PREPARATION AND CAPACITANCE PROPERTIES OF BARIUM, CALCIUM AND TIN DOPED STRONTIUM TITANATE THIN FILMS

May Kalayar Kyaing[1], Amy Aung[2], Moht Moht Than[3], San San Oo[4] and Hnin Yu Wai[5]

Abstract

Sol-gel method was used in this study to prepare barium, calcium and tin doped strontium titanate thin films deposited onto silicon substrates by spin-coating technique. The effects of the dopant materials on the structural and capacitance properties of the films were examined by various characterization procedures. Morphological analysis of the samples was performed using scanning electron microscopy and all the films were found to be well grown and homogeneous structure. The structural modification was investigated by X-ray diffraction and the crystalline phases of the films were observed to be cubic perovskite structure. Measurements of capacitance-voltage characteristics were carried out by using LCR meter in the frequency range of 1 kHz to 100 kHz with the various applied voltages. From Mott-Schottky analysis, built in potential "V_{bi}", effective dopant concentration "N_D" and depletion layer width "W" of the films were also evaluated.

Keywords: Sol-gel, Doped strontium titanate, Capacitance-voltage measurements

Introduction

In the coming years, capacitors will be increasingly fabricated into microelectronic substrates in some manner since there are clear benefits in functional density, performance, and reliability relative to surface mount discretes [Woong Choi. et al., (2010)]. The main questions to be resolved involve the choice of materials, configurations, and fabrication processes to implement integrated capacitors in a cost effective manner. The purpose of this article is to compare and contrast, for integrated capacitor applications, the two major classes of dielectric materials: paraelectrics and ferroelectrics, respectively [Victor Williams, R., (2015)]. First, the mechanisms of charge storage are briefly reviewed for the two classes in order to elucidate the differences in fabrication options, electrical performance, and the effects of operational conditions such as temperature, bias, frequency, and film thickness [Malic, B. et al., (2007)]. Then, the two types of dielectrics are compared, based on these physical and electrical properties, for use in the integrated capacitor applications of decoupling, analog functions, and termination. It will be shown that the fundamental difference in the way the two materials store charge is very important to their respective suitability for these applications [S. Maletica and D. Maleticb, (2014)]. It will also be shown that selecting the dielectric with the largest k is not always the optimal choice. The ability of a dielectric material to store energy under the influence of an electric field results from the separation and alignment of electric charges brought about by that field. The larger the dipole moment arm the separation of charges in the direction of the field, and the larger the number of these dipoles, the higher the material's dielectric constant [Jae-Yeol Hwang et al., (2006)]. There are several possible contributions to this polarizability which, depending on the mechanisms operative in a given dielectric, determine not only the value of k, but also how it varies with frequency, temperature, bias, impurity concentration, and crystal

[1] Dr, Assistant Lecturer, Department of Physics, University of Yangon
[2] Assistant Lecturer, Department of Physics, University of Yangon
[3] Associate Professor, Department of Physics, Mohnyin Degree College
[4] Assistant Lecturer, Department of Physics, University of Yangon
[5] Assistant Lecturer, Department of Physics, University of Yangon

structure. The three general mechanisms important to candidate materials for integrated capacitors are electronic, atomic, and ionic polarization [F. M. Pontes et al., (2000)].

Strontium titanate in the perovskite structure exhibits high charge storage capacity, good insulating properties and excellent optical transparency in the visible region. Thus it is a potential material for a wide range of electronic and optical applications, such as dielectric thin film memory capacitors in microwave integrated circuits, dynamic random access and insulating layers for limiting current in thin film electroluminescent displays [Xiaoyong Wei and Xi Yao, (2007)]. In the present research, the influence of doping by the barium, calcium and tin ions on the capacitance properties of the strontium titanate thin films were examined. In order to understand the study of changes in the structural and electrical properties of the films that arise as a result of the incorporation of different cations is essential.

Experimental Procedure

The perovskite samples of barium, calcium and tin doped strontium titanate were prepared by conventional solid state reaction method and the starting materials were SrO, TiO_2, BaO, CaO and SnO_2. All the powders were having more than 99% purity and the stoichiometric composition of the $SrBaTiO_3$, $SrCaTiO_3$ and $SrSnTiO_3$ powders were thoroughly mixed in an agate mortar to obtain the homogeneity. The mixed powders were calcinated at 700˚C for 1 hr. Each mixture of the powders was mixed with 2-methoxyethanol ($CH_3OCH_2CH_2OH$) solution and then heated up to 100˚C with indirect heat treatment for 1 hr. Finally, homogeneous precursor solutions or coating solutions were obtained. The silicon substrates were cleaned by standard cleaning method and the resulting precursor solutions were deposited on silicon substrates by spin coating technique. After spin coating, deposited thin films were heat treated at 700˚C for 1hr. The surface morphologies of the films were studied using scanning electron microscope (SEM) and the crystallographic properties of the films were investigated by X-ray diffractiometer. Measurement of capacitance was carried out using LCR Meter in a frequency range of (1 kHz- 100 kHz) for the three $SrTiO_3$ thin films with different doping materials.

Results and Discussion

Surface Morphology and Microstructure

The surface morphologies of the thin films deposited on silicon substrates were examined by using SEM with accelerating voltage 15 kV and photo magnification 5,500. SEM images of the Ba, Ca and Sn doped $SrTiO_3$ thin films are shown in Figure 1 (a-c). All the films showed the formation of uniformly distributed microcrystalline grains over the entire surface of the substrates. According to the result, it was observed that calcium doped strontium titanate thin film has the smallest grain size. In this Ca^{2+} has smaller ionic radius than Sr^{2+} and the grain sizes of the film depend on the dopant materials incorporated into the structure. The average grain sizes of the films were estimated using the line intercept method and the determined values were collected in Table 1.

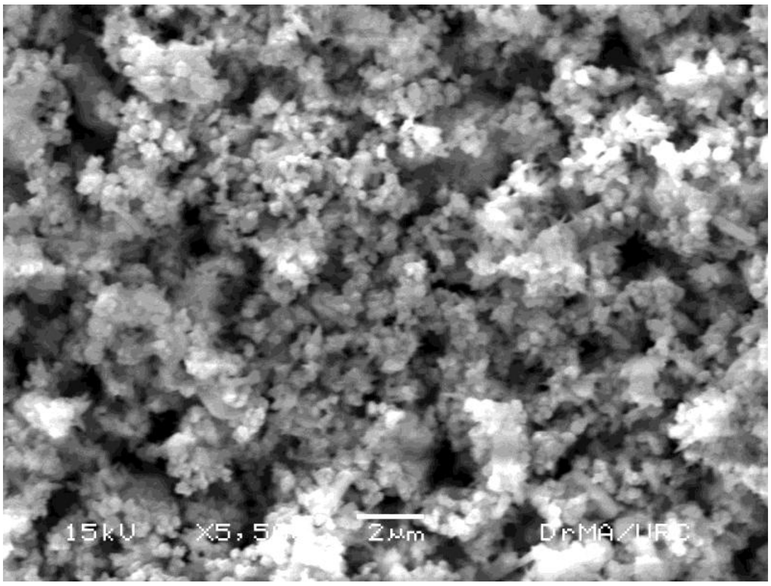

Figure 1 (a) SEM image of barium doped strontium titanate thin film

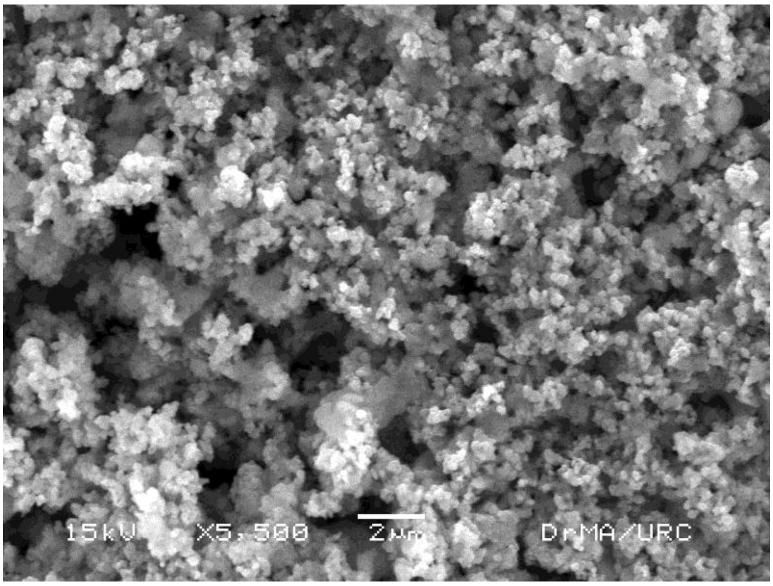

Figure 1 (b) SEM image of calcium doped strontium titanate thin film

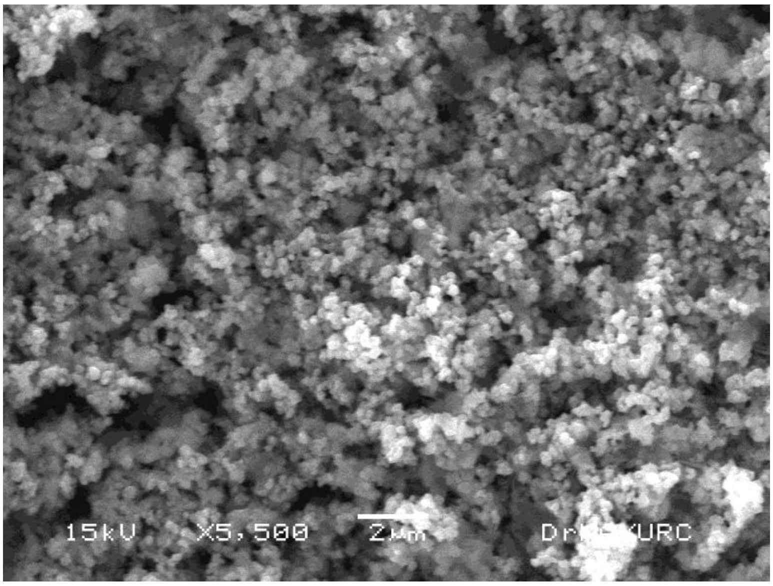

Figure 1 (c) SEM image of tin doped strontium titanate thin film

Table 1 Grain sizes of the Ba, Ca and Sn doped $SrTiO_3$ thin films

Thin Film	Average Grain Size (μm)
Ba doped $SrTiO_3$	0.475
Ca doped $SrTiO_3$	0.350
Sn doped $SrTiO_3$	0.413

Crystallographic Structure

The crystallographic structures of the thin films were determined by X-ray diffraction and Figure 2 show the XRD patterns of barium, calcium and tin doped strontium titanate thin films. XRD was usually used for identification of the crystalline nature and estimation of the crystallite size. The variation in the lattice parameters of doped strontium titanate thin films with the change in dopant materials may be attributed to the change in ionic radius. From the investigation of dopant materials, XRD analysis indicated that all deposited films are cubic perovskite structure. Average crystallite sizes were calculated based on widening the diffraction using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where D is the crystallite size(nm), λ is the wavelength of the X-ray source (1.59 nm), B is the full-width at half maximum (FWHM) in radians, and θ is half of the diffraction angle. The results showed that the widening the diffraction pattern was influenced by the crystallite size, where the wider diffraction pattern indicated the smaller crystallite size. The average crystallite sizes were determined using the diffraction peaks with preferred orientation at (110) planes. The determined crystallite sizes are shown in Table 2.

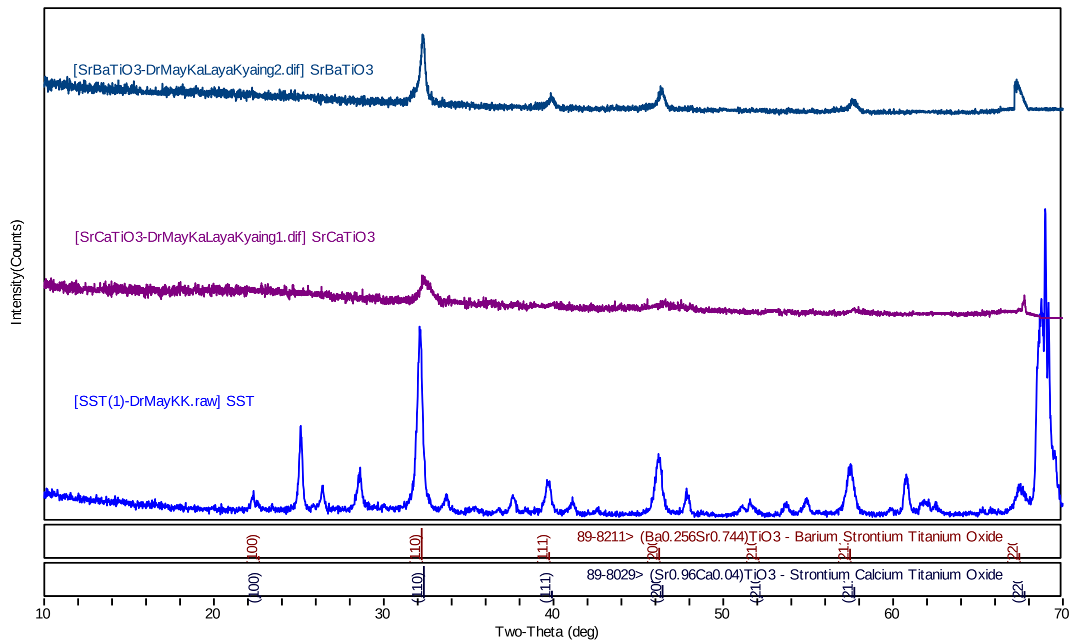

Figure 2 X-ray diffraction patterns of barium, calcium and tin doped strontium titanate thin films

Table 2 The peak positions (2θ), intensity, full width half maximum (FWHM), lattice parameters (a) and average crystallite sizes (D) of the thin films at (110) plane

Thin Film	Peak position (2θ)	Intensity (cps)	FWHM	a (nm)	D(nm)
Ba doped $SrTiO_3$	32.311	277	0.390	3.915	21.2081
Ca doped $SrTiO_3$	32.320	108	0.560	3.914	14.782
Sn doped $SrTiO_3$	32.135	724	0.368	3.935	22.467

Capacitance Properties

The capacitance-voltage (C-V) measurements as a tool of analyzing the electrical properties of the films were examined by a LCR Meter at the frequency range of 1 kHz to 100 kHz. The maximum capacitance value was occurred at the tin doped strontium titanate thin film at a frequency of 1 kHz. Figure (3) shows the frequency dependence of the capacitance of the thin films and the measured values are presented in Table 3. The capacitance-voltage characteristics are useful in obtained information about the potential barrier at the junction, the semiconductor doping density and the presence of traps in materials. Figure 4 (a-c) shows the $1/C^2$ versus V graphs for Ba, Ca and Sn doped $SrTiO_3$ thin films. Measurement of “C” as a function of applied voltage can be used to determine the built - in voltage and the dopant concentration near the junction. According to equation (2),

$$C = A\left[\frac{q\varepsilon_s}{2(V_{bi} - V)} N_D\right]^{1/2} \qquad (2)$$

a plot of $1/C^2$ as a function of V is a straight line whose intercept on the voltage axis gives V_{bi}, and the slope can be used to determine the effective dopant concentration N_D. The depletion layer capacitance associated with a Schottky device is given by equation (3),

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \varepsilon_s N_D} \tag{3}$$

where "N_D" is the effective dopant concentration, "A" is the diode area, "V_{bi}" is the built in voltage and "ε_s" is the permittivity of the diffusion layer. The value of depletion layer width "W" was given by equation (4),

$$W = \frac{\varepsilon_s A}{C} \tag{4}$$

The values of V_{bi}, N_D, and W of the thin films are summarized in Table 4.

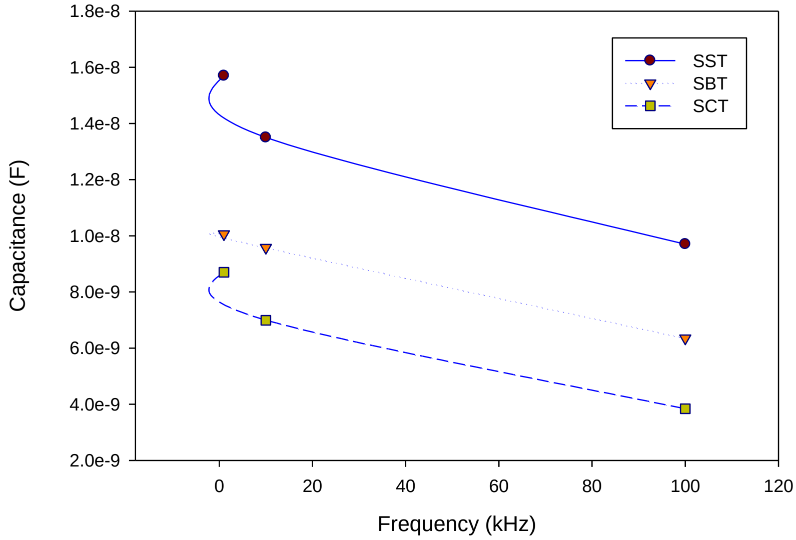

Figure 3 Frequency dependence of the capacitance of Ba, Ca and Sn doped $SrTiO_3$ thin films

Table 3 The capacitance values of the thin films as a function of frequency

Thin film	f(1 kHz)	Capacitance (nF) f(10 kHz)	f(10 kHz)
Ba doped $SrTiO_3$	10.06	9.58	6.35
Ca doped $SrTiO_3$	8.70	6.99	3.84
Sn doped $SrTiO_3$	15.70	13.54	9.70

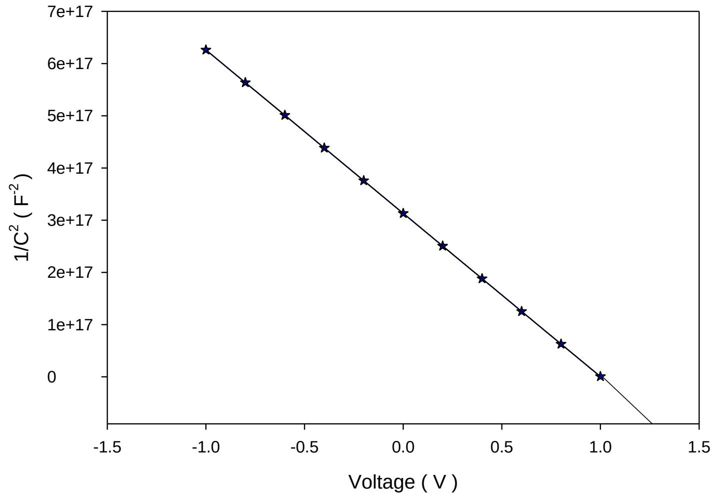

Figure 4 (a) $1/C^2$ versus V characteristics of Ba doped $SrTiO_3$ thin film

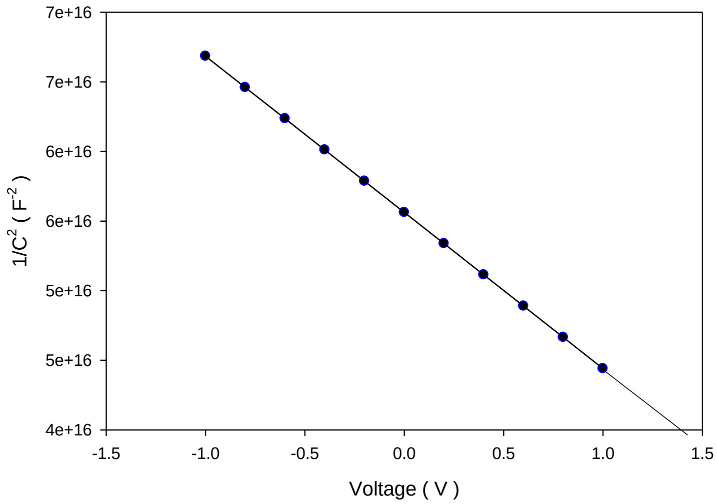

Figure 4 (b) $1/C^2$ versus V characteristics of Ca doped $SrTiO_3$ thin film

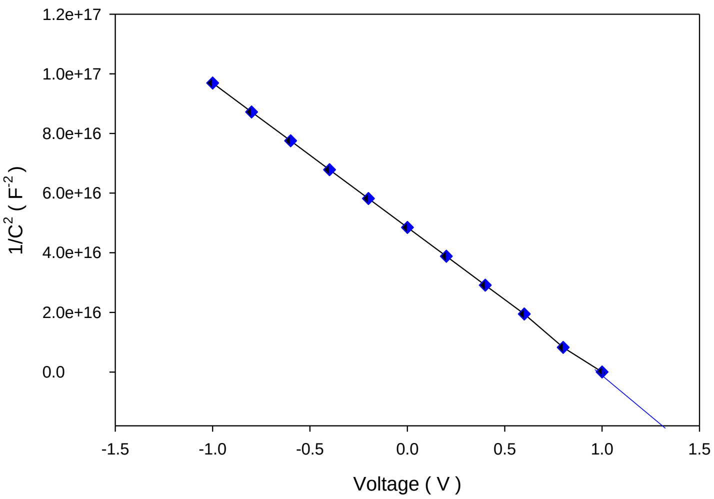

Figure 4 (c) $1/C^2$ versus V characteristics of Sn doped $SrTiO_3$ thin film

Table 4 The values of V_{bi}, N_D, and W of Ba, Ca and Sn doped $SrTiO_3$ thin films

Thin Film	V_{bi} (V)	$N_D(cm^{-3})$	W (cm)
Ba doped $SrTiO_3$	1.2574	8.81×10^{14}	10.11×10^{-4}
Ca doped $SrTiO_3$	1.3872	1.96×10^{14}	10.08×10^{-4}
Sn doped $SrTiO_3$	1.2598	2.43×10^{15}	10.09×10^{-4}

Conclusions

Barium, calcium and tin doped strontium titanate thin films deposited onto silicon substrates were prepared by sol-gel method. Morphological analysis of the samples was performed using scanning electron microscopy and all the films showed the compact structures which composed of small and densely packed microcrystals. The structural modification was investigated by X-ray diffraction and all the crystallographic planes and orientations were expressed with reference to the cubic perovskite unit cells. Measurements of capacitance-voltage characteristics were carried out by using LCR meter in the frequency range of 1 kHz to 100 kHz with the various applied voltages. From Mott-Schottky analysis, built in potential "V_{bi}", effective dopant concentration "N_D" and depletion layer width "W" of the films were also evaluated. According to the results of good characteristics and electrical properties, Ba, Ca and Sn doping effects on $SrTiO_3$ are useful for selecting materials in the manufacturing of technological applications.

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References

F. M. Pontes et al., (2000), "High dielectric constant of $SrTiO_3$ thin films prepared by chemical process," *Journal of Material Science*, 35, 4783 - 4787

Jae-Yeol Hwang et al., (2006) " Dielectric Properties of Artificially Textured $(Ba_{0.5}Sr_{0.5})TiO_3$ Thin Film Prepared by Pulsed Laser Deposition," *Journal of the Korean Physical Society*," 49, 447- 696

Malic, B. et al., (2007) "Processing and dielectric characterization of $Ba_{0.3}Sr_{0.7}TiO_3$ Thin Films" *Journal of the European Ceramic Society*, 27, 2945-2948

S. Maletica) and D. Maleticb, (2014) "Dielectric and infrared properties of SrTiO3 single crystal doped by 3d (V, Mn, Fe, Ni) and 4f (Nd, Sm, Er) ions" *Chinese Physical Society and IOP*, 23, 026102

Victor Williams, R., (2015) "Structural and Electrical behavior of Tin Doped $Ba_{0.6}Sr_{0.4}TiO_3$ Thin Films," *International Journal of Development Research*, 5, 5725-5732

Woong Choi et al.,(2010),"Capacitance-voltage characteristics of SrTiO3 /LaVO3 epitaxial heterostructures ," *Applied Physics Letters*, 96, 212903

Xiaoyong Wei and Xi Yao, (2007) "Preparation, structure and dielectric property of barium stannate titanate ceramics," *Materials Science and Engineering B*, 137, 184-188