Optical properties of Cu and Ru doped BST thin films with additive glycerol and MESA surfactant

N G Pamungkas¹, M Dahrul², Irzaman² and H Alatas²

¹ Biophysics Program, Department of Physics, Bogor Agricultural University, Indonesia
² Departement of Physics, Bogor Agricultural University, Indonesia

Email: novita.galih@gmail.com

Abstract. In this paper, barium strontium titanate (BST) thin films were deposited by chemical solution deposition (CSD) with addition glycerol and methyl ester sulfonic acid (MESA) surfactant as additive materials. The effect of variation spinning speed (5500 and 8000 rpm), different dopant (Cu and Ru dopants), and also additive materials on optical properties were studied by Spectrophotometer Vis-NIR. As a result, BST thin films with additive MESA have higher absorbance and similar spectrum pattern than additive glycerol. Generally, BST thin films with MESA surfactant had band gap smaller than glycerol of BST thin films. Absorption and extinction coefficient of BST with glycerol were observed and we reported Ru doped BST at spinning speed 5500 rpm had higher value than other films. On other hand, Cu doped BST at 8000 rpm had absorption and extinction coefficient higher than other films.

1. Introduction

Ba₀.₅Sr₀.₅TiO₃ (BST) is a ferroelectric perovskite materials has been well studied in thin film and bulk form. BST as thin film has been under investigation for about 15 years starting from 90’s[1]. The initial interest in BST thin films was due to its high dielectric constant, low dielectric loss, high dielectric breakdown and composition dependent Curie temperature [2]. These advantages make the thin film BST as a candidate replace SiO₂ as the dielectric mass storage (capacitor), dynamic random access memory (DRAM), application of acoustic waves, and tunable microwave [3-6]. Besides having ferroelectric properties, BST thin films have the sensitivity to light (opto-electronic), sensitive to temperature stimuli (pyroelectric), and sensitive to the influence of pressure (piezoelectric) [7-9]. The pyroelectric characteristics of BST have been applied as a switch thermal infrared and infra-red sensors [7, 8]. Opto-electronic properties of BST has been applied as photodiode [10, 11]. In addition, its sensitivity to light has been applied in the model of automatic drying in agriculture [12].
Dopant material is a material that is expected to change the lattice constant, dielectric constant, pyroelectric properties, opto-electronic properties, piezoelectric properties of the ceramic and thin film BST become well. Addition of hard dopant and soft dopant in BST thin films increase optical and electrical properties of BST thin films [5, 11]. Another factor affecting the characteristics of the thin film is deposition process on substrate. Chemical solution deposition (CSD) method is of particular interest because of its good control of stoichiometry, ease of fabrication and low temperature synthesis. There are mainly two methods for the coating of solutions in CSD process: dip coating and spin coating. Spin speed of spin coating influence coating process and thickness film [13].

Here, utilization of material additives in deposition process especially spin coating technique such as polymer or surfactant, increase homogeneous in thin film surface [14,15]. Surfactant is material agent that reduces the surface tension of water or solution by forming a molecular or atomic layer on the surface. The addition of surfactant to the solution can enhance various properties of the films, such as increasing optical absorbance, energy gap, and the thickness of films [15]. Methyl Ester Sulfonic (MES) surfactants produced from palm oil and has been investigated for Enhanced Oil Recovery (EOR) applications in the petroleum industry [16]. Materials for methyl esters are palm olein, methanol and potassium hydroxide (KOH). Sulfonation process methyl ester from palm olein produce methyl ester sulfonate surfactant acid (MESA), dark and blackish. Glycerol is the residue of transesterification process palm olein into methyl ester [17].

In this study, BST thin films were deposited by chemical solution deposition on Silicon substrates using spin-coating. Glycerol and MESA surfactant additive were used to BST solution. BST thin films use doping variation, Copper (Cu) and Ruthenium (Ru) with variation spinning speed, 5500 and 8000 rpm. Optical properties, namely absorbance, band gap, absorption coefficient, and extinction coefficient were investigated to study the potential of using glycerol, MESA surfactant, and also dopants for optical properties in thin film.

2. Research and Method

2.1. Material Preparation

BST solution with 1 M concentration have been synthesized by CSD method. Barium acetate [Ba(CH₃COO)₂, 99%] and strontium acetate [Sr(CH₃COO)₂, 99%] were dissolved in acetic acid [CH₃COOH, ≥ 99.7%] and stirring for 60 minutes. Titanium isopropoxide was added in solution and stirring for 30 minutes. Then, Ruthenium oxide and copper acetate were added to the different solution and stirring again for 30 minutes as dopants. Finally, glycerol and MESA was mixed to the solution and continuously stirred for 1 hours. Silicone as substrate was cleaned in acetone solution. Films were prepared by depositing the solution on the surface silicone. Coating thin film use spin coating technique. Thin layer was spin-coated with variation spinning speed 5500 and 800 rpm on substrate for 40 s. Thin layer was dried on hotplate. This process was repeated for the 3 layers. BST Films were annealed for 8 hours in an air atmosphere using furnace Vulcan model 3-130. BST films were annealed 850°C.

2.2. Analysis

Spectroscopy is one of analysis to observe the optical properties of the surface material. Optical properties were observed in this research are absorbance, band gap, absorption coefficient, and extinction coefficient. The Optical properties of BST thin films were characterized using Spectrophotometer Vis-NIR USB 1000 Oceanoptic in range 339 – 1022 nm.
3. Results and discussion

3.1. Absorbance BST thin films
Absorbance BST thin film aims to observe the maximum absorption and wide absorption spectra of thin films of BST. It is based on that electromagnetics wave radiation from the sun has the greatest intensity in the visible region (black box radiation). From the Figure 1, BST thin films with MESA surfactant additive have higher absorbance than BST thin films with glycerol additive. Glycerol additive leads surface of thin films inhomogeneous. Surfaces formed glossy but not flat. This is due to viscous solution. Viscous solution causes centrifugal process in the spin-coating was not optimal. MESA surfactant additions in the deposition process to result thin films with higher absorbance than glycerol. The addition of additive ethylene has been done in some previous studies. The addition of the additive in the film coating process causes the film surface to form more homogeneous. Homogeneous layer formation with MESA additive result increasing film thickness.

![Figure 1. Absorbance of BST thin films with (a) glycerol additive and (b) MESA additive](image)

Figure 1. Absorbance of BST thin films with (a) glycerol additive and (b) MESA additive

Figure 1. (a) showed the absorbance curve BST thin films with dopants variation (Cu and Ru), variation speed of spin coater (5500 and 8000 rpm), and with glycerol additive. BST thin film with dopant Ru has a higher absorbance than dopant Cu. Absorbance peaks of BST thin films with Ru dopants shifted towards smaller wavelengths on a speed of 5500 rpm, from 500 nm to 700 nm. However, BST thin film with Cu dopants no shifting (400 nm). Figure 2. (b) showed variation of BST thin films with MESA surfactant additive. Generally, the absorbance peaks for all types of films have the same curve shape and there is no shifting. Speeds of 8000 rpm have higher absorbance than 5500 rpm. MESA surfactant leads films surface homogeneous and deposition thin film (3 layers) well formed.

3.2. Band gap of BST thin films
Determination of the gap energy BST thin films using optical absorbance characteristics, by plotting \((\alpha h\nu)^n\) with \(h\nu\). The resulting gap energy using indirect transition value that is \(n = 2\) [18,19]. This can be explained that the transition of electrons between the valleys of the conduction band and valence band peak occurs indirectly but absorb or emit energy phonons. The smaller the gap energy of a semiconductor material, the more easily an electric current flows. Figure 2 showed gap energy for all films type with glycerol additive. Addition of Ru dopants lowering gap energy. Speeds of 8000 rpm lead gap energy decreasing at Cu doped BST and increasing at Ru doped BST. Figure 3 showed BST thin films with MESA surfactant additive. Addition of Ru dopants lead gap energy increasing. Variation speeds of spin-coating leads the gap energy constant at Cu doped BST and increasing at Ru doped BST. Smaller gap energy, electrical and optical properties increasing.
Figure 2. Band gap of BST thin films with glycerol additive and variation a) Cu dopant at 5500 rpm b) Cu dopant at 8000 rpm c) Ru dopant at 5500 rpm d) Ru dopant at 8000 rpm
Figure 3. Band gap of BST thin films with MESA additive and variation a) Cu dopant at 5500 rpm b) Cu dopant at 8000 rpm c) Ru dopant at 5500 rpm d) Ru dopant at 8000 rpm

3.3. Absorption coefficient and extinction coefficient of BST thin films

The others parameter in optical properties are absorption coefficient and extinction coefficient. The absorption coefficient is a function of the absorbance and thickness so that the thickness difference factor can be ignored. Extinction coefficient have been used to calculate the damping or reduction factor of light intensity when passing through thin films. Figure 4 and 5 showed absorption coefficient and extinction coefficient. Absorption coefficient of BST thin films with MESA surfactant additive higher than glycerol additive. Ru doped BST thin films higher absorption coefficient than Cu dopants. Figure 5 showed small extinction coefficient for all films.

Figure 4. (a) Absorption and (b) extinction coefficient of BST thin film with additives glycerol
1.3 1.7 2.1 2.5 2.9
Absorption coefficient 
(10^4 cm^-1)
Photon energy (eV)
Cu dopant // 5500 rpm
Cu dopant // 8000 rpm
Ru dopant // 5500 rpm
Ru dopant // 8000 rpm
(a)
380 480 580 680 780 880
Extinction coefficient 
(10^-6)
Wavelength (nm)
Cu dopant // 5500 rpm Cu dopant // 8000 rpm
Ru dopant // 5500 rpm Ru dopant // 8000 rpm
(b)

Figure 5. (a) Absorption and (b) extinction coefficient of BST thin film with additives MESA

4. Conclusions

BST thin films were successfully deposition onto silicone substrate by CSD and sol-gel method with glycerol and MESA surfactant additive. BST thin films with MESA surfactant additive have higher absorbance and absorption coefficients than BST thin films with glycerol additive. Ru dopants in BST increase absorbance and absorption coefficients. BST Thin films with MESA surfactant additive, absorption coefficients and extinction coefficients increase with Ru dopants. Absorbance BST thin films with MESA surfactant additive and spinning speed 5500 rpm higher than 8000 rpm. These result indicate that MESA additive has the potential to be used as surfactant at deposition thin film.

References

[1] Baumert B A, Chang L -H, Matsuda A T, Tsai C JT -L, Tracy C J, Gregory R B, Fejes P L, Cave N G, Chen W, Taylor D J, Otsuki T, Fuji E, Hayashi S and Suu K 1998 J. Appl. Phys 13 197-204
[2] Adem U 2003 Preparation of BaxSr1-xTiO3 Thin Films by Chemical deposition and their Electrical Characterization (Thesis) (Ankara: The Middle East Technical University) p 34-36
[3] Manavalan S G 2005 Structural and Electrical Properties of Barium Strontium Titanate Thin Films for Tunable Microwave Application (Thesis) (South Florida: University of South Florida) chapter 2 pp 20-27
[4] Gurumurthy V 2007 Barium Strontium Titanate Films for Tunable Microwave and Acoustic Wave Application (Thesis) (South Florida: University of South Florida) p 19
[5] Irzaman, Syafutra H, Darmasetiawan H, Hardhienata H, Erviansyah R, Huriawati F, Akhiruddin, Hikam M, Arifin P 2011 Atom Indoneia 37 133-138
[6] Bhachandran R, Ong B H, Wong H Y, Tan K B and Rasat M M 2012 Int. J. Electro chem. Sci. 7 11895-11903
[7] Okatan M B, Cole M W and Alpay S P 2008 J. App. Phys. 104 104-107
[8] Irzaman and Barmawi M 2008 J. SAINS MIPA 14 5-7
[9] Kanareykin A, Nenasheva E, Kozyrev A, Kazakov S, Yakovlev V 2010 Proc. Int. Particle Accelerator Conf. (May, 23-28; Kyoto) vol 7 (Geneva: JACoW ) pp 3896-3898
[10] Kocanda M, Mohiudin S F and Abdel-Motabeb I 2012 CSTA 12 17-20
[11] Dahrul M, Syafutra H, Arif A, Irzaman, Indro M N, Siswadi 2010 AIP Conf. Proc. (October 10-13; Bandung) vol 1325 (New York: AIP Publishing) pp 43-46
[12] Irzaman, Putra I R, Aminullah, Syafutra H, Alatas H 2016 Proc. Environmental Science (November 17-18; Bogor) vol 33 (Amsterdam: Elsevier B.V.) pp 607-614
[13] Bornside D E, Macosko C W and Scriven L E 1987 J. Image Tech. 13 122-129
[14] Doshi D A, Gibaud A, Goleeto V, Lu M, Gerung H, Ocko B, Han S M and Brinker CJ 2003 J. Am. Chem. Soc. 125 11646-11655
[15] Halin D S C, Talib I A, Daud A R and Hamid M A A 2014 Int. J. Pho. 2014 1-6
[16] Hambali E, Suarsana P, Sugihardjo, Rivai M, Zulchaidir E and Handoko H 2010 Peningkatan Nilai Tambah Minyak Kelapa Sawit Melalui Pengembangan Teknologi Proses Produksi Surfaktan Metil Ester Sulfonat (MES) dan Aplikasinya untuk Meningkatkan Produksi Minyak Bumi Menggunakan Metode Huff dan Puff (DIKTI) p 14

[17] Irzaman, Hambali E, Suryani A and Alatas H 2016 Pengembangan Fotovoltaik Berbasis Bahan Alam untuk Kebutuhan Energi Masyarakat dan Mendukung Penerapan Biosurfaktan untuk Peningkatan Produksi Minyak Bumi (DIKTI) pp 59-62

[18] Lim Y F, Chua C S, Lee C J J and Chi D 2014 Phys. Chem. Chem. Phys. 14 241-250

[19] Halin D S C, Talib I A, Daud A R and Hamid MAA 2014 2014 Int. J. Pho. 1-6 Dahrul M, Alatas H, Irzaman 2016 Proc. Environmental Science (November 17-18; Bogor) vol 33 (Amsterdam: Elsevier B.V.) pp 661–667