**PREPARATION AND CHARACTERIZATION OF LEAD LANTHANUM
TITANATE THIN FILMS BY METALORGANIC DECOMPOSITION**

by

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(ABSTRACT)

There is a critical need for materials with very high dielectric constant to be integrated in the next generation of 64- and 256-Mb ULSI DRAMs. Materials in the Pb-based perovskite family have high relative permittivities and have consequently attracted a world wide attention. Cubic Lead Lanthanum Titanate (PLT) is one of the prime candidates in this respect and its structure and properties in the thin film form were investigated in the present study, for potential application in the ULSI DRAMs.

Thin films of Lead Lanthanum Titanate corresponding to 28 atomic percentage of lanthanum were prepared by metalorganic decomposition (MOD) process. Solutions were prepared from lead acetate, lanthanum acetate and titanium iso-propoxide and thin films were then spin-coated from these solutions on Pt/Ti/SiO₂/Si and sapphire substrates. The films were fabricated from two solutions of different compositions. The composition of the first solution was determined assuming that the incorporation of La³⁺ in the PbTiO₃ structure gives rise to A-site or Pb vacancies whereas for the composition of the other solution the creation of B-site or Ti vacancies was assumed. The effect of excess lead on

the structure and the properties was also studied for 0% to 20% of excess PbO. The x-ray diffraction patterns of all films at room temperature indicated a cubic structure with lattice constant of 3.92 Å. Optical and electrical measurements showed that the films made assuming B-site vacancies had better properties. In general, excess PbO was found to improve the optical as well as the electrical properties of films. However, in films with B-site vacancies this improvement occurred only up to 5-10% of excess PbO, while higher PbO additions had a deleterious effect. The films had high resistivity, good relative permittivity, low loss, very low leakage current density, and high charge storage density. A type-B film with 10 % excess Pb had a permittivity of 1336 at 100 kHz. It also had a charge storage density at room temperature of around $16.1 \mu\text{C}/\text{cm}^2$ at a field of 200 kV/cm and no sign of polarization loss or breakdown was observed up to 10^{10} cycles under the accelerated degradation/breakdown test.

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Chapter 1. Introduction

Prior to the 1970s, magnetic core technology was the primary source of large computer memory where each memory cell consisted of a small magnetic ring through which two wires were strung in order to perform the read and write functions of the cell. As one might expect, this technology had limitations in achievable density, cost, speed, and performance. The announcement of the first 1-kbit DRAM in 1970 [1], which contained three transistors, ushered in a new era of memory technology in terms of size, cost and performance. An immediate further improvement in design introduced the one transistor-one capacitor arrangement which since then has been the memory cell of choice in dynamic random access memories (DRAMs) because it is relatively fast, cheap, and compact in design [2]. The key invention of the one-transistor one-capacitor (1-T) cell or one-device memory cell along with important MOS technology advances in the late 1960s and the early 1970s has led to a tremendous growth of MOS technology and products.

1.1 The 1-T Dynamic Random Access Memory Cell

The basic concept of the 1-T cell is depicted in Fig. 1.1. It consists of a single transistor, or transfer gate, and a capacitor. The "1" or "0" binary information is stored on the capacitor by charging or discharging the capacitor through the transistor. That is, the transistor isolates the memory cell from the bit line and the rest of the memory array, and it is connected to the word line. When the transistor is turned on, the capacitor is connected to the bit line through which information is written or read. Thus only two lines are required to access each memory cell; an x-line (word line) and a y-line (bit line) [3].

Fig. 1.1 A one transistor one capacitor, or 1-T memory cell. (a) Schematic diagram of the cell. (b) Cross section of the cell showing the structure.

The total memory capacity is determined by how many of such 1-T cells can be packed into the available total memory area.

In the twenty years since the first 1-kbit MOS dynamic random access memory integrated circuit product, there has been a continuous effort to increase the total memory capacity by increasing the level of integration so much so that 16-Mbit products are now available. The major factors contributing to this progress have been decreasing feature size and MOS transistor scaling, process and circuit design ingenuity, and improved manufacturing processing equipment and practices which have resulted in higher yields on larger die sizes with steadily decreasing feature sizes [4]. Most notable among the cell and process technology advancements are ion implantation, dry etching (plasma, RIE, etc.), local oxidation of silicon (LOCOS), device isolation, silicides, optical projection lithography, implementation of CMOS technology, progress in stacked and trench capacitor development and a greatly improved understanding of diffusion and of the roles of oxygen, carbon and nitrogen in silicon [3-4].

By these efforts significant improvement in the total memory capacity and reduction in cost have been achieved. However, these improvements seem to have reached their technological limits and the next generation of 64- and 256-Mb DRAMs would require further improvement in the capacitance volumetric efficiency. The capacitance per unit volume or the packing density is given by

$$\frac{C}{V} = \frac{(k \epsilon_0 A / d)}{A d} = \frac{k \epsilon_0}{d^2} \quad (1.1)$$

where k is the dielectric constant or relative permittivity and d the thickness of the active dielectric material of the capacitor. Reduction in thickness of the dielectric layer or

employing materials with higher dielectric constant are, therefore, the two ways in which the memory capacity can be increased. The thickness, however, cannot be reduced below a certain limit as the field inside increases with decreasing thickness and may reach the breakdown strength at some point [5]. Therefore, the obvious alternative to increase the capacitance per unit volume is to employ materials with higher dielectric constant than those being used currently, i. e., SiO_2 or $\text{Si}_3\text{N}_4\text{-SiO}_2$ sandwich layers. There have been several studies on higher dielectric constant materials such as Ta_2O_5 [6] and Y_2O_5 [7]. The net improvement in charge capacity with these materials, however, over that of $\text{Si}_3\text{N}_4\text{-SiO}_2$ ($\epsilon_r < 10$) layers is only a factor of two at best. An analysis [2] shows that a planar dielectric film ($0.02\text{ }\mu\text{m}$) must have a permittivity higher than 150 in order to meet the minimum charge storage requirement in 256-Mb DRAMs.

The ferroelectric perovskites in general and the $(\text{Pb,L a})(\text{Zr,Ti})\text{O}_3$ family ($\epsilon_r = 10^3\text{-}10^4$) in particular have very high relative permittivities and hold excellent promise in this respect. There are, however, other technological requirements and material characteristics that must be met by the material before it can be incorporated in the ULSI DRAM technology as discussed in the next section.

1.2 Projected Electrical Parameters and Material Characteristics

Parker and Tasch have done an extensive analysis of the material issues and technology requirements for 64-Mb and 256-Mb DRAMs [2, 8]. This analysis produced projected requirements for the memory-cell area, ratio of cell-area to storage-capacitor area, total storage charge, storage-charge density, and leakage current as presented in Table 1.1 for both trench and planar configurations. The range for planar configuration

Table 1.1 Projected requirements for electrical parameters in ULSI DRAMs [8].

Parameter	64 Mb	256 Mb	Capacitor type
Storage charge density, ($\mu\text{C}/\text{cm}^2$)			
Successful SOI	1 - 5 10 - 50	2 - 11 20 - 115	Trench Planar
Partially successful SOI	2 - 7 20 - 75	4 - 17 45 - 170	Trench Planar
Leakage current density, max ($\mu\text{A}/\text{cm}^2$)	2 - 25 20 - 250	3 - 35 30 - 360	Trench Planar
Memory cell area (μm^2)	0.7 - 1.0	0.25 - 0.34	
Capacitor area, (μm^2)	2 - 6 0.2 - 0.5	0.7 - 2 0.07 - 0.17	Trench Planar
Dielectric thickness (nm)	10 - 200	10 - 100	

specifies the parameters if the process limitations of the new dielectric necessitate a planar configuration.

The ferroelectric materials exhibit a characteristic temperature, known as the Curie temperature, at which the ferroelectric to non-ferroelectric or paraelectric transition takes place. This transition, attributed to a change in the crystal structure of the material, results in a large variation in material characteristics around this temperature. Therefore, it would appear desirable to use a material whose transition temperature is located outside the normal range of DRAM operation — 0-70 °C ambient and 0-100 °C on the chip. In other words, the active dielectric material of the DRAM should always be in one phase — ferroelectric or paraelectric — to avoid substantial variation of key parameters over the operating temperature range [8, 9].

The use of switching ferroelectric thin films in unipolar non-switching DRAM operation, however, presents a number of disadvantages such as aging, fatigue, and microcracking [8, 10-11]. The ferroelectric materials show hysteresis in their polarization vs. applied field (P-E) behavior. There is usually a large difference between their maximum or saturation polarization and the remanent polarization which is due to the contributions of the linear capacitive charges and the relatively slow and time dependent polarization reversal processes [10, 12]. These latter processes, namely, domain reorientation and phase switching, not only pose a potential fatigue problem but can increase the dielectric loss tangent, $\tan \delta$, and severely limit the charging and discharging speeds of the capacitor. Therefore, paraelectric or nonferroelectric materials with very high permittivity are more desirable for DRAM applications than their ferroelectric counterparts.

Based on the available experimental data, cubic paraelectric (Pb,La)TiO₃ compositions have dielectric constant in the range of 1000-3000 and a possible charge storage density of 12 $\mu\text{C}/\text{cm}^2$ [8]. In the light of the electrical requirements projected in

Table 1.1, therefore, these materials are one of the prime candidates for 64- and 256-Mb DRAMs with simple 1-T cell structure.

1.3 Lanthanum modified Lead Titanate

Lead titanate (PbTiO_3) is an ABO_3 type ferroelectric material which has a tetragonal perovskite structure as shown in Fig. 1.2. The corner or A sites of the unit cell are occupied by Pb^{2+} ions, the Ti^{4+} ions are at the center or the B site of the cell, and O^{2-} ions are located in the face centers. Its Curie temperature is 490°C , below which it is ferroelectric and has a tetragonal structure [13]. At room temperature the lattice parameters for PbTiO_3 unit cell are $a = 3.895 \text{ \AA}$ and $c = 4.146 \text{ \AA}$ which gives a c/a ratio of 1.064 [13]. The addition of aliovalent substituents such as lanthanum (La) was found to cause a unit cell contraction, or decrease in the value of c/a ratio, with a corresponding drop in the Curie temperature (T_c). At around 28 atomic % of lanthanum the c/a ratio becomes unity and the T_c falls below room temperature [12, 14]. It, therefore, has a cubic perovskite structure at room temperature and is paraelectric as shown in the room temperature phase diagram of the $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ system in Fig. 1.3. Therefore, PLT (28 mol % La) in the chip integrated form would be a suitable choice for the aforementioned applications, due in part to the simple composition that would lend itself to ease of processing. Preparation of PLT in the thin film form and characterization of its structure and properties is, therefore, needed to make it directly compatible for integration in the memory technology.

Because La^{3+} has an ionic radius comparable to Pb^{2+} ions as shown in Table 1.2, it is incorporated in the tetragonal perovskite structure of PbTiO_3 at the A-sites by replacing the Pb^{2+} ions [15]. There are two possible ways of neutralizing the extra

Fig. 1.2 An ABO_3 perovskite unit cell.

Fig. 1.3 Room temperature phase diagram of PLZT system [16].

Table 1.2 Comparison of radii of Pb^{2+} , La^{3+} , and Ti^{4+} ions.

Ion type	Radius ($\text{\AA}$)
Pb $^{2+}$	1.32
La $^{3+}$	1.22
Ti $^{4+}$	0.64

positive charge as a result of La^{3+} substitution in the A-sites — by the creation of either lead (A-site) or titanium (B-site) vacancies [17]. Since La_2O_3 brings an extra oxygen atom compared to PbO it is expected to inhibit the oxygen vacancies created as result of removal of Pb in the form of PbO [3]. Therefore, assuming there are no oxygen vacancies, the creation of Pb^{2+} vacancies as a result of La^{3+} incorporation can be expressed by the following equation:

while the one for extra charge compensation by the creation of Ti^{4+} vacancies would be:

The composition of PLT for x mol % of La can, correspondingly, be expressed in either of the following two forms depending on the type of vacancies produced:

A few authors have reported the synthesis of PLT thin films of various mol % of La using sputtering [18-24] or sol-gel [12, 25-26] methods. For the preparation of bulk PLT and the thin films, some authors have assumed the formula A [27-28], others have

* For 28 atomic % La they are, (A) $\text{Pb}_{0.58}\text{La}_{0.28}\text{TiO}_3$, and (B) $\text{Pb}_{0.72}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$, respectively.

assumed the formula B [18-21], and yet others have used a vacancy distribution factor or lead elimination factor [12, 14-15, 22, 29-30] and have reported a range of values for the electrical properties.

According to the vacancy distribution theory [14] the charge imbalance upon incorporation of La in the PbTiO_3 structure is compensated by the creation of both Pb and Ti vacancies for $\text{La} > 5$ mol % and their relative proportions are dependent on the La content incorporated [14]. That is, for x mol % of La incorporated the actual mol % of Pb is somewhere between $1-1.5x$ and $1-x$ and the exact number is determined by the mol % of La. Sometimes the formula in (1.5) is normalized with respect to Ti and expressed as

$$\text{(B) Pb}_{(1-x)/(1-0.25x)} \text{La}_{x/(1-0.25x)} \text{Ti O}_{3/(1-0.25x)} \quad (1.6)$$

The distribution of vacancies between the A site and the B site is usually expressed in terms of a parameter α known as the lead elimination parameter or the vacancy distribution parameter. For the incorporation of x mol % of La the resulting mol % of Pb is represented as $1-\alpha x$ where $0.75 \leq \alpha \leq 1.5$ if the normalized version of the composition formulae are used. In the case of 28 mol % of La in bulk PbTiO_3 , Hennings and Härdtl determined this parameter to be around 1.3 [14]. This result is based on the studies done on bulk PLT where the processing temperatures are very high (1000-1400 °C) and significant Pb loss is expected by PbO volatilization. The value of α , evidently, is dependent on the processing conditions because Pb loss increases with temperature and also depends on the ambient vapor pressure of PbO in during annealing. Even at the very high temperatures of bulk processing where Pb loss in the form of PbO is expected to be significant, it was found that less than 1.5x mole of PbO per x mole of La (i. e., $\alpha = 1.3$ for 28 mol % La) is eliminated; the remaining charge being balanced by the formation of

Ti vacancies [14]. It can, therefore, be argued that at relatively low processing temperatures of thin films there might be even less Pb loss giving more Ti vacancies with Pb content approaching the non-normalized value of $1-x$ for x mol % of La. Since the heat treatment temperatures used in this study never exceeded 700 °C it is possible that La incorporation may result in only B-site vacancies.

Since the composition has a very strong influence on the structure and properties of materials in the perovskite family it is important to characterize the stoichiometry-structure-property relationship in the PLT films corresponding to 28 mol % of La for the two different compositions resulting from A-site and B-site vacancy compensation.

It has also been a common practice to add excess Pb during the fabrication of Pb based bulk ceramics to compensate for the Pb loss due to its volatility at high processing temperatures. Though Pb loss is not significant at the MOD or sol-gel processing temperatures, extra Pb is still added as it has been found to improve the electrical properties [31-33]. Therefore, it is also of interest to investigate the effect of excess Pb on the structure and properties of PLT films of both compositions.

Among all the deposition methods for multicomponent ferroelectric thin films, chemical solution deposition methods (i. e., sol-gel or MOD) are well known for allowing best composition control as the constituents are dissolved at the molecular level. It is, however, extremely important to optimize the solution deposition procedure with the right choice of precursors as it has profound impact on the structure and properties of the final films [34-35]. Most of the data available on the preparation and electrical properties of PLT films corresponds to sputtering. There are very few reports on the solution deposition of PLT films — only one for PLT with 28 mol % La [12] — and understandably there is a variation in the reported values of the properties. It was, therefore, considered important from the point of view of having good control over the

composition and ease of handling to come up with a solution deposition technique that should be simple to implement, should give stable solutions with good shelf life and should result in good reproducibility of the structure and properties.

1.4 Objectives

In the light of the discussion in the preceding sections the objectives of this research can be summarized as follows:

1. To develop a metalorganic decomposition technique with stable solutions, that is easy to use, and gives reproducible films of good quality.
2. To study the effect of stoichiometry (difference in composition as a result of different vacancy compensation mechanisms) on the structure and properties of PLT thin films.
3. To study the effect of excess Pb on the structure and properties of PLT thin films.
4. To characterize the electrical properties for the projected electrical parameters requirements.

In the present study, thin films of PLT (28 mol %) were fabricated using both formula A and formula B and their properties were investigated and compared. The effect of excess Pb on the properties was studied by adding various amounts of extra Pb in the range of 0% through 20%. X-ray diffraction, high resolution Scanning Electron Microscopy and UV-VIS-NIR spectrophotometry were employed to study the structure and its development. Metalorganic Decomposition (MOD) process was used for film fabrication because similar to sol-gel, it offers several advantages such as low processing temperatures, close composition control, ease of fabrication, relative inexpensive, and greater homogeneity [26].

Chapter 2. Experimental Procedure

Thin film fabrication through chemical solution deposition route typically consists of three steps; namely, preparation of an appropriate metalorganic solution, coating of a film (which is amorphous) of the solution on a substrate, and heat treatment of the film to obtain the desired crystalline structure.

2.1 Solution Preparation

The solution preparation is of critical importance for film fabrication through the solution deposition techniques. The choice of the metalorganic precursors and organic solvents, and the order in which they are mixed profoundly affect the structure and properties of the film [34-35]. The stoichiometry of the films is also primarily determined by the composition of the solution.

For the present study, ten solutions of different compositions were prepared as listed in Table 2.1, five each for type-A and type-B. The type-A solutions were made for five different excess Pb concentrations, namely no excess Pb or 0%, 5%, 10%, 14%, and 18%. Five solutions were similarly made for type-B with 0%, 5%, 10%, 15%, and 20% excess Pb concentrations.

The precursors used to make the solution for PLT film fabrication were lead acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (from Fisher Scientific), aqueous solution of lanthanum acetate, $\text{La}(\text{CH}_3\text{COO})_3$ (from Molycorp), and titanium iso-propoxide, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (from Fisher Scientific). Acetic acid and n-propanol (both from Fisher Scientific) were used as the solvent and the chemical modifier. 0.4M solutions of PLT (28

Table 2.1 Composition of the ten solutions prepared for the study.

**Type-A
Compositions**

Excess Pb Content	Composition
0 %	$\text{Pb}_{0.58}\text{La}_{0.28}\text{TiO}_3$
5 %	$\text{Pb}_{0.63}\text{La}_{0.28}\text{TiO}_3$
10 %	$\text{Pb}_{0.68}\text{La}_{0.28}\text{TiO}_3$
14 %	$\text{Pb}_{0.72}\text{La}_{0.28}\text{TiO}_3$
18 %	$\text{Pb}_{0.74}\text{La}_{0.28}\text{TiO}_3$

**Type-B
Compositions**

Excess Pb Content	Composition
0 %	$\text{Pb}_{0.72}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$
5 %	$\text{Pb}_{0.77}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$
10 %	$\text{Pb}_{0.82}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$
15 %	$\text{Pb}_{0.87}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$
20 %	$\text{Pb}_{0.92}\text{La}_{0.28}\text{Ti}_{0.93}\text{O}_3$

mol %) were made for all ten compositions described above using the procedure shown in Fig. 2.1. The required amount of titanium iso-propoxide was weighed in a beaker. Approximately 10 g of propanol was added to titanium iso-propoxide and the solution was stirred in an ultrasonic bath ('USB' in the figure) for 5 minutes to facilitate proper mixing. Then approximately 5 g of acetic acid was added to this system and was mixed in the ultrasonic bath for 5 minutes. Desired amount of lanthanum acetate was then added to the system followed by the addition of the required amount of lead acetate. Proper dissolution was obtained by heating the system to 60-70 °C in the ultrasonic bath for 10-15 minutes. After the precursors dissolved completely, 5 g acetic acid was further dissolved in it. Finally, propanol was added to make the total volume 50 ml. By this process, very clear solutions were consistently obtained. All solutions were made using the same procedure described above and differed only in their composition.

2.2 Fabrication of Thin Films

Spin-coating is one of the most commonly employed techniques by which a coating of the solution is deposited on to a substrate surface. The substrate, placed on a platform, is first covered with a layer of the solution to be deposited. The platform is then made to spin resulting in a thin amorphous coating of the metalorganic solution. This process is repeated until the desired thickness is obtained.

Thin films of PLT from the ten solutions were spin-coated on the substrates using a photoresist spinner (Headway Research Inc.) at an rpm of 1500 for 30 seconds. Sapphire substrates were used for optical property characterization while Pt/Ti/SiO₂/Si substrates were used for electrical measurements. Initially, after each coating, the films were baked at

Fig. 2.1 Flow diagram for solution preparation.

150 °C for 5 minutes to dry out the volatile organic medium. This cycle was repeated three times (to obtain the desired thickness of 300-400 nm). In the preliminary studies it was observed that the multilayered films wherein each layer was baked for 5 minutes showed the presence of interfaces between the layers in the optical transmittance spectra. It was suspected to be due to the difference in total baking times of the layers. For instance, in a film with three spin-coated layers the first layer got baked for 15 minutes while the last layer was baked for only 5 minutes. Though subsequent heat treatment at elevated temperatures for the formation of perovskite phase should remove this discrepancy but it was not observed to do so. Therefore, after the last coating, the films were dried for 15 minutes to homogenize the baking of all the layers. It was found to result in a continuous film.

The films were then annealed at elevated temperatures to obtain the perovskite phase and their structure was studied. The heat treatments were always done in a quartz tube furnace in air for 30 minutes.

2.3 Characterization Procedure

The films were characterized with respect to their microstructure, optical transmittance behavior, and the electrical properties and their degradation behavior. The crystal structure of the films was characterized by x-ray diffraction. Scanning electron microscopy was used to study the microstructure. The thickness of the film was estimated by weight difference and also more accurately by the optical transmission spectra.

The optical properties of the films deposited on sapphire were measured using a UV-VIS-NIR spectrophotometer (UV-3101PC, Shimadzu Corp.). The envelope method [36] was used to calculate the refractive index and the thickness of the film.

The structure development of the films was studied as a function of annealing temperature. After spin-coating and associated baking at 150 °C, the films were annealed at temperatures increasing in steps of 50 °C. After each annealing the x-ray diffraction pattern and optical transmittance spectra were obtained. In this way, the evolution of crystallinity and variation in optical behavior were studied for each of the films annealed at various temperatures from 150 °C to 700 °C.

For electrical measurements the films were spin-coated on Pt/Ti/SiO₂/Si substrates and after appropriate heat treatment top electrodes of palladium were deposited using vacuum evaporation. The area and thickness of the top electrodes were $2.1 \times 10^{-4} \text{ cm}^2$ and 400 nm respectively. The dielectric constant and loss measurements were done using the HP4192A low frequency impedance analyzer. The time dependent dielectric breakdown, fatigue, and charge storage density were measured on the RT-66A standardized ferroelectric test system (from Radiant Technologies, Inc.). The leakage current measurements were done on a Keithley 617 programmable electrometer.

Chapter 3. Crystal Structure and Morphology

3.1 Crystal Structure

As mentioned in the introduction thin films were prepared assuming both A- and B-site vacancies. For convenience, they will henceforth be referred to as type-A film and type-B film, respectively. The x-ray diffraction patterns for both films were similar. The variation in the x-ray diffraction pattern as a function of annealing temperature is shown in Fig. 3.1 for a type-A film with no excess Pb. The x-ray diffraction peaks correspond to a cubic perovskite structure with the lattice parameter $a = 3.92 \text{ \AA}$.

In Fig. 3.2 the x-ray diffraction pattern of type-A as well as type-B films with different excess Pb concentrations annealed at 700 °C are compared. The patterns were almost identical and there was no discernible difference in the lattice parameters of any of these films. It, therefore, appears that the perovskite phase in all the films had the same crystal structure. The low sensitivity or resolution of the x-ray diffraction equipment, however, does not preclude the presence of other phases in small amounts. Also before perovskite phase formation no peaks corresponding to any other phase, such as the pyrochlore phase, appeared. As can be seen from the x-ray diffraction patterns shown in Fig. 3.1, the perovskite phase formation initiated somewhere between 450 °C and 500 °C for a type-A film with no excess Pb. There was no change in the intensity of the diffraction peaks beyond 600 °C indicating that the perovskite phase formation completed between 550 and 600 °C. Same ranges for initiation and completion of the perovskite phase were observed for other compositions.

Fig. 3.1 X-ray diffraction pattern as a function of annealing temperature for a type-A film with no excess Pb.

Fig. 3.2 Comparison of the x-ray diffraction pattern of both type of films with different amounts of excess Pb annealed at 700 °C.

3.2 Morphology

The films had very smooth surface and did not show much morphological features under the conventional scanning electron microscope investigation. High resolution scanning electron microscopy was then employed with back scattered (BSD) and secondary electron detectors (SED) to look at the microstructure of these films deposited on Pt/Ti/SiO₂/Si substrates and annealed at different temperatures.

3.2.1 Microstructure of type-A Films

Fig. 3.3(a) through 3.3(d) show the secondary electron and back scattered detected micrographs at two different magnifications for a type-A film with no excess Pb annealed at 700 °C for 30 minutes. The SED micrographs of the film show dense and uniform clusters embedded in a matrix which has small dark spots distributed throughout. The SED micrograph reflects the topography and the secondary electron yield depends on the surface structure [37]. The dark spots embedded in the matrix, therefore, might be micropores or regions of uneven topography.

The corresponding BSD micrographs of the same film show the grain clusters as bright regions while the matrix appears dark. The back scattered electron yield increases with the atomic number [37] and consequently the bright regions in the micrograph must have a higher average atomic number distribution than the dark regions. In materials such as Pb(Zr_xTi_{1-x})O₃ where the formation of Pb deficient pyrochlore phase has been reported besides the desired perovskite phase, because of the higher atomic number of Pb, the perovskite phase has a higher back scattered electron emission yield and appears

(a)

0.5 μm

(c)

2 μm

(b)

0.5 μm

(d)

2 μm

Fig. 3.3 Two different magnifications of the SED (a) and (c), and the BSD (b) and (d) micrographs for a type-A film with no excess Pb annealed at 700 °C.

brighter in the BSD micrograph [31]. The back scatter coefficient, η is 0.51, 0.44, and 0.25 for Pb, La, and Ti, respectively [37]. Therefore the presence of a phase deficient in either Pb or La, compared to the perovskite phase, might give rise to the dark regions in the BSD micrographs of type-A films with no excess Pb. The x-ray diffraction patterns of the type-A film with no excess Pb, shown in Fig. 3.1, did not indicate the presence of any crystalline phase other than the cubic perovskite phase. The dark region, consequently, could be a lead or lanthanum deficient amorphous phase. It could also be the perovskite phase mixed with a distribution of micropores since the presence of micropores would decrease the average atomic number of the region and decrease the back scattered yield of electrons.

The effect of excess Pb on the microstructure of type-A films is shown in the SED micrographs of Fig. 3.4(a) through 3.4(d) for increasing contents of excess Pb. As the amount of excess Pb increased the number of the uniform dense clusters in the SED micrographs increased while their size decreased and the dark spots embedded in the matrix decreased.

Similar trend was observed for the BSD micrographs of these films with increasing excess Pb and is shown in Fig. 3.5(a) through 3.5(d). The dark regions were observed to diminish with increasing excess Pb and therefore it is unlikely that the dark regions were a result of lanthanum depletion, since the lanthanum content of these films was the same for all compositions.

3.2.2 Microstructure of type-B Films

The SED micrographs for type-B films annealed at 700 °C are shown in Fig. 3.6(a) through 3.6(e) as the excess Pb increased from 0% to 20%. The corresponding BSD

(a)

0.5 μm

(b)

0.5 μm

(c)

0.5 μm

(d)

0.5 μm

Fig. 3.4 SED micrographs of type-A films with (a) 5%, (b) 10%, (c) 14%, and (d) 18% excess Pb annealed at 700 °C.

(a)

2 μm

(b)

2 μm

(c)

2 μm

(d)

2 μm

Fig. 3.5 BSD micrographs of type-A films with (a) 5%, (b) 10%, (c) 14%, and (d) 18% excess Pb annealed at 700 °C.

Fig. 3.6 SED micrographs of type-B films with (a) 0%, (b) 5%, (c) 10%, (d) 15%, and (e) 20% excess Pb annealed at 700 °C.

micrographs for the same films are shown in Fig. 3.7(a) through 3.7(e). A type-B film with no excess Pb, in Fig. 3.6(a), showed densely packed uniform microstructure. Increasing excess Pb in type-B films improved the packing of the grain clusters and decreased their size, as was observed in type-A films also. Beyond 10% excess Pb, however, there was not much improvement and the structure appeared more or less saturated. It is noteworthy, however, that for 10% excess Pb and beyond on type-B films the microstructures showed the appearance of sinuous and continuous channel-like structure whose prominence increased as the excess Pb increased beyond 10%. Similar structures were obtained as a result of annealing for sputtered PLT films by Fox et al [22-24] who believe them to be the result of PbO evaporation. They also showed that PbO loss increased with increasing excess Pb in the as deposited film and at an annealing temperature of 650 °C there was very little Pb loss for up to 5 mol % excess Pb on their formula beyond which there was a sharp increase in loss. For 10% extra Pb and beyond on our type-B films, therefore, the appearance of the channel-like structure would suggest PbO evaporation.

3.2.3 Interpretation of the Differences in Morphology

On type-A films no channel-like structure was seen even as 18% excess Pb was added and therefore evaporation of PbO from type-A films is ruled out. A comparison of the composition formulae of the films given in Table 2.1 indicate that if formula B represents the right stoichiometry of the perovskite phase then formula A is highly Pb deficient or, conversely, formula B would have excess Pb if formula A gives the right stoichiometry.

Fig. 3.7 BSD micrographs of type-B films with (a) 0%, (b) 5%, (c) 10%, (d) 15%, and (e) 20% excess Pb annealed at 700 °C.

Absence of the sinuous channels in the micrographs of type-A films along with the considerable improvement in the uniformity of the microstructure with excess Pb addition indicate formula A to be Pb deficient rather than formula B being Pb rich.

The microstructure of films annealed at 600 °C showed the same general trend as the ones annealed at 700 °C for both type of films as well as with respect to the effect of excess Pb. The SED and the BSD micrographs of a type-A film with 10% excess Pb, annealed at 600 °C, are shown as representative examples in Fig. 3.8(a) and 3.8(b), respectively. The respective micrographs for the same film annealed at 700 °C were shown in Fig. 3.4(b) and 3.5(b).

Heat treatment of the films has one or all of the following three possible effects: Pb loss due to the volatilization of PbO, perovskite phase formation, or sintering of the nucleated perovskite particles. Increment of the annealing temperature from 600 to 700 °C should result in the enhancement of these effects and would be accordingly manifest in the microstructure. An increase in the perovskite phase formation would result in an increase in the fraction of bright perovskite regions of the BSD micrograph. The x-ray diffraction pattern of the films, however, did not show any increase in the intensity of the peaks beyond the annealing temperature of 600 °C implying that perovskite phase formation completed by this temperature and therefore should not have any significant effect on the microstructure evolution from 600 to 700 °C. If there was any Pb loss at these heat treatment temperatures it would give rise to Pb deficient dark regions. Increasing Pb loss at higher annealing temperature would tend to increase the fraction of the dark region as the annealing temperature is increased from 600 to 700 °C while densification would have the opposite effect. A comparison of the BSD micrographs at the two temperatures shows a decrease in the fraction of the Pb deficient region while the SED pictures clearly show the "agglomerate-like" structure of small perovskite particles at 600 °C which coalesce

(a)

0.5 μm

(b)

2 μm

Fig. 3.8 (a) SED and (b) BSD micrographs of a type-A film with 10% excess Pb annealed at 600 °C.

together to form dense and large clusters of perovskite at 700 °C. Pb loss from these films, therefore, appears unlikely and is not the cause of Pb deficient dark regions. Consequently it is the formula A itself that is Pb deficient compared to the perovskite stoichiometry. This conclusion is also supported by the fact that as the Pb content was increased the microstructure became more uniform, fine, and densely packed and the dark regions diminished.

Addition of excess Pb, therefore, seems to increase the nucleation of the perovskite phase and promote the densification of the structure as has also been observed in other Pb based perovskite [5, 20]. The SED micrographs are shown at a higher magnification because with increasing excess Pb the films became smoother and did not show the features very well at lower magnification.

Chapter 4. Optical Properties

Measurement of optical properties also brought about the striking difference between type-A and type-B films. As deposited, both type-A and type-B films had excellent transparency. Upon heat treatment type-A films invariably started to get cloudy as the amorphous to perovskite phase transformation took place. That is, as the annealing temperature was increased beyond 450 °C, they started to lose their transparency and the maxima and minima in the transmission spectra broadened with decreasing amplitudes and the transmittance decreased sharply. Shown, for example, are the specular and the total transmittance curves for a type-A film with no excess Pb annealed at 450 °C in Fig. 4.1. The film was transparent; there was very little scattering and the two transmittance curves were reasonably close to each other. The same film when annealed at 500 °C lost its transparency, became cloudy, and showed a considerable gap between the specular and the total transmittance around the visible wavelengths as shown in Fig. 4.2. As the annealing temperature was increased further the film became more cloudy and the gap between the two transmission spectra increased indicating increased scattering. The behavior is similar to that reported for bulk PLZT which when prepared assuming A-site vacancies consistently did not give transparent samples [16]. The envelope method calculations from the transmittance vs. wavelength pattern are, therefore, not very reliable for type-A films annealed at higher temperatures. The pattern, however, was observed to improve with increasing excess Pb resulting in a continuous decrease in the gap between the two transmission spectra. A type-A film with 18% excess Pb in Fig. 4.3, for instance, showed less mismatch between the two transmittance patterns.

Fig. 4.1 Transmittance vs. wavelength for a type-A film with no excess Pb on sapphire heat treated at 450 °C.

Fig. 4.2 Transmittance vs. wavelength for a type-A film with no excess Pb on sapphire heat treated at 500 °C.

Fig. 4.3 Transmittance vs. wavelength for a type-A film with 18% excess Pb on sapphire heat treated at 500 °C.

Type-B films, on the contrary, had very good transparency and transmittance vs. wavelength curves. The specular and total transmission curves were almost identical for all type-B films. For example, there was excellent match between the two transmission curves for a type-B film without any excess Pb annealed at 600 °C as shown in Fig. 4.4. In type-B films also the transparency improved with increasing extra lead content though this improvement was marginal beyond 10% excess Pb.

The refractive index at 633 nm and the thickness of the film were calculated from the transmittance vs. wavelength curve using the envelope method [21] and the results are shown in Fig. 4.5 for a type-B film with no extra lead. The refractive index vs. the annealing temperature for type-A film with 18% extra lead, albeit not very reliable above 500 °C, is shown for comparison in Fig. 4.6. The variation in the refractive index with extra lead is shown in Fig. 4.7 for type-B films annealed at 700 °C. As can be seen from the figure, the refractive index increased with extra lead up to 10% beyond which the value saturated at around 2.15 for type-B films which is slightly smaller than the value reported for sputtered PLT films [5].

There was a slight variation in the film thickness with excess Pb. Thickness values after annealing at 700 °C for all the films with three coatings were in the range of 320-360 nm. The variation in the thickness as a function of excess lead content for type-A and type-B films annealed at 700 °C after three coatings is shown in Fig. 4.8 and Fig. 4.9, respectively. The values obtained from weight difference measurements were in reasonable agreement with the thickness calculated from the optical transmission spectra and are compared in Table 4.1.

From the compositional formulae given in the introduction it is evident that formula-A films are Pb deficient compared to formula-B films. Addition of extra Pb on type-A films increased the perovskite phase consequently decreasing the fraction of Pb-

Fig. 4.4 Transmittance vs. wavelength for a type-B film with no excess Pb on sapphire heat treated at 600 °C.

Fig. 4.5 Refractive index and thickness of a type-B film with no excess Pb as a function of annealing temperature.

Fig. 4.6 Refractive index of a type-A film with 18% excess Pb as a function of annealing temperature.

Fig. 4.7 Variation in the refractive index of type-B films annealed at 700 °C with excess Pb content.

Fig. 4.8 Variation in thickness with excess Pb for a type-A film annealed at 700 °C.

Fig. 4.9 Variation in thickness with excess Pb for a type-B film annealed at 700 °C.

Table 4.1 A comparison of thickness of the films obtained by weight difference and envelope method.

Type-B

Excess Pb	Thickness (nm)	
	Weight difference	Envelope method
0%	343	339
5%	341	347
10%	358	353
15%	354	358
20%	361	357

deficient scattering regions and resulting in an increase in the refractive index and better transparency. In other words, increase in the refractive index can be attributed to the improvement in the packing density of the film under the effective medium approximation [36]. Excess Pb improved the packing density of type-B films up to 10% resulting in an improvement in the refractive index. Beyond 10% excess Pb, however, there was not much improvement in the packing density and consequently the value of refractive index saturated beyond this point. This is supported by the microstructural differences between type-A and type-B films as mentioned earlier. The result of dielectric measurements also seemed to indicate that formula A is Pb deficient rather than formula B being Pb rich, as discussed in the following chapter.

Chapter 5. Electrical Properties

5.1 Dielectric Constant and Polarization

Type-A films showed very low values of the dielectric constant and the charge storage density. There was a continuous improvement in the values with the addition of excess Pb. Type-B films on the other hand had very good values of the dielectric constant and the charge storage. Addition of excess Pb improved these values up to 10% excess Pb after which there was a decline in these values. The variation of the dielectric constant and the loss factor with applied frequency at 1 V rms (or, applied field ≈ 30 kV/cm) is plotted for a type-A film with 18% extra Pb, which had the best dielectric constant among the type-A films, and a type-B film without any extra Pb, which had the lowest value among the type-B films, in Fig. 5.1 and Fig. 5.2, respectively. The permittivity and the loss in general both decreased with increasing frequency. The type-B films showed higher dielectric constant as well as slightly higher loss values than type-A films. The room temperature dielectric constants for the aforementioned type-A and type-B films at 100 kHz were 946 and 1107 respectively. The best dielectric constant value at 100 kHz was 1336 for a type-B film with 10% excess Pb. The dielectric constant remained more or less constant for low fields while at higher fields it decreased with the field and showed a tendency to saturate indicating a nonlinearity in the dielectric behavior which was very clearly observed in the P-E curve. The nonlinearity results from the broad phase transition of PLT (for $\text{La} \geq 23\%$) [27,30] attributable to the chemical inhomogeneity at the micro level.

Fig. 5.1 Dielectric constant and loss tangent for a type-A film with 18% excess Pb as a function of frequency.

Fig. 5.2 Dielectric constant and loss tangent for a type-B film with no excess Pb as a function of applied frequency.

The dielectric constant as well as the loss values started to increase rapidly at around 1 MHz. Other researchers who used the same equipment (HP 4192A) also observed this behavior and suspect it might be a result of resonance in the electrical test circuit [12].

The dielectric constant decreased for both type of films as the temperature was increased above room temperature. The variation in dielectric constant with temperature is shown in Fig. 5.3 for a type-A film with 18% excess Pb and in Fig. 5.4 for a type-B film without any excess Pb. All the films showed similar behavior with temperature indicating that the Curie temperature for all films was below room temperature.

Small signal capacitance measurements were done using the RT-66A test system to study the polarization vs. applied field (P-E) behavior of these films. As was also observed in the case of dielectric constant, the type-A films showed low values of the charge storage density while type-B films had very good values. For type-A films the polarization continuously improved with the addition of excess Pb while for type-B films the improvement was only observed up to 10% excess Pb, after which the values degraded. In other words, for type-A films the best polarization values were obtained for a film with 18% excess Pb while for type-B films it was with 10% excess Pb. The P-E behavior of these films, annealed at 700 °C for 30 minutes, is shown in Fig. 5.5 and Fig. 5.6, respectively.

The effect of addition of excess Pb on the dielectric constant and the polarization for both type of films is illustrated in Fig. 5.7 and Fig. 5.8, respectively. The addition of excess Pb had a strong influence on the microstructure of these films and consequently on the properties. In general, in Pb based perovskites a deficiency of PbO results in the formation of Pb deficient phases and poor densification while excess PbO promotes

Fig. 5.3 Dependence of dielectric constant on temperature for a type-A film with 18% excess Pb.

Fig. 5.4 Dependence of dielectric constant on temperature for a type-B film with no excess Pb.

Fig. 5.5 P-E characteristic for a type-A film with 18% excess Pb.

Fig. 5.6 P-E characteristic for a type-B film with no excess Pb.

Fig. 5.7 Variation in room temperature dielectric constant with excess Pb at 100 kHz for both type of films.

Fig. 5.8 Variation in polarization with excess Pb for both type of films.

perovskite phase and densification. Beyond a certain limit, however, excess PbO might form Pb rich non-perovskite phases, might go in the grain boundaries, or evaporate leaving continuous porosity resulting in a decrease in the values as well as leading to degradation and aging of the material. Usually an addition of 5-10% excess Pb has been found to give the best electrical properties for several Pb based perovskites [5, 24, 31-33].

For instance, for sol-gel derived $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ thin films it has been shown that 10% Pb deficient films had very poor electrical properties while 9-10% excess Pb gave the best values for polarization as well as coercive field and beyond 10% excess Pb they either degraded or leveled off [31-33]. In type-A films in the present case the dielectric constant and polarization kept improving even at 18% excess Pb. In formula-B, on the other hand, though there was a definite improvement in properties with excess Pb the refractive index value leveled off beyond 10% while the dielectric constant and polarization values fell. A type-B film with 10% excess Pb would be effectively 25% excess Pb on formula A and consequently should show severe degradation in the optical and the electrical properties if formula A was the right composition for the perovskite phase. Since the films were annealed at 600-700 °C only, expulsion of excess PbO should not be significant enough to compensate for that high an excess Pb concentration and consequently type-B could not be an excessively Pb rich film. The trend with excess Pb, on the contrary, suggests that formula A more probably is Pb deficient. Another way to look at the behavior with excess Pb is to realize that increasing excess Pb is nothing but increasing the value of $1-\alpha x$ from $1-1.5x$ towards $1-x$. Improvement in the properties, in general, upon further Pb addition (beyond $1-x$; up to 10% in our case) can be attributed to the compensation of Pb loss, improved densification, and enhancement of perovskite phase. In the present case of films annealed at 600-700 °C, densification seems to be the major cause of improvement in

properties though PbO volatilization is also possible for type-B films with 10% and higher excess Pb as suggested by the microstructure of these films.

A comparison of the microstructures with the dielectric properties of these films clearly supports the basic hypothesis of type-B formula being closer to the perovskite phase stoichiometry, if not the same, than type-A. The very high value of the dielectric constant of the oxide ferroelectrics ABO_3 has been shown to be due to their perovskite structure and consequently a higher fraction of the perovskite phase in the microstructure gives a higher dielectric constant value [5]. In the type-A film without any excess Pb there are big clusters of perovskite embedded in a Pb deficient matrix. The structure can be schematically expressed as a capacitor with two layers of dielectric—one with very high dielectric constant and the other with a very low dielectric constant. The effective dielectric constant of the material depends on the dielectric constant values as well as the volume fraction of these layers [38]:

$$1 / k_{\text{eff}} = v_1 / k_1 + v_2 / k_2 , \quad (5.1)$$

and therefore the measured values of the dielectric constant are very small for a type-A film with no excess Pb which has a considerable fraction of low dielectric constant Pb-deficient regions seen in the micrographs. As the excess Pb was increased on these films the volume fraction of the low permittivity dark regions decreased resulting in higher values of the dielectric constant.

The type-B films, on the contrary had very dense and uniform microstructure with small grain size and no trace of low permittivity dark regions. As the excess Pb increased there was improved densification and packing resulting in an improvement in the permittivity and polarization values. Beyond 10%, however, the extra Pb in the form of

PbO which has very low permittivity (≈ 20) might distribute itself at the grain boundaries [39] and may result in an overall decrease in the value of the effective dielectric constant. The presence of the sinuous channel like structure in type-B films with extra Pb beyond 10% seems to support the decrease in the dielectric constant values observed from the measurements. Even if these channels do not contain excess PbO, and are continuous porous structures, their presence would decrease the permittivity. The purpose of this study, however, is not to prove the defect structure of the film but to report that type-B films showed better electrical and optical properties and also that with increasing excess Pb type-A films approached the dielectric constant and refractive index values of type-B films.

A comparison of the projected electrical parameter requirements for 256-Mb DRAMs presented in Table 1.1 shows that the type-B films with 5-10 % excess Pb are excellent in terms of the storage-charge density requirements.

5.2 Leakage Current

The leakage current tests were performed on a Keithley 617 programmable electrometer and the measurements were taken when the current had stabilized. The initial currents, attributable to the accumulation of charge in the cathode depletion zone [40-41], were considerably higher which gradually decreased and after a prolonged period of time reached the equilibrium value that resulted solely from the conductivity of the dielectric material.

The leakage current levels were observed to decrease with excess Pb on type-A films and the lowest values were obtained for a film with 18% excess Pb. Within the range of measurements performed, breakdown was observed only for a film with no excess Pb.

For type-B films the leakage current was lower for 5% excess Pb compared to a film without any excess Pb. Beyond 5% excess Pb the current levels were observed to increase with excess Pb. A comparison of the leakage current behavior of the best type-A and type-B films with applied field is shown in Fig. 5.9. The effect of excess Pb on the leakage current density at a fixed applied field is illustrated in Fig. 5.10 which shows that a type-B film with 5% excess Pb had the lowest current density among all films.

Since the quality of the dielectric material is strongly dependent on its structure the reduction in leakage current levels in type-A films with increasing excess Pb is hardly surprising. As the low permittivity Pb deficient regions decrease (or, the high permittivity perovskite phase increases) the possibility of formation of conducting paths through these regions decreases leading to a reduction in the current levels. On type-B films, however, this improvement is observed only up to 5 % excess Pb. For 10 % and beyond the appearance of the dark "channel-like" structure might lead to a continuous conducting path increasing the current levels specially if these contain excess PbO. The measurements of resistivity and degradation studies also showed similar behavior with excess Pb and are discussed in the following section.

5.3 Dielectric Degradation

The breakdown of the dielectric after a certain period of time under a fixed applied field lower than its breakdown strength is an important parameter that governs the performance of the dielectric in a device. RT-66A test system was used to study the performance of the films on Pt/Ti/SiO₂/Si substrates under a fixed applied dc field. The measurements were taken at increasing intervals of time. The resistivities of the films annealed at 700 °C were found to be in the range of 10⁹-10¹¹ ohm-cm at room

Fig. 5.9 Films of each type with lowest leakage current levels.

Fig. 5.10 A comparison of leakage current densities at a fixed applied field for both type of films.

temperature at an applied field of 200 kV/cm and their behavior with time is compared in Fig. 5.11 and 5.12 respectively for type-A and type-B films. In general the resistivity was found to increase with excess Pb for both type of films though the values were all very close together. The values were also found to be dependent on the applied field and were found to decrease as the field was increased. Except in a film with 18% excess Pb no sign of aging, degradation or breakdown was observed in the resistivity of type-A films for up to around 25-30 hours at which the tests were terminated. The film with 18% excess Pb showed very little decay as depicted in Fig. 5.11.

Type-B films showed increasing effects of aging for up to 10% excess Pb as can be seen in Fig. 5.12. A sharp drop in resistivity was observed for 15 and 20% excess Pb indicating breakdown. This aging behavior can be attributed to excess Pb which in the form of PbO helps in densification of the microstructure through liquid phase sintering, which might be the reason for improved resistivity, but is unlikely to go in the perovskite phase and therefore either evaporates leaving porous channels or is present in the grain boundaries promoting the degradation of dielectric with time [40]. Furthermore, the resistivity of PbO ($\sim 10^8$ ohm-cm) being much lower than that of the PLT material, excess of PbO beyond a certain limit has a deleterious effect on both the overall resistivity and the leakage current of these films [42].

5.4 Fatigue

The capacitor in the DRAM requires to be refreshed periodically, which is usually on the order of milliseconds, to compensate for the charge loss by the capacitor through the dielectric as leakage current. Therefore, in reality there is a unipolar cyclic loading of the dielectric material (at a frequency on the order of MHz in present day DRAM's) that

Fig. 5.11 TDDB behavior of type-A films with varying excess Pb under a fixed applied field of 200 kV.

Fig. 5.12 TDDDB behavior of type-B films with varying excess Pb under a fixed applied field of 200 kV.

might lead to earlier degradation. A study of the degradation behavior under unipolar cyclic field is of interest from that point of view. It has been shown that the degradation in ferroelectric materials (and usually in all materials) is faster under bipolar field (alternating current) compared to unipolar field. Therefore, to get a faster estimate of the fatigue behavior, degradation studies were done at a frequency of 1 MHz under an ac field for a type-B film without any excess Pb using an accelerated test technique [43]. At room temperature the storage charge density was $15.6 \mu\text{C}/\text{cm}^2$ at a field of 200 kV/cm for a type-B film with no excess Pb. At room temperature the films showed almost no loss in the polarization up to 10^{10} cycles. Frequently, the temperature inside the device increases and may effect degradation earlier. In Fig. 5.13, the polarization degradation behavior at room temperature as well as at elevated temperatures is shown. The charge density was observed to decrease as the temperature increased and at 200 °C the polarization started to fall off at around 10^9 cycles. For the same time (10^3 - 10^4 seconds), as described in the previous section, there was no loss in polarization when the test was done under dc fields.

In the light of the values for the aforementioned electrical parameters obtained the PLT films corresponding to 28 mol % of La appear to be excellent candidates for 64- and 256-Mb ULSI DRAM applications.

Fig. 5.13 Unified accelerated test for loss of polarization with time (no. of cycles) for a type-B film with no excess Pb.

Chapter 6. Summary

Thin films of Lead Lanthanum Titanate having 28% La were successfully fabricated using metalorganic decomposition process. The films were made corresponding to two different formulae: assuming A-site and B-site vacancy compensation, respectively. Type-B films were found to have better optical as well as electrical properties. The films showed an improvement in the dielectric permittivity and the refractive index with the addition of excess Pb over the formula. The data seems to suggest that films made according to formula A might be Pb deficient. The best properties were obtained for a type-B film with 5-10% excess Pb. The films were found to be cubic at room temperature and had fine microstructure. High permittivity, low loss, high resistivity, and no significant degradation up to 10^{10} cycles make these films excellent candidates for high density DRAM applications. Other than their potential application in high capacity DRAMs, owing to their variable capacitance (nonlinear C-V characteristic at high fields) these PLT films can also be utilized in the circuit to compensate for any stray inductance, viz., as decoupling capacitors.

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