Chapter 1

Introduction to ferroelectrics

Hysteresis loops come in all sizes and shapes, and, similar to a fingerprint identify the material in a very special way

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The phenomenon of ferroelectricity was discovered in 1921 by J. Valasek who was investigating the dielectric properties of Rochelle salt (NaKC₄H₄O₆·4H₂O). The name ferroelectricity refers to certain magnetic analogies, though it has no connection with iron (ferrum) at all. Ferroelectricity has also been called Seignette electricity, as Seignette or Rochelle Salt (RS) was the first material found to show ferroelectric properties such as a spontaneous polarization on cooling below the Curie point, ferroelectric domains and a ferroelectric hysteresis loop [1].

Oxide materials has wide range of applications since these oxides exhibit properties ranging from insulator to high T_c superconductors and from ferroelectric to ferromagnetics. Research on high T_c superconducting thin
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films has brought a rapid development on the growth technique and have promoted the application of oxide thin films for device fabrication.

The potential for device application drove a tremendous volume of research beginning in the mid 1940’s when BaTiO$_3$ was discovered to have a high dielectric constant (1000-3000) and possess the largest ferroelectric response then known to exist. Since then, many other ferroelectric ceramics including lead titanate (PbTiO$_3$), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), and relaxor ferroelectrics like lead magnesium niobate (PMN) have been developed and utilized for a variety of applications. But the interests diminished in 1960’s and 1970’s when industrial demands for the ease of processing and device durability dictated the use of alternate materials and approaches. Fatigue and aging associated with polycrystalline bulk materials were detrimental to many applications [2].

The development of ceramic processing and thin film technology lead to the emergence of new applications of ferroelectrics. A renewed interest in ferroelectric thin films has arisen with the new growth techniques like plasma sputtering, ion beam sputtering, metal organic vapour chemical deposition (MOCVD), sol-gel, spin coating, metal organic decomposition (MOD) and pulsed laser deposition (PLD) to produce high quality thin films of ferroelectrics. The PLD technique has matured rapidly with the discovery of high temperature superconducting oxides in 1986 [3]. These oxides have a perovskite based structure similar to many ferroelectric materials and have been deposited as epitaxial films by PLD. Epitaxial films can be deposited by PLD at low substrate temperature and high deposition rates over a range of target phases and composition with few experimental parameters to optimize.
The most promising application of ferroelectric ceramics have been in the areas such as dielectric ceramics for capacitors, ferroelectric thin films for non volatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro-optic materials for data storage and displays. The potential commercial and defense related applications of thin ferroelectric film with thickness 0.2-5\(\mu m\) are widespread and include acoustic wave transducers [4, 5], electro optic switches [6] radiation hard, NVRAM [7] and pyrosensors [8]. Ferroelectrics have recently gained attention as potential smart materials and as active sensors in smart devices [9]. Ferroelectric composition mostly contain a volatile component (Pb,Bi,Li or K) and small deviations from stoichiometry can lead to films that comprise undesirable non ferroelectric phase. Control over the process is required to preclude loss of volatile components and formation of metastable phases [2].

### 1.1 Ferroelectric phase transition

A ferroelectric phase transition is a structural phase transition which results in the ability of the crystal to sustain a spontaneous polarization caused by the relative displacement of the ions of each unit cell of the crystal [1].

The ferroelectric phase transition occurs at a temperature \(T_c\) analogous to the curie temperature of a ferromagnet. Above the Curie temperature the crystal is usually a centrosymmetric paraelectric. Below the curie temperature the crystal is no longer centrosymmetric which results in ferroelectric behavior.

In the ferroelectric phase at least one set of ions in the crystal sits in a double well potential where either of the two positions is equally energiti-
cally favorable. Above $T_c$ the particle in a double well have enough kinetic energy to move back and forth over the barrier that separates the wells so that the time average position of the atom is midway between the wells. Figure 1.1 shows the thermodynamic potential of the system as function of the atom position [9].

![Figure 1.1: Thermodynamic potential as a function of atom position for a ferroelectric material below its curie temperature.](image)

If the shape of the well stays the same above $T_c$ but ion kinetic energy $k_B T$ becomes large, the transition is an order disorder phase transition. If the minima of the well actually move together to form a single well above $T_c$ then the transition is displacive. These are the extrema of the phase transition phenomena most ferroelectric phase transition are combination
Ferroelectric phase transition

Ferroelectric phase transitions can be described mathematically with some success by Landau theory often called Landau-Devonshire theory as credit to Devonshire who developed it specifically for the ferroelectric case. Phase transitions in ferroelectric are usually second-order transitions meaning that the distortions of the crystal lattice occur continuously with temperature. When the transition are discontinuous (first-order) they are usually close to second-order transitions and are still described well by Landau-Devonshire theory.

In Landau-Devonshire theory the Helmhotz free energy of the system is described by a power series in the order parameter $\eta$ [1]. For a ferroelectric crystal the order parameter is the polarization, $\eta$ where $0 \leq \eta \leq 1$

$$F(\eta, T, E) = A\eta^2 + B\eta^4 + C\eta^6 + D$$

where $D$ is a constant. $A$ has the form $A_0(T-T_c)$ where $T_c$ is the Curie temperature. If the transition is first order there is hysteresis in the temperature dependence. This form for $A$ is a result of mean field theory which is often used in ferromagnetism and analogously can be used in ferroelectrics as well. $B$ and $C$ are likely to be temperature dependent as well. The order (first or second) of the transition depends on the sign of $B$ with $C$ being necessarily positive for stability. At thermal equilibrium the free energy of any systems is minimized.

$$\frac{\partial F}{\partial \eta_{T,x}} = 0$$

$$0 = 2A\eta + 4B\eta^3 + 6C\eta^5$$

where $A$, $B$, and $C$ are constants dependent on temperature and the specific material.
If $B$ is positive, the last term is negligible. Then

$$\eta^2 = 2A_0 \frac{T_c - T}{4B} \eta(0)^2 = 2A_0 \frac{T_c}{4B} \eta(T) = \eta(0) \sqrt{\frac{T_c - T}{T_c}}$$

(1.4)

This describes the change in the order parameter as a function of temperature in the second order continuous phase transition. If $B$ is negative the transition is first order and discontinuous.

1.2 Domains and Ferroelectric polarization

Ferroelectric behavior arises from the fact that in the ferroelectric phase at least one set of ions in the crystal has a double well potential as shown in the figure 1.1. A local region where all of the ions in the crystal sit on the same side of the well is called domain[9].

If a ferroelectric phase transition takes place in an ideal crystal with an infinitely slow decrease in temperatures (to maintain thermal equilibrium in the crystal) then a single domain would form in the crystal. All ions in the crystal would be thermodynamically coupled and hence sit on the same side of the double well, the probability of the ion residing in one side or the other being equal. In real crystals different regions form ferroelectric phase independently resulting in domains with different directions of polarization

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$$

(1.5)

which relates the electric displacement $\mathbf{D}$ and electric field $\mathbf{E}$ to the polarization $\mathbf{P}$. The dielectric polarization $\mathbf{P}$ is due to both the polarizability of the material due to the applied field, $\mathbf{P}_E$, and from the spontaneous alignment of dipoles in the materials, $\mathbf{P}_s$. 
\[ \mathcal{P}_E = \chi E \]  
(1.6)

The free charge density must satisfy poisson's equation

\[ \nabla \cdot \mathcal{D} = \rho \]  
(1.7)

so that

\[ \nabla \cdot \mathcal{E} = \frac{1}{\epsilon \epsilon_0} \left( \rho - \nabla \cdot \mathcal{P}_s \right) \]  
(1.8)

In an infinite ideal ferroelectric crystal, \n\[ \nabla \cdot \mathcal{E} = \frac{\rho}{\epsilon \epsilon_0} \] as in ordinary dielectrics. For a real crystal, \( P_s \) goes to zero at the crystal surface and may differ from the bulk crystal value at defect sites. For these reasons

\[ \nabla \cdot \mathcal{P}_s \]  
(1.9)

acts as a polarizing field opposed to the dielectric polarization. It is this depolarizing field which can be compensated by the flow of free charge in the crystal. The energy associated with the depolarization of the crystal is zero for a totally compensated crystal in equilibrium. Domains form in fresh crystals to compensate for depolarization energy before free charge compensation takes place.

In a fresh crystal the net polarisation of the crystal should be zero due to the many domains of random polarization. In a nonconducting finite crystal a complex branched domain system is predicted to eliminate the electric field due to the surface. In real crystals even a low conductivity can compensate the surface effects and allow for a simpler columnar domain structure to form [1].
Polarization of ferroelectric crystals is accomplished by aligning the cells in the material in the same direction by the application of a field. This is done by increasing the size of domains in the desired direction while decreasing the size of domains in all the other direction until the crystal is one domain pointing in the direction of field.

Domain walls in ferroelectric are only a few unit cells wide with the polarization going to zero at the center of the wall. The domain width is dependant on the thickness of the crystal. If the thickness of the crystal decreases so that the domain width approaches the thickness of the domain wall the depolarizing field can no longer be compensated and there is a minimum film thickness for which ferroelectricity to be a stable state [1]. The occurrence of a finite thickness has considerable implications for applications of ferroelectrics because it limits the useful thickness of these materials.

The primary property of a ferroelectric is the reversibility of its spontaneous polarization accomplished by reversing the direction of the applied field. Polarization reversal is demonstrated by a hysteresis loop in the plot of polarization versus applied electric filed (P-E). This is measured using a Sawyer Tower circuit.

The coercive field $E_c$ is the field at which half of the polarisation has been reversed. The remnant polarisation $P_r$ is the polarisation which remains when the field is removed. A high polarisation and a low well defined coercive field results in a square shaped loop and the crystal is ideal for ferroelectric application.

Defects in ferroelectric crystals are evident from P-E plot. When the polarisation is reversed the polarisation due to defects will not reverse or may reverse at a different field than the rest of the crystal. If the defects do
reverse the value of coercive field is affected. if it doesnt reverse, the whole loop is biased along field axis.

1.3 Ferroelectric domains and hysteresis loop

A ferroelectric material is characterized by reversible spontaneous polarization arising from non centro symmetric arrangements of ions in its unit cell which produces a permanent electric dipole moment. Adjacent dipoles also tend to orient themselves in the same direction to form a region called ferroelectric domains. Ferroelectricity is commonly observed in ABO$_3$ perovskite structures and hence do not exhibit any spontaneous polarization (para-electric phase). As the temperature is lowered below the curie point phase transformation take place from paraelectric state to ferroelectric state. The center ion is displaced from its body center position and cubic unit cell deforms to one of the non centrosymmetric structures such as tetragonal rhombohedral or monoclinic structure. The polarization response with the electric field of these materials is highly nonlinear and exhibits a hysteresis loop as shown in figure 1.2.

Ferroelectrics are a subgroup of the pyroelectric materials which are in turn a subgroup of piezoelectric materials. These materials have a characteristic temperature -transition temperature- at which the material makes a structural phase change from a polar phase (ferroelectric) to a non polar called paraelectric phase [10].
As the applied field is increased ferroelectric domains which are favorably oriented with respect to the applied field grow at the expense of other domains. This continues till the total domain growth and reorientation of all the domains has occurred in a direction favorable to the external field. At this stage the material is assumed to possess saturated polarization ($P_{sat}$). If the electric field is removed at this point some of the domains do not reorient into a random configuration and thus leaving the material still polarized. This polarization is the remnant polarization ($P_r$). The strength of the electric field required to return the polarization to zero is the coercive field ($E_c$).
The drive towards miniaturization in electronic devices has motivated scientists to focus on ways to improve the properties of dielectric and ferroelectric oxide thin film. The fabricated capacitors based on these oxide thin film are useful for the development of dynamic random access memories (DRAM)[11] or microwave devices [12]. An ideal capacitor based on these ferroelectric oxides should have high dielectric constant, high dielectric break down field strength, low leakage current density and low dissipation factor. Apart from electronic application ferroelectric films are of interest to various micro electromechanical and optical applications.

1.4 Oxygen octahedra

A very important group of ferroelectric is that known as the perovskite from the mineral perovskite CaTiO₃. The perfect perovskite structure is an extremely simple one with general formula ABO₃ where A is a monovalent or divalent metal and B is a tera or pentavalent one (figure 1.3).

Figure 1.3: Perovskite structure with general formula ABO₃
The perovskite structure is cubic with A atoms at the cube corners, B atoms at the body centers and the oxygen at the face centers. The structure can also be regarded as a set of BO$_6$ octahedra arranged in a simple cubic pattern and linked together by shared oxygen atoms with A atoms occupying the spaces between.

The first ferroelectric perovskite to be discovered was BaTiO$_3$. This rose the interest in ferroelectrics as it was earlier believed that H bond crystals alone show ferroelectricity.

Much simpler in their ferroelectric soft mode behaviour are the near ferroelectric KTaO$_3$ and SrTiO$_3$ and the actual ferroelectric PbTiO$_3$. Lead titanate in addition has a single ferroelectric phase whereas BaTiO$_3$ undergoes successive transitions to three different ferroelectric phases as the temperature is lowered. The great fascination of the perovskite structure is that it readily undergoes structural transitions involving non polar phonons (tilt in oxygen octahedron) in addition to both ferro and antiferroelectric transitions.

The O$_6$ group in particular can be thought of as a hard unit in the sense that it is little distorted from regular octahedron symmetry. In the cubic phase the O$_6$ octahedron are parallel but the bond angles at their corners are soft and tilting is easy. The simplest set tilt are those in which all octahedra tilt in alternating fashion about the same axis. There are three such possibilities a

- two fold symmetry (diad-axis) tilt
- three fold (triad axis) tilt
- four fold (tetrad axis) tilt

The triad axis tilt then requires 3 equal non zero components and the diad axis tilt then requires two equal non zero components. However un-
equal tilt components and many other arrangement are possible. The off centering of the B cation is a relatively independent process that can occur in any structure built from hard octahedra. It is this off centering which leads to the presence of dipoles and to ferroelectric and antiferroelectric behaviour.

The types of ferroelectric materials have been grouped according to their structure. The four main types of structures include the corner sharing oxygen octahedra, compounds containing hydrogen bonded radicals, organic polymers and ceramic polymer composites. A large class of ferroelectric crystals are made up of mixed oxides containing corner sharing octahedra of $O^{2-}$ ions (as shown in figure 1.4). The corner sharing oxygen octahedra discussed includes the perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structured compounds, and lithium niobate and tantalate [13].

**Figure 1.4:** (a) A cubic ABO$_3$ (BaTiO$_3$) perovskite-type unit cell and (b) three dimensional network of corner sharing octahedra of $O^{2-}$ ions
All most all the materials (except KNO$_3$) described by the general formula ABO$_3$ possess the perovskite crystal structure. The A element is a large cation situated at the corners of the unit cell (monovalent or divalent metal) and the B element is a smaller cation located at the body center (tetravalent or pentavalent metal). The oxygen atoms are at the face centers [1]. In the ferroelectric phase, perovskite structure assumes one of the three Bravis lattice: tetragonal, orthorhombic or rhombohedral.

In tetragonal symmetry a cubic cell stretches along one side (c axis) and shrinks along the other two sides (a axis) forming a rectangular prism. The spontaneous polarization aligns itself parallel to the longest side. The orthorhombic structure is formed by stretching the face diagonal along which the polarization aligns. In a rhombohedral structure cube is stretched along a body diagonal and polarization aligns in that direction.

In a paraelectric phase, the perovskite structure has cubic symmetry - neither stretched nor distorted. Ferroelectric materials for 64 and 256 Mb RAM [10]. It is the off centering of the B cation that leads to ferroelectric and antiferroelectric behaviour. The B cations have two stable positions relative to the neighboring ions. A potential barrier separates one from the other. The ion can exchange position if enough energy is supplied to the system for the ion to overcome the barrier.

Some of the important compounds crystallizing in perovskite phase is discussed in detail.

1.4.1 Barium Titatate (BaTiO$_3$)

Barium titanate (BaTiO$_3$ / BT) has a paraelectric cubic phase above its Curie point of 130°C. In the temperature range of 130°C to 0°C the ferroelectric tetragonal phase with a c/a ratio of ~ 1.01 is stable. The sponta-
neous polarization is along one of the [001] directions in the original cubic structure. Between 0°C and -90°C, the ferroelectric orthorhombic phase is stable with the polarization along one of the [110] directions in the original cubic structure. On decreasing the temperature below -90°C the phase transition from the orthorhombic to ferroelectric rhombohedral phase leads to polarization along one of the [111] cubic directions. The spontaneous polarization on cooling BaTiO₃ below the Curie point $T_c$ is due to changes in the crystal structure. As shown in figure 1.5a the paraelectric cubic phase is stable above 130°C with the center of positive charges (Ba²⁺ and Ti⁴⁺ ions) coinciding with the center of negative charge (O²⁻). On cooling below the Curie point $T_c$, a tetragonal structure (figure 1.5b) is evolved where the center of Ba²⁺ and Ti⁴⁺ ions are displaced relative to the O²⁻ ions, leading to the formation of electric dipoles. Spontaneous polarization developed is the net dipole moment produced per unit volume for the dipoles pointing in a given direction [14].

**Figure 1.5:** The crystal structure of BaTiO₃ (a) above the Curie point the cell is cubic; (b) below the Curie point the structure is tetragonal with Ba²⁺ and Ti⁴⁺ ions displaced relative to O²⁻ ions
Various A and B site substitutions in different concentrations have been tried to see their effect on the dielectric and ferroelectric properties of BaTiO$_3$. Sr$^{2+}$ substitutions to the A site have been found to reduce the Curie point linearly towards room temperature. The substitution of Pb$^{2+}$ for Ba$^{2+}$ raises the Curie point. The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of BaTiO$_3$. The effect of various isovalent substitutions on the transition temperatures of BaTiO$_3$ ceramic [15].

**Figure 1.6**: The effect of isovalent substitutions on the transition temperatures of BaTiO$_3$ ceramic [15]
temperatures of BaTiO$_3$ ceramic are shown in figure 1.6 [15–18].

The dielectric properties of BaTiO$_3$ are found to be dependent on the grain size [19–21]. Figure 1.7 shows the variation of dielectric constant with temperature for BaTiO$_3$ ceramics with a fine ($\sim$1 $\mu$m) and coarse ($\sim$50$\mu$m) grain size. Large grained BaTiO$_3$ ($\geq$1$\mu$m) shows an extremely high dielectric constant at the Curie point.

This is because of the formation of multiple domains in a single grain, the motion of whose walls increases the dielectric constant at the Curie point. For a BaTiO$_3$ ceramic with fine grains ($\sim$1 $\mu$m), a single domain forms inside each grain. The movement of domain walls are restricted by the grain boundaries, thus leading to a low dielectric constant at the Curie
point as compared to coarse grained BaTiO$_3$ [22]. The room temperature dielectric constant ($\epsilon_r$) of coarse grained ($\sim$10 $\mu$m) BaTiO$_3$ ceramics is found to be in the range of 1500-2000. On the other hand, fine grained ($\sim$1 $\mu$m) BaTiO$_3$ ceramics exhibit a room temperature dielectric constant between 3500-6000. The grain size effect on the dielectric constant at room temperature has been explained by the work of Buessem et. al. [23] and Arlt et. al [24]. Buessem and coworkers proposed that the internal stresses in fine grained BaTiO$_3$ must be much greater than the coarse grained ceramic, thus leading to a higher permittivity at room temperature. Arlt studied the domain structures in BaTiO$_3$ ceramics and showed that the room temperature $\epsilon_r$ reached a peak value at a critical grain size of $\sim$ 0.7 $\mu$m.

As the BaTiO$_3$ ceramics have a very large room temperature dielectric constant, they are mainly used multilayer capacitor applications. The grain size control is very important for these applications.

### 1.4.2 Barium Stronion Titanatae (Ba$_x$Sr$_{1-x}$TiO$_3$)

Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) is the solid solution between barium titanate (BaTiO$_3$) and strontium titanate (SrTiO$_3$) over the entire range of concentration. The dielectric and ferroelectric properties of Ba$_x$Sr$_{(1-x)}$TiO$_3$ depend on Sr content. At room temperature Ba$_x$Sr$_{(1-x)}$TiO$_3$ is ferroelectric, when $x$ is in the range of 0.7-1 and is paraelectric when $x$ is in the range 0-0.7[25]. As a result the electrical and optical properties of BST can be tailored over a broad range for various electronic applications [26].

The utilization of the BaTiO$_3$ - SrTiO$_3$ solid solution allows the Curie temperature (ferroelectric-paraelectric transition temperature, Tc) of BaTiO$_3$ can be shifted from 120$^0$C to around room temperature for Ba$_x$Sr$_{(1-x)}$TiO$_3$ films. For Sr addition into BaTiO$_3$, the linear drop of Tc is ca. 3.4$^0$C per
mol%. Therefore, 30mol% Sr (x = 0.3) would bring the Tc down to room temperature. BST films are not only paraelectric at the dynamic random access memory (DRAM) operating temperature range (0–70°C ambient and 0–100°C on chips) [27], but also achieve maximum permittivity around the operating temperature. On the other hand, the volatilities of the BST components are lower than Pb-based ferroelectric materials, thereby making it relatively easier to introduce into fabrication facilities [27, 28]. BST films are polycrystalline. Their properties heavily depend on composition, stoichiometry, microstructure (grain size and size distribution), film thickness, characteristics of electrode, and homogeneity of the film. The BST thin film growth method significantly affects the composition, stoichiometry, crystallinity, and grain size of the film and, consequently, its dielectric properties [29].

Barium strontium titanate (Ba,Sr)TiO3 (BST) thin films are being widely investigated as alternative dielectrics for ultra large scale integrated circuits (ULSIs) DRAM storage capacitors [29–32] due to its

1. high dielectric constant (\(\epsilon_r >200\))
2. low leakage current
3. low temperature coefficient of electrical properties
4. small dielectric loss
5. free from fatigue or aging problems
6. high compatibility with device processes
7. linear relation of electric field and polarization
8. low Curie temperature

. However, whether BST thin film can be successfully applied largely depends on more thorough understanding the materials properties. The deposition techniques and electrical properties of BST films have received increasing interest. According to those investigations the electrical and dielectric properties and reliability of BST films heavily depend upon the deposition process, post-annealing process, composition, base electrodes, microstructure, film thickness, surface roughness, oxygen content and film homogeneity.

A variety of techniques such as rf-sputtering [33–35], laser ablation [36] and solgel processing [37] have been used to deposit BST thin films. Above methods are highly competitive, each having advantages and disadvantages in terms of homogeneity, processing temperature, and processing costs. Because of the multicomponent nature of BST materials precise microscopic control of stoichiometry is essential for obtaining uniform single phase films. The basic parameters for applying capacitor thin films on DRAMs are dielectric constant, leakage current density and reliability. The targets for ideal Gbit era DRAM dielectrics include the followings [27]: (i) SiO$_2$ equivalent thickness $<0.2$ nm for Gbit; (ii) leakage current density $<1<10^{-7}$ Acm$^{-2}$ at 1.6V; (iii) life time 10 years at 85$^0$C and 1.6V; (iv) stability $10^{15}$ cycles at $>100$ MHz; and (v) general compatibility to semiconductor processing.

1.4.3 Lead Titanate (PbTiO$_3$)

Lead titanate (PbTiO$_3$/PT) is a ferroelectric material having a structure similar to BaTiO$_3$ with a high Curie point (490$^0$C). On decreasing the
temperature through the Curie point a phase transition from the paraelectric cubic phase to the ferroelectric tetragonal phase takes place. Lead titanate ceramics are difficult to fabricate in the bulk form as they undergo a large volume change on cooling below the Curie point. It is the result of the cubic \((c/a = 1.00)\) to tetragonal \((c/a = 1.064)\) phase transformation leading to a strain of >6%. Hence, pure \(\text{PbTiO}_3\) ceramics crack and fracture during fabrication. The spontaneous strain developed during cooling can be reduced by modifying the lead titanate with various dopants such as Ca, Sr, Ba, Sn, and W to obtain a crack free ceramic.

### 1.4.4 Lead Zirconate Titanate (Pb(Zr\(_x\)Ti\(_{1-x}\))O\(_3\))

Lead Zirconate Titanate (PZT) is a binary solid solution of \(\text{PbZrO}_3\) an antiferroelectric (orthorhombic structure) and \(\text{PbTiO}_3\) a ferroelectric (tetragonal perovskite structure). PZT has a perovskite type structure with the Ti\(^{4+}\) and Zr\(^{4+}\) ions occupying the B site at random. The PZT phase diagram is shown in figure 1.8. At high temperatures PZT has the cubic perovskite structure which is paraelectric. On cooling below the Curie point line, the structure undergoes a phase transition to form a ferroelectric tetragonal or rhombohedral phase. In the tetragonal phase, the spontaneous polarization is along the \(<100>\) set of directions while in the rhombohedral phase the polarization is along the \(<111>\) set of directions [38].
Figure 1.8: The PZT phase diagram

As shown in figure 1.8 most physical properties such as dielectric and piezoelectric constants show an anomalous behavior at the morphotropic phase boundary (MPB). The MPB separating the two ferroelectric tetragonal and orthorhombic phases has a room temperature composition with a Zr/Ti ratio of $\sim 52/48$. PZT ceramics with the MPB composition show excellent piezoelectric properties. The poling of the PZT ceramic is also easy at this composition because the spontaneous polarization within each grain can be switched to one of the 14 possible orientations (eight [111] directions for the rhombohedral phase and six [100] directions for the tetragonal phase). Below the Zr/Ti ratio of 95/5 the solid solution is antiferroelectric with an orthorhombic phase. On the application of an electric field to this composition a double hysteresis loop is obtained. This is because of the strong influence of the antiferroelectric PbZrO$_3$ phase [15].
In order to suit some specific requirements for certain applications, piezoelectric ceramics can be modified by doping them with ions which have a valence different than the ions in the lattice. Piezoelectric PZT ceramics having the composition at the MPB can be doped with ions to form "hard" and "soft" PZT. Hard PZT are doped with acceptor ions such as K$^+$, Na$^+$ (for A site) and Fe$^{3+}$, Al$^{3+}$, Mn$^{3+}$ (for B site), creating oxygen vacancies in the lattice [39, 40]. Hard PZT usually have lower permittivities, smaller electrical losses and lower piezoelectric coefficients. These are more difficult to pole and depole, thus making them ideal for rugged applications. On the other hand, soft PZT are doped with donor ions such as

**Figure 1.9:** The effect of composition on the dielectric constant and electromechanical coupling factor $k_p$ in PZT ceramics


La$^{3+}$ (for A site) and Nb$^{5+}$, Sb$^{5+}$ (for B site) leading to the creation of A site vacancies in the lattice [41–44]. The soft PZT have a higher permittivity, larger losses, higher piezoelectric coefficient and are easy to pole and depole. They can be used for applications requiring very high piezoelectric properties.

### 1.4.5 Lead Lanthanum Zirconate Titanate

(Pb$_{1-x}$La$_x$)(Zr$_{1-y}$Ti$_y$)$_{1-x/4}$O$_3$

(Pb$_{1-x}$La$_x$)(Zr$_{1-y}$Ti$_y$)$_3$O$_3$ PLZT is a transparent ferroelectric ceramic formed by doping La$^{3+}$ ions on the A sites of lead zirconate titanate (PZT). The PLZT ceramics have the same perovskite structure as BaTiO$_3$ and PZT. The transparent nature of PLZT has led to its use in electro-optic applications. Before the development of PLZT, the electro-optic effect was seen only for single crystals. The two factors that are responsible for getting a transparent PLZT ceramic include the reduction in the anisotropy of the PZT crystal structure by the substitution of La$^{3+}$ and the ability to get a pore free ceramic by either hot pressing or liquid phase sintering.

The general formula for PLZT is given by $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-x/4}\text{O}_3V^B_{0.25x}\text{O}_3$ and $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)V^A_{0.5x}\text{O}_3$. The first formula assumes that La$^{3+}$ ions go to the A site and vacancies ($V^B$) are created on the B site to maintain charge balance. The second formula assumes that vacancies ($V^A$) are created on the A site. The actual structure may be due to the combination of A and B site vacancies.

The room temperature phase diagram of PLZT system is shown in figure 1.10. The different phases in the diagram are a tetragonal ferroelectric phase (FE$_{tet}$), a rhombohedral ferroelectric phase (FE$_{Rh}$), a cubic re-

laxor ferroelectric phase (FE\textsubscript{Cubic}), an orthorhombic antiferroelectric phase (AFE) and a cubic paraelectric phase (PE\textsubscript{Cubic}) [45].

**Figure 1.10:** Room temperature phase diagram of the PLZT system. The regions in the diagram are, a tetragonal ferroelectric phase (FE\textsubscript{Tet}); a rhombohedral ferroelectric phase (FE\textsubscript{Rh}); a cubic relaxor ferroelectric phase (FE\textsubscript{Cubic}); an orthorhombic antiferroelectric phase (AFE); and a cubic paraelectric phase (PE\textsubscript{Cubic}).

The electro-optic applications of PLZT ceramics depends on the composition. Figure 1.11 shows the hysteresis loops for various PLZT compositions from the phase diagram. PLZT ceramic compositions in the tetragonal ferroelectric (FE\textsubscript{Tet}) region show hysteresis loops with a very high coercive field (E\textsubscript{C}). Materials with this composition exhibit linear electro-optic behavior for E < E\textsubscript{C}. PLZT ceramic compositions in the rhombohedral ferroelectric (FE\textsubscript{Rh}) region of the PLZT phase diagram have loops with a low coercive field. These PLZT ceramics are useful for optical memory.
applications [45].

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig11.png}
\caption{Representative hysteresis loops obtained for different ferroelectric compositions (a) $\text{FE}_{\text{Tet}}$ (b) $\text{FE}_{\text{Rh}}$ (c) $\text{FE}_{\text{Cubic}}$ and (d) AFE regions of the PLZT phase diagram.}
\end{figure}

PLZT ceramic compositions with the relaxor ferroelectric behavior are characterized by a slim hysteresis loop (figure 1.11). They show large quadratic electro-optic effects which are used for making flash protection goggles to shield them from intense radiation. This is one of the biggest applications of the electro-optic effect shown by transparent PLZT ceramics. The PLZT ceramics in the antiferroelectric region show a hysteresis loop expected from an antiferroelectric material. These components are used for memory applications [45–48].
Material process issues in PZT

A good ferroelectric film has a high remnant polarization ie a large amount of charge can be stored in a small area and a small coercive field ie it can be polarized at low voltages. For use in transparent devices a high optical transmittance is also needed. Most defects in PZT is due to vacancies, usually lead and oxygen. PbO is volatile and PZT can accommodate large amounts of lead and oxygen vacancies which can interact with one another [49]. Low resistivity is also attributed to lead loss in PZT films. Lead loss is avoided by adding 2 to 10% excess lead in the starting material [50, 51]. Oxygen vacancies is inhibited by including donor dopants in PZT.

Lead loss causes PZT to behave like a p-type semiconductor. The lead vacancies ($V_{Pb}$) act as acceptors and cause the Fermi level to move towards the valence band [52]. When it is thermodynamically more favorable to create an oxygen vacancy ($V_0$) to compensate the lead vacancy than it is to further modulate the Fermi level, oxygen vacancies form concomitantly with lead vacancies and the materials exhibits fatigue and conductivity. Figure 1.12 shows the relationship between oxygen and lead vacancies and the Fermi level in the PZT band gap.
The migration of oxygen vacancies during polarisation causes fatigue [1]. Intentional donor doping has been shown to counteract fatigue in ferroelectric capacitors by the suppression of the formation of oxygen vacancies. Fatigue occurs when upon repeated switching of a crystal the polarisation becomes clamped while the coercive field increases and become less well defined. Fatigue causes a longer switching time for the crystal. The fatigue can be reduced or eliminated by choosing oxide electrodes.

It is common practice to include donor dopants in PZT to improve electrical and optical properties. The most common A site donor dopants are trivalent lanthanum (La) and yttrium (Y). Lanthanum donor dopants in PZT compensate the lead vacancy acceptors thereby inhibiting the formation of oxygen vacancies. Figure 1.13 shows La donor sites in the band gap. \((\text{Pb,La})(\text{Zr,Ti})\text{O}_3\) (PLZT) is valued for its exceptional electro optical properties and its increased transparency compared to PZT [51]. But PLZT has a smaller amount of polarization and a less squareness hysteresis loop.

**Figure 1.12:** Energy level due to lead and oxygen vacancies in the PZT band gap
when compared to PZT with the same Zr/Ti ratio [49].

![Diagram of energy levels in PZT]

**Figure 1.13:** La donors levels in the band gap of PZT compensate lead vacancies leading to the suppression of compensation induced oxygen vacancies

Common B-site donor dopants are pentavalent niobium (Nb) and the tantalum (Ta) which substitute for quadrivalent Zr or Ti. A thin layer of PbTiO$_3$ (PT) grown before the deposition of PZT or PLZT has been shown to assist in the crystallisation in the perovskite phase since PbTiO$_3$ always crystallise in the perovskite phase. Very thin layer of PbTiO$_3$ will facilitate the growth of the perovskite phase and have little effect on the dielectric properties of the film but increasing the thickness of PbTiO$_3$ buffer layer causes a decrease in the dielectric constant due to the lower dielectric constant of PbTiO$_3$ layer compared to the PZT.

**1.4.6 Lead Magnesium Niobate (Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$)**

Relaxor ferroelectric are a class of lead based perovskite type compounds with the general formula Pb(B$_1$B$_2$)O$_3$ where B$_1$ is a lower valency cation
Introduction to ferroelectrics

(like Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Fe$^{3+}$) and $B_2$ is a higher valency cation (like Nb$^{5+}$, Ta$^{5+}$, W$^{5+}$). Pure lead magnesium niobate (PMN or Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$) is a representative of this class of materials with a Curie point at -10º C. The main differences between relaxor and normal ferroelectrics is shown in Table 1.1.

Table 1.1: Differences between normal and relaxor ferroelectrics.[53]

<table>
<thead>
<tr>
<th>Property</th>
<th>Normal Ferroelectric</th>
<th>Relaxor Ferroelectric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric temperature dependence</td>
<td>Sharp 1$^{st}$ or 2$^{nd}$ order transition at Curie point $T_c$</td>
<td>Broad diffused phase transition at Curie maxima</td>
</tr>
<tr>
<td>Dielectric frequency dependence</td>
<td>Weak Frequency dependence</td>
<td>Strong frequency dependence</td>
</tr>
<tr>
<td>Dielectric Behavior in paraelectric range ($T &gt; T_c$)</td>
<td>Follows Curie - Weiss law</td>
<td>Follows Curie - Weiss square law</td>
</tr>
<tr>
<td>Remnant polarization ($P_R$)</td>
<td>Strong $P_R$</td>
<td>Weak $P_R$</td>
</tr>
<tr>
<td>Scattering of light</td>
<td>Strong anisotropy</td>
<td>Very weak anisotropy to light</td>
</tr>
<tr>
<td>Diffraction of x-rays</td>
<td>Line splitting due to deformation from paraelectric to ferroelectric phase</td>
<td>No x-ray line splitting</td>
</tr>
</tbody>
</table>
Table 1.2: Major families of ferroelectric oxides [54]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Characteristics</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$, BST, SrTiO$_3$</td>
<td>Dielectric, Pyroelectric, Ferroelectric, electro-optic</td>
<td>DRAM capacitors, sensors, Phase shifters, SHG</td>
</tr>
<tr>
<td>PbTiO$_3$ PT, Pb(ZrTi)O$_3$, PZT, (Pb,La)(Zr,Ti)O$_3$ PLZT</td>
<td>Dielectric, Pyroelectric, Ferroelectric, Piezoelectric, electro-optic</td>
<td>Pyrodetectors, transducers, Non volatile memory, SHG, optical memory</td>
</tr>
<tr>
<td>SrBi$_2$Ta$_2$O$_9$</td>
<td>Ferroelectric</td>
<td>Non volatile memory</td>
</tr>
<tr>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)O$_3$ PMN-PT</td>
<td>Dielectric, electro-optic</td>
<td>Capacitor memory, waveguide devices</td>
</tr>
<tr>
<td>LiNbO$_3$, LiTaO$_3$</td>
<td>Piezoelectric devices, electro-optic</td>
<td>Pyrodetectors, waveguide applications, SHG, optical modulators</td>
</tr>
<tr>
<td>KNbO$_3$, K(Ta, Nb)O$_3$</td>
<td>Pyroelectric, electro-optic</td>
<td>Waveguided devices, frequency doublers, holographic storage, pyro-detector</td>
</tr>
</tbody>
</table>

Relaxor ferroelectrics like PMN can be distinguished from normal ferroelectrics such as BaTiO$_3$ and PZT, by the presence of a broad diffused and dispersive phase transition on cooling below the Curie point. The dif-
fused phase transitions in relaxor ferroelectrics are due to the compositional heterogeneity seen on a microscopic scale.

Major families of ferroelectric oxides with their important properties and application are listed in table 1.2.

1.5 Application

Ferroelectric thin films have attracted attention for applications in many electronic and electro-optic devices. Some of the important ferroelectric materials being used for making thin films include the perovskite type materials such as BaTiO$_3$, (Ba$_x$Sr$_{1-x}$)TiO$_3$, PbTiO$_3$, Pb(Zr$_x$Ti$_{1-x}$)O$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. Applications of ferroelectric thin films utilize the unique dielectric, piezoelectric, pyroelectric, and electro-optic properties of ferroelectric materials. Some of the most important electronic applications of ferroelectric thin films include nonvolatile memories, thin films capacitors, pyroelectric sensors, and surface acoustic wave (SAW) substrates. The electro-optic devices being studied include optical waveguides and optical memories and displays.

There are three important ferroelectric thin film non volatile random access memory (NVRAM) concepts. Two are based on nondestructive read-out (NDRO) approach which avoids repolarisation of the ferroelectric after a read operation. In one of these designs a ferroelectric thin film controls the source to drain current through the FET. However the charge injection from the ferroelectric semiconductor interface can be a limiting problem.

The second NDRO approach is less developed. It uses a polarisation dependent photoinduced current from a capacitor to read the memory cell. This
concept would be especially useful for more advanced memory application such as high capacity parallel processor or an optical image comparator.

The final NVRAM approach has received more widespread attention. It uses the remanent polarisation of a ferroelectric capacitor to store information. The polarisation state is read by measuring the current drawn through the capacitor by an applied voltage pulse. Since this read operation can reverse the polarisation state it is known as destructive read out (DRO) device.

1.5.1 Novel microelectronic devices

Novel devices make use of the large dielectric constant or the desirable piezoelectric and electrooptic properties of ferroelectric thin film materials. In ultra large scale integrated (ULSI) circuits the decreasing area for capacitors requires a concomitant but unattainable decrease in layer thickness of standard dielectrics. Use of a large dielectric constant material would allow thicker films and ferroelectric materials having high dielectric constant is employed for such applications.

High dielectric constant ferroelectric materials could also be used in microwave monolithic integrated circuits (MMIC). For example on chip bypass capacitor. Another potential microwave application of ferroelectric thin film is for phase shifting. A DC bias applied across the ferroelectric layer controls the dielectric constant and hence its phase velocity through MIM structure. The large piezoelectric properties of ferroelectric thin films can be useful for the fabrication of surface acoustic wave devices (SAW). Interdigital transducers (IDTs) with finger like pattern on the surface can be used to launch acoustic wave into the underlying material at resonant frequencies. Similar IDTs can act as receivers for the launched acoustic
waves. This structure can function as a high frequency filter or be used to diffract an optical signal in an acoustic devices. The strong electro optical coupling of many ferroelectric materials provide a number of application in thin film form. Optical wave guides fabricated in ferroelectric thin films could be used in directional couplers, Mach-Zehndar intensity modulators and total internal reflection switches.

1.5.2 Sensors and Actuators

The research area of micro electro mechanical systems (MEMS) has been receiving much attention lately. In MEMS, sensors and actuators are constructed on a microscale using lithographic techniques developed for integrated circuit fabrication. A number of devices have been conceived and studied that utilize the peizoelectric and pyroelectric properties of ferroelectric materials. Devices require epitaxial growth, coherent interfaces with an underlying semiconductor substrate and lower processing temperatures. High quality epitaxial films may offer advantages in terms of sensitivity and reduced leakage current under dc bias.

1.5.3 Smart materials and adaptive structures

Smart materials are able to alter their performance in response to their environment or an external stimulus. By designing they should perform this function automatically although separate sensing component may provide the stimulus. An example is the use of adaptive optics to compensate for turbulence in the atmosphere.
1.5.4 Thin film Capacitors

The high dielectric permittivity of ferroelectric ceramics such as BaTiO$_3$, BST, PMN and PZT make them very useful for capacitor applications. The MLC (multilayer ceramic capacitors) have a very high volumetric efficiency (capacitance per unit volume) because of the combined capacitance of thin ceramic tapes of thickness $\sim$ 10-20 $\mu$m stacked one on top of the other. The volumetric efficiency of the MLC capacitor can be further increased if the thickness of the ceramic sheets can be made lower ($< 10 \mu$m). Thin film technology can be used to make dielectric layers as thin as 1 $\mu$m. BaTiO$_3$ and PMN are the two important materials being looked at for thin film MLC applications [55].

1.6 Ferroelectric RAM memory

There are worldwide considerable efforts to develop nonvolatile random access memories. Portable electronic equipment such as the personal digital assistant, cellular phones or digital cameras need secure and fast data transfer in combination with nonvolatile storage. Another main development route is that of contact less smart cards with multiple functions including e.g. personal banking, transport access and medical data. The market for non-volatile random access memories (NVRAMs) has been drastically increased over the last years, although by far not reaching the market volume of (volatile) dynamic random access memories (DRAMs). The required performance of NVRAMs, such as, storage density, endurance, write and access time or power consumption are related to a particular application. Therefore it is not astonishing that a number of different NVRAMs technologies exist to fulfill all requirements.
1.6.1 History of FeRAM

Ferroelectric RAM was proposed and published in 1952. Development of FeRAM began in the late 1980s. Work was done in 1991 at NASA’s Jet Propulsion Laboratory on improving methods of read out, including a novel method of non-destructive readout using pulses of UV radiation [56]. Much of the current FeRAM technology was developed by Ramtron, a fabless semiconductor company. One major licensee is Fujitsu, who operate what is probably the largest semiconductor foundry production line with FeRAM capability. Since 1999 they have been using this line to produce standalone FeRAMs, as well as specialized chips (e.g. chips for smart cards) with embedded FeRAMs within. Fujitsu produces devices for Ramtron. By 2005, Ramtron reported that they were evaluating prototype samples of an 8 megabit FeRAM manufactured using Texas Instruments’ (TI) FeRAM process. Fujitsu and Seiko-Epson were in 2005 collaborating in the development of a 180 nm FeRAM process. FeRAM research projects have also been reported at Samsung, Matsushita, Oki, Toshiba, Infineon, Hynix, Symetrix, Cambridge University, University of Toronto and the Interuniversity Microelectronics Centre, Belgium.

1.6.2 Working of FeRAM

The reversible spontaneous polarization of ferroelectric materials make them attractive for memory applications. An ideal memory device has low power consumption fast read and write access times and infinite re writability. Memory devices should also be scalable. A ferroelectric non volatile (NV) memory must be able to maintain its orientation in the absence of
applied power for more than ten years in order to compete with modern devices [57].

Designs for ferroelectric memory have two basic types; capacitor type memories have ferroelectric capacitor in series with field effect transistor (FRAM) and transistor type memories have a ferroelectric material as the
gate dielectric of the ferroelectric field effect transistor (FEFET) [34]. Non volatile ferroelectric random access memory (NVFRAM) are the first ferroelectric devices to be commercially available [58].

Memory arrays of capacitor type FRAM have advantages over current magnetic hard disks and floppy disks. FeRAM have no moving parts, more reliable and have faster read/write access time. Moreover the ferroelectric materials have dielectric constants up to 500 times larger than current memory dielectrics so more charge can be stored in a smaller surface area [57].

FRAM is based on the DRAM structure in which a capacitor is connected in series with a transistor. Figure 1.14 shows a circuit diagram of a FRAM devices. The success of DRAM is largely due to its small cell size. DRAM and FRAM store one bit on one capacitor and one transistor [59].

Data are stored in an array of capacitors each connected to the sources of a metal oxide semiconductor (MOS) transistor. The drains of the transistors are connected to the bit lines and the gates are connected to the word lines. Data are written to the capacitors by applying a voltage to the word lines to turn on the transistors. those which connects each capacitor to its bit line. Then a voltage greater than the ferroelectric capacitors positive coercive voltage or a voltage greater than the capacitors negative coercive voltage is applied to the bit line to write 1 or 0 to the cell, respectively.

To read the cell the transistors are turned on and the capacitors discharge onto the bit line. At the end of each bit line a sense amplifier determines whether the cell was written with 1 or a 0 and then rewrites the cell by applying the appropriate voltage. DRAM is volatile, the capacitors must be refreshed occasionally to maintain the memory (charge).
The advantage of using a ferroelectric capacitor in DRAM cell is the nonvolatility of the ferroelectric polarization. An FRAM is non volatile memory that is as small as a DRAM cell with no moving parts. When a material has a higher dielectric constant more charge can be stored in a smaller area.

Like DRAM, FRAM is a destructive read out (DRO) device, which means that the information stored in the cell is lost when the cell is read and must be written after it is read. Reading an FRAM cell requires that the polarization on the capacitor be reversed. This means that FRAM devices will be read and rewritten more often than nondestructive read out (NDRO) devices. The quality of the capacitor is integral to the device properties.

It is also important that the devices be symmetric that is the positive and negative coercive voltages have approximately the same value, which remains constant in time. Since the device is written with a 1 or 0 with a voltage pulse that is greater than the coercive voltage, the coercive voltage must remain the same over time in order to properly polarize the device with that pulse. Hence only capacitors which exhibit low fatigue and imprint properties can be used in FRAM devices. The two coercive voltage points should be symmetrical and less than 2.5V in order to operate from standard memory voltage power supply’s [57].

A schematic representation of FeRAM is shown in the figure 1.15. Ferroelectric capacitors are usually integrated on to a CMOS processed chip in a back end process to keep from contaminating the CMOS facility. All the process involved in the patterning and deposition of ferroelectric capacitors have to be safe for CMOS devices [58] and must not damage the ferroelectric layer [34].
1.6.3 Comparison with other systems

Density

The main factor that determine the memory system’s cost is the density of the components used to make it up. Smaller components, and less of them, means that more cells can be packed onto a single chip, which in turn means more can be produced from a single silicon wafer. This improves yield, which is directly related to cost.

The lower limit to this scaling process is an important point for comparison, generally the technology that scales to the smallest cell size will end up being the least expensive per bit. FeRAM and DRAM are constructionally similar, and can generally be built on similar lines at similar sizes. In both cases the lower limit seems to be defined by the amount of charge needed to trigger the sense amplifiers. For DRAM, this appears to be a
problem at around 55 nm, at which the charge stored in the capacitor is too small to be detected. It is not clear if FeRAM can scale to the same size, as the charge density of the PZT layer may not be the same as the metal plates in a normal capacitor.

An additional limitation on size is that materials tend to stop being ferroelectric when they are too small [60, 61]. This effect is related to the ferroelectric’s "depolarization field". There is ongoing research on addressing the problem of stabilizing ferroelectric materials; one approach, for example, uses molecular adsorbates.

To date, the commercial FeRAM devices have been produced at 350 nm and 130 nm.

**Power Consumption**

The key advantage of FeRAM over DRAM is the low power consumption which could be understood from read and write cycles. In DRAM, the charge deposited on the metal plates leaks across the insulating layer and the control transistor, and disappears. In order for a DRAM to store data for anything other than a microscopic time, every cell must be periodically read and then re-written, a process known as refresh. Each cell must be refreshed many times every second (65ms) [62] and this requires a continuous supply of power.

In contrast, FeRAM only requires power when actually reading or writing a cell. The vast majority of power used in DRAM is used for refresh, indicating power usage about 99% lower than DRAM.

Another non-volatile type memory is Flash RAM, and like FeRAM it does not require a refresh process. Flash works by pushing electrons across a high-quality insulating barrier where they get "stuck" on one terminal of
a transistor. This process requires high voltages, which are built up in a charge pump with time. This means that FeRAM could be expected to be lower power than Flash, at least for writing, as the write power in FeRAM is only marginally higher than reading. For a "mostly-read" device the difference might be slight, but for devices with more balanced read and write the difference could be expected to be much higher.

Performance

DRAM performance is limited by the rate at which the charge stored in the cells can be drained (for reading) or stored (for writing). Generally this ends up being defined by the capability of the control transistors, the capacitance of the lines carrying power to the cells, and the heat that power generates.

FeRAM is based on the physical movement of atoms in response to an external field, which happens to be extremely fast, settling in about 1 ns. In theory, this means that FeRAM could be much faster than DRAM. However, since power has to flow into the cell for reading and writing, the electrical and switching delays would likely be similar to DRAM overall. It does seem reasonable to suggest that FeRAM would require less charge than DRAM, because DRAMs need to hold the charge, whereas FeRAM would have been written to before the charge would have drained. That said, there is a delay in writing because the charge has to flow through the control transistor, which limits current somewhat.

In comparison to 'Flash' the advantages are much more obvious. Whereas the read operation is likely to be similar in performance, the charge pump used for writing requires a considerable time to "build up" current, a process that FeRAM does not need. Flash memories commonly need about
1 ms to write a bit, whereas even current FeRAMs are at least 100 times that data rate.

Existing 350 nm devices have read times of the order of 50-60 ns. Although slow compared to modern DRAMs, which can be found with times of the order of 2 ns, common 350 nm DRAMs operated with a read time of about 35 ns, so FeRAM performance appears to be comparable given the same fab [62].

1.6.4 Recent trends in ferroelectric materials

FeRAM remains a relatively small part of the overall semiconductor market. Flash memory is currently the overwhelmingly dominant NVRAM technology, and this situation seems likely to continue for at least the rest of the decade. The much larger sales of flash memory compared to the alternative NVRAMs support a much larger research and development effort. Flash memory is produced using semiconductor linewidths of 30 nm at Samsung (2007) while FeRAMs are produced in linewidths of 350 nm at Fujitsu and 130 nm at Texas Instruments (2007). Flash memory cells can store multiple bits per cell (currently 2 in the highest density NAND flash devices), and the number of bits per flash cell is projected to increase to 4 or even to 8 as a result of innovations in flash cell design. The areal bit densities of flash memory are consequently much higher than FeRAM, and thus the cost per bit of flash memory is orders of magnitude cheaper than FeRAM.

The density of FeRAM arrays might be increased by improvements in FeRAM foundry process technology and cell structures, such as the development of vertical capacitor structures (in the same way as DRAM) to reduce the area of the cell footprint. However, reducing the cell size may cause the
data signal to become too weak to be detectable. Theoretically, it should be possible to embed FeRAM cells using two additional masking steps during conventional CMOS semiconductor manufacture. Flash typically requires nine masks. This could make possible for example, the integration of FeRAM on microcontrollers, where a simplified process would reduce costs. However, the materials used to make FeRAMs are not commonly used in CMOS integrated circuit manufacturing. Both the BST/PZT ferroelectric layer and the noble metals used for electrodes raise CMOS process compatibility and contamination issues.

The FM22L16 is the semiconductor industry’s highest density FRAM, a 4-Mbit, 3V, parallel nonvolatile RAM that breaks new technological ground. It is manufactured on TIs advanced 130nm CMOS process. The FM22L16 is a 256Kx16 nonvolatile memory that reads and writes like a standard static RAM. A ferroelectric random access memory or FRAM is nonvolatile, which means that data is retained after power is removed. It provides data retention for over 10 years while eliminating the reliability concerns, functional disadvantages and system design complexities of battery-backed SRAM (BBSRAM). Fast write timing and high write endurance make FRAM superior to other types of memory.

The FM22L16 includes a low voltage monitor that blocks access to the memory array when virtual device driver (VDD) drops below a critical threshold. The memory is protected against an inadvertent access and data corruption under this condition. The device also features software-controlled write protection. The memory array is divided into 8 uniform blocks, each of which can be individually write protected.