switching static currents is smaller at higher voltage. Especially for 6 s delay time, shown in Fig. 5.5 (b), the non-switching static current is almost the same as the full-switching static current at 6 V.

The delay time effects on both static currents at low and high electric fields are shown in Fig. 5.6. At low voltage, 1V (18.5 kV/cm), the full-switching static current is much larger than the non-switching static current even for 100 s delay time. The relation between the full-switching static current and delay time \(t_d\) can be expressed empirically as

\[
J = 4.6 \times 10^{-7}(t_d)^{-1}. \tag{5.2.1}
\]

According to Eq. (5.1.3), the full-switching current must be related to the delay time exponentially. The discrepancy between the theoretical and the empirical relationship (exponential and inverse) may be attributed to the difference in time scale. Because the delay time (second order) is much larger than the switching time (micro-second order), the full-switching current measured in this experiment has only the
residual switching current component. Therefore, it can be represented using Eq. (5.2.1), rather than the exponential relationship.

The same slope in non-switching static current as full-switching static current indicates that switching current is the major component even in the non-switching static current at low electric field. Further, the smaller static current at the longer delay time is consistent with the exponential decay of the switching current. At high field, 6V (111 kV/cm), the switching current component is suppressed significantly even for a delay time of 2 s, resulting in the same level of full-switching and non-switching static currents. The continuous decrease of static currents in proportion to $t_d^{-0.9}$ shows that both static currents still include a switching current component for a delay time less than 10 s. As the delay time increases longer than 10 s, the leakage current becomes dominant.

These results suggest that non-switching static current with a long delay time is a good way to measure the leakage current. At high electric field, a relatively short delay time, such as 2 s, can measure the leakage current within an order of magnitude. However, at low electric field, quite a long delay time, longer than 100 s, is necessary to measure the leakage current alone.
Fig. 5.5. Comparison of the full- and the non-switching currents for different delay times. (a) 0 s. (b) 6 s.
Fig. 5.6. Delay time effect on the full-switching and the non-switching static currents. (a) At low voltage (1V or 18.5kV/cm). (b) At high voltage (6V or 111kV/cm).
5.3 Application of I-V Measurement to Examining Fatigue Effects

The fatigue effects on the PZT thin films were examined with the static current measurement methods described above. As stated before, a long delay time is required to eliminate the switching current component and to measure the leakage current alone. However, it takes an impractically long time to obtain an I-V curve. In the experiment described below, a compromised value of 2 s is used for a delay time to reduce the total measurement time. Even though a 2 s delay time is relatively short, non-switching current at high electric field can estimate the leakage current quite closely. At the same time, with this delay time, full-switching current at low electric field can give some insight on the switching characteristics.

Along with the static current measurements, the continuous hysteresis curve and the pulse polarization were measured using the virtual ground mode of an RT66A ferroelectric tester. The details of the pulse polarization were already discussed in Chapter 4.

Because the switching polarization ($P^*$) and the non-switching polarization ($P^n$) are measured under similar conditions to those used for measuring the full-switching and non-switching static current, respectively, the fatigue effects due to bipolar and unipolar stresses were analyzed in terms of these polarizations.

Fig. 5.7 shows typical changes in the pulse polarization due to bipolar ($\pm 8$ V) and unipolar (0 to 8 V) electrical cycling at 100 kHz. For these films, bipolar cycling decreases the switching polarization ($P^*$) rapidly after $10^8$ cycles and changes the shape of the hysteresis curve. In contrast to bipolar stress, no significant degradation in the polarization is observed for unipolar stress in these films. These results are consistent with the hysteresis loop changes due to bipolar and unipolar stresses shown in Chapter 4.
Fig. 5.7. Changes in the switching ($P^*$) and non-switching ($P^\perp$) polarization due to bipolar and unipolar stress.

The changes in the static currents after the bipolar stress ($\pm 8$ V, 100 kHz) up to $8.4 \times 10^9$ cycles are shown in Fig. 5.8. In the full-switching static current in Fig. 5.8 (a), the initial bipolar cycling increases the peak current and decreases the current at 6 V ($\sim 111$ kV/cm). The increase in the switching polarization in Fig. 5.7 and the peak current in Fig. 5.8 (a) after the initial bipolar cyclings indicate that the domain reorganization [49] activates some domains, otherwise unswitchable, to increase the number of domains in the switching process. Simultaneously, more domains switch at the lower electric field with the faster switching time. Therefore, the switching current increases at the low electric field and decreases at the high field. The further cycling reduces the number of the switching dipoles and decreases the switching current at low voltage. However, the increase of the current at high voltage shows that the film is degraded by the bipolar stress. The non-switching static current after $8.4 \times 10^9$ cycles in Fig. 5.8 (b) clearly shows leakage current increase. For convenience, the peak current density of the full-switching
static current and the non-switching static current at the maximum electric field are defined as \( J_{\text{peak}} \) and \( J_{@6V} \), respectively.

For the various bipolar cycling conditions, fatigue effects on the static currents are examined by correlating the changes in the switching polarization \( (\Delta P^*) \) with the changes in the key parameters of the static currents such as \( \Delta J_{\text{peak}} \) and \( \Delta J_{@6V} \). Fig. 5.9 (a) shows that the decrease in the switching polarization is strongly correlated with the decrease of the peak current in the full-switching static measurement. As shown in Fig. 5.9 (b), a larger decrease in the switching polarization generally accompanies the larger leakage current.

These experimental results suggest that the static I-V measurement method developed here is useful to characterize the ferroelectric thin films. From the full-switching static current, the changes in domain switching behaviors can be monitored. Further, from the non-switching static current, the leakage characteristics can be detected.
Fig. 5.8. I-V curves after the bipolar stress with a ± 8 V, 100 kHz square wave. (a) Full-switching static currents with a 2 s delay time. (b) Non-switching static currents with a 2 s delay time.
Fig. 5.9. Correlation of variations in static currents and pulse polarizations (a) $\Delta J_{\text{peak}}$ with $\Delta P^*$ and (b) $\Delta J_{@6V}$ with $\Delta P^*$. 
CHAPTER 6

MODELING OF A FERROELECTRIC THIN FILM CAPACITOR

In the previous chapter, the method for measuring static current flowing through a ferroelectric capacitor was discussed. It has been found that the static currents depend on the initial polarization states. This was simply interpreted in terms of domain switching behavior. In this chapter, to understand the characteristics of a metal-ferroelectric-metal (MFM) structure, a model for the MFM system is presented. The objective of the modeling is to develop an energy band structure which can explain the experimentally observed capacitance-voltage (C-V) and current-voltage (I-V) characteristics of a Pt-PZT-Pt capacitor.

6.1 Energy Band Diagram for Ferroelectric PZT Thin Films

6.1.1 PZT as a P-type Semiconductor

It has been reported that ferroelectric PZT thin films can be regarded as a wide band gap p-type semiconductor [54,55]. The energy band gap of PZT thin films with a Zr/Ti ratio of 40/60 was calculated to be 3.6 eV by assuming that PZT is a direct band gap material [56]. During high temperature sintering in an oxidizing atmosphere, some lead reacts with oxygen to produce volatile PbO. This reaction results in lead-loss and the formation of lead and oxygen vacancies [57]

\[ \text{Pb}_{\text{Pb}} + O_{\text{O}} \leftrightarrow \text{PbO} + V_{\text{Pb}}^{-2} + V_{\text{O}}^{2+}. \]  (6.1.1)
In the above notation, the main symbol (Pb, O, etc.) identifies the species, V represents a vacant site, the subscript indicates the lattice site involved, and the superscript is the local charge discrepancy relative to the ideal lattice. For instance, $V_{Pb}^{-2}$ means that lead with two positive charges, Pb$^{+2}$, is missing from its ideal site and this vacancy acts as if it had two negative charges. In addition to the above reaction, some of the oxygen vacancies can be filled and this creates two holes for each filled vacancy

$$V_{O}^{-2} + \frac{1}{2}O_{2} \leftrightarrow O_{O} + 2h.$$  \hspace{1cm} (6.1.2)

As the PZT thin film cools down toward room temperature, some holes may be trapped by the negatively charged lead vacancies as follows [7]

$$V_{Pb}^{-2} + 2h \leftrightarrow V_{Pb}.$$  \hspace{1cm} (6.1.3)

These lead vacancies can be acceptors and free holes will produce p-type conductivity in PZT thin films.

For a p-type semiconductor, the location of the Fermi level ($E_f$) can be found from the doping concentration ($N_A$) and the effective density of states in the valence band ($N_v$). The doping concentration of PZT films was estimated to be at a level of $1 \times 10^{18}$ cm$^{-3}$ by assuming that PZT has a constant relative permittivity of 400 [58]. Further, other ferroelectric materials, such as potassium tantalate ($K_TaO_3$) [59] or $BaTiO_3$ [60], were found to be in the range of $10^{18}$ to $10^{19}$ cm$^{-3}$. Even though the effective density of states in the valence band ($N_v$) of PZT thin films has not been reported, it can be estimated from that of other ferroelectric materials which have similar properties. For Barium Titanate ($BaTiO_3$), which has an energy band gap of 3.13 eV, the effective density of states in the
conduction band \((N_C)\) is known to be \(5 \times 10^{19} \text{ cm}^{-3}\) \([61]\). If \(p = N_A\), and \(N_v\) are \(1 \times 10^{18} \text{ cm}^{-3}\) and \(5 \times 10^{19} \text{ cm}^{-3}\), respectively, from

\[
p = N_A = N_v \exp \left( \frac{E_v - E_f}{kT} \right) \]

\[
E_f - E_v = kT \ln \left( \frac{N_v}{N_A} \right),
\]

(6.1.4)

the location of the Fermi level is 0.1 eV above the valence band.

Further, from

\[
n_i = \sqrt{N_C N_v} \exp \left( \frac{-E_v}{2kT} \right) \equiv N_v \exp \left( \frac{-E_v}{2kT} \right),
\]

(6.1.5)

the intrinsic carrier concentration will be \(3.5 \times 10^{-11} \text{ cm}^{-3}\). The low intrinsic carrier concentration means that intrinsic ferroelectric materials are more likely to be an insulator compared to a conventional semiconductor such as silicon.

### 6.1.2 Energy Band for an Unpolarized, Long PZT Capacitor

Fig. 6.1 shows an energy-band diagram of a platinum-PZT-platinum structure before the platinum electrodes make contact to both sides of the PZT thin film. As described earlier, the PZT thin film is assumed to be a p-type semiconductor with a doping concentration of \(1 \times 10^{18} \text{ cm}^{-3}\). For the sake of argument, the polarization state of the PZT thin films is not considered here. For convenience, the right platinum electrode is defined as the top and the left one as the bottom electrode.

In this figure, the energy band gap of PZT is assumed to be 3.5 eV. Further, the work function of PZT (\(q\Phi_{PZT}\)) is considered to be larger than that of platinum (\(q\Phi_m = 5.5\) eV). In other words, the electron affinity of PZT thin films (\(\chi_{PZT}\)) is assumed to be larger.
than 2.1 eV. However, because the electron affinity of PZT thin films ($q\chi_{\text{PZT}}$) is unknown, the possibility that the work function of PZT is smaller than that of platinum can not be excluded. If $q\chi_{\text{PZT}}$ is smaller than 2.1 eV, intimate contacts between PZT and platinum will form hole-accumulation layers at the PZT side of the contacts.

![Energy band diagram of a platinum-PZT-platinum structure before intimate contact](image)

Fig. 6.1. Energy band diagram of a platinum-PZT-platinum structure before intimate contact

If these hole-accumulation layers exist in PZT thin films having a doping concentration of $1 \times 10^{18} \text{ cm}^{-3}$, the current flowing through this PZT capacitor will be much larger than the current density level shown in the previous chapter. For example, from the current density equation for a sample dominated by ohmic conduction

$$ J = q \rho \mu_r F = qN_\delta \mu_r \frac{V}{d}, \quad (6.1.6) $$

the current density for this PZT film with a thickness ($d$) of 5000Å will be at least a few 1000 A/cm² at 1 V even if hole mobility ($\mu_r$) is only 1 cm²/V·sec. To the contrary, the
experimentally observed current density is less than $1 \times 10^{-6}$ A/cm$^2$ for non-switching static current. The current density will be small if the PZT has a very low carrier concentration. However, it is difficult to control the doping concentration to less than $1 \times 10^{15}$ cm$^{-3}$. Further, for BaTiO$_3$, the theoretical electron affinity was reported to be 2.52 eV [62]. As described above, the work function of PZT will be assumed to be larger than that of platinum.

![Energy band diagram for a Pt-unpolarized PZT-Pt structure after intimate contact. PZT thin film is assumed to be infinitely long.](image)

When the platinum electrodes make intimate contact to both sides of unpolarized PZT thin films, holes in the PZT will flow into the platinum electrodes, resulting in depletion layers adjacent to both electrodes. These depletion layers will make the Pt-PZT-Pt capacitor a back-to-back Schottky barrier system as shown in Fig. 6.2. If no polarization state is considered at this point, both sides of the contacts will have the same barrier
heights. This energy band diagram is obtained from the following three factors: constancy of Fermi level ($E_F$), continuity of the vacuum level, and constancy of electron affinity in PZT ($\chi_{\text{PZT}}$) without considering surface states [63].

In this diagram, the PZT film is assumed to be so thick that the depletion layers at both sides do not interact with each other. For the long capacitor, barrier height ($\Phi_B$) and built-in voltage ($V_{bi}$) will be

$$q\Phi_B = q(\chi_{\text{PZT}} + E_g - \Phi_m) \quad (6.1.7)$$

and

$$qV_{bi} = q(\Phi_{\text{PZT}} - \Phi_m). \quad (6.1.8)$$

6.1.3 Polarization Effects on the Energy Band Diagram

When platinum electrodes make intimate contacts with an unpolarized, infinitely long PZT film, the charge distribution in this symmetric back-to-back Schottky system is as shown in Fig. 6.3. The total negative fixed charges in the PZT ($-Q_{sc}$) are balanced with a sheet of holes ($+Q_m$) in adjacent metal electrodes.

If a positive voltage larger than the coercive voltage is applied to the top electrode with the bottom electrode at ground and the positive voltage is subsequently removed, dipoles in the PZT align along the electric field produced by the positive voltage and a spontaneous polarization is generated. Positive charges in the dipoles will direct towards the bottom electrode and negative charges towards the top electrode. The dipole movements will induce positive and negative sheet charge layers at the left (bottom electrode side) and the right (top electrode side) end of PZT thin film, respectively. Because the whole Pt-PZT-Pt system is short circuited, the spontaneous polarization must be canceled, or screened, to
make the net electric field of the whole system be zero [61]. For example, if a spontaneous polarization induces positive and negative ionic charge layers of $\pm 20 \, \mu C/cm^2$ at each end of the PZT thin film, the same amount of hole charge, corresponding to $1.25 \times 10^{14}$ holes/cm$^2$, will be depleted and accumulated at the bottom and the top electrode, respectively. The electric field produced by these holes, opposing the spontaneous polarization, is called a depolarization field [64]. In Fig. 6.4, the charge distributions when a spontaneous polarization in the PZT thin film is directed towards the bottom electrode (from right to left) are shown.

From the charge distribution shown in Fig. 6.4, it can be expected that ionic charges in the PZT thin film and the corresponding image charges in the metal electrodes change the potential distribution and produce different barrier heights at each Pt-PZT contact. Therefore, the current flow from top to bottom electrode is different from that flowing in the opposite direction. For the same reason, current levels in one direction also depend on the polarization state in PZT thin films.
Fig. 6.3. Charge distribution for a Pt-unpolarized PZT-Pt capacitor. PZT film is assumed to be infinitely long.

Fig. 6.4. Charge distribution in a Pt-polarized PZT-Pt system assuming that PZT is infinitely long.
6.2 Back-to-Back Schottky Barrier System

In the last section, it was shown that the polarization state in PZT thin films could produce a back-to-back Schottky barrier system with different barrier heights at each contact. These asymmetric barriers may explain the difference in non-switching and full-switching static currents observed in Chapter 5. In this section, the qualitative behavior of a back-to-back Schottky barrier system will be reviewed.

6.2.1 Infinitely Long Back-to-Back Schottky Barrier Structure

A study on a metal-semiconductor-metal (MSM) structure was performed by Sze in the early 70s [65]. This study focused on a symmetric barrier system with uniformly doped n-type semiconductor. In the discussion below, this previous study will be modified for an asymmetric barrier system with p-type semiconductor. An equilibrium energy-band diagram of an asymmetric MSM structure with uniformly doped p-type semiconductor is shown in Fig. 6.5.

![Equilibrium energy-band diagram of a metal-semiconductor-metal structure with uniformly doped p-type semiconductor.](image)

Fig. 6.5. Equilibrium energy-band diagram of a metal-semiconductor-metal structure with uniformly doped p-type semiconductor. Semiconductor is assumed to be infinitely long.
For convenience, consider that the barrier height of contact 1 (top electrode) is larger than that of contact 2 (bottom electrode). If a positive voltage is applied to the top electrode with the bottom electrode at ground, it makes contact 1 reverse-biased and widens the depletion layer near the top electrode. At the same time, contact 2 will be forward-biased and its depletion layer width will be reduced. In this analysis, the semiconductor is assumed to be infinitely long, so that the reverse-biased depletion region does not reach to the forward-biased depletion region.

A positive voltage \( V_A \) applied to the top electrode will be split into voltage drops across contact 1 \( V_1 \) and across contact 2 \( V_2 \). If thermionic emission is the dominant current transport mechanism in this system, hole currents flowing through contact 1 \( J_{p1} \) and contact 2 \( J_{p2} \) from right to left (direction from top to bottom electrode) are given by

\[
J_{p1} = A_p T^2 \exp\left(-\frac{q\Phi_{p1}}{kT}\right) \left[1 - \exp\left(-\frac{qV_1}{kT}\right)\right] \tag{6.2.1}
\]

\[
J_{p2} = A_p T^2 \exp\left(-\frac{q\Phi_{p2}}{kT}\right) \left[\exp\left(\frac{qV_2}{kT}\right) - 1\right]. \tag{6.2.2}
\]

Because these two currents must balance each other and the sum of the voltage drops across the contacts are the same as the applied voltage, \( V_1 \) and \( V_2 \) will satisfy the following relations

\[
\exp\left(-\frac{q\Phi_{p1}}{kT}\right) \left[1 - \exp\left(-\frac{qV_1}{kT}\right)\right] = \exp\left(-\frac{q\Phi_{p2}}{kT}\right) \left[\exp\left(\frac{qV_2}{kT}\right) - 1\right] \tag{6.2.3}
\]

\[
V = V_1 + V_2. \tag{6.2.4}
\]
From Eq (6.2.3), it can be expected that most of the voltage drop occurs at contact 1 because \( \Phi_{p1} \) is larger than \( \Phi_{p2} \). For example, if \( \Phi_{p1} \) is larger than \( \Phi_{p2} \) by only twice the thermal voltage (~50 mV), then

\[
\left[ 1 - \exp\left( -\frac{qV_1}{kT} \right) \right] = 7.4 \times \left[ \exp\left( \frac{qV_2}{kT} \right) - 1 \right].
\] (6.2.5)

If \( V_1 \) is 0.01 V, then \( V_2 \) will be only 0.0001 V. In other words, if a positive voltage is applied to the larger barrier height Schottky junction with the smaller barrier height junction grounded, almost all the voltage drop happens at the larger barrier junction.

On the other hand, suppose that a small positive voltage is applied to the bottom electrode (contact 2) with the top electrode (contact 1) at ground. Because contact 2 is reverse-biased and contact 1 is forward-biased, the hole currents from left to right (from the bottom to the top electrode) are given by

\[
J_{p1} = A_p^* T^2 \exp\left( -\frac{q\Phi_{p1}}{kT} \right) \left[ \exp\left( \frac{qV_1}{kT} \right) - 1 \right]
\] (6.2.6)

\[
J_{p2} = A_p^* T^2 \exp\left( -\frac{q\Phi_{p2}}{kT} \right) \left[ 1 - \exp\left( -\frac{qV_2}{kT} \right) \right].
\] (6.2.7)

Because \( \Phi_{p1} \) is larger than \( \Phi_{p2} \), it can be expected that \( V_1 \) increases more rapidly than \( V_2 \) does until \( V_1 \) reaches the value of \( \Phi_{p1} - \Phi_{p2} \). After \( V_1 \) reaches \( \Phi_{p1} - \Phi_{p2} \), most of the voltage drop occurs at contact 2. The voltage drops across contact 1 and 2 can be found by solving \( J_{p1} = J_{p2} \) numerically. Fig. 6.6 shows the numerically solved voltage drops when the barrier height of contact 1 is larger than that of contact 2 by 50 mV. As described before, the voltage drop across contact 1 remains the same after it reaches 53 mV, which is almost identical to \( \Phi_{p1} - \Phi_{p2} \).
Fig. 6.6. Voltage drops across contacts in an MSM structure when a positive bias is applied to contact 2 with contact 1 at ground. The barrier height of contact 1 is assumed to be larger than that of contact 2 by 50 mV.

These results indicate that the current through a MSM structure is determined by the reverse-biased junction saturation current. If a reverse-biased junction has larger barrier height than the forward-biased junction (a positive voltage to the top electrode here), almost all the voltage drops occur at the reverse-biased junction. However, if the barrier height of the reverse-biased junction is smaller than that of the forward-biased one (a positive voltage to the bottom electrode here), a portion of the voltage drop approximately equal to the difference between the two barrier heights occurs at the forward-biased junction and the rest of the voltage drop occurs at the reverse-biased junction. Therefore, the barrier height difference in an asymmetric MSM structure can be estimated by comparing the current flowing in one direction with that in the opposite direction.
6.2.2 Wholly Depleted Model

As a voltage applied to the back-to-back Schottky barrier structure with a finite thickness increases, the depletion layer of the reverse-biased junction becomes larger and it eventually reaches through to the forward-biased depletion layer. If the sample is quite thin, the depletion layers may spread out into each other at small voltage. For a ferroelectric material, this reach-through may happen at an even smaller voltage, or in equilibrium, because it has very high permittivity. In this section, the characteristics of a reach-through back-to-back Schottky barrier, or a wholly depleted, structure will be discussed. For convenience, it will be assumed that reach-through has already happened in equilibrium.

![Energy-band structures](image)

Fig. 6.7. Energy-band structures of the wholly depleted model (thick black line) and the infinitely long structure (thin gray line)

Fig. 6.7 shows equilibrium energy-band diagrams of the wholly depleted structure and the infinitely long back-to-back Schottky barrier structure. Here, once again, the top electrode (right side) is assumed to have a larger barrier height than that of the bottom electrode (left side). For the sake of comparison, it is further assumed that the infinitely
long sample and the wholly depleted sample have the same surface potential. As shown in this figure, the wholly depleted structure has smaller built-in hole barriers ($V_{i1}$ and $V_{i2}$ in this figure) and a less effective electron barrier ($\Phi_n$) than those of the infinitely long sample.

Fig. 6.8 (a) is an energy-band diagram when a small positive voltage is applied to the top electrode of the wholly depleted structure with the bottom electrode at ground. As the applied bias increases, the hole built-in voltage on the left (bottom electrode) side ($V_{i2}$) and the effective electron barrier height ($\Phi_n$) become smaller.

If the electron effective barrier is low, the electron injection from the bottom electrode is significant. However, as shown in Fig. 6.2, if the doping concentration is $1 \times 10^{18}$ cm$^{-3}$, the effective electron barrier height is 3.4 eV for the infinitely long sample. Even if it is reduced in the wholly depleted structure, it may be too large for electrons to surmount. Based on this, electron injection will not be taken into account in the analysis below.

As the applied voltage increases, the built-in voltage of the bottom electrode will disappear eventually as shown in Fig. 6.8 (b). This situation is generally called the flat-band condition [65]. If the voltage on the top electrode increases further beyond the flat-band voltage ($V_{FB}$), the energy barrier will becomes thinner and the tunneling of holes can be expected. More discussion on the current behavior of the Pt-PZT-Pt capacitor based on the back-to-back Schottky barrier system will be presented in the next section.
Fig. 6.8. Energy-band diagrams when a positive voltage is applied to the wholly depleted structure. (a) before flat-band. (b) at flat-band.
6.2.3 Experimental I-V vs. a Back-to-Back Schottky Barrier System

Before proceeding with further analysis of the back-to-back Schottky barrier system, we must consider whether the back-to-back Schottky barrier model can explain the experimental current-voltage characteristics of a Pt-PZT-Pt capacitor. In Fig. 6.9, non-switching and full-switching static current behaviors are shown in log-log scale. The same methods as described in Chapter 5 were used to measure these currents. To find the current behavior over a wider voltage range, the voltage was swept from 0 V to 12 V, increasing in 0.2 V steps. Delay time used for this measurement was 20 s to obtain more static behavior. The poling voltage before measuring the static currents is +6 V for non-switching and -6 V for full-switching, respectively.

![Current-voltage curves for a Pt-PZT-Pt capacitor. The curve with filled symbols was measured after negative (-6 V) poling. The other curve with hollow symbols was after positive (6 V) poling. Delay time used is 20 s.](image)

Fig. 6.9.
As shown in Fig. 6.9, the static current behavior can be divided into three different regions; the low voltage range less than coercive voltage (Region I), the medium voltage range (Region II), and the high voltage range (Region III). Below the coercive voltage (Region I), the full-switching static current is larger than the non-switching static current by an order of magnitude. Because the polarization reverses at the coercive voltage, full-switching static current gradually approaches the non-switching static current in Region II. Eventually, both currents are quite similar to each other in Region III.

The back-to-back Schottky barrier model can explain the static currents in Region II and III. The almost constant value of the non-switching static current in Region II can be explained by the reverse-biased junction saturation current. The rapid increase in Region III can be explained by the tunneling.

However, this model is not adequate to explain the current increase in the low voltage range shown in Fig. 6.9. When the barrier heights do not differ from each other significantly, no matter which electrode is chosen for applying voltage with the other at ground, almost all the voltage drop occurs at the reverse-biased junction. Once the voltage drop across the reverse-biased junction is larger than a few thermal-voltages, current becomes independent of the applied voltage. For instance, if the reverse-biased junction voltage drop is only 3 thermal-voltages (76 mV), the current will be already 95% of the saturation value.

\[ J_p = A_p \cdot T^2 \exp \left( -\frac{q\Phi_p}{kT} \right) \left[ 1 - \exp \left( -\frac{qV}{kT} \right) \right] \]

\[ = A_p \cdot T^2 \exp \left( -\frac{q\Phi_p}{kT} \right) \left[ 1 - \exp(-3) \right] = 0.95J_{ps} \]

where \( J_{ps} = A_p \cdot T^2 \exp \left( -\frac{q\Phi_e}{kT} \right) \).
Fig. 6.10. Full- and non-switching static currents measured with 100 s delay time.

The current increase in the low voltage range may be explained by the transient current effect. Fig. 6.10 shows the full-switching and non-switching static currents measured with 100 s delay time. With this long delay time, the current level of the non-switching static current in the voltage range up to 3 V is not distinguishable from the noise level. This observation indicates that the current increase in the low voltage range is mostly due to the switching current. Up to the coercive voltage, about 1 V, switching current increases as the applied voltage increases. Because most of the domain switching is completed by the time the coercive voltage is reached, switching current becomes negligible above the coercive voltage and the current remains at the level of the reverse saturation current of the back-to-back Schottky barrier system. If the current is determined by the reverse saturation current, it should be the same for different delay times. However, as shown in Fig. 5.5, the current in the voltage range between 1 V and 5 V also gets smaller as the delay time increases. It may be related to the barrier height increase due to charge variation. Above the coercive voltage, the charge distribution in the MFM system is as
shown in Fig. 6.4. If a positive voltage is applied to the top electrode longer, it will induce more negative charges near the top electrode side of the PZT film. In this way, the larger barrier height will be produced near the top electrode for the longer delay time, resulting in the reduction in the reverse saturation current.

The difference between non-switching and full-switching currents in the low voltage range (Region I in Fig. 6.9) is related to an increased transient switching current in the full-switching case. However, if the barrier height variation with respect to time is taken into account, this difference can be explained by the barrier height difference in an asymmetric back-to-back Schottky barrier structure. Because the spontaneous polarizations are in opposite directions, the energy-band diagrams for non-switching and full-switching conditions are mirror-images of each other. From the experimental result that full-switching static current is larger than non-switching static current, it can be expected that the energy-band for non-switching is the same shape as Fig. 6.5, while full-switching has a mirror-image structure. In other words, in the non-switching case, the barrier height near the top electrode is larger than that near the bottom electrode. In the full-switching case, the top electrode barrier height is smaller than the bottom electrode barrier height. If the difference between the full-switching and the non-switching static currents is determined by the barrier height difference, it should be the same amount. In contrast to this, the experimental results show that the full-switching and the non-switching static current in the low voltage range differ each other not by the same amount, but by an order of magnitude. As mentioned before, this can be explained by the barrier height variation with respect to time. When a positive voltage is applied to the top electrode with the other at ground, the rate of the negative charge accumulation inside PZT near the top electrode is the same regardless of the initial polarization state. Therefore, the barrier height difference between the non-switching and full-switching situations remains the same. Based on this, the barrier height difference in the asymmetric back-to-back Schottky barrier system can be estimated.
As mentioned before, from thermionic emission theory, the current through a back-to-back Schottky barrier structure is determined by the reverse-biased junction saturation current

\[ J_p = A_p e^{\frac{q\Phi_p}{kT}}. \]  

(6.2.9)

In the low voltage range less than 1 V, the full-switching static current is larger than the non-switching static current by an order of magnitude. Therefore, one barrier height is larger than the other by 60 mV because

\[ \exp\left(\frac{q(\Delta\Phi_p)}{kT}\right) = 10, \]

\[ \Delta\Phi_p = \frac{kT}{q}\ln10 \approx 60\text{mV}. \]  

(6.2.10)

In this way, the current level difference between non-switching and full-switching static currents can be explained using a back-to-back Schottky barrier structure having asymmetric barrier heights.
6.3 Numerical Analysis Method for a Wholly Depleted Structure

In the last section, a back-to-back Schottky barrier system was proposed as a model for a platinum-PZT-platinum capacitor. Further, the possibility of full depletion due to the finite thickness and the large permittivity of the ferroelectric film was considered. Except for the current behavior in the low voltage range, the wholly depleted model can explain qualitatively the experimental current behavior. The wholly depleted model can be applied to a capacitor with a finite thickness also. If the thickness of the capacitor is so thin that the capacitor is wholly depleted at relatively low voltage, the wholly depleted model can explain the characteristics of the capacitor in most of the voltage range. Therefore, for the sake of simplicity, a wholly depleted model will be considered first in the discussion below.

To examine the validity of the wholly depleted model, the capacitance-voltage (C-V) characteristics of this model will be predicted and compared with the experimental results. In this section, as a first step for predicting the C-V characteristics, the numerical analysis method for calculating potential and electric field distributions in the wholly depleted structure will be discussed.

6.3.1 C-V Characteristics of Non-constant Permittivity Materials

The capacitance of a back-to-back Schottky barrier system is given by a series combination of two Schottky barrier capacitors. If permittivity is constant regardless of electric field and the depletion layer widths of Schottky junctions are $d_1$ and $d_2$, the total capacitance is

$$\frac{1}{C} = \frac{d_1}{\varepsilon} + \frac{d_2}{\varepsilon}.$$  \hspace{1cm} (6.3.1)
In the wholly depleted structure, because the sum of the depletion layer widths is the same as the film thickness \(d\), the capacitance is constant as

\[
C = \frac{\varepsilon}{d}
\]

where \(C\) is the capacitance per unit area.

However, as shown in Fig. 6.11, constant capacitance was not observed in the experimental C-V curves. The experimental C-V measurements were taken at 1 kHz with an HP4192 LF Impedance Analyzer by applying a DC bias from -12 V to 12 V or vice versa, increasing in 0.4 V steps. The small signal-measurement voltage was 5 mV\(_\text{rms}\).

To explain the experimental results, the capacitance vs. voltage relation when the permittivity changes as a function of electric field will be investigated. For a back-to-back Schottky barrier system, whether it is an infinitely long or a wholly depleted system, the charge variation on the top electrode is balanced by the same but opposite polarity charge...
variation on the bottom electrode. If there is a charge of $\delta Q_s$ induced at the surface near the top electrode by a small-signal voltage of $\delta V_s$ applied to the top electrode, a charge of $-\delta Q_s$ will be induced at the surface near the bottom electrode. Therefore, the capacitance per unit area is

$$C = -\frac{\delta Q_s}{\delta V_s}. \quad (6.3.3)$$

From the relation between the surface charge ($Q_s$) and the displacement flux ($D_s$)

$$Q_s = D_s \cdot A, \quad (6.3.4)$$

capacitance will be

$$C = \left| \frac{\delta D_s}{\delta V_s} \right|. \quad (6.3.5)$$

Further, from the definition of small-signal permittivity

$$\varepsilon(F_s) = \frac{\delta D_s}{\delta F_s}, \quad (6.3.6)$$

where $F_s$ is the surface electric field,

the capacitance will be

$$C = \left| \frac{\delta D_s}{\delta V_s} \right| = \left| \frac{\delta D_s}{\delta F_s} \frac{\delta F_s}{\delta V_s} \right| = \varepsilon(F_s) \left| \frac{\delta F_s}{\delta V_s} \right|. \quad (6.3.7)$$

If the permittivity is constant and the surface electric field ($F_s$) is proportional to the applied voltage change ($V_s$), the capacitance will be constant as in Eq. (6.3.2). However, for materials with a field-dependent permittivity, the following two relationships must be found in order to predict the C-V characteristics:

1) permittivity as a function of the electric field; and

2) small-signal surface electric field variation at each applied voltage.
6.3.2 Permittivity of Ferroelectric Materials

Because most of the domain switching occurs at the coercive field \((F_c)\), the permittivity of ferroelectric materials will be very large in the neighborhood of the coercive field, and will have a much lower value everywhere else [58]. Therefore, the permittivity can be described by a Lorentzian function as

\[
\varepsilon(F) = \varepsilon_{\infty} + (\varepsilon_{\text{max}} - \varepsilon_{\infty}) \frac{1}{1 + \left( \frac{F \pm F_c}{F_0} \right)^2}.
\]  

In Eq. (6.3.8), \(\varepsilon_{\text{max}}\) is the maximum permittivity at the coercive field, \(\varepsilon_{\infty}\) is the saturation permittivity at large electric field, and \(F_0\) is a normalization field. If the normalization field \(F_0\) is quite small, it will become an asymptotic form of a delta function. The positive (+) and the negative (-) signs can be selected depending on the initial polarization state.

In order to determine the sign, consider the situation of sweeping the voltage of the top electrode from positive to negative polarity (for example, from +12 to -12 V) with the bottom electrode at ground.

As might be expected from the charge distributions in Fig. 6.3, the electric field inside the PZT film near the top electrode is in the negative direction. For this reason, suppose that the negative sign in Eq. (6.3.8) is adequate in the situation described above. Because the initially applied voltage is positive, a positive voltage can not change the polarization state. If a positive voltage is applied to the top electrode with the bottom electrode at ground, it produces a negative electric field due to positive charges on the metal side and negative ionic charges on the PZT side of the top electrode. Therefore, the polarity of the electric field inside the PZT film near top electrode will not be changed by a positive voltage on the top electrode. On the other hand, it will be changed if a large
negative voltage is applied on the top electrode. Therefore, the negative sign in Eq. (6.3.8) is the correct choice when sweeping the voltage on the top electrode from positive to the negative polarity.

6.3.3 Poisson's Equation for the Ferroelectric Thin Film

To predict the C-V characteristics of the wholly depleted structure, it is necessary to find the small-signal surface field variation at each bias condition. In order to do this, Poisson's equation for ferroelectric materials will be solved first to find the surface electric field \( F_s \) at each applied voltage \( V_s \). Once the relation between the surface electric field and applied voltage \( F_s \) vs. \( V_s \) is obtained, the small-signal surface electric field at each bias voltage can be found by differentiating this relation with respect to the applied voltage. In this section, Poisson's equation for the ferroelectric thin film will be introduced.

In Fig. 6.12, an energy-band diagram for the wholly depleted structure in equilibrium is shown once again. Before the flat-band voltage, the minimum hole energy position exists inside the film. At \( x = 0 \) in this figure, the hole energy will be minimum and the electric field (gradient of the energy band) will be zero. The potential can be defined with respect to the minimum energy position

\[
\phi(x) = -\frac{E_v(x) - E_v(0)}{q} = -\frac{E_c(x) - E_c(0)}{q} \quad (6.3.9)
\]

\[
0 \leq \phi(x) \leq \phi_{sb}.
\]

If the permittivity variation due to the electric field is considered, Poisson's equation will be

\[
e(F)dF = -\rho(\phi)d\phi. \quad (6.3.10)
\]
The electric field is related to the potential as

$$ F = -\frac{d\phi}{dx} \quad (6.3.11) $$

The derivation of the Poisson's equation for the non-constant permittivity materials, Eq. (6.3.10), is shown in detail in Appendix C.

The same Poisson’s equation as Eq. (6.3.10) is applicable to the infinitely long sample. In this case, the minimum hole energy $E_v(0)$ will be located at the same energy level as the valence band in the bulk of the infinitely long sample.

If the depletion approximation is employed, the charge density is simply expressed by a doping concentration of the ferroelectric material

$$ \rho(x) = q[p(x) - n(x) - N_A] \equiv -qN_A. \quad (6.3.12) $$
Therefore, Poisson's equation will be

$$\varepsilon(F)FdF = qN_A d\phi$$

where

$$\varepsilon(F) = \varepsilon_\infty + (\varepsilon_{\text{max}} - \varepsilon_\infty) \frac{1}{1 + \left[ \frac{F - F_c}{F_0} \right]^2}. \quad (6.3.13)$$

Because both the electric field and potential are zero at $x = 0$, at the arbitrary position

$$\int_0^F \left( \varepsilon_\infty + (\varepsilon_{\text{max}} - \varepsilon_\infty) \frac{1}{1 + \left[ \frac{F - F_c}{F_0} \right]^2} \right) FdF = \int_0^\phi qN_A d\phi. \quad (6.3.14)$$

The calculation of the left hand side of Eq. (6.3.14) is given below and, for convenience, it will be called the field function $H(F)$

$$H(F) = \frac{1}{2} \varepsilon_\infty F^2 + F_c F_0 (\varepsilon_{\text{max}} - \varepsilon_\infty) \left\{ \tan^{-1} \left( \frac{F - F_c}{F_0} \right) + \tan^{-1} \left( \frac{F_c}{F_0} \right) \right\}$$

$$+ \frac{1}{2} (\varepsilon_{\text{max}} - \varepsilon_\infty) F_0^2 \ln \left( \frac{F_0^2 + (F - F_c)^2}{F_0^2 + F_c^2} \right). \quad (6.3.15)$$

Because of the truncation error when calculating the arc-tangent function in $H(F)$, the field function expressed in the above form has very small negative values at low electric field. Because the integrand in the field function is greater than zero for positive electric field and negative for negative field, the field function is always larger than zero. To avoid this problem, a Taylor expansion is employed when the magnitude of
the electric field is smaller than 0.5% of that of the coercive field. In this low electric field range, the field function used is

\[ H(F) = \frac{1}{2} \varepsilon_{\infty} F^2 + \frac{1}{2} \left( \frac{\varepsilon_{\text{max}} - \varepsilon_{\infty}}{2} \right) F^2 \left( 1 + \left( \frac{F_c}{F_0} \right)^2 \right). \]  

(6.3.16)

The detailed calculation for \( H(F) \), both complete and Taylor expansion forms, is shown in Appendix C. In Fig. 6.13, the complete (Eq. (6.3.15)) and Taylor expansion (Eq. (6.3.16)) forms of the field function are compared each other. It clearly shows that Taylor expansion is needed at low electric field range.

Fig. 6.13. Comparison between the complete and the Taylor expansion form of the field function at the electric field much less than the coercive field (24 kV/cm in this calculation).
Using the field function, Eq. (6.3.14) will be

\[ H(F) = qN_A \phi. \]  

(6.3.17)

Therefore, the potential and corresponding electric field can be found by solving Eq. (6.3.17). If a surface potential is given as a boundary condition, after dividing potential in many steps from zero to the surface potential, electric field \( F_i \) at each potential \( \phi_i \) can be found. After finding potential \( \phi_i \) at each field \( F_i \), from the relation

\[ F = -\frac{d\phi}{dx} = \frac{\Delta \phi}{\Delta x}, \]  

(6.3.18)

the position can be found

\[ x_i = x_{i-1} - \frac{(\phi_i - \phi_{i-1})}{\frac{1}{2}(F_i + F_{i-1})} \]  

(6.3.19)

where \( x_0 = 0, F_0 = 0, \) and \( \phi_0 = 0. \)

In this equation, the mid-point value is used for electric field.

However, due to the complexity of the field function, it is easier to find a potential at a given electric field than vice versa. Therefore, instead of varying potential, the potential at each electric field is calculated by changing the field from zero to the surface field. Because the surface potential, rather than the surface field, is generally given as a boundary condition, the step-size of the electric field is carefully selected. In other words, as the potential gets closer to the surface potential, the step-size of the electric field is reduced to 1 V/cm to make the final potential within 0.5 mV error of the given surface potential.
6.3.4 Potential Profile Calculation Method for Equilibrium

In this section, the procedures for finding the potential distribution in equilibrium will be explained conceptually. As shown in Fig. 6.14, a back-to-back Schottky barrier system will be an infinitely long model or a wholly depleted model depending on the device parameters, such as sample thickness, doping concentration, and surface potentials etc. If these parameters are given and the permittivity function (permittivity vs. electric field) is known, the potential profile can be obtained by solving Poission's equation (Eq. (6.3.17)) numerically.

![Diagram of a back-to-back Schottky barrier system](image)

Fig. 6.14. Potential profile in a back-to-back Schottky barrier system for various film thicknesses.
As shown in this figure, for given barrier heights ($\Phi_{BR}$ and $\Phi_{BL}$) and doping concentration ($N_A$), if a surface potential on the right side ($\phi_{SR,i}$) is chosen, the film thickness corresponding to this potential ($a_i$) can be calculated using Eqs. (6.3.17), (6.3.18) and (6.3.19). Further using the following relation

$$\phi_{SL,i} = |\Phi_{BR}| - |\Phi_{BL}| - \phi_{SR,i},$$  \hspace{1cm} (6.3.20)

the surface potential on the left side and the corresponding film thickness ($b_i$) can be obtained. If the sum of $a_i$ and $b_i$ is the same as the film thickness, the calculated potentials are the solutions for the given conditions.

In the next two sections, more detailed procedures for finding potential distributions are presented. Especially, the procedures when bias is applied are considered in these sections.

6.3.5 Potential Profile Calculation before Flat-Band

As mentioned previously, there is a zero-field, or minimum hole energy, position in the wholly depleted structure before flat-band occurs. Fig. 6.15 shows the quantities used to find the potential distribution before flat-band. In this section, the algorithm for finding the potential profile will be explained step by step. These procedures are shown as a flow-chart in Fig. 6.16.
Fig. 6.15. Algorithm for finding potential distribution in wholly depleted structure before flat-band. (a) Overall algorithm. (b) Method for finding surface electric field when zero-electric field position is given.
Step 1;

As given conditions, the barrier heights at the top and bottom electrodes ($\Phi_{BR}$ and $\Phi_{BL}$), the doping concentration ($N_A$), and the film thickness ($d$) are assumed to be known. The procedures for determining barrier heights $\Phi_{BR}$ and $\Phi_{BL}$ will be described in section 6.4. If a voltage $V_A$ (larger than negative flat-band voltage and less than positive flat-band voltage) is applied to the top electrode, it will be simply assumed that this voltage changes the top electrode barrier height from $\Phi_{BR}$ to $\Phi_{BR} + V_A$ as shown in Fig. 6.15 (a).

Step 2;

Select the zero-electric field position arbitrarily. Assume the initial guess of the zero-electric field position is located at a distance of $a_i$ from the top electrode as shown in Fig. 6.15 (a).

Step 3;

As shown in Fig. 6.15 (b), the potential distribution from zero-electric field to the top electrode satisfying the arbitrary chosen $a_i$ can be found by iteration. As an initial guess, suppose the top electrode surface potential as $\phi_{SR,i}$. Using Eq. (6.3.17), find potentials by increasing electric field until the potential is the same as the guessed surface potential $\phi_{SR,i}$.

After finding the potential at each electric field, calculate the distance $a_i$ using Eq. (6.3.19). If the distance $a_i$ is smaller than the arbitrarily chosen distance $a_i$ as shown in Fig. 6.15 (b), increase the surface potential near the top electrode. If the distance is larger, decrease the surface potential. By repeating these procedures, the surface potential ($\phi_{SR,i}$) corresponding to the chosen zero-field position ($a_i$) can be found.
Step 4;

If the surface potential near the top electrode ($\phi_{SR,i}$) is known, the surface potential near bottom electrode ($\phi_{SL,i}$) can be found from

$$\phi_{SL,i} = (|\Phi_{BR} - V_A|^2 |\Phi_{BL}|) - \phi_{SR,i}. \quad (6.3.21)$$

Step 5;

Using the same procedures as described earlier, the potential distribution from zero-electric field to the bottom electrode can be found by changing electric field. From the potential and electric field values, the distance ($b_i$) from the zero-electric field point to the bottom electrode can be found.

Step 6;

If the summation of the distances, $a_i + b_i$, is the same the film thickness $d$, the potential and electric field distributions found in the previous steps are the correct solutions satisfying the conditions given in step 1. If $a_i + b_i$ is different from $d$, then choose a new zero-electric field position $a_i$ and repeat step 3 and afterwards until $a_i + b_i$ is equal to $d$. As shown in Fig. 6.14 (a), if $a_i + b_i$ is larger than $d$, then the new $a_i$ will be smaller than the previous value. If $a_i + b_i$ is smaller than $d$, then the new $a_i$ will be larger than the previous value.

These procedures can be used when the voltage on the top electrode is negative, but smaller than the flat-band voltage in magnitude. In Fig. 6.15, the flow-chart of the algorithm before flat-band is shown. In Appendix D, the computer program is listed.
Given Parameters
• Barrier heights; $\Phi_{BR}$, $\Phi_{BL}$
• Doping concentration $N_A$
• Film thickness $d$

Choose initial distance from zero-field position to top electrode $a_i$

Find top electrode surface potential $\phi_{sR,i}$ corresponding to chosen zero-field position by iteration

Calculate bottom electrode surface potential using
$$\phi_{sL,i} = (\Phi_{BR} - N_A \Phi_{BL}) - \phi_{sR,i}$$

Calculate distance from zero-field position to bottom electrode $b_i$

Compare with film thickness $d$

If $a_i + b_i > d$, choose smaller $a_i$
If $a_i + b_i < d$, choose larger $a_i$

STOP

Fig. 6.16. Flow-chart for calculating potential distribution before flat-band.
6.3.6 Potential Profile Calculation After Flat-Band

When the applied voltage is larger than the flat-band voltage (or smaller than the negative flat-band voltage), no zero-electric field position exists in the film. For convenience, the case of applying positive voltage as shown in Fig. 6.17 will be discussed first.

![Diagram of potential profile](image)

Fig. 6.17. Algorithm for finding potential distribution in the wholly depleted model after flat-band (Positive voltage larger than flat-band voltage).

If the electric field and the potential on the bottom electrode are assumed to be $F_L$ and zero, respectively, Poisson's equation will be

$$\int_{F_L}^{F} F e(F) dF = qN_A \phi.$$  \hspace{1cm} (6.3.22)
Therefore, using the field function $H(F)$, Poisson's equation will be expressed as

$$H(F) = qN_A \phi + H(F_L). \quad (6.3.23)$$

In Fig. 6.16, the potential drop across the film is

$$\Delta \phi = V_a + (|\Phi_{BR}| - |\Phi_{BL}|). \quad (6.3.24)$$

Therefore, the surface field near the top electrode $F_R$ must satisfy

$$\int_{F_L}^{F_R} F \epsilon(F) dF = H(F_R) - H(F_L) = qN_A \Delta \phi = qN_A (V_a + |\Phi_{BR}| - |\Phi_{BL}|). \quad (6.3.25)$$

Based on these relations, the algorithms for finding potential and electric field distributions when the applied positive voltage is larger than the flat-band voltage can be described as follows.

**Step 1:**

Assume the left-side (bottom electrode) surface electric field $F_{L,i}$.

**Step 2:**

Calculate potential at each electric field using Eq (6.3.23), by increasing electric field until the right-side (top electrode) surface field satisfies Eq. (6.3.25).

**Step 3:**

Calculate distance using

$$x_i = x_{i-1} - \frac{(\phi_i - \phi_{i-1})}{\frac{1}{2}(F_i + F_{i-1})} \quad (6.3.26)$$

where $x_0 = 0$, $F_0 = F_L$, and $\phi_0 = 0$.

and compare with the film thickness $d$.

**Step 4:**

If the calculated thickness is smaller than the film thickness, decrease the
magnitude of the left-side field $F_{L,i}$. If larger, increase the magnitude of $F_{L,i}$. Then, repeat step 1 to 3 until calculated thickness is equal to the film thickness.

In Fig. 6.18, the flow-chart of the algorithm described above is shown. In Appendix E, the computer program is listed.

---

**Fig. 6.18.** Flow-chart for calculating potential distribution after flat-band (positive voltage case).
If the voltage on the top electrode is negative and large enough in magnitude to cause flat-band as shown in Fig. 6.19, it is convenient to assume that the right-side (top electrode) surface field is $F_R$ and the right-side potential is zero. In this case, the same procedures used for the positive voltage case can be used with the following equations.

\[
\int_{F_R}^{F} \! F \epsilon(F) dF = qN_A \phi \tag{6.3.27}
\]

\[
H(F) = qN_A \phi + H(F_R) \tag{6.3.28}
\]

\[
\Delta \phi = (|V_A| - |\Phi_{BR}|) + |\Phi_{BL}| \tag{6.3.29}
\]

\[
\int_{F_L}^{F_R} \! F \epsilon(F) dF = qN_A \Delta \phi = qN_A (V_a + |\Phi_{BR}| - |\Phi_{BL}|) \tag{6.3.30}
\]

Fig. 6.19. Algorithm for finding potential distribution when the voltage on the top electrode is negative and is larger than flat-band voltage in magnitude.
If the voltage on the top electrode is larger than the coercive voltage in magnitude, it will change the polarization state. In order to take into account polarization reversal, once the top electrode surface electric field, which is negative in equilibrium, becomes the same as the positive coercive electric field, the barrier heights on both sides are switched with each other. In other words, the top electrode barrier height changes to $\Phi_{BL}$ and the bottom electrode's changes to $\Phi_{BR}$. 
6.4 Numerical Analysis for C-V Characteristics

In the last section, a numerical method for finding the potential and the electric field distributions in a wholly depleted ferroelectric capacitor was explained. In this section, using numerical analysis, potential and field profiles will be found. Further, based on these numerical results, C-V characteristics will be predicted and compared with the experimental results.

6.4.1 Barrier Height Calculation from I-V Characteristics

When solving Poisson's equation, barrier heights on both top and bottom electrode were considered to be given parameters. Here, it will be discussed how to determine barrier heights. In the previous analysis, the difference between the two Schottky barrier heights was found to be 60 mV. Therefore, if one barrier height is known, the other can be found.

In a back-to-back Schottky barrier system, current is mainly determined by the reverse-biased current. Further, if the voltage drop across the reverse-biased junction is larger than a few thermal voltages \(kT\), the current is almost the same as the reverse saturation current.

\[
J = A^* T^2 \exp \left( - \frac{q \Phi_B}{kT} \right) \left[ 1 - \exp \left( - \frac{q V_R}{kT} \right) \right]
\]

\[
= A^* T^2 \exp \left( - \frac{q \Phi_B}{kT} \right) = J_s \quad \text{(if \( V_R \gg \frac{kT}{q} \)).}
\]

(6.4.1)

Therefore, by measuring current densities at different temperatures, the barrier height of the reverse-biased junction can be found. In Fig. 6.20, the non-switching static current-voltage curves at different temperatures ranging from room-temperature to 200 °C are shown.
In this figure, the I-V curves at room-temperature and 40°C are almost identical to each other. The delay time used for these measurements was 20 s. Because the reverse-biased barrier is larger than the forward-biased barrier in the non-switching condition, the magnitude of the larger barrier can be estimated.

Using these I-V characteristics, $J / T^2$ vs. $1 / T$ for different voltages are plotted as shown in Fig. 6.21. In the low temperature range (from room-temperature to 80 °C), the barrier height can not be obtained because the data are scattered. In elevated temperatures from 80 to 160 °C, the barrier height ranges from 0.3 to 0.6 eV. The data points at 12 V show that $J / T^2$ changes from $1 \times 10^{-14}$ to $4 \times 10^{-10}$ when $1 / T$ changes by $1.5 \times 10^{-3}$. 

Fig. 6.20. Non-switching static current vs. voltage curves at different temperatures.
Therefore, from

\[
\ln \left[ \frac{J}{T^2} \right] = \ln A^* - \frac{q\Phi_B}{kT}
\]

and

\[
\ln \left[ \Delta \left( \frac{J}{T^2} \right) \right] = -\frac{q\Phi_B}{k} \left[ \Delta \left( \frac{1}{T} \right) \right],
\]

(6.4.2)

\[
\Phi_B = \frac{8.617 \times 10^{-5} \text{eV}}{e} \times \frac{\ln(4 \times 10^4)}{1.5 \times 10^{-3}} = 0.61 \text{ V}.
\]

(6.4.3)

The data points at 0.2 V do not have a constant slope in the temperature range between 80 and 160°C. If the two data point at 125 and 160°C are used, the barrier height is

\[
\Phi_B = \frac{8.617 \times 10^{-5} \text{eV}}{e} \times \frac{\ln(10)}{0.7 \times 10^{-3}} = 0.28 \text{ V}.
\]

(6.4.4)

At temperatures higher than 160 °C, the slope of \( J / T^2 \) vs. \( 1 / T \) becomes steeper.

Fig. 6.21. \( J / T^2 \) vs. \( 1 / T \) plot from non-switching currents in Fig. 6.20.
In section 6.2.3, room-temperature I-V characteristics were explained by the reverse saturation current in the low voltage range and by tunneling in the high voltage range. Current-voltage behaviors at different temperatures can be described on the same basis. Randomly scattered data at low temperatures in Fig. 6.20 indicate that thermionic emission is not the main contribution to the current conduction. As temperature increases, thermionic emission becomes important. Larger current at high voltage in all the temperature ranges can be attributed to the tunneling effect. A rapid increase in current due to thermionic process can be expected at even higher temperatures (higher than 160 °C), resulting in a steeper slope in the $J / T^2$ vs. $1 / T$ plot.

Because the barrier height is significantly affected by temperature and bias conditions, it is difficult to choose a specific value. In the numerical analysis below, the magnitude of the larger barrier will be considered to be from 0.3 to 0.6 eV.

### 6.4.2 Permittivity Calculation

In order to solve Poisson's equation, the parameters in the permittivity function, $\varepsilon_\infty$, $\varepsilon_{\text{max}}$, $F_c$ and $F_0$ must be known. From Eqs. (6.3.7) and (6.3.8), the capacitance will be

$$C(V_s) = \left| \varepsilon_\infty \frac{\delta F}{\delta V_s} + (\varepsilon_{\text{max}} - \varepsilon_\infty) \frac{1}{1 + \left( \frac{F_s - F_c}{F_0} \right)^2} \frac{\delta F}{\delta V_s} \right|. \quad (6.4.5)$$
If a surface electric field $F_s$ can be represented as a function of an applied voltage $V_s$, Eq. (6.4.5) will be

$$\varepsilon(V_s) = \left. \frac{C(V_s)}{\delta F_s} \right|_{\delta V_s} = \varepsilon_\infty + (\varepsilon_{\max} - \varepsilon_\infty) \frac{1}{1 + \left( \frac{F_s(V_s) - F_c}{F_0} \right)^2}. \tag{6.4.6}$$

Therefore, the parameters in the permittivity function can be found by fitting the $C(V_s)$ curve divided by $|\delta F_s / \delta V_s|.$

In section 6.3.1, C-V curves measured using an HP4192 LF Impedance Analyzer were shown. However, as expressed in Eq. (6.3.5), the derivative of the displacement flux with respect to a voltage is a more appropriate definition of the capacitance. Because the hysteresis curve measured in this experiment is actually the displacement vs. voltage, its derivative with respect to the voltage will be used as a C-V curve in the next discussion.

As a first approximation, assume that the surface electric field is proportional to the applied voltage like a normal dielectric

$$F_s = K_f V_s + F_{s,0} \tag{6.4.7}$$

where $F_{s,0}$ is the surface electric field at 0 V.

Then

$$\varepsilon(V_s) = \left. \frac{C(V_s)}{|K_f|} \right|_{V_s} = \varepsilon_\infty + (\varepsilon_{\max} - \varepsilon_\infty) \frac{1}{1 + \left( \frac{K_f V_s + F_{s,0} - F_c}{F_0} \right)^2}. \tag{6.4.8}$$

Therefore,

$$\varepsilon(V_s) = \left. \frac{C(V_s)}{|K_f|} \right|_{V_s} = \varepsilon_\infty + (\varepsilon_{\max} - \varepsilon_\infty) \frac{1}{1 + \left( \frac{V_s + V_c}{V_0} \right)^2} \tag{6.4.9}$$

where

$$V_c = \frac{F_{s,0} - F_c}{K_f} \quad \text{and} \quad V_0 = \frac{F_0}{K_f}.$$
Further, assume that the absolute value of a constant $K_f$ is the same as the inverse of the film thickness

$$K_f = -\frac{1}{d}.$$  \hfill (6.4.10)

Then, dividing the derivative of the hysteresis loop by $|K_f|$ (1/5400 Å in this film), $\varepsilon(V_s)$ can be obtained as shown in Fig. 6.22. By doing curve-fitting, it has been found that the permittivity function can be represented in the overall voltage range with a relation of

$$\varepsilon(V_s) = 380\varepsilon_0 + \frac{(8530\varepsilon_0 - 380\varepsilon_0)}{1 + \left(\frac{V_s + 1.3}{1.4}\right)^2}.$$  \hfill (6.4.11)

---

**Fig. 6.22.** Curve fitting for relative permittivity. Open circle is the derivative of the hysteresis loop multiplied by the film thickness.
Therefore,

\[ \varepsilon_{\infty} = 380\varepsilon_0, \]
\[ \varepsilon_{\text{max}} = 8530\varepsilon_0, \]
\[ V_c = \frac{F_{s,0} - F_c}{1K_f 1} = \frac{F_{s,0} - F_c}{1/5400\text{A}} = 1.3, \]

and

\[ V_0 = \frac{F_0}{1K_f 1} = \frac{F_0}{1/5400\text{A}} = 1.4 \]

For simplicity, if the zero-volt electric field \( F_{s,0} \) and the coercive field \( F_c \) are assumed to be the same as each other in magnitude, then

\[ F_c = -F_{s,0} = \frac{1.3}{5400\text{A}} \times \frac{1}{2} = 12.04\text{kV/cm} \]

and the normalization field \( F_0 \) will be

\[ F_0 = \frac{1.4}{5400\text{A}} = 25.93\text{kV/cm}. \]

With these parameters, the initial guess of the permittivity function will be

\[ \varepsilon(F_s) = 380\varepsilon_0 + (8530\varepsilon_0 - 380\varepsilon_0) \frac{1}{1+\left(\frac{F_s-10.03}{25.93}\right)^2} \quad (6.4.12) \]

where the unit of \( F_s \) is kV/cm.

### 6.4.3 Numerical Analysis for Equilibrium

In the last two sub-sections, the barrier height calculation and parameter fitting for the permittivity function were performed. The barrier height at moderately high temperatures was found to be from 0.3 eV to 0.6 eV. In the first numerical analysis, the top
electrode barrier height is chosen as 0.3 eV. In the non-switching case, the barrier height of the bottom electrode is smaller than that of the top electrode by 60 meV, so the bottom electrode barrier is chosen as 0.24 eV. With these barrier heights and the permittivity function of Eq. (6.4.12), numerical analyses are performed using the algorithms described in section 6.3.

In Fig. 6.23 and 6.24, the equilibrium potential and electric field distributions of PZT films with doping concentrations of $1 \times 10^{18}$ and $1 \times 10^{19}$ cm$^{-3}$ are shown, respectively. The wholly depleted profile is obtained for the doping concentration of $1 \times 10^{18}$ cm$^{-3}$ as shown in Fig. 6.23 (a). In this wholly depleted case, the surface potentials near the top and bottom electrodes are found to be 0.128 and 0.068 V, respectively. The zero-electric field position is located 3030 Å from the top electrode. As shown in Fig. 6.23 (b), the electric field is almost uniformly distributed in the PZT film. The surface electric field near the top electrode is -8.84 kV/cm, which is quite close to the initial guess of -12.04 kV/cm. For the doping concentration of $1 \times 10^{19}$ cm$^{-3}$, the film is no longer wholly depleted as shown in Fig. 6.24. Further numerical analyses show that the PZT film is not wholly depleted even at large bias (such as 12 V) with this doping concentration. In the next two sub-sections, the C-V characteristics for doping concentrations of $1 \times 10^{18}$ and $1 \times 10^{19}$ cm$^{-3}$ will be calculated and compared with the experimental C-V curve. For a doping concentration of $1 \times 10^{18}$ cm$^{-3}$, the capacitance will be calculated using a numerical method for the wholly depleted model described in section 6.3. For a doping concentration of $1 \times 10^{19}$ cm$^{-3}$, the numerical method in section 6.3 will be modified slightly to calculate the C-V characteristics for an infinitely long sample.
Fig. 6.23. (a) Potential and (b) electric field distribution for \( N_A = 1 \times 10^{18} \text{ cm}^{-3} \).
Fig. 6.24. (a) Potential and (b) electric field distribution for $N_A=1\times 10^{19}$ cm$^{-3}$.
6.4.4 C-V Prediction for a Wholly Depleted Structure

The C-V characteristics are calculated for a PZT film having a doping concentration of $1 \times 10^{18}$ cm$^{-3}$ and a permittivity expressed as Eq. (6.4.12). With these device parameters, the PZT thin film was found to be wholly depleted, even in equilibrium. If a smaller permittivity is used, a doping concentration less than $1 \times 10^{18}$ cm$^{-3}$ is needed to make the film wholly depleted. In the previous analysis, however, the top electrode barrier height was chosen as the lowest value (0.3 eV) in its possible range (0.3 to 0.6 eV). If a larger barrier height is selected, the film will be more depleted. Therefore, it can be concluded that the wholly depleted model holds for the given device parameters such as a doping concentration of $1 \times 10^{18}$ cm$^{-3}$ and the maximum relative permittivity of ~8000.

To find the C-V characteristics, the small-signal surface electric field variation at each applied voltage was calculated first. Fig. 6.25 shows the top electrode surface electric field for bias voltages from -12 to 12V.

![Fig. 6.25. Surface electric field for different voltages obtained by the numerical analysis (open circle) and its curve fitting.](image)
This surface field vs. voltage curve can be considered as superimposing a Lorentzian function with a relatively large normalization constant on the linear function as

\[ F_s [\text{kV/cm}] = -18.7V_s - 109 + \frac{103}{1 + \left( \frac{V_s + 1.2}{6} \right)^2}. \]  

(6.4.13)

This result indicates that the surface electric field responds to the applied voltage quite linearly at large voltages, like a normal dielectric. At low voltages, the switching process produces a non-linear effect as the third term in Eq. (6.4.13). Especially, the coefficient of the linear term \(18.7 \times 10^3 \text{fcm}\) is almost the same as the inverse of the thickness \(1/5400 \text{Å} = 18.5 \times 10^3 \text{fcm}\).

By differentiating this relation, the small-signal variation of the surface electric field with respect to voltage can be obtained as

\[ \frac{\delta F_s}{\delta V_s} [10^3/\text{cm}] = -18.7 - 103 \times \frac{2 \left( \frac{V_s + 1.2}{6} \right) \frac{1}{6}}{\left[ 1 + \left( \frac{V_s + 1.2}{6} \right)^2 \right]^2}. \]  

(6.4.14)

Finally, using Eq. (6.3.7), the C-V curve is obtained as shown in Fig. 6.24. The numerically predicted C-V curve is quite close to the C-V curve obtained from the hysteresis curve. The larger peak capacitance and shift in positive direction of the numerical C-V curve can be attributed to errors in the fitting parameters in the permittivity function.

To reduce the differences in the previous results, another numerical analysis was attempted. In this analysis, the maximum relative permittivity of 7250, which is 85% of the previous value, and the same doping concentration of \(1 \times 10^{18} \text{cm}^{-3}\) were used. In spite of the decrease in the maximum permittivity, the PZT film was found to be wholly depleted in equilibrium. The C-V curve obtained using the same procedures as described before has better agreement than the previous result as shown in Fig. 6.27.
Fig. 6.26. C-V for a wholly depleted structure (open circle) with the maximum relative permittivity of 8530 and comparison with a C-V from hysteresis loop.

Fig. 6.27. C-V for a wholly depleted structure (open circle) with the maximum relative permittivity of 7250 and comparison with a C-V from hysteresis loop.
Key results in this numerical analysis can be summarized as follows:

1) Positive flat-band voltage is 0.5 V;
2) Negative flat-band voltage is -0.5 V; and
3) Coercive voltage is -1.1 V.

Besides these results, the potential and electric field distribution does not depend on the magnitude of the barrier heights as long as the wholly depleted model holds. In other words, if the barrier heights are large enough to cause reach-through in equilibrium, their magnitude does not affect the potential and electric field distributions.

6.4.5 C-V Prediction for an Infinitely Long Sample

For a doping concentration of $1 \times 10^{19}$ cm$^{-3}$, the depletion layers near the top and the bottom electrode do not spread out into each other even if a large voltage (such as 12 V) is applied to the Pt-PZT-Pt capacitor. Before calculating the C-V characteristics for this doping concentration, the difference between an infinitely long and a wholly depleted sample will be discussed in order to find out how the numerical methods described in section 6.2.6 & 6.2.7 are modified for the infinitely long structure.

In the wholly depleted structure, the depletion layers near the top and the bottom electrodes are merged into each other, so the whole system can be regarded as one capacitor. If a voltage $V_s$ is applied to the top electrode with the bottom electrode at ground, the Fermi level of the top electrode is shifted by the applied voltage. Before the flat-band condition (from the negative flat-band voltage to the positive flat-band voltage), this Fermi level shift of the top electrode is converted to the barrier height change near the top electrode. Because the whole film responds to the applied voltage on the top electrode, the
numerical methods based on the change in the barrier height can be used even if a negative voltage is applied to the top electrode.

Above the flat-band condition, the potential distribution is calculated to produce the potential drop across the film as

$$\Delta \phi = V_s + (|\Phi_{BR}| - |\Phi_{BL}|) \quad \text{for a positive } V_s, \quad (6.4.15)$$

or

$$\Delta \phi = |V_s| + (|\Phi_{BL}| - |\Phi_{BR}|) \quad \text{for a negative } V_s. \quad (6.4.16)$$

Because the surface electric field near the top electrode can be found for all the voltages (from some negative voltage to some positive voltage), the capacitance is calculated from

$$C = \left| \frac{\delta D_s}{\delta V_s} \right| = \left| \varepsilon(F_s) \frac{\delta F_s}{\delta V_s} \right|. \quad (6.4.17)$$

For an infinitely long sample, the depletion layers do not interact with each other, so the Pt-PZT-Pt capacitor can be divided into three regions; depletion layers near the top and the bottom electrode and a neutral PZT layer between the depletion layers. If a positive voltage is applied to the top electrode with the bottom electrode at ground, the depletion layer near the top electrode widens. In the positive voltage ranges, the same procedures used for the wholly depleted case can be used. Therefore, the positive applied voltage shifts the Fermi level of the top electrode downwards and this shift can be converted to an increase in the barrier height near the top electrode.

However, when a negative voltage is applied to the top electrode of the infinitely long sample with the bottom electrode at ground, different numerical methods are needed. If the same numerical methods used for the wholly depleted structure is used, the negative voltage on the top electrode will decrease the depletion layer near the top electrode without
changing the depletion layer near the bottom electrode. Because the contact near the top electrode is forward-biased in this case, the voltage drop at the top electrode contact can not exceed a few thermal voltages. Based on this, when a negative voltage is applied to the top electrode, the numerical analysis is performed by assuming that a positive voltage with the same magnitude is applied to the bottom electrode with the top electrode at ground.

Another thing to be considered for the infinitely long sample is how to determine the voltage at which the direction of the spontaneous polarization switches. In the numerical analysis for the wholly depleted structure, it is assumed that the spontaneous polarization switches its direction when the surface field near the top electrode is equal to the positive coercive field. As shown in Fig. 6.23 (b), the electric field in the wholly depleted structure is uniformly distributed from a positive value near the bottom electrode to a negative value near the top electrode in equilibrium. As the magnitude of a negative voltage on the top electrode increases, all the electric fields in the PZT film become more positive and the zero-field position moves towards the top electrode. At the negative flat-band voltage, the zero-field position is located at the top electrode. When the magnitude of the negative voltage increases further and all the electric fields in the PZT film are larger than the positive coercive field, it is assumed that the direction of the spontaneous polarization switches and the barrier heights near the top and the bottom electrodes also change their magnitudes. From the uniform electric field distribution, it is expected that the switching occurs gradually. Because the electric field near the bottom electrode reaches the positive coercive field earlier than the other region of the film, the switching process takes place near the bottom electrode first and it propagates to the top electrode. However, because of the simplicity, it is assumed that the switching occurs only when the surface electric field near the top electrode is equal to the positive coercive field in the analysis of the wholly depleted structure.
As described before, if a negative voltage is applied to the top electrode of the
infinitely long sample, it will be treated as an application of a positive voltage to the bottom
electrode in the later analyses. If these numerical analyses are employed, the surface electric
field near the top electrode remains the same in the negative voltage ranges. Therefore, the
switching voltage can not be determined by the surface electric field near the top electrode.
Instead, the average electric field in the PZT film will be used to determine the switching
voltage in the later analyses for the infinitely long sample. If the average field in the PZT
film is larger than the positive coercive field, the voltage at this condition will be considered
as the switching voltage.

Because the surface electric field near the top electrode remains the same in the
negative voltage range, capacitance calculation by differentiating the surface electric field
with respect to the applied voltage as in Eq. (6.4.17) is not applicable, either. In this case,
the capacitance is given by the series combination of the depletion layer capacitances and
the neutral region capacitance. Therefore, the total capacitance will be

\[
\frac{1}{C} = \frac{1}{C_{\text{Bot}}} + \frac{1}{C_{\text{Neu}}} + \frac{1}{C_{\text{Top}}} \tag{6.4.18}
\]

where \( C_{\text{Bot}} \) and \( C_{\text{Top}} \) are the depletion capacitances near the bottom electrode and the top
electrode, respectively, and \( C_{\text{Neu}} \) is the neutral region capacitance.

Kahng and Wemple [59] previously derived the expression for the depletion
 capacitance of a non-constant permittivity material under the assumption of an infinitely
long sample. According to their derivation, the depletion layer capacitances can be
calculated from

\[
\frac{1}{C_{\text{Bot}}} = \int_0^{w_b} \frac{dx}{\epsilon(F(x))} \tag{6.4.19}
\]

and

\[
\frac{1}{C_{\text{Top}}} = \int_0^{w_t} \frac{dx}{\epsilon(F(x))} \tag{6.4.20}
\]
In the above equations, $W_R$ and $W_L$ are the widths of the depletion layers from the top and the bottom electrodes, respectively.

In the numerical analysis, these depletion capacitances are calculated using the equations below

$$\frac{1}{C_{Dep}} = \sum_{i=1}^{n} \frac{1}{2} \left( \frac{1}{\varepsilon(F(x_i))} + \frac{1}{\varepsilon(F(x_{i-1}))} \right) (x_i - x_{i-1}) \quad (6.4.21)$$

where $x_0 = 0$ and $x_n = W_R$ or $W_L$.

Further, the average electric field in each depletion region is calculated from

$$\bar{F} = \frac{1}{W_0} \int_{0}^{W} F(x) dx$$

$$= \frac{1}{W} \sum_{i=1}^{n} \frac{1}{2} [F(x_i) + F(x_{i-1})] (x_i - x_{i-1}) \quad (6.4.22)$$

where $x_0 = 0$, $x_n = W_R$ or $W_L$, and $W$ is also either $W_R$ or $W_L$.

Because the electric field in the neutral region is zero, the capacitance of the neutral region can be found from

$$C_{Neu} = \frac{\varepsilon(F = 0)}{d - (W_R + W_L)} \quad (6.4.23)$$

where $d$ is the PZT film thickness.

Using these procedures, the C-V curve for a doping concentration of $1 \times 10^{19}$ cm$^{-3}$ was calculated as shown in Fig. 6.28 and 6.29. In this analysis, the same barrier heights as for the previous analysis (0.3 eV for the top electrode and 0.24 eV for the bottom electrode) and the maximum relative permittivity of 8530 were used.

The calculated C-V curve shown in Fig. 6.28 does not consider the capacitance due to the neutral region. If the neutral region capacitance is considered, the capacitance in the low voltage range (from -2 V to 2 V) decreases significantly as shown in Fig. 6.29.
Fig. 6.28. C-V for an infinitely long sample and comparison with a C-V from hysteresis loop. Neutral region capacitance is not considered.

Fig. 6.29. C-V for an infinitely long sample and comparison with a C-V from hysteresis loop. Neutral region capacitance is considered.
In these analyses, the switching voltage is chosen as -0.7 V. At -0.7 V, the net electric field (difference between the average fields in the depletion layers) is found to be 15 kV/cm, which is larger than the coercive field (~ 12 kV/cm) calculated in section 6.4.2. Therefore, for a negative voltage with a magnitude larger than 0.7 V, the numerical analyses were performed with the changed barrier heights (0.24 eV for the top electrode and 0.3 eV for the bottom electrode).

The calculated C-V curves in Fig. 6.28 and Fig. 6.29 have the maximum at 0 V. In the analysis here, if a voltage is applied to the top electrode, the depletion layer near the top electrode widens for a positive voltage, while the depletion layer near the bottom electrode widens for a negative voltage. These simple algorithms result in the maximum at 0 V.

In order to shift the maximum point to a negative voltage, more rigorous numerical methods are needed. One approach was proposed by Brennan [58]. In his work, a depolarization field and a corresponding voltage drop ($V_{pol}$) in the neutral region were assumed. Because no potential drop and no electric field are shown in the neutral region in Fig. 6.24, it may not be reasonable to assume any voltage drop in the neutral region. However, this also can be regarded as a voltage drop due to the series resistance of the neutral region. Further, he assumed a constant permittivity in each region; the saturation permittivity in depletion layers and the maximum permittivity in the neutral region. He analyzed the C-V characteristics in three different voltage ranges; positive voltage, small negative voltage, and large negative voltage.

If a voltage applied to the top electrode is positive or large negative, he used the same procedures as in this work. In these voltage ranges, one depletion layer widens while the other depletion layer remains in equilibrium condition. In the small negative voltage ranges, he calculated the voltage drops across the depletion layers ($V_{top}$ near top electrode and $V_{bot}$ near bottom electrode) and $V_{pol}$ across the neutral region numerically by
considering the sum of the voltage drop (Eq. (6.4.24)) and charge conservation (Eq. (6.4.25))

\[ V = V_{\text{top}} + V_{\text{pol}} + V_{\text{bot}} \]  \hspace{1cm} (6.4.24)

and

\[ W_{\text{top}}(V_{\text{top}}) + W_{\text{bot}}(V_{\text{bot}}) = W_{\text{top}}(0) + W_{\text{bot}}(0). \]  \hspace{1cm} (6.4.25)

Eq. (6.4.25) means that the space charge loss in one depletion region must be compensated by the space charge gain in the other depletion region. Because of a constant permittivity at each region, Eq. (6.4.25) can give the relationship between \( V_{\text{top}} \) and \( V_{\text{bot}} \). If the values of \( V_{\text{top}} \) and \( V_{\text{bot}} \) at particular conditions (such as at 0 V etc.) are known, the voltages of \( V_{\text{top}} \), \( V_{\text{bot}} \), and \( V_{\text{pol}} \) can be found numerically. Therefore, all the voltage drop is not occurred across the depletion region near the bottom electrode and the maximum capacitance is obtained at some negative voltage.

However, if the permittivity is a function of an electric field, the analytical relationship between \( V_{\text{top}} \) and \( V_{\text{bot}} \) is no longer available from Eq. (6.4.25). Because more rigorous methods are needed to consider the charge conservation when solving Poisson's equation, the numerical methods described earlier were used in the analysis here.

The previous numerical analyses show that the C-V curve for the wholly depleted model (doping concentration of \( 1 \times 10^{18} \text{ cm}^{-3} \) here) has better agreement with the experimental C-V curves than that for the infinitely long model (doping concentration of \( 1 \times 10^{19} \text{ cm}^{-3} \) here). Further, a uniformly distributed field in the wholly depleted structure can explain the switching behavior of the ferroelectric film more easily. Therefore, even if the limitation of the numerical methods for the infinitely long sample in this work is considered, it can be concluded that the characteristics of the Pt-PZT-Pt capacitor in this experiment can be explained by the wholly depleted model.
6.5 Application and Limitation of Ferroelectric Modeling

6.5.1 Application of the Modeling

In the last section, it was found that the C-V curve predicted using the wholly depleted model is quite close to the C-V curve obtained from the derivative of the hysteresis curve. This result suggests that, along with the wholly depleted model, the estimated doping concentration of $1 \times 10^{18}$ cm$^{-3}$ and the permittivity function expressed using a Lorentzian form as Eq. (6.4.12) can explain the characteristics of the PZT capacitor in this experiment.

Further, from these results, the characteristics of a PZT capacitor can be predicted when different materials other than platinum are used as electrodes. Suppose that the same material is used for both top and bottom electrodes and the Schottky barriers are large enough to cause full depletion. Because the potential and field distributions are independent of the barrier heights, the same C-V characteristics, or hysteresis behavior, as platinum electrodes would be expected. For I-V characteristics, the current density levels may be different for different materials. However, the difference in the non-switching and full-switching static currents, one order of magnitude in this experiment, should be the same for other electrodes because spontaneous polarization produces the 60 mV difference between the top and bottom barrier heights.

If different materials are used for the top and the bottom electrodes in an MFM capacitor, for instance Au-PZT-Pt, more asymmetry in the barrier heights can be expected. Even in a symmetric electrode system, spontaneous polarization produces an asymmetry, which is 60 meV in this film. If the two electrode materials have different contact potentials with the ferroelectric film, either due to the different work functions or due to the different surface states, the difference in contact potentials must be considered. Suppose that Au
(\(\Phi_m=5.1\ \text{eV}\)) and Pt (\(\Phi_m=5.5\ \text{eV}\)) are used as the top and bottom electrodes, respectively. If no surface state is considered, the barrier height of the top electrode is larger than that of the bottom electrode by 0.46 eV for the non-switching case. Because of the surface states, this large barrier height difference cannot be expected in reality. However, Au-PZT-Pt structure should produce a larger barrier height difference than the symmetric electrode system.

### 6.5.2 Limitation of the Modeling

The previous numerical result shows that the wholly depleted model agrees well with the C-V characteristics of the Pt-PZT-Pt structure. However, this model has some limitations in explaining the I-V characteristics of the PZT capacitor. First, as described before, whether it is infinitely long or wholly depleted, the back-to-back Schottky barrier system has difficulty in explaining the current increase in the low voltage range (less than 1 V). In section 6.2.3, the current increase in the low voltage range was explained by the transient current effect. The current level decrease in the medium voltage range (from 1 V to 5 V) for longer delay time was explained by the barrier height increase due to the larger charge accumulation. One order of magnitude difference between the full-switching and the non-switching static currents for low voltages was explained by the different barrier heights at the top and the bottom electrode. Further, the one order of magnitude difference, instead of a fixed difference, for different delay times was explained by the same rate variation of the barrier height. However, the transient model, including the barrier height variation with respect to time, was not developed in this work.

Secondly, the calculated electric field is not strong enough to cause tunneling in the voltage range larger than 6 V. The conceptual potential configuration after flat-band voltage can be drawn as in Fig. 6.30.
From the WKB approximation of quantum mechanics [66], the tunneling probability is given by

\[ T = \exp \left( \frac{4 \sqrt{2m} (q\phi)^{3/2}}{3 \hbar \mid qF \mid} \right). \tag{6.5.1} \]

As shown in Fig. 6.25, the surface electric field is about 200 kV/cm at 6 V. Therefore, the tunneling probability will be

\[
T = \exp \left( -\frac{4 \sqrt{2 \times 9.11 \times 10^{-28} \text{g} \times (0.3 \text{eV})^{3/2}}}{3 \times 1.055 \times 10^{-27} \text{erg} \cdot \text{s} \times 200 \text{keV} / \text{cm}} \right) \\
= \exp \left( -\frac{4 \times 0.3 \times \sqrt{2 \times 9.11 \times 10^{-28} \text{g} \times (0.3 \text{eV})}}{3 \times 2.11 \times 10^{-22} \text{erg} \cdot \text{s} / \text{cm}} \right) \\
= \exp \left( -\frac{4 \times 0.3 \times \sqrt{2 \times 9.11 \times 10^{-28} \text{g} \times 0.3 \times 1.6 \times 10^{-12} \text{g} \cdot \text{erg}}}{3 \times 2.11 \times 10^{-22} \text{erg} \cdot \text{s} / \text{cm}} \right) \\
= \exp(-56).
\]
This estimate shows that the tunneling probability is extremely low at this electric field. Even though a rapid increase of the tunneling probability can be expected as the voltage increases, this estimate is too low to explain the current conduction entirely by the tunneling effect. Therefore, other mechanisms for current conduction in the high electric field range, such as avalanching, must be considered in the further study.
CHAPTER 7

CONCLUSIONS

7.1 Summary and Conclusions

In this work, electrical characterization of ferroelectric PZT thin films was performed. To understand the experimentally observed electrical characteristics of ferroelectric PZT thin films, a model for the platinum-PZT-platinum system was presented.

Because no standard characterization method has been established yet, the measurement methods for the polarization and leakage-current were discussed first.

As for polarization, the traditional Sawyer-Tower method and the pulse polarization method were explained. Using a commercial RT66A ferroelectric tester, correlation between the two methods was attempted. The polarization characteristics of a Pt-PZT-Pt capacitor were investigated using these polarization measurement methods. Temperature effect, fatigue, and retention properties of the sol-gel derived PZT thin film were examined in terms of the polarization changes. At 100 °C, remanent polarization falls to 65% of the room temperature value. With ± 6 V bipolar stress, remanent polarization decreases to 50% of the initial value after 1x10^9 cycles. Even though this fatigue property is not sufficient to meet the endurance requirement of 1x10^{12} cycles, the charge storage capability of 4 μC/cm^2 after 1x10^{10} cycles is still much larger than that of conventional silicon dioxide. In contrast to bipolar stress, no significant reduction in polarization was found for unipolar stress in this experiment. At room temperature, stored
charge decreased by only 0.5 μC/cm² for 10,000 s. This result indicates that the room temperature retention is not a concern for ferroelectric memories.

Total-dose radiation effects (Appendix A) were also investigated up to a total dose of 1 Mrad(Si). After irradiation, the distortion in the hysteresis loop and the decrease in the polarization were observed. However, fatigue and retention properties of the irradiated PZT capacitors were found to be the same as those of the non-irradiated capacitors except for the polarization reduction.

To measure the leakage current of ferroelectric thin films, a static I-V measurement method for ferroelectric thin films was developed. The objective of this measurement method is to distinguish the leakage current from the switching current. This measurement technique considers the initial polarization state and the exponential decay behavior of the switching current. Depending on the initial polarity, the static currents are defined as a full-switching and a non-switching static current. At each voltage step, a delay time is inserted before the current measurement in order to investigate the exponential decay behavior of the switching current. At low electric field, a significant difference between full-switching and non-switching static currents was found even for a 100 s delay time. At high electric field, both static currents are close to each other for a short delay time. These results suggest that non-switching static current with a long delay time is a good way to measure the leakage current alone.

The feasibility of this method as a practical characterization tool was tested by examining the fatigue effects on PZT thin films. The polarization reduction after bipolar electrical stress accompanies the decrease in the switching current at low electric field and the increase in the leakage current at high electric field.

To understand the current-voltage and capacitance-voltage characteristics of the Pt-PZT-Pt capacitor, a model for the ferroelectric thin film capacitor was presented. By assuming that the ferroelectric PZT is a p-type semiconductor, a back-to-back Schottky
barrier model was introduced. Because the spontaneous polarization will induce positive and negative ionic charges at each end of the PZT thin film, it will produce different barrier heights at each Pt-PZT contact. Therefore, a back-to-back Schottky barrier system having asymmetric barriers was proposed as a model for the Pt-PZT-Pt capacitor.

The barrier heights for this system are determined by measuring the I-V characteristics for different temperatures from room temperature to 200 °C. Using thermionic theory, the magnitude of the larger barrier was found to be in the range of 0.3 eV to 0.6 eV. Because the full-switching static current was always larger than the non-switching static current by one order of magnitude for all the delay times in the low voltage range, the other barrier was assumed to be smaller than the larger barrier by 60 meV.

The potential and electric field distributions were calculated by solving Poisson's equation numerically. In contrast to other reported modeling efforts [58], the permittivity variation with respect to the electric field was considered in this numerical analysis. From the C-V characteristics obtained by differentiating the hysteresis curve, the permittivity function was chosen to have the Lorentzian form

\[
\varepsilon(F) = \varepsilon_\infty + (\varepsilon_{\text{max}} - \varepsilon_\infty) \frac{1}{1 + \left[ \frac{F - F_c}{F_0} \right]^2}.
\]

(7.1.1)

If the doping concentration is chosen to be 1x10^{18} \text{ cm}^{-3}, the depletion layers near the top and the bottom electrode reach through to each other even in equilibrium. If the doping concentration is 1x10^{19} \text{ cm}^{-3}, the depletion layers do not merge even if a large voltage is applied.

The C-V characteristics of the PZT capacitor were predicted for these two doping concentrations by solving Poisson's equation for different applied voltages. For a doping
concentration of $1 \times 10^{18}$ cm$^{-3}$, the C-V curve for a PZT film was calculated using the permittivity function of (7.1.1) and the small-signal surface field variation with respect to the applied voltage

$$C = \epsilon(F) \left| \frac{\delta F}{\delta V} \right|.$$  (7.1.2)

Using this doping concentration ($1 \times 10^{18}$ cm$^{-3}$), the predicted C-V curve agrees well with the C-V curve derived from the hysteresis loop with the following parameters of the permittivity function

$$\epsilon_{\text{max}} = 7250 \epsilon_0$$
$$\epsilon_{\infty} = 380 \epsilon_0$$
$$F_c = 12.04 \text{kV/cm}$$
$$F_0 = 25.93 \text{kV/cm}.$$  (7.1.3)

For a doping concentration of $1 \times 10^{19}$ cm$^{-3}$, the PZT capacitor was considered as a series combination of depletion capacitors near the top and the bottom electrodes and a capacitor in the neutral region. However, the predicted C-V did not show a good agreement with the C-V curve derived from the hysteresis loop.

These results suggest that the back-to-back Schottky barrier structure with merged depletion layers, the so-called wholly depleted model, is a good model for the Pt-PZT-Pt capacitor used in this experiment. Further, it was found that the potential and electric field distribution in PZT film is independent of the magnitude of the barrier heights as long as the wholly depleted model holds.

However, the back-to-back Schottky barrier system, whether it is wholly depleted or not, has some limitations in explaining the I-V characteristics of the PZT capacitor. Because the current conduction in this system is mainly determined by the voltage-independent reverse saturation current, the current increase in the low voltage range can
not be explained by this model. The current increase in the low voltage range may be related to the switching current. If a delay time longer than 100 s is used, the current level at low voltages decreases to the noise level. This result indicates that the switching current is the major component in the low voltage range. Up to the coercive voltage, switching current increases as the applied voltage increases. Because most of the domain switching is completed up to the coercive voltage, the switching current component becomes negligible and the current remains at the same level for the voltages larger than the coercive voltage.

In the large voltage range (larger than 6 V), the current increase was explained by tunneling. Because the electric field near the hole injecting electrode is estimated to be only a few hundred kV/cm, which is not strong enough to cause tunneling, the current conduction can not be entirely attributed to tunneling. However, the rapid increase in the tunneling process can be expected after the flat-band condition occurs.

7.2 Areas for Further Studies

As mentioned before, no standard measurement method for characterizing the ferroelectric materials has established been yet. Standard measurement methods for polarization and leakage current must be provided to characterize the film under the same conditions.

As discussed earlier, the electrical model for the metal-ferroelectric-metal system developed in this work has some limitations in explaining the I-V characteristics. The transient response model in the low voltages and the current conduction mechanism in the high voltages must be studied.

Further, the study on the properties of domain for ferroelectric thin films is needed. In this work, the permittivity function was empirically obtained from the C-V
curve. Because it was derived empirically, the individual properties of domains were not considered. However, as the film gets thinner and the area of the capacitor gets smaller, the capacitor will consist of a fewer number of domains and the permittivity will be strongly affected by the properties of each domain. Therefore, the domain properties, such as the size and the domain motion under the applied voltage etc., of ferroelectric thin films must be studied.

Up to now, most research on the ferroelectrics used the platinum as the electrode materials. Recently, different electrode materials other than platinum have been used to improve the properties of the ferroelectric capacitor. The modeling of ferroelectric materials presented in this work will be useful to understand the property of the ferroelectric capacitor with other electrode materials. If the barrier height for a given electrode material can be estimated by the similar procedures used in this work, the properties, such as leakage current, associated with the material can be predicted.
APPENDIX A

RADIATION EFFECTS

In this appendix, total-dose radiation effects on sol-gel derived PZT thin films at moderate total dose levels (less than 1 Mrad(Si)) are discussed. Among many experimental results, which were already reported [67], some important results related to the reliability of ferroelectric memories in radiation environments are presented here.

The ferroelectric capacitors were prepared using the same procedures as described in section 2.2. Because these experiments were done at the early stage of the research, all the samples were fabricated without an additional heat-treatment after formation of the top electrode.

The ferroelectric capacitors were irradiated with Co-60 gamma rays at various dose rates from 4 to 170 rad(Si)/min. under open circuit conditions. These capacitors were irradiated to a total dose of ~ 1 Mrad(Si). After irradiation, the fatigue and retention properties of the irradiated capacitors were measured and compared with those of the non-irradiated samples.

Fig. A.1 shows the typical changes in the hysteresis loops after a total dose of 0.85 Mrad(Si). The post-rad hysteresis curve was obtained using a different capacitor than the pre-rad capacitor in order to avoid the polarization change effects due to the electrical measurements. If a capacitor is subjected to electrical tests and subsequently irradiated, the electrical test condition before the irradiation affects the radiation response. For example, if the electrical measurements end with positive bias, this positive voltage changes the polarization state of the capacitor and affects the following radiation
response. The polarization effects on radiation response were explained in detail in a previous report [67].

As shown in Fig. A.1, the hysteresis curve shifts downward and shows a narrower loop for positive electric field after irradiation. This can be explained by an increase in the internal bias field [68]. The initial distortion in the pre-rad hysteresis curve results from the different heat-treatment histories of the top and bottom electrodes. This asymmetry in electrodes causes an internal field. During irradiation, radiation-induced charges increase the internal bias field and makes the hysteresis curve more asymmetric.

![Graph showing changes in hysteresis due to radiation](image)

**Fig. A.1.** Changes in the hysteresis curve due to radiation.

In Fig. A.2, the fatigue properties of irradiated capacitors were compared with those of the non-irradiated capacitors. The fatigue behavior was obtained using 1 MHz, ± 6 V bipolar stress. The fatigue behaviors of the non-irradiated capacitor can be divided into two phases: 1) an initial increase due to domain reorganization followed by 2)
logarithmic decay [49]. Because no additional heat-treatments were performed after top electrode formation, the fatigue behavior of the non-irradiated capacitors showed more initial increase than the top-electrode annealed sample shown in section 4.2.2. For irradiated samples, during the initial period of electrical cycling, redistribution of the radiation-induced defects and the domain reorganization take place simultaneously and compensates the following logarithmic decay. On completing the defect redistribution, the irradiated capacitor shows nearly the same decay as the non-irradiated capacitor.

Figure A.3. shows retention properties of the irradiated and the non-irradiated capacitors. Because $P^*$ is not available in the retention measurement, $P^*$ is used instead of $P^*-P^\wedge$. As shown in this figure, both samples show almost the same the polarization decay rate. These results indicate that retention and fatigue properties are not degraded by irradiation except for the polarization reduction.

![Figure A.2. Comparison of fatigue properties between non-irradiated and irradiated PZT capacitors, cycled with 1 MHz, ± 6 V square wave.](image-url)
Fig. A.3. Comparison of retention properties between non-irradiated and irradiated PZT capacitors.
APPENDIX B

REVIEW OF THE SWITCHING THEORY

In this appendix, the theoretical switching current equation will be derived in order to understand how the dynamic motion of domains is related to the switching current.

In Chapter 5, the displacement current density was expressed as

\[ j(t) = \frac{dD(t)}{dt} = \varepsilon_0 \frac{dF(t)}{dt} + \frac{dP(t)}{dt}. \]  \hspace{1cm} (B.1)

If the direction of the applied electric field is opposite to that of the initial polarization, the second term of Eq. (B.1) is much larger than the first term. In this situation, the polarization \( P(t) \) can be assumed to change from \(-P_s\) to \(+P_s\). If there are \( N \) domains in the film, these whole domains are initially aligned to have a polarization value of \(-P_s\) and later they are switched to obtain a polarization value of \(+P_s\). Therefore, if one domain switches at arbitrary time, the change of the polarization will be \( 2P_s \times (1/N) \). In this context, the polarization \( P(t) \) can be represented as

\[ P(t) = 2P_s Q(t) \]  \hspace{1cm} (B.2)

where \( Q(t) \) is a fraction of the volume which has been switched from the initial polarization direction to the opposite direction at time \( t \).

As a result, the switching current density is

\[ j(t) = 2P_s \frac{dQ(t)}{dt}. \]  \hspace{1cm} (B.3)

To find an analytical form of \( Q(t) \), the dynamic properties of domains are discussed below.
In Chapter 1, the hysteresis loop of ferroelectric materials was explained by domain movements in response to an electric field. The domain movement was simply considered as nothing but a re-alignment, or switching, of the pre-existing domains. However, more precisely, this switching process can be divided into three steps [69,70,71]:

1) nucleation of new domains, with their polarization orientation antiparallel to the original polarization, at the surfaces of the crystal;

2) forward growth of these domains through the thickness of the crystal; and

3) sideways expansion of the domains.
Fig. B.1 schematically illustrates the above domain switching processes. These three processes can occur in sequence [71] or simultaneously [52]. Here, the latter theory will be discussed.

After nucleation, the domain growth can proceed in one, two, or three dimensional ways. In Fig. B.2, the three dimensional domain growth is shown. Before taking further analysis, several assumptions will be made here [52]:

1) the nucleation is an instant process. In other words, the nucleation site with a radius of $r_c$ appears instantaneously;

2) the nucleation rate $R$ is constant throughout switching period when the constant field is kept applied; and

3) domain expands with a velocity $v$.

![Diagram of nucleation and domain growth in three dimensional way](image)

**Fig. B.2** Nucleation and domain growth in three dimensional way [52].
As shown in Fig. B.2, suppose that the i-th domain is formed during the time interval between \((i-1)\Delta \tau\) and \(i \Delta \tau\). The probability of nucleation during this time interval is \(R \Delta \tau\), where \(R\) is the nucleation rate per unit volume per unit time. At time \(t\), this domain will cover a volume of \(S(t,i \Delta \tau)\)

\[
S(t,i \Delta \tau) = C [r_c + \nu(t-i \Delta \tau)]^n
\]

where \(C = 4\pi / 3\) and \(n = 3\).

In one and two dimensional cases, the corresponding covered width and area are also represented by the above equation simply replacing appropriate \(C\) and \(n\) values. At time \(t\), the probability \(p_i\) that a specific point \(P_i\), shown in Fig. B.2, is included in the i-th domain is

\[
p_i = R \Delta \tau S(t,i \Delta \tau) = R \Delta \tau C [r_c + \nu(t-i \Delta \tau)]^n.
\]

Therefore, the probability \(q_i\) that this point \(P_i\) is not covered by the i-th domain is

\[
q_i = 1 - p_i = 1 - R \Delta \tau S(t,i \Delta \tau) = 1 - R \Delta \tau C [r_c + \nu(t-i \Delta \tau)]^n.
\]

On the same logical basis, the probability \(q(t)\) that a specific volume remains unswitched at time \(t = j \Delta \tau\) is given by

\[
q(t) = \prod_{i=0}^{j} [1 - R S(j \Delta \tau, i \Delta \tau) \Delta \tau].
\]

By taking a logarithm and using the approximation of \(\ln(1-x) = -x\),

\[
\ln q(t) = \sum_{i=0}^{j} [1 - R S(j \Delta \tau, i \Delta \tau) \Delta \tau] = - \sum_{i=0}^{j} [R S(j \Delta \tau, i \Delta \tau) \Delta \tau].
\]
And
\[
\ln q(t) = -\int_0^t R S(t,i \Delta \tau) \, d\tau .
\] (B.9)

From Eq. (B.4) and Eq. (B.9)
\[
\ln q(t) = \frac{RC}{v(n+1)} \left[ (r_e)^{n+1} - (r_e + vt)^{n+1} \right]
\] (B.10)
and
\[
q(t) = \exp \left\{ -\frac{RC \, v^n}{(n+1)} \left[ (t + \frac{r_e}{v})^{n+1} - \left( \frac{r_e}{v} \right)^{n+1} \right] \right\} .
\] (B.11)

If the characteristic switching time \( t_0 \) and the critical time \( t_c \) for nucleation are defined as
\[
t_0 = \left( \frac{n+1}{RC \, v^n} \right)^{1/(n+1)} \quad \text{and} \quad t_c = \frac{r_e}{v},
\]
then
\[
q(t) = \exp \left\{ -\left[ \left( t + \frac{t_c}{t_0} \right)^{n+1} - \left( \frac{t_c}{t_0} \right)^{n+1} \right] \right\} .
\] (B.12)

In general, the characteristic switching time is in the micro-second (\( \mu s \)) range and the critical time for nucleation is in the nano-second (\( ns \)) range. Therefore,
\[
q(t) = \exp \left\{ -\left( \frac{t}{t_0} \right)^{n+1} \right\} .
\] (B.13)

Finally, \( Q(t) \), the fraction of the switched volume relative to the whole volume, can be obtained as
\[
Q(t) = 1 - \exp \left\{ -\left( \frac{t}{t_0} \right)^{n+1} \right\} .
\] (B.14)
By putting $Q(t)$ into the switching current density equation,

$$j(t) = 2P_s \frac{n+1}{t_0} \left( \frac{t}{t_0} \right)^n \exp \left[ - \left( \frac{t}{t_0} \right)^{n+1} \right].$$  \hspace{1cm} (B.15)

In the preceding derivations, it was assumed that the nucleation rate $R$ is constant throughout switching period. However, it can be also assumed that the nucleation only happens at the beginning of the switching process. In other words, every domain is assumed to grow from $t = 0$. In this case, the integrand of Eq. (B.9) can be treated as a delta function and

$$\ln q(t) = R S(t,0) = R C \left[ -(r_c + vt)^n \right]. \hspace{1cm} (B.16)$$

With the same manipulation, $Q(t)$ and $j(t)$ will be expressed as

$$Q(t) = 1 - \exp \left[ - \left( \frac{t}{t'_0} \right)^{n+1} \right]. \hspace{1cm} (B.17)$$

and

$$j(t) = 2P_s \frac{n}{t'_0 t_0} \left( \frac{t}{t'_0} \right)^{n-1} \exp \left[ - \left( \frac{t}{t'_0} \right)^n \right]. \hspace{1cm} (B.18)$$

where $t'_0 = \left( \frac{1}{RC v^n} \right)^{1/n}$. 
APPENDIX C

POISSON'S EQUATION FOR FERROELECTRIC MATERIALS

In this appendix, Poisson's equation for non-constant material will be derived first. Later, it will be shown how the field function $H(F)$ in section 6.3 is obtained. Further, the Taylor expansion form at low electric field is derived.

C.1 Poisson's Equation for Non-Constant Permittivity Materials

The one dimensional Poisson's equation is

$$\frac{\partial}{\partial x} D(x) = \rho(x). \quad (C.1.1)$$

Because the permittivity is defined as

$$\varepsilon(F) = \frac{\partial D}{\partial F} \quad (C.1.2)$$

where $F$ is an electric field,

Poisson's equation will be

$$\frac{\partial D(x)}{\partial x} = \frac{\partial D(x)}{\partial F} \frac{\partial F}{\partial x} = \varepsilon(F) \frac{\partial F(x)}{\partial x} = \rho(x). \quad (C.1.3)$$

Because the electric field is given by

$$F = -\frac{d\phi}{dx}, \quad (C.1.4)$$

Poisson's equation is

$$\varepsilon(F) \left[ -\frac{d^2}{dx^2} \phi(x) \right] = \rho(x). \quad (C.1.5)$$

Multiplying by $\frac{d\phi}{dx}$ on both sides, Eq. (C.1.5) will be
From Eq. (C.1.4) and Eq. (C.1.5), Poisson's equation will be

$$\varepsilon(F) \frac{\partial F}{\partial x} = -\rho(\phi) \frac{d\phi}{dx}.$$

Because the left side of the above equation is only field-dependent and the right side is only potential-dependent, Poisson's equation is

$$\varepsilon(F) F \frac{dF}{dx} = -\rho(\phi) \frac{d\phi}{dx}.$$  \hspace{1cm} (C.1.7)

If the film is assumed to be p-type and the depletion approximation is used,

$$\rho(\phi) = -qN_A.$$  \hspace{1cm} (C.1.9)

Therefore,

$$\varepsilon(F) F dF = qN_A d\phi.$$  \hspace{1cm} (C.1.10)

### C.2 Field Function $H(F)$ Calculation

In section 6.3, the field function $H(F)$ is defined as

$$H(F) = \int_0^F F \varepsilon(F) dF.$$  \hspace{1cm} (C.2.1)

If the permittivity is

$$\varepsilon(F) = \varepsilon_{\infty} + (\varepsilon_{\text{max}} - \varepsilon_{\infty}) \left( \frac{1}{F - F_c} \right) \left( \frac{F_c}{F_0} \right)^{\gamma},$$  \hspace{1cm} (C.2.2)

then the field function will be

$$H(F) = \frac{1}{2} \varepsilon_{\infty} F^2 + (\varepsilon_{\text{max}} - \varepsilon_{\infty}) \left[ \frac{F}{(F - F_c)} \right]_{0}^{F} \left( \frac{F - F_c}{F_0} \right)^{\gamma} dF.$$  \hspace{1cm} (C.2.3)
Now, let

\[ I = \int_{0}^{F} \frac{F}{1 + \left( \frac{F - F_c}{F_0} \right)^2} dF. \]  

(C.2.4)

By changing variables

\[ t = \frac{F - F_c}{F_0} \quad dF = F_0 dt, \]  

(C.2.5)

\[ I = \int_{-F_c/F_0}^{(F_c/F_0)} \frac{F_0 t + (F - F_c)}{1 + t^2} dt + \int_{-F_c/F_0}^{(F - F_c)/F_0} \frac{t}{1 + t^2} dt + \int_{-F_c/F_0}^{(F_c/F_0)} \frac{dt}{1 + t^2}. \]  

(C.2.6)

The first term in the right-most side is a log function and the second term is an arctangent function. The final calculation is

\[ I = F_c F_0 \left[ \tan^{-1} \left( \frac{F - F_c}{F_0} \right) - \tan^{-1} \left( \frac{-F_c}{F_0} \right) \right] + \frac{1}{2} F_0^2 \ln \left[ \frac{F_0^2 + (F - F_c)^2}{F_0^2 + F_c^2} \right] \]  

(C.2.7)

and

\[ H(F) = \frac{1}{2} \varepsilon_{\infty} F^2 + (\varepsilon_{\max} - \varepsilon_{\infty}) I. \]  

(C.2.8)
C.3 Taylor Expansion of Field Function at Low Electric Field

When calculating an arc-tangent function in Eq. (C.2.7) at very low electric field, a truncation error makes the field function $H(F)$ have negative values. To avoid this problem, a Taylor expansion is used at low field.

To find the Taylor expansion form of the arc-tangent function $\tan^{-1}\left(\frac{F + F_c}{F_0}\right)$, let

$$f(F) = \tan^{-1}\left(\frac{F}{F_0}\right), \quad \text{(C.3.1)}$$

then

$$f'(F) = \frac{1}{F_0} \frac{1}{1 + \left(\frac{F}{F_0}\right)^2} \quad \text{and} \quad f''(F) = -\frac{1}{F_0^3} \frac{2F}{\left[1 + \left(\frac{F}{F_0}\right)^2\right]^2}. \quad \text{(C.3.2)}$$

Therefore,

$$f(F + F_c) = \tan^{-1}\left(\frac{F + F_c}{F_0}\right)$$

$$= f(F_c) + F f'(F_c) + \frac{F^2}{2} f''(F_c) + \cdots \quad \text{(C.3.3)}$$

$$= \tan^{-1}\left(\frac{F_c}{F_0}\right) + \frac{F}{F_0} \frac{1}{1 + \left(\frac{F_c}{F_0}\right)^2} - \frac{F^2}{2F_0^3} \frac{2F_c}{\left[1 + \left(\frac{F_c}{F_0}\right)^2\right]^2} + \cdots.$$

Finally,

$$\tan^{-1}\left(\frac{F + F_c}{F_0}\right) - \tan^{-1}\left(\frac{F_c}{F_0}\right) = \frac{F}{F_0} \frac{1}{1 + \left(\frac{F_c}{F_0}\right)^2} - \frac{F^2}{2F_0^3} \frac{F_c}{\left[1 + \left(\frac{F_c}{F_0}\right)^2\right]^2}. \quad \text{(C.3.4)}$$
The log function in Eq. (C.2.7) can be rearranged as

\[
\ln \left[ \frac{F_0^2 + (F - F_c)^2}{F_0^2 + F_c^2} \right] = \ln \left[ 1 + \left( \frac{F + F_c}{F_0} \right)^2 \right] - \ln \left[ 1 + \left( \frac{F_c}{F_0} \right)^2 \right]. \quad (C.3.5)
\]

To expand \( \ln \left[ 1 + \left( \frac{F + F_c}{F_0} \right)^2 \right] \) in Taylor series, define \( g(F) \) as

\[
g(F) = \ln \left[ 1 + \left( \frac{F}{F_0} \right)^2 \right]. \quad (C.3.6)
\]

Then,

\[
g(F + F_c) = \ln \left[ 1 + \left( \frac{F + F_c}{F_0} \right)^2 \right]
= g(F_c) + Fg'(F_c) + \frac{F^2}{2} g''(F_c) + \cdots.
\]

\[
= \ln \left[ 1 + \left( \frac{F_c}{F_0} \right)^2 \right] + \frac{2F}{F_0^2} \frac{F_c}{F_0} \left( \frac{F_c}{F_0} \right)^2 + \frac{F^2}{2} \left[ 1 - \left( \frac{F_c}{F_0} \right)^2 \right] + \cdots. \quad (C.3.7)
\]

Therefore,

\[
\ln \left[ \frac{F_0^2 + (F - F_c)^2}{F_0^2 + F_c^2} \right] = \frac{2F}{F_0^2} \frac{F_c}{F_0} \left( \frac{F_c}{F_0} \right)^2 + \frac{F^2}{2} \left[ 1 - \left( \frac{F_c}{F_0} \right)^2 \right]. \quad (C.3.8)
\]

By substituting Eqs. (C.3.4) and (C.3.8) into the field function (Eqs. (C.2.7) and (C.2.8)), the Taylor expansion form can be obtained as

\[
H(F) = \frac{1}{2} \varepsilon \omega F^2 + \frac{1}{2} \frac{(\varepsilon_{\text{max}} - \varepsilon_\infty)}{\varepsilon_\infty} F^2.
\]
APPENDIX D

SUBROUTINES: BEFORE FLAT-BAND

Included in this appendix is the computer program that calculates the potential and electric field distributions in the metal-semiconductor-metal (MFM) system. This program applies before the MFM system reaches the flat-band condition. The program is written in FORTRAN language.
**PROGRAM FOR DISTANCE VS. POTENTIAL CALCULATION FOR THIN FILM**

*PROPOSED MODEL IS DEPLETION APPROXIMATION*

*CALCULATE FIELD VS POTENTIAL BEFORE FLAT BAND*

*CALCULATE POTENTIAL AT THE SPECIFIC ELECTRIC FIELD*

```
DIMENSION POTR(20000),FIER(20000),DISTR(20000),
1 POTL(20000),FIEL(20000),DISTL(20000),
1 DISA(200),DISB(200),TDIS(200),SURPA(200),SURPB(200)
```

INPUT PARAMETERS

WRITE (6,500)
500 FORMAT (1X,'ENTER INPUT BIAS VOLTAGE')
WRITE (6,501)
501 FORMAT (1X,'FORWARD BIAS: ENTER POSITIVE VALUE',/
1 1X,'REVERSE BIAS: ENTER NEGATIVE VALUE',/)
READ (6,502) BIAS
502 FORMAT (F10.3)
FTHICK=5.4E-5
BHRO=-0.3
BHL=-0.24

INPUT DOPING CONCENTRATION

WRITE (6,504)
504 FORMAT (5X,'ENTER DOPING CONCENTRATION',/)
READ (5,505) DOPING
505 FORMAT (E15.8)
DEFEV=0.0252*ALOG(5.0E19/DOPING)
SPINF=ABS(DEFEV+(BHRO»

CONFIRM PARAMETERS

WRITE (6,503) DOPING,FTHICK, BHRO, BHL, SPINF, BIAS
503 FORMAT (1X,'MATERIAL PROPERTIES:',//
1 1X,'DOPING CONCENTRATION=',2X,E15.8,2X//
1 1X,'FILM THICKNESS (CM)=',2X,E15.8,2X/
1 1X,'TOP ELECTRODE BARRIER @eq (eV)=',2X,F10.3,2X/
1 1X,'BOTTOM ELECTRODE BARRIER @eq (eV)=',2X,F10.3,2X/
1 1X,'SURFACE POTEN. FOR INFINITE SAMPLE=',2X,E15.8,2X/
1 1X,'BIAS ON TOP ELECTRODE=',2X,F10.3,2X//)

BHR=BHRO-BIAS

FIND TOP ELECTRODE SURFACE POTENTIAL FOR CHOSEN THICKNESS

JITER=1
WRITE (6,15)
15 FORMAT (1X,'GUESS ZERO FIELD POSITION',5X,/)
```
1X,'GUESS INITIAL SURFACE POTENTIAL',5X,/
READ (5,16) TEMPDA,TEMPSPR
16 FORMAT (E15.8,F15.8)
C
CALCULATE POTENTIAL DISTRIBUTION USING THE FIRST GUESS
C
22 CONTINUE
C
NITER=0
C
25 NITER=NITER+1
C
********************************************************************************
C
CALCULATE POTENTIAL
C
FSTARTR=0.0
SPOTFR=FSTARTR
I=1
C
50 CONTINUE
C
XR=HFIELD(SPOTFR)/(1.6E-19*DOPING)
FIER(I)=SPOTFR
POTR(I)=XR
C
100 CONTINUE
C
CHANGE FIELD UP TO VALUE SATISFYING RIGHT-SIDE SURFACE POTEN.
C
DELTAR=TEMPSPR-XR
IF (DELTAR.LE.0.5E-3) GO TO 200
C
FIELD STEP SIZE CONTROL
C
IF (DELTAR.GT.0.05) FSTEPR=100.0
IF (DELTAR.GT.0.005.AND.DELTAR.LE.0.05) FSTEPR=10.0
IF (DELTAR.GT.0.0005.AND.DELTAR.LE.0.005) FSTEPR=1.0
IF (SPOTFR.LE.0.0) FSTEPR=FSTEPR*(-1.0)
SPOTFR=SPOTFR+FSTEPR
I=I+1
GO TO 50
C
CALCULATE DISTANCE AND COMPARE WITH FILM THICKNESS
C
200 DISTR(1)=0.0
DO 210 J=2,I
  DELPOTR=POTR(J)-POTR(J-1)
  AVGFIER=0.5*(FIER(J)+FIER(J-1))
  DISTR(J)=DISTR(J-1)-(DELPOTR/AVGFIER)
  IF (J.EQ.I) CALTHR=ABS(DISTR(J))
210 CONTINUE
C
WRITE (6,611) NITER,CALTHR
611 FORMAT (5X,'ITERATION:',5X,I4,5X,'THICKNESS=',2X,E15.8,2X)
C
ERRTHICK=ABS(CALTHR-TEMPDA)
C
IF ESTIMATED VALUE IS THICKER, THEN REDUCE SURFACE POT. MAG.
IF THINNER, THEN INCREASE SURFACE POT. MAG.
C
RELLER=ERRTHICK/TEMPDA
IF (RELLER.LT.0.005) GO TO 212
IF (RELLER.GE.2.0) POLSTEP=0.05
IF (RELLER.GE.1.0.AND.RELLER.LT.2.0) POLSTEP=0.01
IF (RELLER.GE.0.5.AND.RELLER.LT.1.0) POLSTEP=0.005
IF (RELLER.GE.0.1.AND.RELLER.LT.0.5) POLSTEP=0.002
IF (RELLER.GE.0.02.AND.RELLER.LT.0.1) POLSTEP=0.001
IF (RELLER.GE.0.01.AND.RELLER.LT.0.02) POLSTEP=0.0002
IF (RELLER.GE.0.005.AND.RELLER.LT.0.01) POLSTEP=0.0001
IF (CALTHR.GT.TEMPDA) THEN
   TEMPSPR=TEMPSPR-POLSTEP
   IF (TEMPSPR.LE.0.0) TEMPSPR=0.000001
   GO TO 25
END IF
SPRMAX=SPINF+BIAS
C
IF (CALTHR.LT.TEMPDA.AND.TEMPSPR.EQ.SPRMAX) THEN
WRITE (6,209)
209 FORMAT (5X,'IT IS NOT WHOLLY DEPLETED MODEL ANY LONGER',/)
GO TO 212
END IF
C
IF (CALTHR.LT.TEMPDA.AND.TEMPSPR.LT.SPRMAX) THEN
   TEMPSPR=TEMPSPR+POLSTEP
   IF (TEMPSPR.GT.SPRMAX) TEMPSPR=SPRMAX
   GO TO 25
END IF
C
212 CONTINUE
DISA(JITER)=CALTHR
SURPA(JITER)=TEMPSPR
C
C ******************************************************************
C
C CALCULATE LEFT SIDE SURFACE POTENTIAL
C
C TEMPSPL=BHR-BHL+TEMPSPR
C
C IF (TEMPSPL.LE.0.0) THEN
   TEMPA=TEMPDA+0.2E-6
   IF (TEMPA.GT.FTHICK) THEN
      WRITE (6,310)
310 FORMAT (1X,'TOP ELEC DEP. WIDTH EXTENDS TO BOTTOM ELEC',/)
      END IF
   GO TO 770
END IF
C
C CALCULATE LEFT SIDE DISTANCE
C
C CALCULATE POTENTIAL
C
FSTARTL=0.0
SPOTFL=FSTARTL
IL=1
C
350 CONTINUE
XL=HFIELD(SPOFL)/(1.6E-19*DOPING)
FIELD(IL)=SPOFL
POTL(IL)=XL

CHANGE FIELD UP TO THE VALUE SATISFYING LEFT SIDE SURFACE POT.

DELTAL=TEMPSPL-XL
IF (DELTAL.LE.0.5E-3) GO TO 400

FIELD STEP SIZE CONTROL

IF (DELTAL.GT.0.05) FSTEPL=100.0
IF (DELTAL.GT.0.005.AND.DELTAL.LE.0.05) FSTEPL=10.0
IF (DELTAL.GT.0.0005.AND.DELTAL.LE.0.005) FSTEPL=1.0
SPOTFL=SPOTFL+FSTEPL
IL=IL+1
GO TO 350

DETERMINE LEFT SIDE DISTANCE

400 DISTL(1)=0.0
DO 410 JL=2,IL
   DELPOTL=POTL(JL)-POTL(JL-1)
   AVGFIELD=0.5*(FIELD(JL)+FIELD(JL-1))
   DISTL(JL)=DISTL(JL-1)-(DELPOTL/AVGFIELD)
   IF (JL.EQ.IL) CALTHL=ABS(DISTL(JL))
410 CONTINUE

DISB(JITER)=CALTHL
SURPB(JITER)=TEMPSPL
TDIS(JITER)=DISA(JITER)+DISB(JITER)
WRITE (6,420) JITER,DISA(JITER),DISB(JITER),TDIS(JITER),
SURPA(JITER),SURPB(JITER)
FORMAT(1X,'******** ITERATION #:',5X,I5,5X,'***************',/)
   1X,'RIGHT SIDE DEPLETION WIDTH=',5X,E15.8,2X,
1X,'LEFT SIDE DEPLETION WIDTH=',5X,E15.8,2X,
1X,'TOTAL DEPLETION WIDTH=',5X,E15.8,2X,
1X,'RIGHT SIDE SURFACE POTENT=',5X,F15.8,2X,
1X,'LEFT SIDE SURFACE POTENT=',5X,F15.8,2X,/
C
IF (TEMPSPR.EQ.SPRMAX) GO TO 430
IF (TDIS(JITER).GT.FTHICK) GO TO 430
DELTICL=FTHICK-TDIS(JITER)
IF (DELTICL.GE.0.0.AND.DELTICL.LE.0.15E-6) GO TO 430
CHANGE DEPLETION WIDTH NEAR TOP ELECTRODE
DELTEMP=2.E-7
IF (DELTICL.GT.5.0E-7.AND.DELTICL.LE.1.0E-6) THEN
   DELTEMP=5.E-8
END IF
IF (DELTICL.GT.1.5E-7.AND.DELTICL.LE.5.0E-7) THEN
   DELTEMP=1.E-8
END IF
TEMPDA=TEMPDA+DELTEMP
JITER=JITER+1
GO TO 22
C
430 CONTINUE
C
CALULATE RIGHT SIDE SURFACE PERMITTIVITY
C
SURPER=FUNEPS(FIER(I))/8.854E-14
WRITE (6,437) FIEL(IL),FIER(I),SURPER
FORMAT (5X,'LEFT SURFACE FIELD=','5X,E15.8,5X,/
1 5X,'RIGHT SURFACE FIELD=','5X,E15.8,5X,/
1 5X,'SURFACE PERMITTIVITY=','5X,E15.8,5X,/
C
C
DOWN LOAD DATA
DO 700 K=1,I
WRITE (1,630) FIER(K)
CONTINUE
DO 710 L=1,I
WRITE (2,630) POTR(L)
CONTINUE
DO 720 M=1,I
WRITE (4,630) DISTR(M)
CONTINUE
DO 730 KL=1,IL
WRITE (7,630) FIEL(KL)
CONTINUE
DO 740 LL=1,IL
WRITE (8,630) POTL(LL)
CONTINUE
DO 750 ML=1,IL
WRITE (9,630) DISTL(ML)
CONTINUE
630 FORMAT (5X,E15.8)
STOP
END

C
FUNCTION F: FINDING POTENTIAL FOR A GIVEN FIELD

FUNCTION F(POTEN,DOPING,FIELD)

PERINF=380.0*8.854E-14
PERMAX=8530.0*8.854E-14
FIECO=(1.3/5400.0E-8)/2.0
FIEZE=1.4/5400.0E-8
H1=0.5*PERINF*FIELD*FIELD

CRIFIE=ABS(0.005*FIECO)
IF (ABS(FIELD).GT.CRIFIE) GO TO 10

COEF1=0.5*(PERMAX-PERINF)
COEF2=1.0+(FIECO/FIEZE)*(FIECO/FIEZE)
H2=(COEF1/COEF2)*FIELD*FIELD
H=H1+H2
GO TO 20

C

EXACT FOMULAR AT FIELD LARGER THAN .5% COERCIVE FIELD

10 CONST2=FIECO/FIEZE*(PERMAX-PERINF)
H2=CONST2*(ATAN((FIELD-FIECO)/FIEZE)+ATAN(FIECO/FIEZE))
CONST3=0.5*(PERMAX-PERINF)*FIEZE*FIEZE
H3=CONST3 ALOG((FIEZE**2+(FIELD-FIECO)**2)/(FIEZE**2+FIECO**2))
FUNCTION HFIELD(FIELD)

PERINF=380.0*8.854E-14
PERMAX=8530.0*8.854E-14
FIECO=(1.3/5400.0E-8)/2.0
FIEZE=(1.4/5400.0E-8)
H1=0.5*PERINF*FIELD*FIELD
CRIFIE=ABS(0.005*FIECO)
IF (ABS(FIELD).GT.CRIFIE) GO TO 10
COEF1=0.5*(PERMAX-PERINF)
COEF2=1.0+(FIECO/FIEZE)*(FIECO/FIEZE)
H2=(COEF1/COEF2)*FIELD*FIELD
H=H1+H2
GO TO 20

FUNCTION FUNEPS(FIELD)

PERINF=380.0*8.854E-14
PERMAX=8530.0*8.854E-14
FIECO=(1.3/5400.0E-8)/2.0
FIEZE=(1.4/5400.0E-8)
DENOM=1.0+((FIELD-FIECO)/FIEZE)**2
FUNEPS=PERINF+(PERMAX-PERINF)/DENOM
RETURN
APPENDIX E

SUBROUTINES: AFTER FLAT-BAND

Included in this appendix is the computer program that calculates the potential and electric field distributions in the metal-semiconductor-metal (MFM) system. This program applies after the MFM system reaches the flat-band condition. Further, the program is limited only for applying a positive voltage on the top electrode. The program is written in FORTRAN language.
C ********************************************************************
C * PROGRAM FOR DISTANCE VS. POTENTIAL CALCULATION FOR THIN FILM *
C * PROPOSED MODEL IS DEPLETION APPROXIMATION *
C * CALCULATE FIELD & POTENTIAL AFTER REACHING FLAT BAND *
C ********************************************************************

DIMENSION POTR(10000),FIER(10000),DISTR(10000)

INPUT PARAMETERS

WRITE (6,500)
500   FORMAT (1X,'ENTER INPUT BIAS VOLTAGE')
WRITE (6,501)
501   FORMAT (1X,'FORWARD BIAS; ENTER POSITIVE VALUE',/)
READ (6,502) BIAS
502   FORMAT (F10.3)
FTHICK=5.4E-5
BHR0=-0.3
BHL=-0.24

INPUT DOPING CONCENTRATION

WRITE (6,504)
504   FORMAT (5X,'ENTER DOPING CONCENTRATION',/)
READ (5,505) DOPING
505   FORMAT (E15.8)
DEFEV=-0.0252*ALOG(5.0E19/DOPING)
SPINF=ABS(DEFEV+(BHR0-BHL))

CONFIRM PARAMETERS

WRITE (6,503) DOPING,FTHICK, BHR0, BHL, SPINF, BIAS
503   FORMAT (1X,'MATERIAL PROPERTIES:',//
1 1X,'DOPING CONCENTRATION='='',2X,E15.8,2X//
1 1X,'FILM THICKNESS (CM)='='',2X,E15.8,2X/
1 1X,'TOP ELECTRODE BARRIER @eq (eV)='='',2X,F10.3,2X/
1 1X,'BOTTOM ELECTRODE BARRIER @eq (eV)='='',2X,F10.3,2X/
1 1X,'SURFACE POTEN. FOR INFINITE SAMPLE','='',2X,E15.8,2X/
1 1X,'BIAS ON TOP ELECTRODE='='',2X,F10.3,2X//

BHR=BHR0-BIAS

FIND TOP ELECTRODE SURFACE POTENTIAL FOR CHOSEN THICKNESS

WRITE (6,15)
15   FORMAT (1X,'GUESS INITIAL LEFT SIDE SURFACE FIELD',5X,/
1    1X,'INITIAL GUESS MUST BE LESS THAN ZERO',5X)
READ (5,16) SFL
16   FORMAT (F15.8)
JITER=0
POTEN=ABS(BHR)-ABS(BHL)
**CONTINUE**

JITER = JITER + 1

**HSFL = HFIELD(SFL)**

**********************************************************************

CALCULATE POTENTIAL DISTRIBUTION USING GUESSED FIELD

SPOTF = SFL

I = 1

**CONTINUE**

X = (HFIELD(SPOTF) - HSFL)/(1.6E-19*DOPING)

FIER(I) = SPOTF

POTR(I) = X

CHANGE FIELD UP TO THE VALUE SATISFYING RIGHT SIDE FIELD

DELTA = POTEN - X

IF (DELTA.LE.0.5E-3) GO TO 200

FIELD STEP SIZE CONTROL

IF (DELTA.GT.0.05) FSTEP = 100.0

IF (DELTA.GT.0.005 .AND. DELTA.LE.0.05) FSTEP = 10.0

IF (DELTA.GT.0.0005 .AND. DELTA.LE.0.005) FSTEP = FSTEP*(-1.0)

SPOTF = SPOTF + FSTEP

I = I + 1

GO TO 50

CALCULATE DISTANCE, COMPARE WITH FILM THICK., DECIDE GO NO-GO

200

DISTR(I) = 0.0

DO 210 J = 2, I

DELPOTR = POTR(J) - POTR(J-1)

AVGFIER = 0.5*(FIER(J) + FIER(J-1))

DISTR(J) = DISTR(J-1) - (DELPOTR/AVGFIER)

IF (J.EQ.I) CALTHR = ABS(DISTR(J))

CONTINUE

WRITE (6, 611) JITER, CALTHR

611

FORMAT (5X, 'ITERATION: ', 5X, I4, 5X, 'THICKNESS= ', 2X, E15.8, 2X)

ERRTHICK = ABS(CALTHR - FTHICK)

IF ESTIMATED VALUE IS Thicker, INCREASE LEFT SURFACE FIELD MG.

IF THINNER, THEN DECREASE RIGHT SURFACE FIELD MG.

RELERR = ERRTHICK/FTHICK

IF (RELERR.LT.0.005) GO TO 212

IF (RELERR.GE.1.0) SFLSTEP = 1000.0

IF (RELERR.GE.0.5) SFLSTEP = 200.0

IF (RELERR.GE.0.1 .AND. RELERR.LT.0.5) SFLSTEP = 100.0

IF (RELERR.GE.0.02 .AND. RELERR.LT.0.1) SFLSTEP = 10.0

IF (RELERR.GE.0.01 .AND. RELERR.LT.0.02) SFLSTEP = 2.0

IF (RELERR.GE.0.005 .AND. RELERR.LT.0.01) SFLSTEP = 1.0
IF (CALTHR.GT.FTHICK) THEN
    SFL=SFL-SFLSTEP
    GO TO 25
END IF

IF (CALTHR.LT.FTHICK) THEN
    IF (SFL.EQ.0.0) THEN
        WRITE (6,209)
        209 FORMAT (5X,'IT IS NOT FLAT BAND MODEL ANY LONGER',/)
        GO TO 212
    END IF
    SFL=SFL+SFLSTEP
    IF (SFL.GT.0.0) SFL=0.0
    GO TO 25
END IF

CONTINUE

C ******************************************************************
C
420
C
C ******************************************************************
C
WRITE (6,420) FIER(I),POTR(I),CALTHR,FIER(I),POTR(I)
420 FORMAT (1X,'******** SOLUTION ********',/)
    1 IX,'LEFT SIDE ELECTRIC FIELD=' ,5X,E15.8,2X,/ 
    1 IX,'LEFT SIDE POTENTIAL='  ,5X,E15.8,2X,/ 
    1 IX,'CALCULATED FILM THICKNESS=' ,5X,E15.8,2X,/ 
    1 IX,'RIGHT SIDE ELECTRIC FIELD=' ,5X,E15.8,2X,/ 
    1 IX,'RIGHT SIDE POTENTIAL='  ,5X,E15.8,2X,/)

CONTINUE

CALULATE RIGHT SIDE SURFACE PERMITTIVITY

SURPER=FUNEPS(FIER(I))/8.854E-14
WRITE (6,437) FIER(I),SURPER
437 FORMAT (5X,'SURFACE ELECTRIC FIELD=' ,5X,E15.8,5X,/ 
    1 5X,'SURFACE PERMITTIVITY='  ,5X,E15.8,5X,/)

DO 700 K=1,I
700 WRITE (1,630) FIER(K)
CONTINUE
DO 710 L=1,I
710 WRITE (2,630) POTR(L)
CONTINUE
DO 720 M=1,I
720 WRITE (4,630) DISTR(M)
CONTINUE

FORMAT (5X,E15.8)
STOP
END

C ******************************************************************
C
C FUNCTION F: FINDING POTENTIAL FOR A GIVEN FIELD
C
FUNCTION F(POTEN,DOPING,FIELD,HSFL)

PERINF=380.0*8.854E-14
PERMAX=8530.0*8.854E-14
FIECO=(1.3/5400.0E-8)/2.0
FIEZE=1.4/5400.0E-8
H1=0.5*PERINF*FIELD*FIELD

TAYLOR EXPANSION AT LOW ELECTRIC FIELD

CRIFIE=ABS(0.005*FIECO)
IF (ABS(FIELD).GT.CRIFIE) GO TO 10
COEF1=0.5*(PERMAX-PERINF)
COEF2=1.0+(FIECO/FIEZE)*(FIECO/FIEZE)
H2=(COEF1/COEF2)*FIELD*FIELD
H=H1+H2
GO TO 20

EXACT FORMULAR AT FIELD LARGER THAN .5% COERCIVE FIELD

10
CONST2=FIECO*FIEZE*(PERMAX-PERINF)
H2=CONST2*(ATAN(FIELD-FIECO)/FIEZE)+ATAN(FIECO/FIEZE))
CONST3=0.5*(PERMAX-PERINF)*FIEZE*FIEZE
H3=CONST3*ALOG((FIEZE**2+(FIELD-FIECO)**2)/(FIEZE**2+FIECO**2))
H=H1+H2+H3
GO TO 20

CONTINUE

TR=H
TL=1.6E-19*DOPING*POTEN-HSFL
F=TL-TR
RETURN
END

FUNCTION HFIELD(FIELD)

PERINF=380.0*8.854E-14
PERMAX=8530.0*8.854E-14
FIECO=(1.3/5400.0E-8)/2.0
FIEZE=1.4/5400.0E-8
H1=0.5*PERINF*FIELD*FIELD

TAYLOR EXPANSION AT LOW ELECTRIC FIELD

CRIFIE=ABS(0.005*FIECO)
IF (ABS(FIELD).GT.CRIFIE) GO TO 10
COEF1=0.5*(PERMAX-PERINF)
COEF2=1.0+(FIECO/FIEZE)*(FIECO/FIEZE)
H2=(COEF1/COEF2)*FIELD*FIELD
H=H1+H2
GO TO 20

EXACT FORMULAR AT FIELD LARGER THAN 0.5% COERCIVE FIELD

10
CONST2=FIECO*FIEZE*(PERMAX-PERINF)
H2=CONST2*(ATAN((FIELD-FIECO)/FIEZE)+ATAN(FIECO/FIEZE))
CONST3=0.5*(PERMAX-PERINF)*FIEZE*FIEZE
H3=CONST3*ALOG((FIEZE**2+(FIELD-FIECO)**2)/(FIEZE**2+FIECO**2))
H=H1+H2+H3
FUNCTION FUNEPS(FIELD)

PERINF = 380.0 * 8.854E-14
PERMAX = 8530.0 * 8.854E-14
FIECO = (1.3 / 5400.0E-8) / 2.0
FIEZE = 1.4 / (5400.0E-8)
DENOM = 1.0 + ((FIELD - FIECO) / FIEZE) ** 2
FUNEPS = PERINF + (PERMAX - PERINF) / DENOM
RETURN
END
REFERENCES


