The Impact of Deposition Layer And Annealing Temperature Towards BST Thin Film Characteristics

by

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A thesis submitted in fulfilment of the requirements for the degree of
Master of Science in Microelectronic Engineering

School of Microelectronic Engineering
UNIVERSITI MALAYSIA PERLIS

2016

ACKNOWLEDMENT

I would like to acknowledge the following people for their support and assistance with this Master Project. Special thanks to Supervisor; Prof. Dr Zaliman Sauli and Co-Supervisor; Dr Vithyacharan Retnasamy for the supervision and support that they gave truly help the progression and smoothness of the master project. The co-operation is much indeed appreciated. A big contribution and hard worked from them is very great indeed. This study during the program would be nothing without the enthusiasm and imagination from

Next, I would like to thanks to our School of Microelectronic Engineering School's Dean; Assoc. Prof. Dr Rizal Affandi and Program Chairman Dr Norhawati for helping me to complete the study. Not to forget, Dr Rozana, Dr Sobri, Dr Asri for sharing their ideas and guidance during my study.

Besides, this study makes me realized the value of working together as a team and is a new experience in working environment, which challenges us every minutes. Not to forget, great appreciation go to the Failure Analysis and Clean room staff; Encik Bahari Man, Encik Zul and Encik Hafiz that help me from time to time.

The whole program really brought us together to appreaciate the true value of friendship and respect of each other. Great deals appreciated go to contribution of my parent and family. I also would like to thankful all my friends; Shakirina, Syuhada, Ong Tee Say, Puan Norlida, and other fellow friends who shared their ideas, expertise, and excitements during the study.

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LIST OF ABBREVIATIONS

AC	Alternating Current
AFM	Atomic Force Microscopy
Al	Aluminum
BST	Barium Strontium Titanate
CVD	Chemical Vapour Deposition
DC	Direct Current
MOCVD	Metal Organic Chemical Vapour Deposition
MOSD	Metal-Organic Solution Deposition
PLD	Pulsed Laser Deposition
Ra	Surface Roughness
RF	Radio Frequency
RMS	Root Means Square
SEM	Scanning Electron Microscope
Sol-gel	Solution-gelation
Sol	Solution
SPA	Semiconductor Parametric Analyzer
TEM	Transmission Electron Microscope
TGS	Triglycine Sulphate
XRD	X-ray Diffraction

LIST OF SYMBOLS

A	Area
Al	Aluminium
Ba	Barium
C	Capacitance
cm	Centimeters
E	Electric Field
FOM	Figure of Merit
g	Grams
Ga	Gallium
hrs	Hours
Hz	Hertz
K	Potassium
k	Kilo
L	Liters
La	Lanthanum
m	Meters
Mg	Magnesium
ml	Milliliters
Na	Natium
nm	Nano Meters
P	Polarization
Pt	Platinum
Si	Silicon
Sr	Strontium

tan δ	Loss Tangent
Tc	Curie temperature
Ti	Titanium
V	Voltage
ε_r	Dielectric Constant/Permittivity
η	Tunability
$Ba(CH_3COO)_2$	Barium Acetate
$Sr(CH_3COO)_2$	Strontium Acetate
$C_{12}H_{28}O_4Ti$	Titanium Isopropoxide
CO_2	Carbon Dioxide
H_2O	Water
CH_3COOH	Glacial Acetic Acid
$C_3H_8O_2$	2-Methoxyethanol

KESAN LAPISAN ENDAPAN DAN SUHU PENYEPUHLINDAPAN KEATAS CIRI-CIRI BAHAN LAPISAN BARIUM STRONTIUM TITANATE

ABSTRAK

Bahan-bahan ferroelektrik yang terdiri daripada oxida kompleks dengan struktur perovskite memberikan pelbagai fungsi telah menarik minat para penyelidik dalam bidang aplikasi peranti elektronik dan optik. Bahagian yang menarik dengan bahan-bahan ini adalah sensitiviti dalam ciri-ciri fizikal terhadap suhu, luaran elektrik, magnetic dan tekanan mekanikal khususnya hampir dengan suhu peralihan fasa. Pelbagai aplikasi elektronik menggunakan bahan-bahan ferroelektrik disebabkan oleh dielektrik, elektrik, suhu, magnetic dan ciri-ciri optik. Ciri-ciri yang terdapat dalam lapisan BST menyebabkan ia menjadi tumpuan penyelidikan dan menggabungkannya ke dalam aplikasi kepadatan tinggi seperti DRAM, fasa perubahan, sensor IR, kelembapan dan sensor gas, penapis tunable, penggerak piezoelektrik, voltage kawalan pengayun dan varaktor. Matlamat penyelidikan ini adalah menyelidik interaksi punca utama jumlah lapisan dan suhu penyepuhlindapan lapisan $Ba_{0.5}Sr_{0.5}TiO_3$ dalam bentuk ciri-ciri mikrostruktur dan elektrik. Selain itu, mencari hubungan punca utama kepada ciri-ciri elektriknya. Penyelidikan ini disediakan dengan menggunakan kaedah sol-gel keatas substrate silikon. Cecair sol-gel yang telah disediakan diendapkan dengan 1 lapisan dan 4 lapisan keatas substrate dimana lapisan BST yang telah disediakan dibahagi dua suhu berbeza iaitu 600°C dan 800°C untuk menjalani proses penyepuhlindapan. Seterusnya, proses pencirian fizikan dan elektrikal dijalankan. Keputusan menunjukkan saiz butiran dan kekasaran permukaan sampel meningkat daripada 38.67 kepada 90.78 dan 1.92 kepada 9.41 dengan jumlah lapisan endapan dan suhu penyepuhlindapan. Di samping itu, pemalar dielektrik juga menunjukkan peningkatan daripada 136.78 kepada 783.91 apabila jumlah lapisan endapan dan suhu penyepuhlindapan meningkat. Oleh itu, pencirian fizikan dan elektrikal lapisan BST berkait rapat antara satu sama lain. Penyelidikan ini menunjukkan hubungan kesan antara pencirian Kristal, saiz butiran, kekasaran permukaan dan ciri-ciri elektrikalnya keatas lapisan BST menggunakan kaedah sol-gel. Dengan itu, hipotesis penyelidikan ini tercapai dengan peningkatan jumlah lapisan endapan dan suhu penyepuhlindapan mempengaruhi ciri Kristal, saiz butiran, kekasaran permukaan dan menyumbang kepada non-ferroektrik seperti sempadan butiran yang seterusnya meningkatkan pemalar dielektrik dan tunability.

THE IMPACT OF DEPOSITION LAYER AND ANNEALING TEMPERATURE TOWARDS BST THIN FILM CHARACTERISTICS

ABSTRACT

Ferroelectric materials which consist of the complex oxides with perovskite structure provided multifunctional have been attracted the eyes of the researchers in the application of electronic and optical devices. The attractive part of these materials is the sensitivity on physical properties to temperature, external electrical, magnetic, and mechanical stress, particularly near the temperatures of phase transitions. Wide range of electronic applications make used of these ferroelectric materials due to its dielectric, electric, temperature, magnetic and optical properties. The properties in Barium Strontium Titanate (BST) thin film causing it become extensively studied and emerged in to the application in high density DRAM, microwave phase shifter, IR sensing, humidity and gas sensor, tunable filters, piezoelectric actuator, voltage controlled oscillators, and varactors. The aim for this study is to investigate the main effect interaction of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin film number of deposition layer and annealing temperature in terms of microstructure and electrical properties to the BST. Besides that, to find the main effect relation of the electrical properties of the BST thin film. The study on the $Ba_{0.5}S_{0.5}TiO_3$ thin film is prepared using sol-gel technique on silicon substrate. Throughout the study, the BST solution is deposited on the $Pt/SiO_2/Si$ substrate by spin coating method in order for the purpose of investigating the microstructure of the thin films. Moreover, all the samples are deposited with combination of 2 different deposition layer and annealing temperature. Physical and electrical characterization of all the samples is done. The results showed that the grain size and surface roughness of the samples increased from 38.67 to 90.78 and 1.92 to 9.41, respectively as the deposition layer and annealing temperature increased. In addition, the dielectric constant of the samples also increased from 136.78 to 783.91 as the deposition layer and annealing temperature increased. Thus, the physical and electrical characteristics of the thin films are related on to another. This study has shown the effects of the deposition layer and annealing temperature of BST sol-gel thin films on the structure, microstructure and dielectric properties. A clear main effect between the surface roughness, grain size and the dielectric properties has been discovered in the BST sol-gel thin films. The objectives achieved where the increase in deposition layer and heat treatment temperature increased the crystallinity, grain size, surface roughness and contribute to the non-ferroelectric materials such as grain boundaries. This resulted in the direct effect on the increase of the thin film dielectric constant and tunability.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Electronic industries nowadays have become part of most important industries in all over the world as its application in a wide range either direct or indirect contact to our daily life. Researches on different areas have been done to produce low cost, high stability, and environmentally friendly products. One of the areas that captured the attention of researchers is on the microelectronic materials which are the basic area to produce a microelectronic device. Ferroelectric materials and related materials has becomes the focus due to its intelligent. Since decades, research and development on these ferroelectric materials in many forms like single crystals, polymers, composites, and thin films. In addition, the ferroelectric materials research is more on the structural types, compositions application and their state of development (Swartz, 1992).

Most of the ferroelectric materials used are found in the perovskite family with general formula ABO_3 which is the compositional modification in solid solution, substitution and/or dopants.

1.2 Overview

Ceramic materials are categorized into inorganic, non-metallic materials which contain of non-metallic and metallic elements that bonded together mainly by covalent and/or ionic bonds (Jones; Kailas, 2004). The chemical compositions for these ceramic materials diverge considerably, from simple compounds to more complex phases bonded together. The differences in bonding makes properties of ceramic materials also vary greatly. Generally, ceramic materials are naturally brittle and hard with low ductility and toughness. Usually, these ceramics are good thermal insulator and electrical caused by the non-attendance of conduction electrons. The stability of the bonding in ceramic materials caused it to have relatively high melting temperatures and chemical stability in many aggressive environments. This ceramic material is indispensable for many engineering designs because of the properties (Jones; Kailas, 2004).

Ceramic materials are used in many electrical and electronic applications. Various forms of ceramics are used as electric insulators for high and low voltage electric currents. Besides that, ceramic materials also find application in various types of capacitors, especially where miniaturization is required (Richard Ulrich, 2000). Another types of ceramics called piezoelectrics which can convert weak pressure signals into electrical signals, and vice versa. Ceramic materials are commonly used as dielectric materials for capacitors, with disk ceramic capacitor being by far the most common type of ceramic capacitor. These very small flat-disk ceramic capacitors consist mainly of barium titanate ($BaTiO_3$) along with other additives. Ceramic chip capacitors are used in some ceramic-based thick-film hybrid electronic circuits. Capacitors can provide appreciably higher capacitance per unit area values and can be added to the thick-film circuit by a simple soldering or bonding operations. Some ceramic ionic crystalline materials have unit cells that do not have a center of symmetry, and as a result their unit cells contain a small electric dipole and are called ferroelectric. An industrially important ceramic material in this class is barium titanate $BaTiO_3$. Above 120^0C, $BaTiO_3$ has the regular cubic symmetrical perovskite crystal structure (Pradhan S, 2013).

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$) compounds are continuous solid solution of strontium titanate ($SrTiO_3$) and barium titanate ($BaTiO_3$). Barium titanate ($BaTiO_3$) is a cubic and consists of large barium ions at each corner and each barium ion are surrounded by 12 nearest oxygen ions. Also, the titanium in the barium titanate ($BaTiO_3$) is at the central and 6 oxygen ions in the octahedral arrangement .The introduction of Sr atoms to the $BaTiO_3$ lattice substitutes the Ba atoms which will influence the crystalline structure and its properties (Adikary, 2004; Marta, 1966). $BaTiO_3$ and $SrTiO_3$ adopt the ABO_3 perovskite structure because of its crystal structure is in the group of material with the mineral name calcium titanate ($CaTiO_3$). When the ceramic materials are in the paraelectric state, there are no spontaneous polarizations, where there are symmetry among the Ti-ion, O-ion and $Ba_xSr_{1-x}TiO_3$. The orientation polarization of the Ti ion in the Perovskite structure results in high tunability and dielectric constant when it is applied bias voltage. In addition, high electrical charge of the Ti-ion induced the high dipole moment, thus high dielectric constant and tunability of the dielectric constant can be obtained. On the hand, spontaneous polarization happens and the structure becomes slightly elongated in ferroelectric state, spontaneous polarization occurs, and the structure becomes slightly elongated. For decades, researches have been working on this BST thin film due to its promising material properties such as tunability, dielectric loss, good temperature behaviour, size and integration (Tiggelman M. P. J, 2010). The most favourable dielectric and ferroelectric properties that attracted researchers' attention include alterable curie temperature ,high dielectric constant, high tunability and low dielectric loss of dielectric behaviour (Smith, 2010). The dielectric properties of BST thin films deposited by numerous depositions reported to be affected by many factors such as oxygen vacancies, film thickness, grain size, dopant types, and Ba/Sr ratio(Tanja Pecnik 2015; V. B. Shirokov, 2015; Xiaohong et al., 2015).

Many techniques can be applied to prepare barium strontium titanate (BST) thin film which includes pulsed laser deposition (PLD), radio-frequency (rf) magnetron sputtering, metal-organic solution deposition (MOSD), chemical vapour deposition (CVD) and sol-gel method. The sol-gel techniques attracted the attention of researches to further their research on sol-gel method because of its significant benefits. Among them are easy stoichiometry control, better homogeneity, ability to coat large area, low cost equipment , complex-shaped area substrates , and ease of doping (Sun et al., 2006). This sol-gel method implies stable colloidal ("sol") solution which gels into a film when dried. There are two steps involved in traditional method for preparing sol-gel that are dissolved organometallic molecular precursor (usually alkoxides) and hydrolysis and polycondensation occur form macromolecular oxide network to obtain gel type solution (Brinker, 1990).

Ferroelectric based devices are well known and being investigated for nearly 50 years since late 1960s and early 1970s. Ferroelectric thin film can be applied in a wide range of microelectronic even now in nanoelectronics application includes memory devices and radio-frequency (rf) devices). Besides that, the ferroelectric based thin films have been developed for various sensor, actuator and microwave devices.

Ferroelectric material is one of the classes of insulating materials which form dielectrics where the materials will sustain a dielectric polarization under the application of an electric field (Whatmore, 2007).

1.2.1 History of Ferroelectric

The history of ferroelectrics has been reported in an excellent way by (Busch, 1987). Many researches were involved in the early development of the ferroelectrics which includes (Brewster, 1824), (Curie, 1880), (Boltzmann, 1873), (Pockels, 1893) and (Debye, 1912). Certainly, this ferroelectricity term was first introduced by (Erwin Schrodinger, 1912). Nevertheless, the discovery of the effect was credited to (Joseph Valasek, 1920), who discovered the switching polarization of sodium potassium tartrate (Rochelle salt) in 1920 by applying an electric field . Therefore, the first demonstration of the process that is the stamp of ferroelectricity is provided. Joseph Valasek in his paper "Piezoelectric and allied phenomena in Rochelle salt" from American Physical Society in Washington dated April 23 in 1920 discussed the reports by Anderson and Cady. Joseph Valasek, 1920 found dielectric where the ballistic galvanometer charge and discharge are unequal for Rochelle salts. Besides that, asymmetry discovered is due to hysteresis of the electric polarization analogous to magnetic hysteresis. Figure 1.1 illustrated the hysteresis loops of the Rochelle Salt.

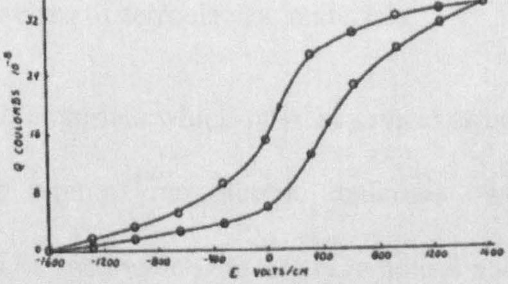

Figure 1.1: Hysteresis Loops of Rochelle Salt. (J. Valasek, 1971)

1.2.2 Ferroelectric Materials

Researches have been attracted to ferroelectric materials which consist of the complex oxides with perovskite structure provided multifunctional in the application of electronic and optical devices. The attractions of these materials are the sensitivity on physical properties to external electrical, magnetic, temperature and mechanical stress, particularly near to the phase transitions temperatures.

Wide range of electronic applications make used of these ferroelectric materials due to its dielectric, electric, temperature, magnetic and optical properties. Below is the summary of the basic properties useful for the applications:

a. Spontaneous polarization observed on ferroelectric (polar phase) that can be switched by an applied electric field (Bottger et al. 2005);
b. Antiferroelectric materials is completely cancel each other due to its antiparallel dipole moments
c. Ferroelastic materials having a stable and switchable spontaneous deformation

Ferroelectric materials can be categorized into its crystal classes such as ferroelectric oxides, Triglycine Sulphate (TGS), and Polymeric ferroelectrics. Common researches were done on the ferroelectric oxides which considered so far the most technologically important class of ferroelectric materials.

Ferroelectric is the materials which possess crystal structures isomorphous with mineral perovskite. This type of ferroelectric materials own its general chemical formula that is commonly be used which are ABO_3, where A and B are cations.

1.3 Problem Statement

Barium Strontium Titanate (BST) is categorized into the ceramics material under perovskite crystal structure. In most of the engineering and traditional ceramic products, they are produced by compacting powders or particles into shapes that are then heated to a high enough temperature in order to bond the particles together. Basically, there are three basic steps involved in processing the ceramics by the agglomeration of particles which includes material preparation, forming or casting, and thermal treatment by drying (which is usually not required) and firing by heating the ceramic shape to a high enough temperature to bond the particles together. Hence, varying the thin film deposition layer, and annealing is crucial steps to fabricate BST thin film (Chilibon, 2012; Smith, 2010).

According to Azhar Ali Haidry (2012), the development of improved and new thin film sensor is still important since they can be prepared by simple and cheap methods. Philippot et al. (2014) states that sol-gel products are much more homogeneous, however the synthesis temperature and duration is still in a challenging stage. Another researcher, Xu, Yan, Xiao, Yu, & Zhu (2013) states that dielectric properties that are based on phase transition phenomena in ferroelectric materials are related to crystal structure of the thin film. In addition, the crystal structure of ferroelectric materials also depends on the thermal condition and fabrication method. According to Kageyama, Sakurai, Ando, & Sakabe (2006), when above the Curie temperatures (Tc), the ferroelectric materials enter paraelectric state and ensuing dielectric loss drastically decreases while the material retains a large permittivity. Therefore, Chilibon (2012) suggested that the correlation of the microstructure and electrical properties of thin film is important.

The aim for this study is to investigate the main effect interaction for the number of deposition layer (thickness) and annealing temperature in terms of microstructure and electrical properties to the BST based on the challenges listed by other researchers. Besides that, this study also investigating the interaction of the electrical properties by changing the number of deposition layer and annealing temperature.

1.4 Scope of Study

The study on the $Ba_{0.5}S_{0.5}TiO_3$ thin film is prepared using sol-gel technique on silicon substrate. Throughout the study, the BST solution is deposited on the $Pt/SiO_2/Si$ substrate by spin coating method in order for the purpose of investigating the microstructure of the thin films. Moreover, all the samples are deposited with two different numbers of deposition layers noted as 1 layer and 4 layers. In addition, the as-deposited samples are annealed with two different annealing temperature which were 600 °C and 800 °C.

1.5 Research objectives

The main objective of this research is to correlate the microstructure and electrical properties of BST thin film. In order to achieve the main objective there are few sub-objectives needed to be done which are listed below:

i. To characterize microstructure of BST by varying the number of deposition layer and annealing temperature

ii. To characterize the electrical of BST by varying the number of deposition layer and annealing temperature.

1.6 Thesis Organization

This thesis is divided into five chapters. Chapter 1 is the introduction that gives a brief review on the background of the research. The research problem also is discussed in this section.

Chapter 2 is the summary of the previous literature on the related works carried out by other researchers. The review is focus on the research about the Barium Strontium Titanate (BST) thin films particularly prepared by sol-gel method. Researches on the other techniques in preparing BST also are reviewed.

Chapter 3 is the discussion on the process flow on the preparation of the $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) solution. Besides the preparation of the BST solution, the preparation of the thin film also is discussed in detail with the characterization of the thin films.

Chapter 4 presents the results of the characterization on BST thin films from physical and electrical study. Firstly, a discussion on the XRD pattern of the BST thin films. Next is the discussion on the physical characterization which consists of the surface and the grain size analysis. Thirdly, the analysis on the electrical characterization of the BST thin films is also discussed in this chapter. Last but not least, the correlation between the physical and electrical characterization on the BST thin films.

Chapter 5 is the conclusion of the overall results that has been done and the future recommendation work.