Physical and electrical characterization of sol-gel derived $Ba_xSr_{1-x}TiO_3$ thin films of various composition ratios and thicknesses

By

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A thesis submitted in fulfillment of the requirements for the degree of Master of Science (Microelectronic Engineering)

School of Microelectronic Engineering
UNIVERSITI MALAYSIA PERLIS

2011

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ACKNOWLEDGEMENT

How should I begin this note of appreciation? There have been so many people involved that I will feel guilty if I don't mention them here. Therefore, if any of them reads this and finds that they are not listed here, I would like to say thank you for your help.

First of all, I am deeply grateful to my supervisor, Mejar Assoc. Prof. Zaliman Sauli for the continuous support, effort and was very willing to take me under his wing. I also feel so honored to have Leftenan R. Charan as my co-supervisor for his patience, motivation, enthusiasm and immense knowledge in helping me complete my thesis. He played such an important role in helping me complete my work. I would also like to take this opportunity to thank Assoc. Prof. Dr Johari Adnan, my second co-supervisor as well as Dean of School of Microelectronic Engineering for his encouragement to fulfill my task.

In my daily work I have been blessed with a friendly and cheerful group of researchers. So, in this brief and short note I would like to expand my appreciation to those people who spend their time and shared their knowledge; Gium, Steven, Mydin, Bojjie, Emma, Syud and many others for their endless support. Without you guys, I would be in disarray.

I am also grateful to the failure analysis and cleanroom staff; En. Bahari, En. Hafizz, En. Hafiz, En. Zul, En. Din for keeping the lab in such superb condition.

Last but not least, to my family, my parents and sisters for their love, patience and support throughout my studies.

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LIST OF ABBREVIATIONS

BST	=	Barium strontium titanate
AFM	=	Atomic Force Microscopy
XRD	=	X-ray Diffraction
PVD	=	Physical Vapor Deposition
RTA	=	Rapid Thermal Annealing
Ba	=	Barium
Sr	=	Strontium
Pt	=	Platinum
Si	=	Silicon
SiO_2	=	Silicon dioxide
Al	=	Aluminum
Rms	=	Root means square
DRAM	=	Dynamic Random Access Memory
T_C	=	Curie temperature
RF	=	Radio Frequency
MOCVD	=	Metal Organic Chemical Vapor Deposition

Pencirian fizikal dan elektrikal berasaskan teknik sol-gel untuk menghasilkan filem nipis $Ba_xSr_{1-x}TiO_3$ untuk pelbagai nisbah komposisi dan ketebalan

ABSTRAK

Antara pelbagai bahan-bahan dielektrik, barium strontium titanate telah dikaji secara meluas kerana mempunyai pemalar dielektrik yang tinggi, kehilangan dielektrik yang rendah dan tunabiliti yang tinggi. Barium strontium titanate adalah komposisi yang bergantung kepada suhu Curie yang menurun secara linear dengan peningkatan jumlah Sr dalam komposisi tersebut. Dalam kajian ini, filem nipis barium strontium titanate dengan empat komposisi berbeza; $Ba_{0.5}Sr_{0.5}TiO_3$, $Ba_{0.6}Sr_{0.4}TiO_3$, $Ba_{0.7}Sr_{0.3}TiO_3$ dan $Ba_{0.8}Sr_{0.2}TiO_3$ telah disediakan dengan menggunakan teknik sol-gel dan difabrikasi atas substrat $Pt/SiO_2/Si$. Filem nipis itu dikristalkan dengan baik, padat, rata dan bebas retak yang diperolehi dengan suhu penyepuhlindapan pada 800 °C. Pemalar dielektrik, tunabiliti, dan kehilangan dielektrik menunjukkan hubungan erat dengan mikrostruktur filem. Pemalar dielektrik, tunabiliti dan kehilangan dielektrik bertambah dengan bertambahnya saiz butiran dan ketebalan filem. Variasi pemalar dielektrik dengan fungsi voltan untuk filem nipis $Ba_{0.5}Sr_{0.5}TiO_3$ dan $Ba_{0.6}Sr_{0.4}TiO_3$ tanpa pengutuban spontan, menunjukkan kewujudan sifat paraelektrik dalam suhu bilik. Bagaimanapun, filem nipis $Ba_{0.7}Sr_{0.3}TiO_3$ dan $Ba_{0.8}Sr_{0.2}TiO_3$ mempunyai bentuk lengkung kupu-kupu menunjukkan kewujudan sifat ferroelektrik. Pemalar dielektrik tertinggi dan tunabiliti, 485.02 dan 34.75 % diperhatikan dalam komposisi $Ba_{0.7}Sr_{0.3}TiO_3$ pada ketebalan 447.6 nm kerana suhu Curie $Ba_{0.7}Sr_{0.3}TiO_3$ hampir kepada suhu bilik. Kerja ini menunjukkan pencirian berjaya dalam sifat-sifat fizikal dan elektrik berbilang lapisan filem nipis $Ba_xSr_{1-x}TiO_3$ dengan nisbah Ba dan Sr yang berbeza.

Physical and electrical characterization of sol-gel derived $Ba_xSr_{1-x}TiO_3$ thin films of various composition ratios and thicknesses

ABSTRACT

Among the various dielectric materials, barium strontium titanate has been extensively studied due to its high dielectric constant, low dielectric loss and high tunability. Barium strontium titanate is a composition dependent to Curie temperature, which decreases linearly with the increasing of Sr amount in the composition. In this study, barium strontium titanate thin films with four different compositions; $Ba_{0.5}Sr_{0.5}TiO_3$, $Ba_{0.6}Sr_{0.4}TiO_3$, $Ba_{0.7}Sr_{0.3}TiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$ and four different thicknesses were prepared by using sol-gel technique and deposited on $Pt/SiO_2/Si$ substrates. The well-crystallized, dense, smooth and crack-free thin films are obtained through annealing process at temperature of 800 °C. The dielectric constant, tunability and dielectric loss shows strong relationship with the films microstructure. The dielectric constant, tunability and dielectric loss increases as the grain size and film thickness increases. The variations of dielectric constant as a function of voltage for $Ba_{0.5}Sr_{0.5}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$ thin films are devoid of any spontaneous polarization, which indicates that the thin film is paraelectric in room temperature. However, $Ba_{0.7}Sr_{0.3}TiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$ thin films with butterfly-shaped curves show the existence of ferroelectric nature. The highest dielectric constant and tunability, 485.02 and 34.75 % were observed in $Ba_{0.7}Sr_{0.3}TiO_3$ composition at thickness of 447.6 nm due to the Curie temperature of $Ba_{0.7}Sr_{0.3}TiO_3$ is close to room temperature. This work demonstrates successful physical and electrical characterization of multiple layers of $Ba_xSr_{1-x}TiO_3$ thin films to its different composition ratios of Ba and Sr.

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter explains the overview of the research done followed by the problem statement. The objectives and scope of this research are described in detail. Finally the dissertation of layout of this thesis is briefly explained.

1.2 Overview of Barium Strontium Titanate

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$/ BST) material is one of the ferroelectric materials which attract great interest among researchers to study its electrical properties due to high dielectric constant and composition dependent to Curie temperature (Roy & Krupanidhi, 1993). Barium strontium titanate compounds are the continuous solid solution of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$). The introduction of Sr atoms to the A site of $BaTiO_3$ lattice substitute the Ba atoms will change the Curie temperature of $Ba_xSr_{1-x}TiO_3$. The Curie temperature of $Ba_xSr_{1-x}TiO_3$ system decreases linearly with the increase of Sr amount in the $BaTiO_3$ lattice which enables the paraelectric-ferroelectric transition temperature to be tailored by adjusting the barium-to-strontium ratio for specific application.

There are few techniques available to fabricate the BST such as radio frequency (RF) magnetron sputtering (Oh et al., 2007), metal organic chemical vapor deposition (MOCVD) (Bogert, 1999), pulsed laser deposition (Zhu et al., 2006), soft-solution processing (Shi, Yao & Zhang, 2005) and sol-gel process (Wang, Uusimäki & Leppävuori, 1997). Among these techniques, sol-gel technique which involves the usage of liquid solution mixture as a starting material offers a homogenous distribution of elements at molecular level, high purity, ease of composition control and better homogeneity. The lower cost of the equipment makes it a great method for preparing new solutions with different compositions. Sol-gel technique also offers easier deposition on large and complex area substrate for thin films fabrication.

Ferroelectric barium strontium titanate thin films have been widely investigated due to its potential in microelectronic devices such as thin films capacitors (Kawakubo et al., 1998), dynamic random access memory (DRAM) (Horikawa et al., 1993), (Kumar & Manavalan, 2005), (Cho et al., 1997), infrared sensors (Zhu et al. 2004), microwave devices (Wang et al. 2003), and hydrogen gas sensor (Zhu et al., 2000). This is mainly because of its high dielectric constant, low dielectric loss, large electric-field tunability, long lifetime and good temperature stability.

The previous work of other researchers show that the electrical properties; dielectric constant, dielectric loss, leakage current and dielectric tunability of barium strontium titanate thin films is affected by the composition of the films that changed the Curie temperature. The film thickness, grain size, surface roughness, deposition technique and type of dopant also influence the electrical properties of barium strontium titanate thin films (Zhu et al., 2006), (Hu, Yang & Zhang, 2008), (Guiying, Ping, & Dingquan, 2007). Therefore, the electrical behavior of BST is extremely dependent on its material properties, including its stoichiometry, microstructure and thickness of the films.

1.3 Problem Statement

Ferroelectric materials are being widely pushed to the forefront for usages in microelectronic field. In this aspect, taking into consideration of the ferroelectric materials capability of high dielectric constant function, it has good potential as a capacitive device. Barium strontium titanate is vastly being researched in the area of ferroelectric and piezoelectric areas, so this material is chosen in this work to study its characteristic in both physical and electrical properties. Many theories and findings have been brought forward in regards of correlation between physical and electrical properties. These relationships are pivotal in device fabrication and functional parameter tuning. To the best of the author's knowledge, most of the previous work done focused on single layer and multiple ratios of $Ba_xSr_{1-x}TiO_3$ composition for the thin films physical and electrical property characterization. Work on multiple thickness or layers is virtually not existence. In this work, multiple layer deposition and its correlation to multiple ratios of $Ba_xSr_{1-x}TiO_3$, physical and electrical were investigated.

1.4 Research Objectives

The main objective of this work is to study the physical and electrical properties of BST thin films by using sol-gel technique. The sub-objectives of this research are:

1. To prepare $Ba_xSr_{1-x}TiO_3$ solutions using sol-gel technique by varying barium-to-strontium ratio with x=0.5, 0.6, 0.7, 0.8.
2. To deposit $Ba_xSr_{1-x}TiO_3$ solutions on $Pt/SiO_2/Si$ substrate with multiple layers noted as 1 layer, 2 layer, 3 layer and 4 layer for physical characterization including microstructure and thickness of the films.
3. To deposit $Al/Ba_xSr_{1-x}TiO_3/Pt$ layer to produce capacitor in order to study the electrical characteristics of the $Ba_xSr_{1-x}TiO_3$ films.
4. To determine correlation between the microstructure of $Ba_xSr_{1-x}TiO_3$ thin films with the electrical properties.

1.5 Research Scope

In this work, the $Ba_xSr_{1-x}TiO_3$ thin films are prepared by using sol-gel technique. The $Ba_xSr_{1-x}TiO_3$ solutions are deposited on $Pt/SiO_2/Si$ substrates by spin coating process in order to study the microstructure of the films. The microstructure of the films consists of the surface roughness and the grain size. The dots of Aluminum are deposited on $Ba_xSr_{1-x}TiO_3/Pt/SiO_2/Si$ to produce metal/ferroelectric/metal layer to study the electrical properties of the $Ba_xSr_{1-x}TiO_3$ thin films. The barium-to-strontium ratio is varied with x=0.5, 0.6, 0.7 and 0.8 in order to study the effect of microstructure and electrical properties of the thin films with four different thicknesses noted as 1 layer, 2 layer, 3 layer and 4 layer.

1.6 Dissertation Layout

This dissertation is divided into five chapters as Introduction, Overview of Barium Strontium Titanate, Research Methodology, Results and Discussions and finally the Conclusion.

The first chapter describe a brief review of the material used, problem statement, objectives and scope of this research.

Chapter two covers review on BST and previous work on related topic by other researchers.

Chapter three discusses the flow and process of the work done. The preparation of the $Ba_xSr_{1-x}TiO_3$ solution is explained in this chapter and also the characterization of the thin films.

Chapter four presents the results obtained from physical and electrical characterization works. The first part displays the XRD pattern of the BST thin films. Physical characterization consists of surface analysis and grain size is discussed. The study of electrical characterization of $Ba_xSr_{1-x}TiO_3$ thin films in sandwiched of Al/BST/Pt is also discussed in this chapter.

Finally, in chapter five, conclusion of overall results has been done with some future work recommendation.

CHAPTER 2

A REVIEW ON BST

2.1 Introduction

This chapter is divided to three subsections which are the overview of ferroelectricity, properties of barium strontium titanate and previous work done by other researchers on barium strontium titanate thin films. The barium strontium titanate films have been studied with different parameters which are preparation technique of the barium strontium titanate films, film composition, film thickness, crystalline temperature, etc which influences the electrical properties of the film itself.

2.2 An Overview of Ferroelectricity

Ferroelectricity is an electrical phenomenon of ferroelectric materials that exhibit a spontaneous polarization in which the direction of the polarization can be switched by the application of an external electric field. This phenomenon was discovered by J. Valasek in 1920 during his study on the analogy between the magnetic properties of ferromagnetic and the dielectric properties of Rochelle Salt (Gonzalo & Jiménez, 2005). Barium titanate, $BaTiO_3$, the first perovskite ferroelectric was discovered during the early 1940's in the United States, Russia and Japan. In 1945 and

1946, Von Hippel, and Wul and Goldman demonstrated first ferroelectric switching in $BaTiO_3$. Thus followed switching found in other perovskites, which is in $KNbO_3$ and $KtaO_3$ discovered by Matthias in 1949, in $LiNbO_3$ and $LiTaO_3$ by Matthias and Remeika in 1949 and in $PbTiO_3$ by Shirane, Hishima and Suzuki in 1950 (Gonzalo & Jiménez, 2005).

Ferroelectric materials with higher dielectric constant has a low dielectric loss and high dielectric tunability compared to ordinary insulating substance. This makes ferroelectric materials a good candidate for a variety of applications such as high dielectric capacitors, tunable microwave devices, DRAM (dynamic random access memory) capacitor, pyroelectric sensors, piezoelectric transducers, and electro optic devices. This wide range of applications is mainly attributed to the phase transitions in ferroelectrics. Most of the ferroelectric materials transforms to paraelectric cubic phase above a transition temperature called Curie temperature, T_C. The ferroelectric materials change from paraelectric cubic phase to ferroelectric tetragonal phase below the T_C. The phase transition of ferroelectrics due to temperature is shown in Figure 2.1 (Manavalan, 2005).

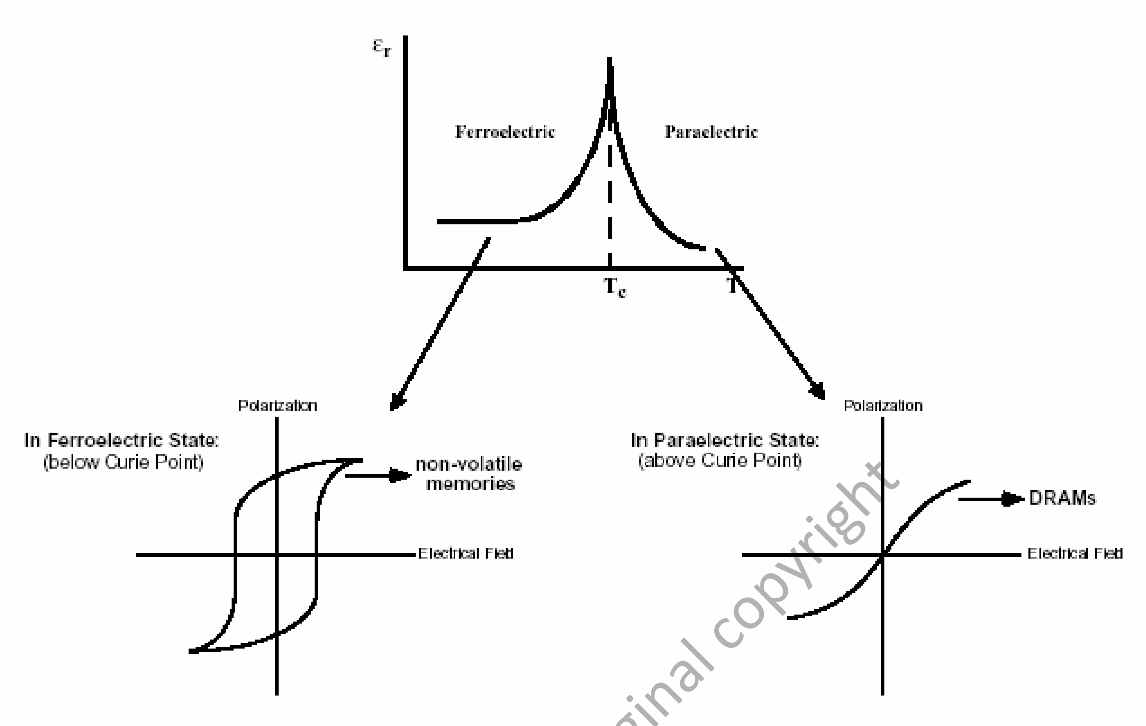

Figure 2.1: Transition characteristic of ferroelectric material

In ferroelectric phase, the dielectric permittivity also known as the dielectric constant (ε_r), increases as the temperature increase while in the paraelectric phase, the dielectric constant decreases with increase in temperature according to the Curie-Weiss,

$$\varepsilon_r = \varepsilon_0 + \frac{C}{T - T_C} \approx \frac{C}{T - T_C} \tag{2.1}$$

where C is the Curie constant, T_C is the Curie temperature and T is temperature. The dielectric constant reaches its maximum value at T_C and for $T > T_C$, ε_r severely decreases. In ferroelectric phase, a highly non-linear loop or hysteresis loop is observed that reveals that the material has memory (Haertling, 1999)). In the paraelectric phase, without spontaneous polarization, the dielectric constant is still high and suitable for tunable microwave and DRAM applications. One of the promising ferroelectric materials is strontium-doped barium titanate ($Ba_xSr_{1-x}TiO_3$) compound due to high dielectric constant and composition dependent Curie temperature (Roy & Krupanidhi, 1993).

2.3 Properties of Barium Strontium Titanate

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$) compounds are continuous solid solution of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$). The introduction of Sr atoms to the $BaTiO_3$ lattice substitutes the Ba atoms which will influence the crystalline structure and its properties (Adikary, 2003). $BaTiO_3$ and $SrTiO_3$ adopt ABO_3 perovskite structure because of its crystal structure is in the group of material with the mineral name calcium titanate ($CaTiO_3$). Figure 2.2 shows the ABO_3 perovskite structure of $Ba_xSr_{1-x}TiO_3$. A (Ba or Sr) represents the large cations located at the corners of the unit cell, B (Ti) represents the smaller cations located at the body center and O is the oxygen atoms positioned at the face centers.

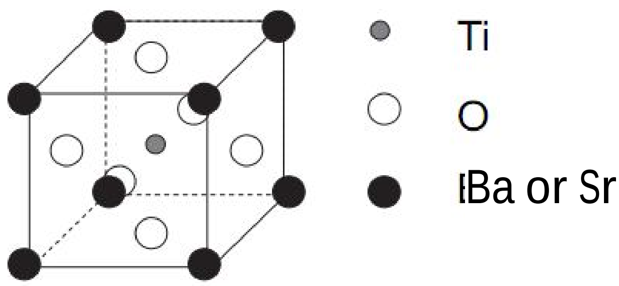

Figure 2.2: The ABO_3 perovskite structure of $Ba_xSr_{1-x}TiO_3$ (Adikary, 2003)

The substitution of Ba^{2+} ion with Sr^{2+} ion to the A site of the $BaTiO_3$ crystal structure is found to reduce the Curie temperature of $BaTiO_3$ while maintaining its high dielectric constant. The structure, dielectric and ferroelectric properties of $Ba_xSr_{1-x}TiO_3$ generally depends on the Sr content because the Curie temperature of $Ba_xSr_{1-x}TiO_3$ system decreases linearly towards room temperature with the increasing amount of Sr in the $BaTiO_3$ lattice as shown in Figure 2.3. The decreasing amounts of T_C enable the paraelectric-ferroelectric transition temperature to be tailored by adjusting the barium-to-strontium ratio for specific application.

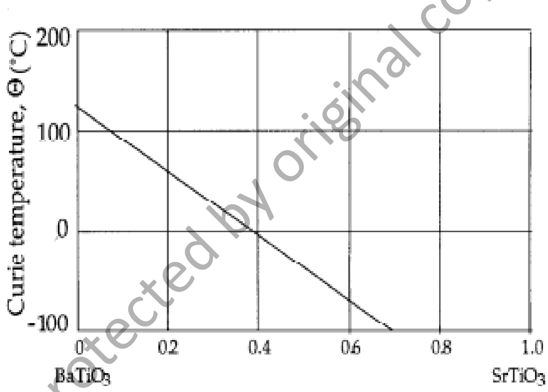

Figure 2.3: Curie temperature of $Ba_xSr_{1-x}TiO_3$ as a function of stoichiometry (Remmel et al., 1999)

$BaTiO_3$ has a paraelectric cubic phase above its Curie temperature at about 120 °C while at room temperature, $BaTiO_3$ exhibit tetragonal perovskite structure. The tetragonality of $Ba_xSr_{1-x}TiO_3$ system decreases with the increasing of Sr content thus at room temperature, the $Ba_xSr_{1-x}TiO_3$ with higher Ba content is tetragonal while with higher Sr content is cubic. Therefore, the $Ba_xSr_{1-x}TiO_3$ with higher Ba content is ferroelectric and tetragonal at room temperature.

The ferroelectric properties of $Ba_xSr_{1-x}TiO_3$ generally depend on the tetragonality of the structure because smaller tetragonal value of c/a ratio may not be sufficient to create separation and spontaneous polarization. Figure 2.4 shows the lattice parameter (a and c) of $Ba_xSr_{1-x}TiO_3$ as a function of Sr (mol %) content at room temperature. From Adikary, it is reported that $Ba_xSr_{1-x}TiO_3$ shows a complete solid solubility over all compositions with a cubic structure at room temperature for $0 \leq x \leq 0.3$, becoming tetragonal for $0.3 \leq x \leq 1$ which shown in Figure 2.4 which x is refer to the Ba content.

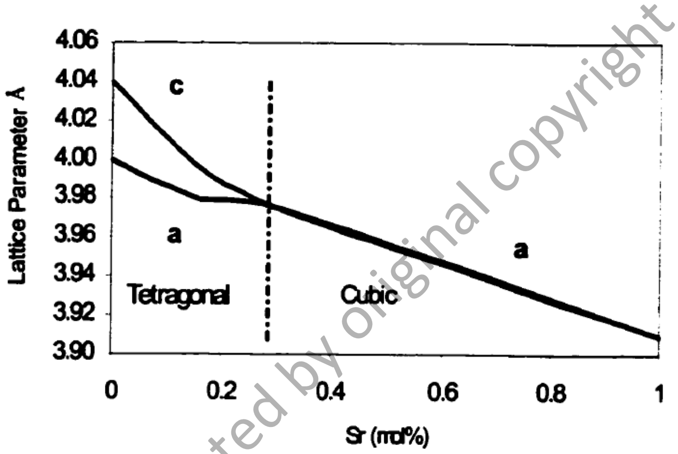

Figure 2.4: Lattice parameter of $Ba_xSr_{1-x}TiO_3$ versus composition at room temperature

2.4 Overview and Previous Work of BST thin films

BST thin films received a large interest because of its potential in the application of microelectronic devices due to high dielectric constant, relatively low dielectric loss tangent and large dielectric field tunability (Chen et al., 2006). In general, a thin film is a layer of material ranging from several nanometers to several micrometers in thickness and is grown on a substrate. The relationship between the film and substrate influences the characteristics of BST thin films (Su & Button, 2001, Su et al., 2003, Yi et al., 2002 & Koutsaroff et al., 2002). Some of the common materials used as a substrate are