Chapter 2
Literature Review

2-1. Structure of ferroelectric oxides

Ferroelectric oxides may be classified into four structure type : (1) perovskite (e.g. $BaTiO_3$, $KNbO_3$ etc.), (2) pyrochlore (e.g. $Cd_2Nb_2O_7$), (3) tungsten bronze and ($PbNb_2O_6$, $PbTa_2O_6$), (4) layer-type bismuth compounds (e.g. $PbBi_2Nb_2O_9$, $SrBi_2Ta_2O_9$). A feature common to these four structures is the presence of ions of small size and large charge in oxygen octahedral, which are linked through corners forming continuous chains of oxygen-metal-oxygen. Among these structures, perovskite and layer bismuth compounds were commonly used in memory devices.

Ferroelectrics with the perovskite structure were introduced by Smolenskii et al. [21]. A wide variety of cations in the complex ABO_3 perovskite can be substituted. Cation A is normally larger than cation B. Barium titanate ($BaTiO_3$) is probably one of the best-cited examples. The crystal structure of $BaTiO_3$ crystal is a cubic unit cell as shown in Fig.2-1. The centers of mass of the negative charges (O^{2-}) and the positive charges of Ba^{2+} and Ti^{4+}, coincide at the Ti^{4+} ion, as shown in the figure. Above the Curie temperature (130), the thermal energy is sufficient to allow the Ti atoms to move randomly from one position to another, so there is no fixed asymmetry, net polarization and P=0. However, below the Curie temperature (130), the whole crystal becomes spontaneously polarized. The onset of spontaneous polarization is accompanied by the distortion of the crystal structure. That is the structure of barium titanate elongates and

the cubic structure is distorted to tetragonal, as shown in Fig.2-1, in which the Ti^{4+} atom is not located at the center of mass of the negative charges. The crystal is therefore polarized by the separation of the center of mass of the negative charges and possesses a finite polarization vector P, which is ferroelectric. As the direction of the polarization is altered by applied electric field, FeRAM using ferroelectric memory cell capacitor can write logic state of "1" and "0" by changing the direction of applied voltage.

Another important structure, recently used in the ferroelectric thin films for nonvolatile memory applications, has been under intensive investigation. These phases are layered perovskites belonging to a group of compounds which were initially described by Aurivillius [22]. He has synthesized a number of mixed bismuth oxides of the general formula $(Bi_2O_2)^{2+}$ $(A_{x-1}B_xO_{3x+1})_m^{2-}$, where A is mono-, di- or trivalent ions or a mixture of them, such as Bi^{3+}, Ba^{2+}, Sr^{2+}, Cu^{2+}, Pb^{2+}, K^+, and B is tetra-, penta-, hexavalent ions or a mixture of them, such as Ti^{4+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, W^{6+}, or Fe^{3+}, and the integer m takes any of the values from 1 to 5. The structure comprises a stacking of m perovskite-like units of nominal composition ABO_3 between Bi_2O_2 layers along the pseudo-tetragonal c-axis (see Fig.2-2). For the example of $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN), there consist of two connected layers of TaO_6 (or NbO_6) octahedral with Sr cations located inside the perovskite-like layers, which are separated by Bi_2O_2 layers as shown in the figure. The structure of SBT, SBN materials have unique ferroelectic properties and spontaneous polarization.
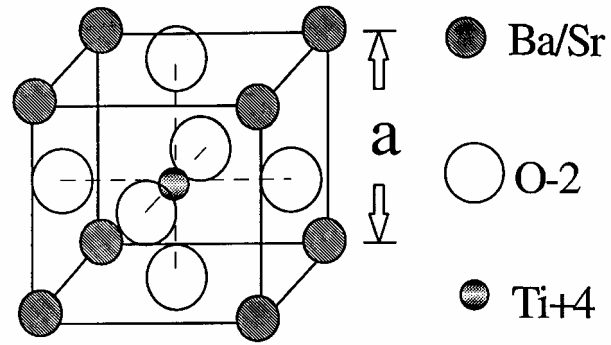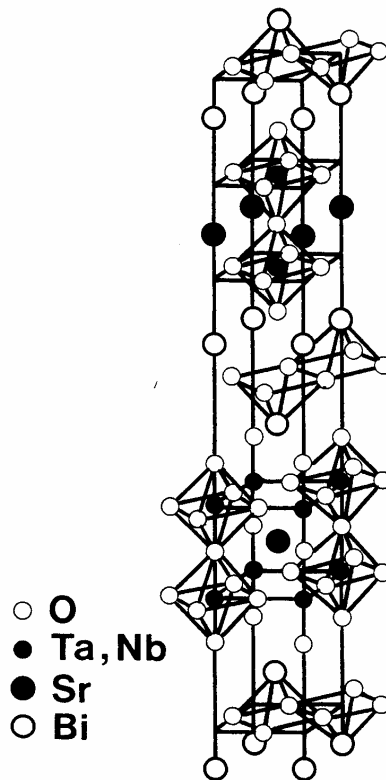
Fig.2-1 The perovskite structure

Fig.2-2 The Bi-base layered perovskite structure of SBT (SBN).

2-2. The composition of ferroelectrics

The effects of Bi/Ta and Sr/Ta mole fraction on ferroelectric properties of $Sr_xBi_yTa_2O_9$ (0.7≤x≤1.0, 2.0≤y≤2.6) thin film were

investigated by Atsuki et al. [23]. They grew SBT thin films by sol-gel method using a spin coating on Pt/Ta/SiO$_2$/Si and Pt/Ti/SiO$_2$/Si substrates. The remanent polarization (P$_r$) depended strongly on the Sr/Ta mole ratio, and increased with decreasing Sr/Ta ratio. On the other hand, P$_r$ was almost independent of the Bi/Ta mole ratio in Fig.2-3. Noguchi et al. [24] reported that the SBT thin films with 20%Sr-deficient and 10% Bi-excess composition showed maximum remanent polarization (P$_r$) values for crystallization temperature of 700   and 800   .

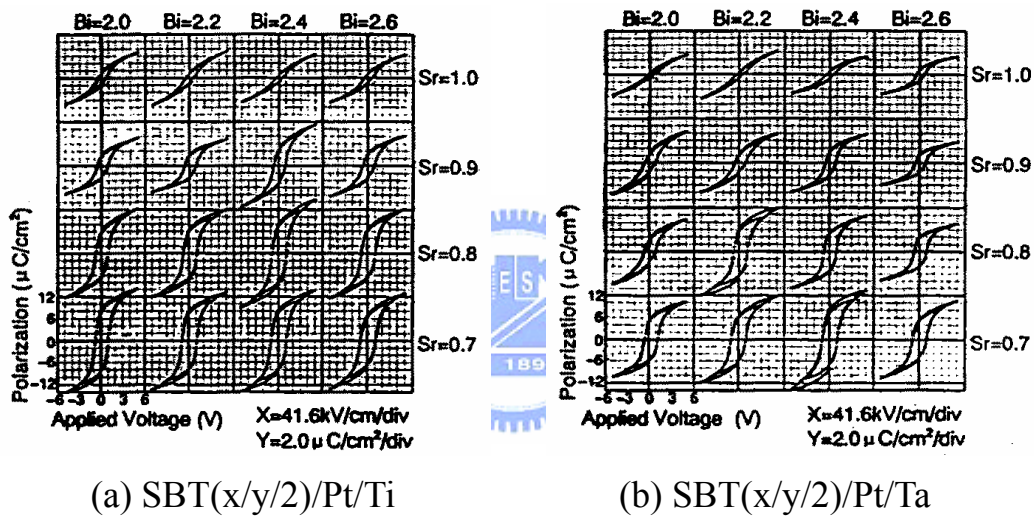(a) SBT(x/y/2)/Pt/Ti   (b) SBT(x/y/2)/Pt/Ta

Fig.2-3   The   P-E   hysteresis   curve   of   SBT(x/y/2)/Pt/Ti   and SBT(x/y/2)/Pt/Ta films

Hase et al. [25] investigated the effects of Sr deficiency to the ferroelectric properties of SBT thin films. The maximum 2Pr was obtained 12.5 μC/cm^2 at Sr deficiency of 20% for both prepared at 700 and 800   . On the other hand, Hase [26] also reports that SBT with Sr deficient composition had a relatively dynamic imprint endurance compared to Sr non-deficient films because of a larger margin against the charge shift and large V$_c$.

Li et al. [27] investigated the effect of excess Bi content on electrical

properties. Strontium bismuth tantalite (SBT) films with excess Bi contents were prepared on $Pt/TiO_2/SiO_2/Si$ substrate by a metal organic decomposition technique. They found the films with 10% excess Bi to be the optimum composition with respect to grain size, morphology, and electrical properties. But another research reported by Chen et al. [28] showed different results. The effect of excess bismuth on ferroelectric electric properties of SBT thin films was investigated for excess bismuth contents ranging from 0% to 100%. The films with 30-50% excess bismuth content were found to be the optimum composition with respecting to grain size, crystallographic orientation and single-phase formation. Koiwa et al. [29] also studied the role of excess bismuth on forming the SBT structure. In SBT films composed of fluorite and Bi-layered structure, Bi-layer structure grains had a higher Bi content than that in fluorite grains. Excess Bi was added to promote crystallization of fluorite to the Bi-layered structure easy. Osaka et al. [30] reported that the fluorite structure was confirmed to form in the initial phase at 650 . They believe that the fluorite changes to pyrochlore in most of Bi-poor composition areas in the film at 750 because a pyrochlore phase is formed during crystallization. Rodriguez et al. [31] has shown that a fluorite phase forms in the 600 temperature range for a film composition near 1:2:2 cation ratio (Sr:Bi:Ta) and a pyrochlore phase forms at the composition 1:0.8:2. The fluorite structure converts to the ferroelectric layered-perovskite phase in the 700 temperature range. This pyrochlore phase has substantial Bi-deficiency and forms with relative ease in low-Bi compositions and can be considered deleterious to perovskite formation.

Watanabe et al. [32] reported that $SrBi_2(Ta_{1-x}, Nb_x)_2O_9$ the films

($0 \leq x \leq 1$) showed the niobium ions substitute for tantalum ions in an arbitrary ratio without any change of the layer structure and lattice constants. The SrBi$_2$(Ta$_{1-x}$, Nb$_x$)$_2$O$_9$ films with various Ta /Nb rations have large enough remanent polarization and high fatigue resistance against 10^{11} cycles of full switching of the remanent polarization. On the other hand, Kaoru Miura et al. [33] describe that the difference in Pr between SBT and SBN is not due to the difference in the displacement of Ta ions and Nb ions in the ab plane of TaO$_6$ (NbO$_6$) octahedral rather than the difference in the displacement of the Sr-Ta(Nb)-O perovskite blocks to the Bi-O layers in the ab plane between SBT and SBN, and the difference in the displacement of the Sr ions in the ab plane between SBT and SBN.

2-3. Fabrication methods of the ferroelectric thin films

In general, there are two major categories of deposition techniques for films [34]: (1) physical vapor deposition and (2) chemical processes involving chemical vapor deposition (CVD) and chemical solution deposition (see the Table 2-1). The advantages of the former methods are (1) dry processing, (2) high integrated-circuit (IC) processing, and (3) possible epitaxial film; however, these are offset by disadvantages, such as (1) slow deposition rates, (2) difficult stoichiometry control in ferroelectrics multi-component systems, (3) high-temperature post-deposition anneal, and (4) high-capital equipment acquisition and maintenance costs. The latter, chemical techniques are usually characterized by (1) higher deposition rates, (2) good stoichiometry control, (3) large area, pinhole-free films, (4) better homogeneity, (5) low processing temperature, and (6) lower initial equipment costs. The wet

chemical solution deposition techniques (sol-gel and MOD) combine the advantages of excellent compositional control, spin-on/spray-on/dip-coating capability, and very low equipment costs, already have been quite successfully and extensively used in producing thin films of PZT, PLZT, and many other materials.

| Table.2-1 Thin Film Deposition Techniques |
| --- |
| Physical vapor deposition |
| Sputtering (rf magnetron, dc, ion beam) |
| Evaporation (e-beam, resistance, molecular beam epitaxy) |
| Laser ablation |
| Chemical vapor deposition (CVD) |
| MOCVD (metal-organic CVD) |
| PECVD (plasma-enhanced CVD) |
| LPCVD (low-pressure CVD) |
| Chemical solution deposition (CSD) |
| Sol-gel (Solution-gelation) |
| MOD (metal-organic decomposition) |
| Melt solution deposition |
| LPE (liquid-phase epitaxy) |

The following research will concern about the fabrication methods of chemical solution deposition. There have been several papers concerning the chemical solution deposition method for synthesis of ferroelectric SBT thin film. It involves sol-gel method, metal-organic deposition method and some new methods like as LSMCD (liquid source misted chemical deposition) and MD (misted deposition) method.

It is now needs to differentiate the sol-gel method from MOD. In general, we consider a process sol-gel if it involves these two characteristic chemical reactions [35]: (1) hydrolysis of at least one precursor compound and (2) poly-condensation of the hydrolyzed precursor compound. A MOD process involves the thermal decompositions of all precursor compounds physically condensed onto substrates through rapid solvent evaporation. Therefore, methods using all alkoxide and partially alkoxide precursors are considered sol-gel processing, and those using precursors other than alkoxides are MOD. One point to emphasize is that one can use all alkoxide precursors in a MOD process. This is possible when neither of the two characteristic reactions for sol-gel is involved and the reactions used to form the oxide are simply thermal decomposition of the metal alkoxides.
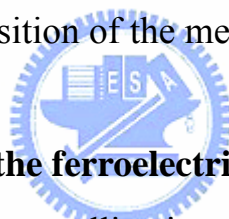
2-4. Precursor solution of the ferroelectrics

The formation of heterometallics is means of overcoming the poor solubility of polymeric metal alkoxides, of achieving homogeneity at a molecular level for multi-component systems, and of providing a better homogeneity of the final material. The presence of functional alkoxy groups around the metals generally results in an increase in its coordination number, and thus hydrolysis becomes more difficult. The reactivity of a variety of glycols $(CH_2)_y(OH)_2$ toward titanium alkoxides, zirconium isopropoxide, and niobium and tantalum ethoxides has been studied by Bradley at al [36]. Complete substitution generally results in poorly soluble products; such derivatives as $M(OR)_n\text{-}2x[O(CH_2)_yO]_x$ generally remain soluble and sometimes volatile.
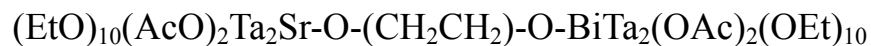
Two kinds of chemical reagents were selected to prepare the SBT

precursor solution in our research. One kind of chemical reagents are strontium acetate, $Sr(CH_3COO)_2$, bismuth acetate, $Bi(CH_3COO)_3$, tantalum pentaethoxide, $Ta(OCH_2CH_3)_5$, and acetic acid as a solvent. We call this chemical route as acetate system. Another is strontium nitrate, $Sr(NO_3)_2$, Bismuth nitrate, $Bi(NO_3)_3$, tantalum pentaethoxide, $Ta(OCH_2CH_3)_5$, and 2-methoxyethanol as a solvent and we call this as nitrate system. In order to obtain a stable solution in air and multi-component homogeneous system, we added a chelating organic ligand into the solution. Several additives were added into solution including the surfactants and drying control chemical additives.

Heteometallic alkoxides are generally obtained either by reaction between Lewis acids and bases or by condensation with elimination of volatile or insoluble by-products. This general Lewis acid-base reactions applies to nearly all alkoxides,

$$yM'(OR')_{n'} + M(OR)_n \qquad MM_y'(OR)_n(OR)_{n'y}$$
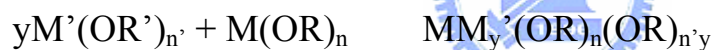
Addition reaction similar to above can also be observed between anhydrous acetates and alkoxides. We also can predict our chemical products as a complex solution of following

$$Bi(OAc)_3 + Ta(OEt)_5 \qquad BiTa_2(OAc)_2(OEt)_{10}$$
$$Sr(OAc)_2 + Ta(OEt)_5 \qquad SrTa_2(OAc)_2(OEt)_{10}$$
$$(EtO)_{10}(AcO)_2Ta_2Sr-O-(CH_2CH_2)-O-BiTa_2(OAc)_2(OEt)_{10}$$

From Guanghua et al.'s report [37], we know that gel films with a thickness less than 1μ m can be dried on a substrate without cracking. In order to solve the problem of the cracking of gel films during drying, cross-linking agents such as ethylene glycol are added to the precursor solution to introduce organic chains in the inorganic network of the gel.

$$2((OR)_nM-O-M(OR_n))+HOCH_2CH_2OH$$

$(OR)_nM-O-M(OR)_{n-1}-O-CH_2CH_2-O-(RO)_{n-1}M-O-M(OR)_n + 2ROH$
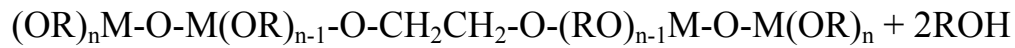
There also can be some inorganic network of the gel in our precursor solution of acetate system.

Lee et al. [38] reported that two kinds of chemical solutions have been prepared for the derivation of strontium bismuth tantalate SBT thin films. One is a single alkoxide sol-gel precursor prepared from 2-methoxyethanol solutions of strontium 2-methoxyethoxide, bismuth( ) 2-methoxyethoxide and tantalum 2-methoxyethoxide. Another is a simple mixture solution prepared from strontium bis(2,2,6,6-tetramethyl-3, 5-heptanedionate, triphenyl bismuth, and tantalum 2-methoxyethoxide. It has been found that the process temperature and the amount of excess Bi, needed to form the ferroelectric phase, are strongly dependent on the sol-gel solution. They have obtained SBT film derived from single alkoxide sol-gel precursor showing a hysteresis loop for the Pt/SBT/Pt capacitor in 250nm thick ferroelectric layer. The remanent polarization (P_r) was 9.0μ C/cm^2, the coercive field (E_c) was 33 kV/cm and leakage current density was 10^{-6} A/cm^2.

Hayashi et al. [39][40] used strontium di-n-butoxide, bismuth tri-i-propoxide and tantalum pentaethoxide as starting materials and 2-methoxyethanol as a solvent to make the precursor of $Sr_{0.7}Bi_{2.2}Ta_2O_9$. The thin films of $Sr_{0.7}Bi_{2.2}Ta_2O_9$ formed by the sol-gel method were prepared at 800 for 1 hr. The thin films are influenced by a metal coordination state that depended upon the metal alkoxides are mixed with acetyl acetone in the solution. This SBT films with a c-axis preferred orientation made by process A and additive acetyl acetone showed stone wall-like grains in their microstructure with a value Pr of 1.6 $\mu C/cm^2$, ε_r of 78, and E_c of 110 kV/cm, while those with random orientation made by

process B and no additive acetyl acetone showed a microstructure of rod-like grain exhibited ε_r of 90, Pr of 6.5μC/cm^2 and E_c of 80kV/cm.

Kim et al. [41] reported that SBT thin films derived by mixed metal esters of 2-ethylhexanoate from a 2-methoxyethanol solution of Sr(OCH$_2$CH$_2$OCH$_3$)$_2$, Bi (OCH$_2$CH$_2$OCH$_3$)$_3$, and Ta (OCH$_2$CH$_2$OCH$_3$)$_5$. The SBT films derived from this precursor deposited on Pt/Ti/SiO$_2$/Si substrate with the stoichiometric amount of 1.0:2.0:2.0 (Sr: Bi: Ta) and a 250mm thick has a remanent polarization Pr of 9μC/cm^2, coercive field (E_c) of 33kV/cm (or 0.8V). Another study reported by kako et al. [42][43] showed the precursor molecules for the layer-structure perovskite thin films of SBT(2/2/3) and SBN(2/2/3) were prepared by the reaction of Sr-Bi (2:2) double methoxyethoxide, [SrBi(OCH$_2$CH$_2$OCH$_3$)$_5$]$_2$, and M(Ta or Nb)methoxyethoxide, M(OCH$_2$CH$_2$OCH$_3$)$_5$. The 210nm thick SBT(2/2/3) thin films did not exhibit a hysteretic loop after rapid thermal annealing at 700 , whereas the 800 post–annealed SBT(2/2/3) thin film exhibited a partial unsaturated hysteresis loop. Kato's report [44] showed that the complex alkoxide functional group, water vapor, and calcinations were found to affect the hydrolysis of the remaining alkoxy groups in the film, the following polycondensation, crystallization, microstructure development, and ferroelectric properties. The calcinations in the water vapor and oxygen flow mixture promoted hydrolysis of the remaining alkoxy groups and oxidation of the alkoxy derived organic compounds in both films. The SBT films which were calcined in the water vapor, oxygen mixture and annealed at 650 in oxygen atmosphere exhibited improved ferroelectric properties.

Zanetti et al. [45, 46] used Strontium carbonate, SrCO$_3$, niobium ammonium oxalate, NH$_4$H$_2$[NbO(C$_2$O$_4$)$_3$]·3H$_2$O, and bismuth oxide,

Bi$_2$O$_3$ as reagents to synthesize polymer precursor of SrBi$_2$Nb$_2$O$_9$ (SBN) and SrBi$_2$Ta$_2$O$_9$ (SBT). The SBN films deposited onto Pt/Ti/SiO$_2$/Si substrate after thermal heat-treatment at temperatures between 600 and 700   , the Bi-layer pervoskite phase is formed. The SBT film crystallized by rapid thermal annealing in a halogen lamp furnace displayed spherical grain structures with dielectric constant values of 121, 248, remanent polarization (2Pr) of 7.1, 18.8 μC/cm^2 and coercive field of 113, 93 kV/cm at 700 and 800   , respectively.

Recently, a chemical liquid solution was made from bismuth 2-ethylhexanoate, strontium 2-ethylhexanoate and tantalum ethoxide as starting materials. Shin-ichi Ohfuji et al. [47] reported that the 200 nm thick SBT films were deposited on Pt/Ti/SiO$_2$/Si substrates by using the above chemical solution and obtained a remanent polarization 2Pr of 10μC/cm^2 with leakage current 1×10^{-6} A/cm^2 at the process temperature of 700   . Chu et al.[48] also used the metal 2-ethylhexanoate and tantalum ethoxide as precursors to make the SBT thin films which obtained the remanent polarization (Pr) value of 5-6 μC/cm^2, coercive field value of 55kV/cm and fatigue endurance of 10^{11} at a process temperature of 800   . Another report by Desu [49] also used the same precursor to deposit the SrBi$_2$Ta$_2$O$_9$ thin films on Pt/Ti/SiO$_2$/Si substrate. The 300 nm thick SBT films were annealed at 700   for 3 hr and 2Pr values greater than 20 μC/cm^2, coercive field E$_c$ less than 60kV/cm, low fatigue rate up to 10^9 and   leakage current density of less than 2×10^{-8}A/cm^2 at 167kV/cm, were obtained.

In Zhou et al.'s study [50], the SBT complex solution was prepared by a sol-gel technique using an alkoxide-carboxylate precursor solution. Strontium isopropoxide, bismuth 2-ethylhexanoate and tantalum ethoxide

were selected as the precursors, and 2-ethylhexanoic acids and 2-methoxyethanol were selected as solvents. This SBT thin films with thickness < 350nm was found to form a pure perovskite phase at 650 and with a remanent polarization of 6.0±0.5 μC/cm^2, and a coercive field of 5.7±0.5 kV/mm.

The SBT thin films from studies by Zhang et al. [51] were prepared on Pt/Ti/SiO$_2$/Si substrates using a metalorganic decomposition (MOD) method. Strontium acetate, bismuth 2-ethylhexanoate and tantalum ethoxide were selected as precursors, and acetic acid, 2-ethylhexanoic acid, and 2-methoxyethanol was selected as solvents. This SBT thin films annealed at 750 had Pr = 8.8 μC/cm^2 and E$_c$ = 29.3 kV/cm at applied voltage. Strontium acetate, bismuth acetate, and tantalum ethoxide were used as a precursor in Boyle's study [52]. The SrBi$_2$Ta$_2$O$_9$ (SBT) thin films were deposited on Pt/Ti/SiO$_2$/Si substrate fired at 750 showed a remanent polarization of 7 to 8μC/cm^2 and a coercive voltage of 45 kV/cm. Another reported by Zhang et al. [53] using strontium acetate, bismuth 2-methoxyethanol, and tantalum ethoxide as precursors; and acetic acid, 2-ethylhexanoic acid and 2-methoxyethanol as solvents. The SBT thin films prepared by laser annealing by a two-step process was crystallized at 550 . There are also similar CSD (chemical solution deposition)[54-57] method was used to prepare the precursor of SBT thin films.

The following research will concern about the new deposition method of liquid source misted chemical deposition (LSMCD). The LSMCD method has some advantage such as good thickness uniformity, conformality and easy for spin-on processing. Park et al. [58] had prepared SrBi$_{2.4}$Ta$_2$O$_9$ (SBT) thin films with 70-400nm thickness was

spin on $Pt/Ti/SiO_2/Si$ substrate by using liquid source misted chemical deposition (LSMCD). In the LSMCD process, a precursor mist is generated from the liquid precursor by an ultrasonic transducer and is carried into the deposition chamber using an inert gas. In their study, strontium ethylhexanoate, bismuth ethylhexanoate and tantalum ethoxide were mixed at a mole ratio of Sr: Bi: Ta=1:2.4:2 and diluted with n-butyl acetate to prepare a coating solution. The 70nm thick SBT thin film exhibited remanent polarization (2Pr) of $13.5\mu C/cm^2$, a coercive field value (E_c) of 63kV/cm at ±3V and fatigue-free up to 10^{12} switching cycles. Other similar result also reported by Solayappn et al. [59-62].

2-5. Annealing atmosphere of the ferroelectrics films

Ogata et al. [63] used the CSD method to fabricated SBT films crystallized in an N_2 ambient atmosphere. The SBT thin films calcined in rich O_2, in which carbon within the films is sufficiently removed, and crystallized in N_2 by the novel N_2 crystallization process, as well as the film crystallized in O_2 by the conventional O_2 crystallization process, have good crystalline quality and electrical properties. Another similar edition were reported by Huiqin Ling et al. [64], in which the films were annealed in vacuum, argon, nitrogen and different ratios of N_2/O_2 atmospheres. It was found that oxygen plays an important role in SBT ferroelectric phase formation and has effect on morphology and electric properties of the films. But only when the film is annealed in pure oxygen can good electric properties be obtained. With the decreasing of O_2 content in annealing atmosphere, electric properties became deteriorated due to increasing oxygen vacancy density on SBT.

In Watanabe et al.'s reports [65], a new process for SBT thin film

growth is to insert forming-gas anneals between the RTA and the crystallization anneal. This forming-gas anneal at 500 for 30-60min in 5% H_2 and 95% N_2 flow is to recover good transistor performance. A forming-gas anneal at 500 for 1hr caused elemental bismuth columnar formation on the SBT surface and a 16% decrease in film thickness. The columnar structures could be removed by additional annealing at 800 for 1hr in flowing oxygen. Moreover, the amount of Bi removed during the recovery annealing can be carefully controlled by parameters in the forming-gas anneal such as temperature, annealing time, and annealing ambient gases.

Ohfuji et al.'s paper [47] showed the effects of annealing processes in Ar gas, added prior to the oxidizing processes of SBT films at 700 . The growth of a bismuth-layered structure was found after annealing at 700 for 5-10s and to be effective in obtaining a saturated polarization , and a remanent polarization 2Pr of more than 10μ C/cm^2. Leakage current of less than 1×10^{-6} A/cm^2 was observed for the annealing time within 100s. Structural and compositional analyses suggest that some Bi atoms in the films are controlled to become free of oxygen and arrive at the lattice sites by the annealing at 700 for short periods in non-oxidizing Ar gas.

Another report studied by Li et al. [66] showed the development of crystalline phase of SBT films were annealed at 550-850 in oxygen, air, or Ar by MOD method. They also found that electrical properties were affects by anneal atmosphere. This implied that oxygen was important in the fabrication of layered perovskite SBT films.

Ito et al. reported [67] that the SBT thin films were annealed before and after the top Pt electrode deposition. The 1st annealing was performed

in a 760 Torr oxygen atmosphere at 600   for 30min, and the 2nd annealing was performed in a 5 Torr oxygen atmosphere at 600   for 30min have good electronic properties. The films annealed at 3 Torr in 2nd annealing showed the (210) peak of Bi_2Pt in addition to the SBT peaks and no SBT peak was observed at 1 Torr or less.

2-6. Electrodes of the ferroelectric films

It has been well documented that for a given SBT ferroelectric film the electrical and reliability properties are strongly influenced by the electrode material. Electrode materials that have been studied so far can be classified into three general groups. The first group consists of noble metals such as Pt, Au, Ir and Ru [68-72]. The second group consists of metal oxides such as IrO_2 and RuO_2 [73]. The third group of electrode materials is the conductive perovskite oxide electrodes such as $LaNiO_3$ (LNO), $SrTiO_3$ (STO), $(La,Sr)CoO_3$ (LSCO), and $SrRuO_3$ (SRO) [74] that exhibit similar structural chemistry as the ferroelectric layer-perovskite structure. The noble metals usually form a Schottky contact to SBT thus limiting the leakage current. Though this is a desirable characteristic, but the interface space charge plays an increasingly dominant role as the thickness of the dielectric layer decreases below 100 nm.

2-7. Sizes effects and thickness effects

In practical application, when the grain size of a ferroelectric material which exists as tetragonal at room temperature decreases, it turns cubic below a critical value and its ferroelectricity disappears. This phenomenon has been discussed in relation to fine particle. This is a property change accompanied by three-dimensional size shrinkage. The

cause of this phenomenon has been though to increase of surface energy against lattice energy or contribution of anti-poling field.

The thickness effects can give important information about interface related properties. Thickness effects on structure and ferroelectric properties have been studied in the PZT family. It has been found that the dielectric constant, remnant polarization, dielectric breakdown fields and tetragonal distortion decrease and the loss tangent, coercive field, band-gap energies, and diffuseness of the phase transition increase with the decrease of film thickness [75-76]. Two models have emerged to explain the thickness effects. One is based on the domain structure transition from multi-domain predominance to singe domain predominance at a critical grain size in the thin film. The other is the film/electrode interfacial blocking layer model. This change in the thickness dependence of E_c in ferroelectrics occurs near a thickness of 200 nm and has a profound practical effect on device construction. When we multiple E_c (coercive field) by d (thickness) to obtain V_s, we find that the $E_c(d)$ dependence discussed above has two effects. It produces an optimum thickness near 250nm, at which V_s is an absolute minimum; and it defines a processing window of film thicknesses, within which V_s will be less than the 5 V CMOS logic levels for Si ICs. The devices will be faster near the thin limit of 100 nm. For thick specimens E_c varies as d where n is number between 1/3 and 1/2 [77] and has been found t o be valid for several materials [78]. The theoretical dependence of switching time is $t_s=AE^{-3/2}$, where A is a constant and E is electric field [79].

2-8. The electrical properties of ferroelectric oxides

1. Hysteresis[80]

Ferroelectricity is the reversible spontaneous alignment of electric dipoles by their mutual interaction. The spontaneous electric polarization can be reversed by application of an external electric field (coercive field E_c) and is increased by the aligning of dipoles in a parallel array with field that is smaller than the breakdown field E_B. The alignment is spontaneous at a temperature T_c (Curie temperature), where the randomizing effect of thermal energy kT is overcome. The spontaneous polarization is defined by the value of the dipole moment per unit volume, or by the value of the charge of the unit area of the surface perpendicular to the axis of spontaneous polarization. The spontaneous alignment of dipoles, which occurs at the onset of Ferroelectricity, is often associated with a crystallographic phase change from a centrosymmetric, non polar lattice to a noncentrosymmetric polar lattice.
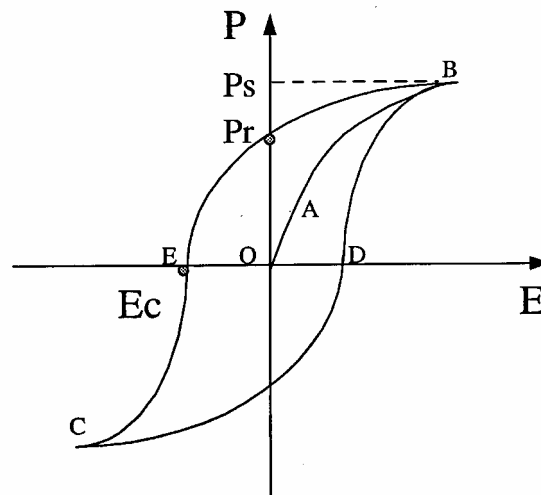

Fig.2-4 The P-E curve (hysteresis loop) of SBT thin films.

The hysteresis loop (see Fig.2-4) is due to the presence of crystallographic domains within which there is complete alignment of electric dipoles. At low field strengths in unpolarized material, the

polarization P is initially reversible and is nearly linear with the applied field. At higher field strengths, the polarization increases considerably as a result of the switching of the ferroelectric domains. The polarization vectors are aligned with the applied field by means of domain boundaries moving through the crystal. Extrapolation of the high field E curve back to E=0 gives P_s, the saturation polarization, corresponding to the spontaneous polarization with all the dipoles aligned in parallel. When E is cut off, P does not go to zero but remains at a finite value called the remanent polarization, P_r. This is due to the oriented domains being unable to return to their random state without an additional energy input by an oppositely directed field. The strength of E required returning P to zero is the coercive field, E_c. Further increase of the field in the negative direction will make a complete alignment of the dipoles in this direction and reversing the direction of electric field once again, also can complete the loop. (as shown in Fig.2-5) It can be observed by means of a Sawyer-Tower circuit.
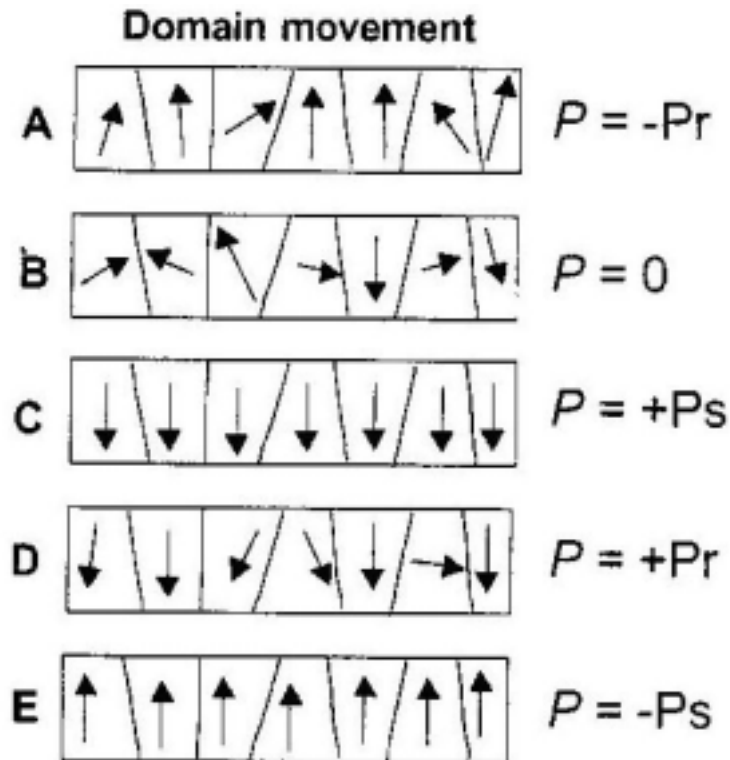
Fig.2-5 Illustration of the polarization reorientation.

2. Dielectric behavior [80][81]

Dielectric properties are of special importance when materials are used as a capacitive element or as insulation in electronic applications. The dielectric constant, dielectric loss factor, and dielectric strength usually determine the suitability of a particular material for such applications. Capacitance is a measure of the ability of any two conductors in proximity to store a charge Q, when a potential difference V is applied across them.

$$C = Q / V$$

Q is proportional to the area A in square meters and the electric field applied E=V/d, where d is the distance between the plates (in meters). The proportionality constant is defined as ε_o, the permittivity of free space, and is equal to 8.854×10^{-12} C^2/m^2 or F/m. Thus, the capacitance of a parallel-plate capacitor will be equal to:

$$Q=\varepsilon_o \,(\, V/d \,) \, A$$

When a material is inserted between the plates the capacitance is increased. The dielectric constant k is defined as the ratio of the capacitance of a condenser, or capacitor, with a dielectric between the plates to that with a vacuum between the plates.

$$k = C/C_o = \varepsilon /\varepsilon_o$$

Thus the dielectric constant of a material is the ratio of the permittivity of the material to the permittivity of free space.

A dielectric material reacts to an electric field differently from a free space because it contains charge carriers that can be displace, which can neutralize a part of the applied field. The total electric flux density D as the sum of the electric field E and dipole charge P:

$$D = \varepsilon_o E + P = \varepsilon E$$

$$P = \varepsilon_o (k-1) E$$

where the polarization is the surface charge density of the bound charge, equal to the dipole moment per unit volume of material.

There are four primary mechanisms of polarization in dielectric materals. The polarization mechanisms include: electronic polarization (P_e), atomic polarization (P_a), dipole polarization (P_d), and interfacial polarization (P_i). The second mechanism of dipolar polarization is an especially important contribution to the room temperature dielectric behavior of glasses and ceramics. It involves the rotation of dipoles between two equivalent equilibrium positions. It is the spontaneous alignment of dipoles in one of the equilibrium positions which gives rise to the nonlinear polarization behavior of ferroelectric materials. The last polarization mechanism, interfacial or space charge polarization, occurs when mobile charge carriers are impeded by a physical barrier that

inhibits charge migration. The charges pile up at the barrier producing a localized polarization of the material.

The total polarizability of the dielectric can be represented as the sum of there:
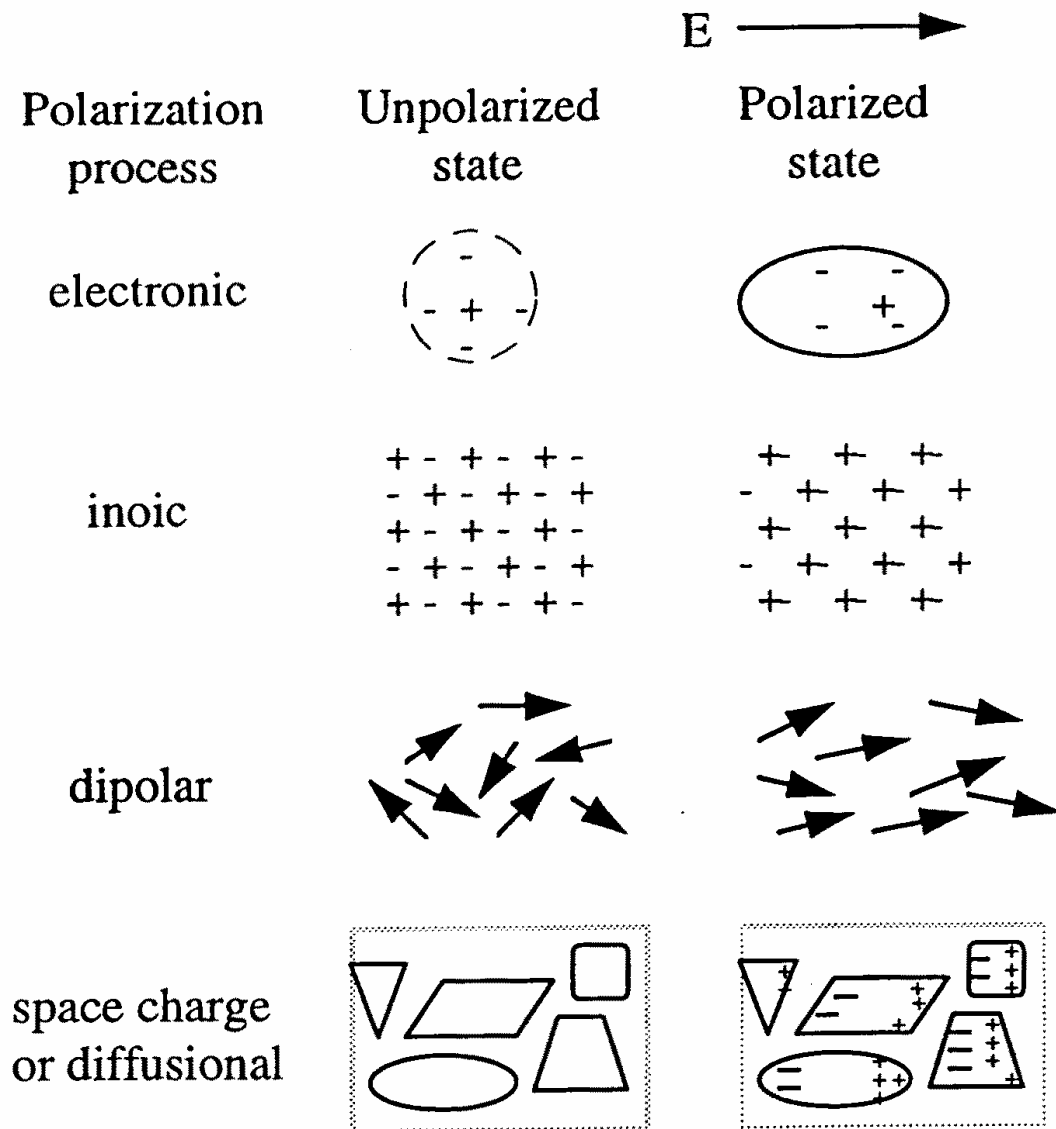
$$P=P_e+P_a+P_d+P_i$$

Fig.2-6 The four various mechanisms of polarization.

2-9. Reliability of ferroelectric films

1. Fatigue [82]

Fatigue is the characteristic of ferroelectrics that the amount of charge q that is switched with repetitive bipolar applied voltages decreases with cycling. This is usually described as a decrease in remanent polarization $P_r(N)$ with switching cycles N. Instead, the number of cells and domains that switch decreases slowly with increasing N, as domain walls become pinned. This pinning can occur at grain boundaries, at surfaces, or at other defect sites, particularly extended defects. Fatigue is a complicated electrochemical process. It arises in part from charge injection at the electrode-ferroelectric interface and is not an intrinsic property of the bulk ferroelectric material. The lack of fatigue in SBT is thought to arise from the fact that domain walls have much smaller pinning energies in SBT, exhibit rather shallow traps, and have a lower concentration of oxygen vacancies near the electrode interface. The lower oxygen vacancy concentration is thought to arise from the fact that the molecular layers adjacent to the electrode are Bi_2O_2 and not TaO_6 octahedral. There were several fatigue mechanisms have been proposed which invoke [83] (a) electronic charge trapping at domain walls, (b) doubly positively charged ionic defect sites such as oxygen vacancies ($V_0^{..}$) pinning domain walls, (c) poling charged defect-dipoles: these dipoles are believed to become aligned during cycling and are very slow to reverse, thus, reducing or canceling some of the switched lattice polarization, (d) decreasing electrode adhesion, as well as (e) micro cracking, to name a few.

2. Retention (or Aging) [82,84,85]

For the use of bismuth-layered perovskite thin film capacitors in nonvolatile memory applications, however, charge retention typically

required to be longer than 10 years under specified temperature stresses. Retention refers to a degradation of polarization parameters (such as the remanent and the saturation polarization) with time. When the remanent polarization P(t) decays with time t at a constant decay rate of $1/\tau$, the exponential dependence of P(t) is

$$P(t)=P_0 e^{-1/\tau} \qquad (1)$$

where $P_0=P(0)$. When the relationship in Eq.(1) is drawn on a logP(t) vs. t plot, $1/\tau$ yields a slope showing polarization decay behavior. However, the actual decay process for long periods of time is described well by the empirical form of

$$P(t)=P_0 - m \ln (t/t_0),$$

where t_0 is a characteristic time at which the linear behavior of P(t) begins with respect to ln t, P_0 is the polarization at $t=t_0$, and m is the slope of the curve in a P(t) vs. ln t plot .

The remanent polarization of poled ferroelectrics decreases rapidly in the initial stages. This may be attributed to space charge migration or polarization reversal caused by an internal field formed due to remanent polarization. After this period, remanent polarization decays linearly with the logarithm of time, which was defined as ageing or retention. The domains stabilization (domain pinning) of ferroelectrics has been proposed the main feature of ageing and can be caused by three effects: volume, domain, and grain boundary effects. The volume effects are defect in ferroelectrics bulk that tends to occupy energetically preferred sites in the lattice. They form anisotropic centers and favor a certain direction for the spontaneous polarization. The domain effects are defect accumulation at the domain walls. When neutralization of internal stresses of compensation of electrical charges occur, defects diffuse into

the domain walls and fix their position. The grain boundary effects are the segregation of impurities and vacancies into domains. For polycrystalline ferroelectrics, second phases can occur at high dopant concentrations when the concentration of the dopant exceeds the solubility limit. These second phases cover the grain surface during sintering and lead to surface charges at the grain boundaries. As a result, the individual crystal is biased by a preferred direction of polarization while the domain wall remains mobile.
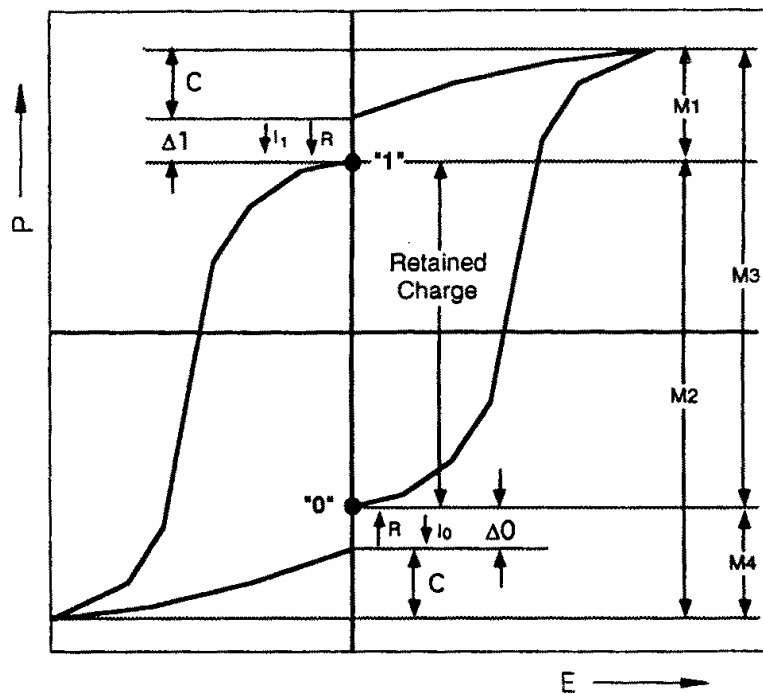

Fig.2-7 A typical P-E hysteresis loop for ferroelectrics.

3. Imprint [84]

Imprint refers to the tendency of a ferroelectric capacitor to prefer one state to another if it stays for a long period of time in that state. Fig.2-6 shows the direction and magnitude of polarization loss $\Delta 1$ and $\Delta 0$. Note that $\Delta 1$ and $\Delta 0$ are vectors, $\Delta 1$ being a negative vector and $\Delta 0$ a positive one. The magnitudes of $\Delta 1$ and $\Delta 0$ are determined by both

retention and imprint effects on ferroelectrics. The polarization losses at the two "stable" states due to retention effects have equal magnitude but opposite directions, i.e., both losses point to the center of the P-E hysteresis loop. The polarization loss in states "1" and "0" due to imprint are only in one direction and their corresponding magnitudes could be different.

4. Leakage current

When a DC field is applied to a dielectric material, the current varies with time typically as shown in Figure 2-8. One can observe three regions in this curve [82]: (1) The initial current decay called charging current, (2) leakage current, where the current stabilizes, and (3) the electrical degradation region. Leakage currents exist in all materials when under an applied electric field. Several types of conduction mechanisms such as simple oxygen diffusion, grain boundary potential barrier height, space charge limiting, Pool-Frenkel emission, and Schottky emission control non-ohmic leakage current. Schottky emission occurs at the interface between the ferroelectric and the electrode where a Schottky barrier is formed. If the top and bottom interfaces are asymmetric, leakage current levels will be different for positive and negative voltage biases. Poole-Frenkel emission occurs via trap levels in the bulk. Therefore, current conduction controlled by Poole-Frenkel emission gives symmetric current level at both positive and negative polarities regardless of asymmetric contacts.
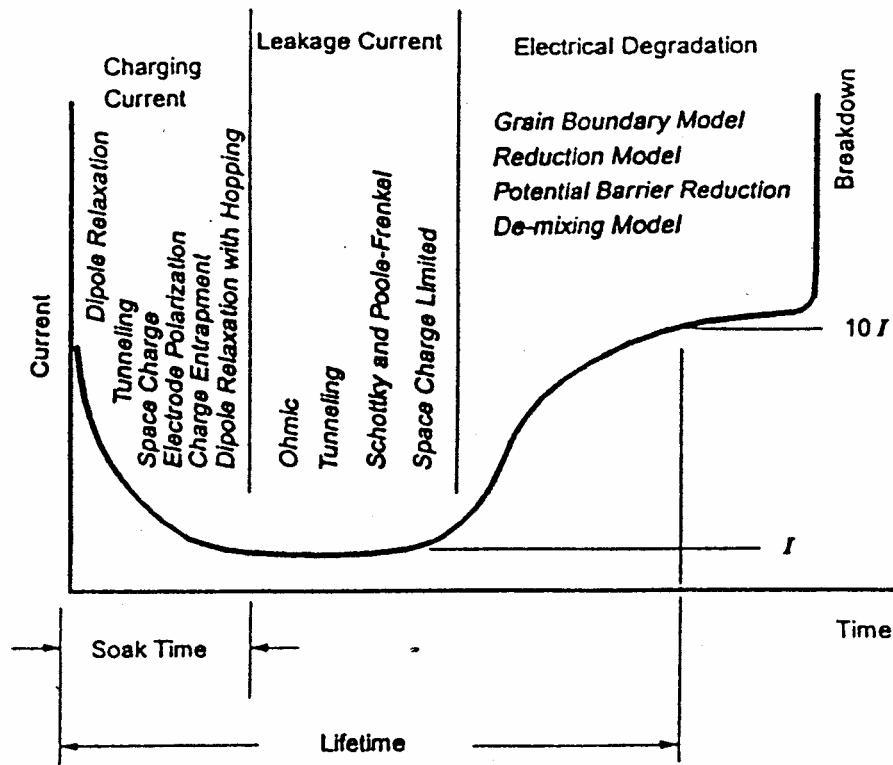
Fig.2-8 Time dependent dielectric breakdown

2-10. Memory operation [86]

The operation model of MFMIS FET is described in Fig.2-9. This device can be operated in the same way as MFS FET and MFIS FET. When a sufficiently large positive bias is applied to the control gate (upper electrode) so that the ferroelectric polarization can occur in the direction shown in Fig.2-3, ferroelectric polarization induces such charge distribution in the floating gate (bottom electrode). As a result, a surface inversion layer (channel) is formed between the source and the drain; the two n^+ regions are then connected by a conductive surface n channel. This is defined as a "ON" state of the FET. Even if the gate bias decreased to 0 V, the FET is in the "ON" state because of the influence of ferroelectric polarization. When a negative bias is applied in order to cause ferroelectric polarization in the opposite

direction, majority carriers (holes) accumulate near the silicon surface. Since the source-to-drain electrodes correspond to two p-n junction connected back to back, almost no current can flow between the source and the drain. This case is defined as the "OFF" state. When the applied voltage increases to 0 V, the FET remains in the "OFF" state because of the remanent polarization.
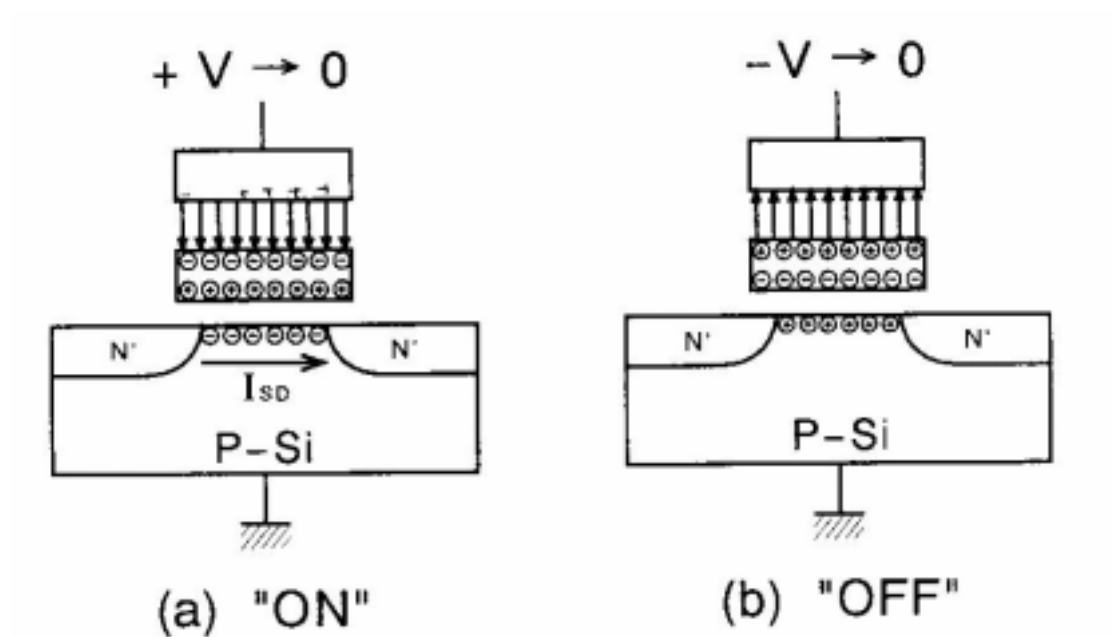

Fig.2-9 The operation of MFMIS FET.