Characterization of ferroelectric thin films materials for FeRAM

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Abstract- **Due to low power consumption levels and high operation speeds, FeRAM are considered as one of the most promising candidates for non-volatile information storage in modern portable electronic devices such as mobile phones and notebook computers. The characteristics of the ferroelectric film, the main element of the FeRAM, are quite important as they determine the quality of the device. In this paper, we discuss the most suitable materials and preparation technologies for FeRAM. Especially, the properties and characteristics of PZT and SBT and their relation to the deposition technique used are presented**

Key words- **FeRAM, PZT, SBT, ferroelectricity $Pb(Zr_xTi_{1-x})O_3$**

I. Introduction

Memories are important and indispensable devices in the electronic industry. Several kinds of memories have been used in computer and communication technology such as static random access memory (SRAM), read only memory (ROM), dynamic random access memory (DRAM), Flash memory, ferroelectric random access memory (FeRAM), etc. FeRAM is a RAM-based device that uses the ferroelectric effect to store information as an electric polarization in the absence of an applied-electric field [1,2].

A FeRAM cell is created by depositing a film of ferroelectric material in crystalline form between two electrode plates to form a capacitor. This construction is very similar to that of the DRAM capacitor. Rather than storing data as charge on a capacitor like a DRAM, a ferroelectric memory stores data within a crystalline structure. Interesting ferroelectric materials include perovskite oxide lead zirconium titanate ceramic (PZT-$PbZr_xTi_{1-x}O_3$), modified barium titanate $(Ba,Sr)TiO_3$, $Pb(Mg,Nb)O_3$, $PbTiO_3$, $BaTiO_3$, $KNbO_3$ with octahedral structure and layered oxide $SrBi_2Ta_2O_9$, $SrBi_2(Ta,Nb)_2O_9$. Among these materials, PZT and SBT have been used in FeRAMs due to their promising ferroelectric properties and large capacity for data storage. PZT and SBT thin films have been grown by different techniques, such as liquid-phase deposition, radio frequency magnetron sputtering, metal-organic chemical vapor deposition (CVD), plasma-enhanced MOCVD, as well as pulsed-laser deposition (PLD) [3].

II. Basic Operation of Non-Volatile FeRAM

A ferroelectric material is characterized by reversible spontaneous polarization arising from noncentrosymmetric arrangements of ions in its unit cells, which produces a permanent electric dipole moment. Adjacent dipoles also tend to orient themselves in the same direction to form a region called ferroelectric domain. Ferroelectricity is most commonly observed in ABO_3 perovskite structures as shown in Figure 1. Above the Curie temperature these materials have a centrosymmetric structure and hence do not exhibit any spontaneous polarization. This phase is known as paraelectric phase. As the temperature is lowered below the Curie point phase transformation takes place from paraelectric state to ferroelectric state. The center ion is displaced from its body center position and the cubic unit cell deforms to one of the noncentrosymmetric structures such as tetragonal rombhohedral or monoclinic structures. The polarization response with the electric field of these materials is highly non-linear and exhibits a hysteresis loop as shown in Figure 2. As the applied electric field is increased, the ferroelectric domains, which are favorably oriented with respect to the electric field, grow at the expense of other domains. This phenomenon continues until total domain growth and reorientation of all the domains has occurred in a

direction favorable to 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 known as remanent polarization (P_r). The strength of the electric field required to return the polarization to zero is called the coercive field (E_c).

Although these features of a ferroelectric material could be used in a wide range of applications the primary focus of the recent research is directed towards development of non-volatile random access memories. In principle the memory application is based on the hysteresis behavior of polarization with electric field as shown in Figure 2. When an external voltage is applied to a ferroelectric capacitor, there is a net ionic displacement in the unit cells of the ferroelectric material. The individual unit cells interact constructively with their neighbors to produce domains within the material. As the voltage is removed a majority of the domains will remain in the direction of the previously applied field, requiring compensating charge to remain on the plates of the capacitor. At zero applied fields, there are two states of polarization ($\pm P_r$), which are equally stable. Either of these two states could be encoded as "1" or "0" and since no external field is required to maintain these states the memory device is non-volatile. Obviously to switch the state of the device a threshold electric field greater than coercive field is required. Since ferroelectric materials have very high coercive fields (in the order of kV/cm), it is necessary to fabricate these materials in the form of thin films in order to be able to switch the domains from one orientation to the other.

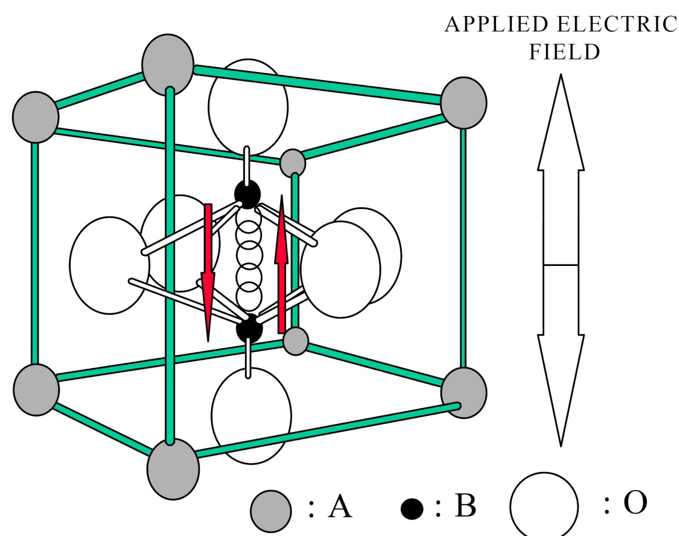

Figure 1. ABO_3 perovskite unit cell.

From a digital point of view if a voltage is applied to a ferroelectric capacitor in a direction opposite to that of previous voltage the remanent domains will switch, requiring a compensating charge to flow on to the capacitor plates. If the field is applied in the direction of the previously applied field, no switching takes place, no change occurs in the compensating charge and hence a very reduced amount of charge flow to the capacitor takes place. This phenomenon can be used to read the state or write a desired state into a ferroelectric storing device. Most often, ferroelectric memory cells are read destructively by sensing the current transient that is delivered to a small load resistor when an external voltage is applied to the cell. For example, if a memory cell is in a negative state (say $-P_r$) and a positive switching voltage is applied to it, there will be a switching charge and a corresponding switching current. This switching current will consist of a linear dielectric response and a displacement current. A non-switching current, for example, is the response of a memory cell in a positive state ($+P_r$) to a positive applied voltage. This current would consist of only a small linear dielectric response. A sense amplifier and other associated circuitry are used in a FRAM device to determine this transient current and thereby read the state of the device.

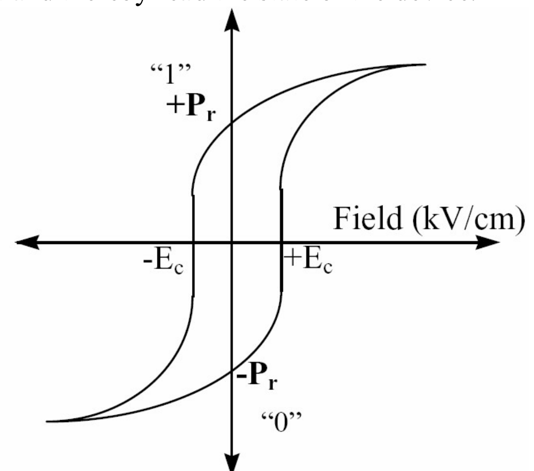

Figure 2. Typical polarization hysteresis loop of a ferroelectric capacitor.

Therefore, an ideal material for use as a FRAM capacitor should have high remnant polarization, low coercive voltage, and a reasonable Curie temperature (much higher than the device operating temperature and lower than the film formation temperature.

III. Ferroelectric Materials

Many ferroelectric materials have been considered for FeRAM, including PZT, SBT, $Bi_4Ti_3O_{12}$, $LiNbO_3$, $Pb(Mg,Nb)O_3$, $PbTiO_3$, $BaTiO_3$, $KNbO_3$, $SrBi_2(Ta,Nb)_2O_9$ and $BaMgF_4$. Among those, PZT and SBT films have received more attention because of their large polarization values and process feasibility. In fact,

the process required to prepare the ferroelectric thin film must not have a detrimental effect on the underlying pattern structure. Two families of materials, PZT and SBT, have been widely investigated for memory application.

PZT is a perovskite material that has a wide range of ferroelectric phase transition temperatures (Curie-temperatures) and two different ferroelectric structures, depending on the Zr/Ti composition ratio [4]. Figure 3 shows the phase diagram of PZT in which the phase transitions are observed. When the Ti content is higher than 0.47, PZT transforms from cubic structure to tetragonal structure at temperatures ranging from 370 to 490 °C. When the Ti content is lower than 0.47, there is a cubic to rhombohedral transition with Curie-temperatures ranging from 230 to 370 °C. The phase diagram clearly shows that the Curie-temperature of PZT increases as the Ti content increases. It is required for the ferroelectric memory to have a wide range of operating temperatures within which the electrical properties are maintained constant. There is morphotropic phase boundary (MPB) region in which the tetragonal and rhombohedral structures are coexisted. The mixture of these two structures in MPB region gives good ferroelectric properties to the PZT films at Ti = 0.47 the lattice parameters of tetragonal structure are changed as a function of Zr/Ti ratio.

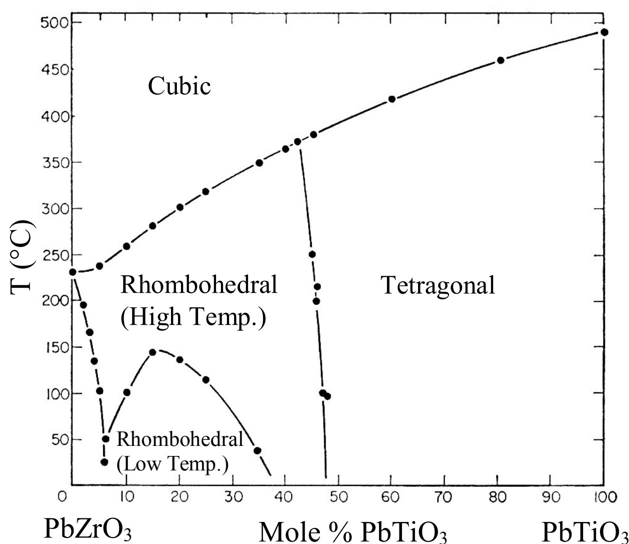

Figure 3. Phase diagram of PZT.

Quite some research on PZT films with various Zr/Ti composition ratios has been reported. Since the ferroelectric properties strongly rely on the film composition, it is desirable to determine the optimal composition for the particular application. In general, the PZT films with 53/47 ratio (MPB region) have been intensively investigated for memory application, because these films exhibit largest P_r and lowest E_c, as required for FeRAM application. The Ti-rich PZT films are also considered as very attractive for process integration due to their low crystallization temperature.

SBT is orthorhombic with lattice constants a=5.531 Å, b=5.534 Å, and c=24.98 Å at room temperature. It belongs to the Aurivillius family with two $(SrTa_2O_7)^{2-}$ perovskite-like structures between $(Bi_2O_2)^{2+}$ layers. The Curie temperature of the SBT is 310^{0}C, and the dielectric constant is 200-300 at the room temperature and 100 kHz. The advantages and disadvantages of both materials are listed as shown in table 1.

Table 1. Properties of PZT and SBT thin films.

Materials	PZT families	SBT families
Crystal structure	ABO_3 type perovskite	Bi layered structure
Formation temperature (^{0}C)	600-700	750-850
Switching polarization ($\mu C/cm^2$)	30-60	10-30
Dielectric constants	400-1500	200-300
Curie temperature (^{0}C)	300-500	-310

IV. Ferroelectric Thin Films Deposition Techniques

Several methods are currently being used for depositing thin films, each of which has its merits and disadvantages. The methods can be classified into three groups:

Physical vapor deposition (PVD), e.g. RF sputtering and pulsed laser deposition.

Chemical vapor deposition (CVD), e.g. metal-organic chemical vapor deposition (MOCVD), PECVD, LSCVD.

Chemical solution deposition (CSD), e.g. sol-gel.

Table 2. Deposition techniques.

Method	Advantages	Disadvantages
PVD	CMOS compatible	Large capital expenditure Difficult to control with complex oxides
CVD	CMOS compatible	Large capital expenditure Requires a source of precursors
CSD	Inexpensive and flexible	Undeveloped for industrial applications

The PVD process was originally developed to deposit materials with a very high melting point (so

called refractive materials). Sputtering involves the removal of material from a solid cathode called target. This is accomplished with Ar gas plasma. The ions are accelerated and knock some of the cathode material loose from the surface. The material is transferred into a physical vapor that deposits on the substrate. The film thickness of the deposited material can be controlled by the sputter time and power. In addition to refractive materials, sputtering is very useful for the deposition of alloys and compound materials as the resulting film structure can be tailored closely to match the composition of the starting target material.

CSD technologies for the fabrication of thin films have gained considerable interest. These novel process routes make the following possible:

- The synthesis of a broad spectrum of materials.
- The ability to co-synthesise two or more materials simultaneously.
- Coating of one or more materials on to other materials (metal or ceramic particulates, and three-dimensional objects).
- Production of extremely homogeneous alloys and composites.
- Synthesis of ultra-high purity materials.
- Very accurate tailoring of the composition even in the early stages of the process, because the synthesis is actually performed on an atomic level.
- Precise control of the microstructure of the final products and.
- Precise control of the physical, mechanical, and chemical properties of the final products.

Although PVD and CVD techniques are currently favored by the semiconductor industry - partly because of their existing investment and experience in using these techniques - CSD is a useful research and development tool requiring very little capital expenditure. The quality of the obtained films is comparable among all three deposition methods.

V. CONCLUSION

In this study, PZT thin films with 53/47 ratio are selected as ferroelectric materials for capacitors because:

- Remnant polarization (P_r) values in PZT capacitors are larger than SBT capacitors;
- The formation temperature of a PZT film is considerably lower than that of an SBT film.
- PZT films show relatively stronger endurance against hydrogen-induced damage compared with that of SBT films.
- PZT 53/47 exhibits the largest remanent polarization (P_r) and lowest coercive field (E_c).

Possibility to use the CSD technique for the deposition of this material will be investigated. CSD technique is good for deposition of PZT materials with high quality, high density and at low cost.

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