Sol-gel BST Thin Films for FeFET Applications : Fabrication and Characterization

by

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ABSTRAK

Kesan komposisi kimia dan ketebalan filem ferroelektrik barium strontium titanate (BST) pada kelakuan bukaan ingatan oleh Al/BST/SiO_2/Si-get-transistor kesan medan telah disiasat. Filem nipis $Ba_xSr_{1-x}TiO_3$ dengan nilai x dan ketabalan filem yang berlainan telah difabrikasi dalam konfigurasi logam-ferroelektrik-penebat-semikondutor (MFIS) dan logam-ferroelektrik-logam (MFM) dengan teknik sol-gel. Suatu mikroskop daya atom (AFM) telah digunakan untuk mengkaji morfologi permukaan dan saiz butiran dengan teliti. Mikrograf AFM menunjukkan bahawa filem BST mempunyai ciri-ciri permukaan yang baik dengan penambahan saiz butiran dan kekasaran permukaan bila kedua-dua kandungan Ba dan ketebalan filem bertambah. Saiz butiran BST untuk nisbah Ba:Sr dan ketebalan filem berubah dari 48 nm hingga 120 nm. Histerisis ferroelektrik untuk filem-filem tersebut telah dikaji untuk memastikan kelakuan ferroelektrik BST berstruktur MFM dengan kedua-dua litar Sawyer-Tower dan kapasitans-voltan (C-V). Walaubagaimanapun, hasil kajian menunjukkan bahawa histerisis ferroelektrik bertambah kuat bila kedua-dua kandungan Ba dan ketebalan filem bertambah. Spektrokopi impedans dengan julat frekuensi dari 1 Hz hingga 1 MHz telah digunakan untuk mengkaji mekanisma kekonduksian dan filem berkurang bila kedua-dua kandungan oleh kesan saiz butiran. Satah impedans compleks (Z*) untuk kesemua filem BST mempunyai dua kawasan yang disebabkan oleh kawasan mekanisma kekonduksian iaitu butiran, dan, sempadan butiran dan electrode. Perubahan pemalar dielektrik (ε) dan tan δ dengan frekuensi telah dikaji untuk memastikan kualiti dielektrik bahan. Hasil kajian menunjukkan bahawa pemalar dielektrik untuk BST berkurangan bila kedua-dua kandungan Ba dan ketebalan filem bertambah, yang juga disebabkan oleh kesan saiz butiran. Nilai pemalar ketelusan dielektrik untuk sample yang diuji berubah antara 151 dan 335 pada frekuensi 10^5 Hz untuk nisbah Ba:Sr yang berlainan dan juga dengan ketebalan filem. Modulus elektrik menunjukan bahawa mekanisma kelonggaran didalam filem-filem BST adalah jenis bukan-Debye (non-Debye). Plot konduktiviti bertentangan frekuensi menunjukkan tiga proses konduksi, iaitu, bahagian frekuensi-rendah disebabkan oleh kekonduksian DC, bahagian frekuensi pertengahan disebabkan oleh gerakan translasi-lompatan dan bahagian frekuensi tinggi disebabkan oleh lompatan setempat dan/atau gerakan orientasi semula. Sebagai tambahan, untuk mendapatkan pemahaman lebih mendalam, suatu litar setara telah diutarakan untuk setiap filem yang dikaji bergantung kepada impedans kompleks dan plot modulus kompleks. Kelakuan ingatan ferroelektrik sampel MFIS telah disiasat menggunakan cirian kapasitans-voltan (C-V). Ciri-ciri C-V menunjukkan bahawa kelebaran bukaan ingatan bertambah dengan pertambahan filem. Ini adalah disebabkan oleh saiz butiran dan kesan dinamik dwikutub. Nilai kelebaran ingatan untuk filem-filem yang telah dikaji berubah antara 0.3 V dan 3.3 V, untuk nisbah Ba:Sr dan ketebalan filem yang berlainan. Sebagai tambahan, bukaan kelebaran ingatan bertambah bila voltan bertambah. Walaubagaimanapun, kadar perubahan voltan tidak menjejaskannya. Mod operasi struktur get, iaitu pengumpulan, susutan dan kaedah penyongsangan juga telah dibincangkan dengan mendalam.

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ABSTRACT

The effect of the chemical composition and film thickness of the ferroelectric barium strontium titanate (BST) at the memory window behavior of Al/BST/SiO_2/Si-Gate-field effect transistor structure has been investigated. $Ba_xSr_{1-x}TiO_3$ thin films with different x values and film thickness have been fabricated as metal-ferroelectric-insulator-semiconductor (MFIS) and metal-ferroelectric-metal (MFM) configurations using a sol-gel technique. The surface morphology and grain size have been studied in detail using an atomic force microscope (AFM). The AFM micrographs show that BST films have good surface properties with increasing in the grain size and surface roughness as both Ba content and film thickness increase. The grain size of BST for different Ba:Sr ratio and film thickness varies between 48 ± 3.56 nm and 120 ± 3.56 nm. In order to confirm the ferroelectric behavior of BST, the ferroelectric hysteresis characteristics of the films have been studied with MFM structure using both Sawyer-Tower circuit and capacitance-voltage (C-V) characteristic tests. The results show that the ferroelectric hysteresis strengthens as both Ba content and film thickness increase. The conduction mechanism and dielectric relaxation mechanism for BST film within MFM structure have been investigated using an impedance spectroscopy in the frequency range of 1 Hz to 1 MHz. The results show that the conductivity of the films decreases as both the Ba content and film thickness increase which are attributed to the grain size effect. The complex impedance (Z) plane for all BST thin films possesses two regions, which attributed to the film's regions conduction mechanism i.e. grains, and grain boundaries and electrodes. The variation of the dielectric constant (ε) and tan δ with frequency have been studied to ensure the dielectric quality of the material. The results show that the dielectric constant for BST films decreases as both of the Ba content and film thickness increase, which also attributed to the grain size effect. The values of the dielectric permittivity constant of the tested samples vary between 151 and 335 at 10^5 Hz frequency for different Ba:Sr ratio and film thickness. The electric modulus results show that the relaxation mechanism within BST films is non-Debye type. The frequency dependent conductivity plots show three regions of conduction processes, i.e. low-frequency region due to DC conduction, mid-frequency region due to translational hopping motion and high-frequency region due to localized hopping and/or reorientational motion. In addition, depending on the complex impedance and complex modulus plots, an equivalent circuit has been suggested for each film in the current study to obtain further understanding for the conduction mechanism of BST film. The ferroelectric memory behavior of the MFIS samples has been investigated using capacitance-voltage (C-V) characteristics. The C-V characteristics show that the memory window width increases with the increase both of Ba content and film thickness. This is attributed to the grain size and dipole dynamics effect. The values of the memory window for the studied films vary between 0.3 V and 3.3 V for different Ba:Sr ratios and film thickness. Furthermore, the width of the memory window increases as the applied voltage increases; however, it is not affected by the voltage sweeping rate. In addition, the operating mode of the gate structure, i.e. accumulation, depletion and inversion conditions, has been also discussed in detail.*

CHAPTER 1

INTRODUCTION

1.1 Research Background

In the past few years, extensive research has been carried out in ferroelectric thin films for microelectronic devices and applications, particularly, in memory devices. Ferroelectric random access memories (FRAMs), which have a transistor as a memory cell, are considered as a promising memory device for the coming times since ferroelectric gates offer simpler circuits and excellent performances (Roy et al, 2008; Wang et al, 2003).

Ferroelectric field effect transistors (FeFET) can be categorized according to the gate structure into two main types; Metal-ferroelectric-metal-insulator-semiconductor (MFMIS) FET and metal-ferroelectric-semiconductor (MFS) FET (Waser, 2005). (MFMIS) FET was introduced for the first time by Nakamora and Nakao (2000) in their patent in 2000, which consists of a ferroelectric capacitor and a conventional MOSFET. Due to the remnant polarization of the ferroelectric materials, the retained charges at the bottom electrode of the capacitor are coupled to the semiconductor and the conducting channel is then induced to allow the current flowing through drain to source (Sing, 2000). On the other hand, (MFS) FET was suggested for the first time by Ross (1957) in a patent in 1957. (MFS) FET is just a MOSFET with a ferroelectric material inserted to represent the gate material instead of the oxide layer.

The structure of the MFS gate has many inherent problems such as difficulty in depositing ferroelectric thin films directly on silicon, high trap densities, and diffusion of elements into silicon (Wang et al, 2007; Lee et al, 2005; Tang et al, 2007). Hence, to overcome these difficulties, an insulating buffer layer, such as $SrTiO_3$, $SrTaO_6$, ZrO, CO2, CeO and Si_3N_4 (Lu, Ishiwara and Maruyama, 2008; Ishiwara, 2009), is often inserted between the ferroelectric film and Si substrate to form a metal-ferroelectric-insulator-semiconductor (MFIS) structure (Lu, Ishiwara and Maruyama, 2008; Ishiwara, 2009). The MFIS structure is more desirable to be used in a FeFET since high density integration of the MFMIS (FET) is difficult, because the gate MIS area must be designed much larger than the MFM capacitor area (Singh, 2004). Therefore MFIS gate structure will be the subject of research in this work.

There are many ferroelectric materials that have been studied to be used as a ferroelectric gate material within the MFIS structure such as lead zirconate titanate (PZT) (Juan et al, 2007), strontium bismuth tantalite (SBT) (Okuyama, Sugiyama and Noda, 1999), lanthanide-substituted bismuth titanate (BLT) (Kim et al, 2005), bismuth vanadate (BVO) (Kumari et al, 2006) and many other materials. Among these materials, barium strontium titanate ($Ba_xSr_{1-x}TiO_3$ or BST) is considered a promising candidate for FeFET applications due to desirable properties such as high permittivity, low dielectric loss and relatively high remnant polarization. Therefore, it is necessary to study and understand the structural, electrical and dielectric properties of the BST in thin film form to ensure the possibility of using it for FeFET applications.

BST thin films can be prepared using different deposition techniques such as sputtering, laser ablation and sol–gel process. The sol-gel technique is advantageous over the other techniques in that it offers a simple method to control the composition, achieve high homogeneity and allows for large area deposition (Wang et al, 2008; Guiying, Ping and Dingquan, 2008). The low cost of the equipments and the simplicity of function, make the sol-gel technique an excellent choice for testing new compositions and modifying conventional fabrication techniques. These advantages make sol-gel method to be the choice technique to fabricate BST thin films in this work.

It is reported in the literature that BST thin films have been fabricated using sol-gel technique via various metal–organic compounds as Barium (Ba) and Strontium (Sr) sources (Ding, Jin and Meng, 2000). The popular precursor compounds that are used to prepare BST thin films are acetate based, i.e. barium acetate and strontium acetate, and carbonate based, i.e. barium carbonate and strontium carbonate. However, many papers reported that the carbonate based BST prepared show carbonate peaks within their X-Ray Diffraction (XRD) patterns (Lazarevic, Romcevic and Stojanovic, 2008; Ries et al, 2003). Therefore, to ensure that the BST thin films in this work crystallized with a perovskite structure without any impurity peaks, acetate based materials have been chosen.

1.2 Problem Statement

The complete study of barium strontium titanate (BST) is a complicated task, involving a multitude of characteristics and an equally varied range of analytical equipment, of which all is not in possession at the current laboratory. As such only a few highly important measurements will be undertaken.

Surface morphology, for one, is a very important indicator of how the interface between dissimilar materials conducts electrons. It is also, in this case, important for the dielectric and ferroelectric properties (Oh et al, 2000). Therefore, an atomic force microscope (AFM) study will be one of the first and foremost studies to be done. Another point of contention, especially when dealing with thin-films deposited by sol-gel spin coating is the formation of cracks and pinholes. Hence the surface morphology is not only foremost but also critical in determining basic as-deposited film quality.

BST is a poly-crystalline compound, whereby there will be like-directional local grouping of material. These local grouping will point towards different regions of space due to the poly-crystalline nature. The local grouping themselves are made up of an agglomeration of basic BST unit cell, or grains, pointing in many directions, give rise to grain boundaries where many interesting and complicated phenomena occur, related to the conduction or leakage mechanisms (Chen et al, 2006). It is therefore very important to study the grain size itself since differing compositions and deposition criteria is expected to alter the granularity of the films. However, studying the grain size will give good understanding for the electrical and ferroelectrical behavior of BST thin films which in turn helps to study the memory behavior for BST films.

The natural progression on the BST characterization should be for ferroelectricity. However, lacking a ferroelectric tester, alternatives, such as capacitance-voltage (C-V) and Sawyer-Tower circuit have to be used. In this work, ferroelectricity tests are just as a basic confirmation that the deposited films are indeed ferroelectric, in line with other published work.

The focus or problem to solve will be one of electrical in nature. The investigated grains and their boundaries as well as other effects will particularly affect the electrical characteristics of the films. Insight into the various electrical functioning of the films can be obtained via AC Impedance Spectroscopy. In this technique, impedance, and its various mathematical manipulations (such as electric modulus, dielectric permittivity and AC conductivity), are investigated as a function of frequency. Furthermore, it will allow identification of electrical regions within and on the surface of the films, such as grain, grain boundaries and electrode (Abrantes, Labrincha and Frade, 2000). Czekaj et al. (2010) have reported sol-gel thin film BST, on a stainless steel substrate, however, not on a silicon or semiconductor substrate. On the other hand Agarwal, Sharma and Manchanda (2001) did perform impedance spectroscopy on silicon as a substrate but for a metal-ferroelectric-semiconductor (MFS) structure.

As stated in the preceding lines, some of the mathematical manipulations of impedance is evident as AC conductivity and dielectric permittivity. The majority of published literature concentrate on the higher frequencies, where the dielectric constant has been found to vary depending on parameters such as fabrication technique, film thickness, Ba:Sr ratio etc. (Wanga et al, 2009; Roya et al, 2004; Lahiry et al, 2000; Kim et al, 2006). As such, AC conductivity and dielectric permittivity will also be investigated in this work.

The main focus in this work is to obtain the memory behavior of BST in a metal-ferroelectric-insulator-semiconductor (MFIS) structure. A literature search shows no work has been carried out for this structure, for BST. There are few studies that have reported the electrical properties for BST in a MFS structure (Jha, Ray and Manna, 2008;