INVESTIGATION OF ULTRASONIFICATION EFFECT ON PHYSICAL AND ELECTRICAL CHARACTERISTICS OF $Ba_x Sr_{1-x} TiO_3$ THIN FILMS PREPARED USING SOL-GEL METHOD

by

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LIST OF ABBREVIATIONS

BST	=	Barium Strontium Titanate
XRD	=	X-ray Diffraction
AFM	=	Atomic Force Microscope
SPA	=	Semiconductor Parameter Analyzer
DIW	=	De-ionized Water
CSD	=	Chemical Solution Deposition
RMS	=	Root-Mean-Square
Al	=	Aluminium
Pt	=	Platinum
RTA	=	Rapid Thermal Annealing
SPM	=	Scanning Probe Microscopes
GaN	=	Gallium Nitride
PVD	=	Physical Vapour Deposition
Sr	=	Strontium
Si	=	Silicon
SiO_2	=	Silicon dioxide
$BaTiO_3$	=	Barium titanate
PZT	=	Zirconate titanate and
STO	=	Strontium titanate
TCD	=	Temperature coefficient of dielectric constant
MOCVD	=	Metal organic chemical vapor deposition
$PbTiO_3$	=	Lead Titanate
PTC	=	Positive temperature coeffiecient
CVD	=	Chemical Vapor Deposition
PECVD	=	Plasma Enhance Chemical Vapor Deposition
MOD	=	Metallorganic Decomposition
DRAM	=	Dynamic random-access memory

LSMCD	=	Liquid source misted chemical deposition
TEM	=	Transmission Electron Microscope
C-V	=	Capacitance - Voltage
P-E	=	Polarization-electric field
Ag	=	Argentum
RF	=	Radio frequency
MgO	=	Magnesium Oxide
I-V	=	Current - Voltage

LIST OF SYMBOLS

V	=	Volts
ε_r	=	Dielectric constant
d	=	Film thickness
C	=	Capacitance
A	=	Area in m^2 of capacitor
ε_o	=	Permittivity of free space, 8.854 x 10^{-12} F/m
n	=	Moles
MM	=	Molecular mass
F	=	Farads
rpm	=	Rotation per minute
cm	=	Centimeter
q	=	Charge
α	=	Polarizability
p	=	Dipole moments
N	=	Number of dipoles per cubic meter
mm	=	Millimeter
nm	=	Nanometer
T_c	=	Curie temperature

Kajian Mengenai Kesan Ultrasonification Terhadap Ciri-Ciri Fizikal Dan Elektrikal Bagi Filem Nipis $Ba_x Sr_{1-x} TiO_3$ Dideposit Menggunakan Kaedah Sol-Gel

ABSTRAK

Pencirian Barium Strontium Titanate (BST) dengan nisbah 60 kepada 40 dan nisbah 80 kepada 20 dari segi morfologi permukaan dan sifat-sifat elektrik telah dilakukan untuk menghasilkan satu campuran BST yang terbaik mengikut applikasi tertentu. Ciri-ciri $Ba_x Sr_x TiO_3$ dan struktur kapasitor BST telah dikaji. Satu wafer silikon jenis p berorientasikan (100) telah dideposit dengan Platinum (Pt), BST, dan Aluminium (Al) dalam susunan berikut, Si / SiO_2 / Pt / BST / Al. BST telah disediakan dengan menggunakan pemendapan kimia penyelesaian (CSD) di mana kaedah yang terlibat dipanggil sol-gel disebabkan oleh keupayaan untuk menghasilkannya pada kos yang rendah. Kaedah sol-gel umumnya menggunakan logam alkoxides hydrolytically yang sensitif sebagai bahan permulaan. Terdapat dua cara penyediaan untuk BST iaitu kaedah sol-gel dengan dan tanpa melibatkan ultrasonic, dan kedua-dua keputusan dibandingkan antara satu sama lain. Kesemua sampel telah melalui proses penyepuhlindapan pada suhu 800 ^oC di dalam suasana oksigen. Kaedah untuk penyediaan BST (60/40 dan 80/20) dijelaskan secara mendalam dan proses fabrikasi filem $Ba_x Sr_{1-x} TiO_3$ diterangkan. Sampel-sampel telah diuji dalam dua kategori iaitu pencirian permukaan dan pencirian elektrik. Bagi pencirian permukaan, pembelauan sinar-X (XRD), telah digunakan untuk mengesahkan pembentukkan fasa pada darjah penteksturan. Pembentukan BST bagi setiap puncak dapat diperhatikan dan menunjukkan sampel-sampel telah menghablur dengan baek bagi kedua-dua kaedah dan nisbah. Mikroskop tenaga atom (AFM) telah digunakan untuk morfologi permukaan dalam imej topografi 2D dan 3D. Filem-filem bagi setiap nisbah amat padat, licin dan bebas retak. Dengan kenaikan nilai x bagi BST menghasilkan saiz butiran yang lebih besar dan penglibatan ultrasonic dalam kaedah penyediaan mengurangkan saiz butiran. Bagi pencirian elektrik, penganalisa parameter semikonduktor (SPA) yang diukur pada 100 kHz dengan perubahan voltan yang diberikan antara 0V kepada +5V bagi pencirian arus – voltan (I-V) dan -8V kepada +8V bagi kapasitan – voltan (C-V) untuk sifat-sifat dielektrik. Kajian mikrostruktur morfologi pada permukaan sampel ini menunjukkan saiz butiran yang kurang daripada 0.1 μm. Dengan pertambahan nilai x pada $Ba_x Sr_{1-x} TiO_3$, pelbagai rantau konduksi menurun. Peningkatan pemalar dielektrik berkadar terus dengan ketebalan filem BST. Kesimpulan adalah selaras dengan keputusan yang diperolehi dengan penglibatan ultrasonic dalam langkah-langkah persediaan mengurangkan saiz butiran dan menghasilkan pemalar dielektrik dan tunabiliti yang lebih kecil.

Investigation Of Ultrasonification Effect On Physical And Electrical Characteristics Of $Ba_x Sr_{1-x} TiO_3$ Thin Films Prepared Using Sol-Gel Method

ABSTRACT

The characterization of Barium Strontium Titanate (BST) with the ratio of 60:40 and 80:20 in terms of surface morphology and electrical properties to produce the best BST solution according to its various applications has been done. Properties of $Ba_x Sr_{1-x} TiO_3$ and the structure of BST capacitor were studied. A (100) oriented p type silicon wafer has been deposited with Platinum (Pt), BST, and Aluminium (Al) in the following order of Si / SiO_2 / Pt / BST / Al. The BST was prepared using the chemical solution deposition (CSD) which involved a method called sol-gel which is of interest due to low capital investment cost. The sol-gel method generally uses hydrolytically sensitive metal alkoxides as the starting materials. There were two ways of preparation, namely the sol-gel method with and without involving ultrasonic and both of their results were compared to each other. All the samples have been annealed at 800 ^oC in oxygen atmosphere. The method for preparation of BST (60/40 and 80/20) was explained in detail and the fabrication process of $Ba_x Sr_{1-x} TiO_3$ films were described. The samples were tested in two categories, namely surface and electrical characterizations. For surface characterization, X-ray diffraction (XRD) was used to confirm phase formation on the degree texturing. BST formation for every peaks were observed and show the samples were well crystallized for both methods and ratio. Atomic force microscopy (AFM) was used to study the surface morhophology in 2D and 3D topography images. The films for each ratio were very dense, smooth and crack free. With the increment of x value of BST produces larger grain size and the involvement of ultrasonic in te preparation method reduces the grain size. For electrical characterization, semiconductor parameter analyzer (SPA) measured at 100 kHz with the variation of applied voltage ranging from 0V to +5V for current – voltage (I-V) and -8V to +8V for capacitance – voltage (C-V) characteristic for its dielectric properties. Microstructural study of the surface morphology of these samples indicated grains of less than 0.1 μm in size. With the increment of x value of $Ba_x Sr_{1-x} TiO_3$, the range of the conduction region decreased. The dielectric constant increase proportional to the thickness of BST films. Conclusion is consistent with the result obtained which with involvement of ultrasonic in the preparation steps reduces the grain size and produces smaller dielectric constant and tunability.

LIST OF PUBLICATIONS

1. Hatta R. M., Juhari N., and Adnan J. (2009). Preparation of $Ba_{0.5}Sr_{0.5}TiO_3$ ferroelectric thin films deposited by the sol-gel method with ultrasonic and reflux technique. *25th Regional Conference on Solid State Science & Technology 2009.*
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3. Retnasamy V., Poopalan P., Sauli Z., Yaacob S., Nor Haimi W. M. W., Taniselass S., Ramli N., Aziz M. H. A., Hatta R. M., Man B., Saif A. A. (2010). Optical Face-Contour Analysis – O. F. - C. A. 21st International Invention, Innovation and Technology Exhibition (ITEX) 2010.

CHAPTER ONE

INTRODUCTION

1.1 Research introduction

This chapter briefly reviews and explains the research problem and the overview of the barium strontium titanate. The research objectives, scopes and approaches are explained in detail in this chapter including the thesis layout.

1.2 Overview of the barium strontium titanate

Barium strontium titanate ($Ba_x Sr_{1-x} TiO_3$) thin films have been investigated as potential candidates for ferroelectric and dielectric materials. The properties depend on the x-value of the barium and strontium (Park et al., 2001). Valasek (1921) has reported that the spontaneous dipole moment in Rochelle salt can be reoriented by an external electric field. Jaffe et al. (1971) indicated that in the early 1940's, critical steps were taken in understanding piezoelectricity and ferroelectricity with the work on $BaTiO_3$ which led to the discovery of the unusually large dielectric constant. The discovery that this high value was due to ferroelectricity and the reorientation of the dipoles with a process called poling. In 1978, Raytheon R&D group, then part of Texas Instruments, patented ferroelectronic infrared detectors, using barium strontium titanate. The BST was coated over the thermal imager's sensor (Bullard Company, 2011).

Kil et al. (1997) stated that barium strontium titanate (BST), lead zirconate titanate (PZT) and strontium titanate (STO) are typical high dielectric constant materials. Among them, BST which is a solid solution consisting of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$) is the most attractive materials for high density DRAM application. This is because of it's paraelectric phase at the device operating temperature.

$Ba_x Sr_{1-x} TiO_3$ have been chosen among researchers who study its electrical properties, high dielectric constant and composition dependent Curie temperature (T_c) in these past years (Roy & Krupanidhi, 1993). The Curie temperature, T_c of $Ba_x Sr_{1-x} TiO_3$ decreases linearly with the increasing amount of strontium in $BaTiO_3$ lattice. Liu et al. (2004) found that ferroelectric BST ceramics with perovskite structure, posses a large temperature coefficient of dielectric constant (TCD) around their Curie temperature. Furthermore, T_c can be easily varied from 0 to 70 ^oC by adjusting the ratio of Ba and Sr. This characteristic indicates the transition of the BST from ferroelectric phase into paraelectric phase. Yamamichi et al. (1994) reviewed electrical properties of $Ba_x Sr_{1-x} TiO_3$ which were varied continuously with a molar ratio from 0 to 1.

Most of the experiments which have been done were intended to improve the dielectric properties by increasing substrate temperature, optimizing sputtering condition and so on (Wang, 1996). There are several different techniques used to fabricate the barium strontium titanate including sputtering (Horikawa, Mikami & Makita, 1993), laser ablation (Saha & Krupanidhi, 2000), metal organic chemical vapor deposition (MOCVD) (Catalan, Mantese & Micheli, 1994) and sol-gel processing (Lahiry, Gupta & Sreenivas, 2000). Among all the techniques that have been stated, sol-gel processing is the most attractive due to low processing temperature (compatible with Si processing), high purity of BST, easier composition control, easier fabrication of large area films and the low cost for preparing the solution and purchase of equipments, which definitely make the sol-gel as the chosen technique for this work.

1.3 Research problem

During this era, almost all parts of the world have been changed by science and technology. Every single thing is changed according to desire and current needs. The same goes to electronic circuits. With ever-increasing development and usage in electronic systems, the continuous miniaturization of electronic circuits has also rapidly increased. Size and functionality are always in parallel with time and technology. Furthermore, new materials need to be produced and the methods can be modified according to the needs of the industry. Barium strontium titanate however has been chosen as the material for the work, due to its potential in the area of ferroelectric and piezoelectric applications.

In this work, two methods of barium strontium titanate preparations, in two ratios namely 60:40 and 80:20 which are sol-gel prepared involving ultrasonic and without involving ultrasonic. The sol-gel method involving ultrasonic has been used in previous researches (Zhang et al., 2006). Investigation on the effect of ultrasonic has been done (Abe et al., 2010). To the best of the author's knowledge, there were very few previous works related to the effect of ultrasonic in term of BST preparation (Chung et al., 2001; Zhang et al., 2006; Abe et al., 2010).

Based on the theories of ultrasonic effects on crystallization in the literature, there are two major hypotheses; first hypothesis states that ultrasonic can assist the crystallization process in several ways, influence the initiation of crystal nucleation and ensuring small and even-sized crystals are formed (Clark, 2008). The second hypothesis claimes that ultrasonic wave traveling through a liquid consists of alternate compressions and rarefactions thus, if the wave is high enough in amplitude, cavitation will occur and disrupt the structure (Howard, 1975).Taking the above hypothesis into consideration, detailed analysis and characterization has to be done for BST crystallization under the influence of ultrasonic factor. The effect of ultrasonic to the crystallization of BST needs to be determined whether it is constructive or destructive in nature.

1.4 Research objectives

The main objective of this project is to improve the current BST thin film in terms of surface and electrical properties through the sol-gel method. The effect of ultrasonification is considered. In order to achieve the main objectives, sub-objectives as detailed below were addressed:

- To study and investigate two methods of $Ba_x\ Sr_{1-x}\ TiO_3$ preparation of which the sol-gel was prepared involving ultrasonic and without involving ultrasonic.
- The layers of $Ba_{0.6}\ Sr_{0.4}\ TiO_3$ and $Ba_{0.8}\ Sr_{0.2}\ TiO_3$ solution were deposited on $Si/SiO_2/Pt$ and subsequently annealed at temperature of 800^oC. XRD analysis also has to be implemented to verify the BST solution.
- To study the physical and electrical properties of BST and compare these two methods of sol-gel preparation in term of XRD peaks, AFM results, I-V, C-V and leakage current density.

1.5 Research scope

In this research, barium strontium titanate thin films were prepared using the sol-gel method. However, an additional technique using ultrasonicator was added. The differences between the two methods in term of surface structure and electrical characterization were studied and investigated. The BST solution was deposited using the spin coating process. The structure of metal-ferroelectric material-metal was been fabricated. Two metal plates which consist of Aluminium (Al) and Platinum (Pt) were used. Pt was used as a bottom electrode while Al was used as the top electrode. Both metal plates were deposited using the sputtering technique in order to study the electrical properties of $Ba_{0.6}$ $Sr_{0.4}$ TiO_3 and $Ba_{0.8}$ $Sr_{0.2}$ TiO_3.

1.6 Research approach

This thesis discusses and analyzes the structure, process and property of thin film layers. A high quality ferroelectric thin film that can be used to power up small electronic or electrical devices such as pH meter. Electrical properties of BST for instance pyroelectric can be used to convert from heat to electricity. In addition, Chemical Solution Deposition (CSD) methods of BST thin films and sputtering process are discussed to provide better understanding for future processing and formation of higher quality of BST thin film. A calculation of mol is needed to make sure a BST with the ratio of 60/40 and 80/20 can be produced. Ultrasonicator was used and the step added into sol-gel method to disperse the barium acetate and strontium acetate powder inside the solution. This technique make common because it produced smaller grains to achieve smoother surface and to obtain a better surface characteristic compared to sol-gel alone (Zhang et al., 2006). XRD was used to characterize the crystallize peak of the samples and compared with other research papers. Samples will be compared based on method and annealing temperature. A comparison in crystallization between the two compositions and two different annealing temperatures will be discussed. The XRD results were required first to confirm the phase formation of the crystalline peak of BST before other experimentations were done. AFM was used to analyze the samples in term of grain size and Root-Mean-Square (RMS) roughness. Optical test, by observation on AFM results will be used to determine whether there were cracks on the samples and the spaces between the grains. Furthermore, all the samples were tested for their electrical properties using SPA 4200. This report presents a complete flow process and analysis. Figures were shown which characterize the preparation process of BST until the electrical characterization. The physical and electrical properties of BST are pivotal in the device fabrication.

The confirmation of the BST material cannot be done without the XRD analysis. Therefore, observations have to be done on the solutions in terms of color and concentration. It is known that BST solution exhibits a yellowish solution (Kribalis et al., 2006).