# Electrical Properties of Photodiode $Ba_{0.25}Sr_{0.75}TiO_3$ (BST) Thin Film Doped with Ferric Oxide on *p*-type Si (100) Substrate using Chemical Solution Deposition Method

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**A R T I C L E I N F O**

*Article history:*
Received 01 February 2010
Received in Revised form 04 October 2011
Accepted 02 November 2011

*Keywords:*
BSFT thin film
Current-voltage characteristics
Ferric oxide doping
Photodiode
*Spin coating*
XRD characteristics

**A B S T R A C T**

In this paper we have grown pure $Ba_{0.25}Sr_{0.75}TiO_3$ (BST) and BST doped by Ferric Oxide $Fe_2O_3$ (BFST) with doping variations of 5%, 10%, and 15% above type-*p* Silicon (100) substrate using the chemical solution deposition (CSD) method with spin coating technique at rotation speed of 3000 rpm, for 30 seconds. BST thin film are made with a concentration of 1 M 2-methoxyethanol and annealing temperature of 850$^{O}$C for the Si (100) substrate. Characterization of the thin film is performed for the electrical properties such as the current-voltage (I-V) curve using Keithley model 2400 as well as dielectric constant, time constant, pyroelectric characteristics, and depth measurement. The results show that the thin film depth increases if the concentration of the Ferric Oxide doping increases. The I-V characterization shows that the BST and BFST thin film has photodiode properties. The dielectric constant increases with the addition of doping. The maximum dielectric constant value is obtained for 15 % doping concentration namely 83.1 for pure BST and 6.89, 11.1, 41.63 and 83.1, respectively for the Ferric Oxide doping based BST with concentration of 5%, 10%, and 15%. XRD spectra of 15 % of ferric oxide doped BST thin film tetragonal phase, we carried out the lattice constant were $a = b = 4.203$ Å; $c = 4.214$ Å; $c/a$ ratio = 1.003.



## INTRODUCTION

The field of electronics continues to develop rapidly due to the synthesis of new materials whose characteristics show promising applications in the future. Ferroelectric materials is one material class whose research is of high interest due to the possible new devices that can be built from its useful and unique characteristics.

Barium Stronsium Titanate (BST) based ferroelectric material posses high dielectric constant and charge capacity so that it can possibly be applied as a Ferroelectric random Access memory (FRAM) and used in Dynamic Random Acces Memory (DRAM) with a storage capacity above 1 Gbyte [1]. Its piezoelectric characteristics can be applied as a microactuator and its pyroelectric properties on infrared sensor. In addition, the polarizability of BST can also be applied as a Non Volatole Ferroelectric RAM (NVRAM) and its electro optic as switch thermal infrared [2]. BST thin films can be produced by various methods such as Pulsed Laser Deposition (PLD), Metal Organic Solution Deposition (MOSD), Sol-Gel Process and RF Magnetron Sputtering [3]. The film can be produced by Chemical Solution Deposition (CSD) which has often been applied to grow perovskite thin film since 1980 popularized by Fukashima *et al.* [4].

In this paper BST and BFST thin films were produced by chemical solution deposition (CSD) due to its benefits when dealing with these materials and easy procedure. In addition, CSD technque are relatively cheap and produces good results. Spin coating is performed above a Si type-p substrate and annealing process at a temperature of 850$^{o}$C whereas the material for thin film uses Etylane

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Glycole rather than 2-methoexcytanol that had often been used during the previous researches. Analysis and characterization its conducted for the produced BST and BFST thin film to test is compatibility as a temperature sensor using multimeter for determining its dielectric constant, electrical characteristics by analizing the voltage-current, XRD characteristics of each thin film that has been doped with ferric oxide.

Ferroelectricity is a class of electronic materials especially dielectric that are spontaneously polarized and has the ability to alter its internal electric polarization. The applied material for producing this thin film is $Ba_xSr_{1-x}TiO_3$ (BST). Barium Stronsium Titanate (BST) is materials with high dielectric constant as well as high charge capacity. The Curie temperature of pure barium titanate is 130°C. By addition of stronsium, the BST temperature decreases to room temperature [5]. BST thin film can be produced by various techniques such as Chemical Solution Deposition, laser ablation, MOCVD, and sol-gel process [6]. The reaction for BST is given by:

$$0.25Ba(CH_3COO)_2 + 0.75Sr(CH_3COO)_2 + Ti(C_{12}H_{28}O_4) + 22O_2 \rightarrow Ba_{0,25}Sr_{0,75}TiO_3 + 17H_2O + 16CO_2$$

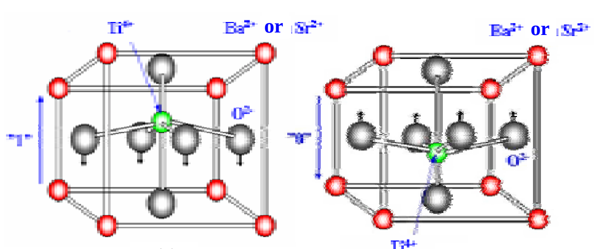



**Fig. 1.** $Ba_{0,5}Sr_{0,5}TiO_3$ Structure (a) Upwards Polarization (b) Downwards Polarization.

Doping is additional material to increase the amount of electrons or holes in a semiconductor. Doping can change the lattice parameter, dielectric constant, electrochemical characteristics, and electro-optical properties as well as pyroelectrical nature of the thin film ceramics [7]. The thin film with a length of one micron is ideal for sensor application. The doping used is ferric oxide ($Fe_2O_3$) which is an acceptor doping $Fe^{3+}$ and has a rhombohedral crystal structure with a lattice constant, $a$ = 5,0329 ± 0.001Å. The density of $Fe_2O_3$ is 5.24 g/ml and melting point is 1565°C. $Fe_2O_3$ cannot dissolve in water but dissolve in acid [8]. Increase od dopant ion ($Fe^{3+}$) will produce an empty space at the $O^{-2}$ ion position. The dopant ion ($Fe^{3+}$) has a valence of more than 4+ this the shortage of positive ion will occur in the perovskyte structure and as a result empty space will be formed at oxygen ion position to keep electroneutrality balance.

The addition of $Fe^{3+}$ ion will produce more oxygen [9,10]. To make this thin film it can be achieved through sputtering, metal organic vapour deposition (MOCVD) and variating the chemical solution deposition (CSD) method. CSD method is a thin film produced by deposition of the chemical material above the substrate preparated using spin coating at a certain rotating speed usually 3000 rpm. Spin coating is an easy and effective way for thin filming above the flat substrate. Spin coating is a thin filming technique by spreading the solution above the substrate and rotating it at constant speed to obtain a new homogenous layer.

## EXPERIMENTAL METHODS

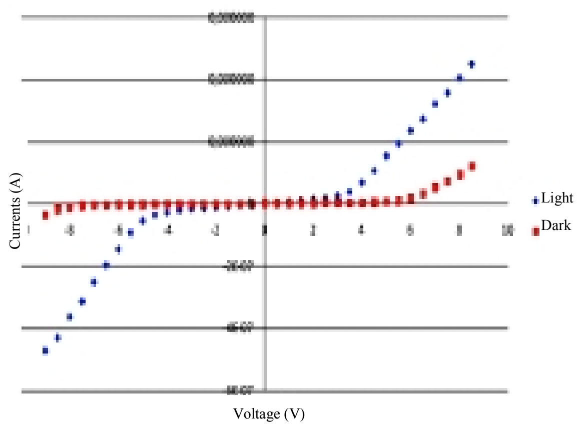
The materials & applied in this research are Barium Acetate [$Ba(CH_3COO)_2$, [99%], Strontium Acetate [$Sr(CH_3COO)_2$, 99%], Titanium Isopropoxide [$Ti(C_{12}O_4H_{28})$, 99.999%], Ferric Oxide [($Fe_2O_3$)], Glycerin Glycol, Acetate Acid, p-type Si (100) substrate, aquades, HF (Fluoride Acid), preparate glass and aluminum foil. This research consists of two stages. The first covers the preparation of type-p Si substrate, BST and BFST solution making, thin film growing, annealing process, and contact installement on thin film prototype. The second stage includes characterization of BST and BFST thin film electrical characterization that consists of voltage-current relationship, dielectric constant, and XRD characteristics to understand whether the thin film can be applied as temperature sensor or not.

## RESULTS AND DISCUSSIONS

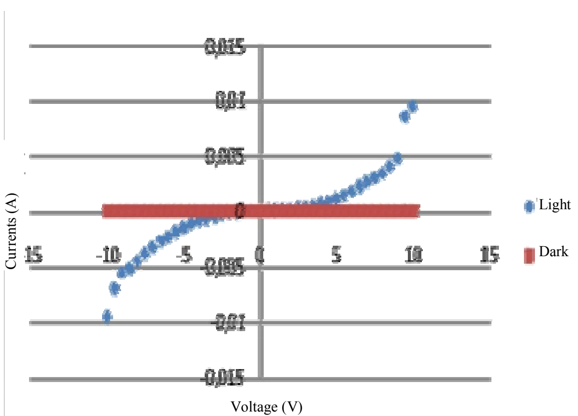
### Current-voltage characteristics

Measurement of the current-voltage (I-V) characteristics is performed using an I-V meter. The measurement is performed using two treatments namely in dark and bright condition, which the later using a 100 Watt neon lamp. The voltage is a free variable depicted by the horizontal axis. The voltage is given up to 10 V with an interval of 0.5V. The output data from the device is the current and voltage values. The I-V characteristics can be obtained which shows that the BST and BFST thin film, grown on type-p substrate has diode characteristics.

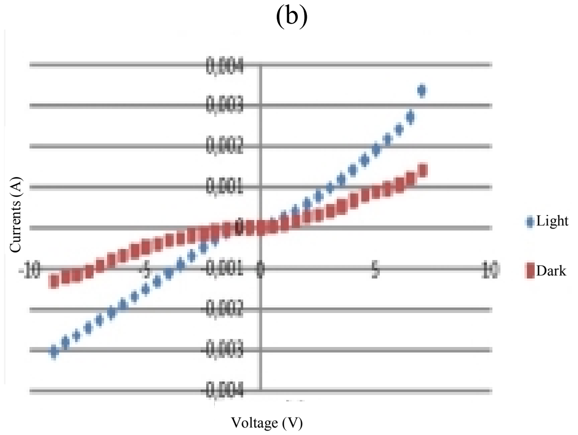
The thin film and p-type Si (100) substrate produced is a junction between two semiconductors. The applied silicon is of p-type whereas the BST and BFST thin films are a type-n semiconductor [11]. The junction between type-p and type-n semiconductor is known as p-n junction [12]. The presence of p-n junction results in similar characteristics between thin film and diode which is a joint of two electrodes namely anodes and cathodes [13,14].



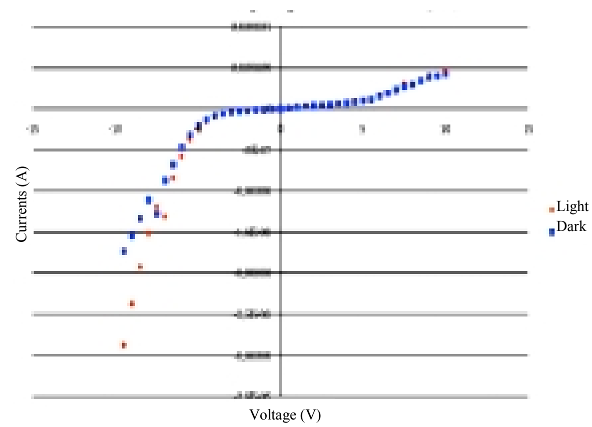

(a)




(b)




(c)




(d)

**Fig. 2.** The knee voltage for BST and BFST from the I-V characteristics, a) Knee voltage of 1.5 V for pure BST, b) Knee voltage of 2.0 V for 5% doped BFST, c) Knee voltage of % 1.0 V for 10% doped BFST, d) Knee voltage of 0.5 V for 15% doped BFST

The voltage that causes the current to start increasing is called the knee voltage. Certain semiconductor materials have different knee Voltages, such as 0.7 V for Silicon and 0.3 V for Germanium. The knee voltage for BST and BFST is depicted in Fig. 2, namely 1.5 V for pure BST thin film, while for BFST thin film with 5%, 10% and 15% doping they are 2 V, 1.5 V, and 1 V respectively. Doping addition decreases the knee voltage and therefore causes more free electrons and holes to form in the crystal [13, 14]. Consequently it will produce more conductive thin films.

Light illumination in thin film causes the film to be more conductive due to photon energy absorbed by the electrons so that the current occurs faster. The I-V characteristics can be used to show that the thin film has diode characteristics and also the differences between illumination and no illumination. The later shows that the thin film has also photodiode characteristics.

## The dielectric constant characteristics

The experimental set up for analyzed of dielectric constant for BST and BFST uses circuits is depicted in Fig. 3. The oscilloscope output (voltage vs time) is used to determine the dielectric constant, a constant of the material that store current along with one of the capacitors nature to store charge. The output also shows the square signal slope shows charge storing in the material (see output from Fig. 4). The factors that affect the dielectric constant is the amount of ferric oxide doping on the thin film.

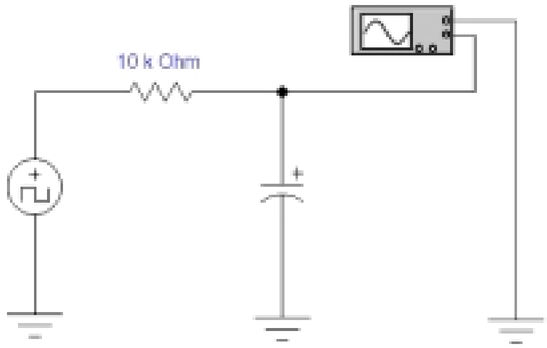
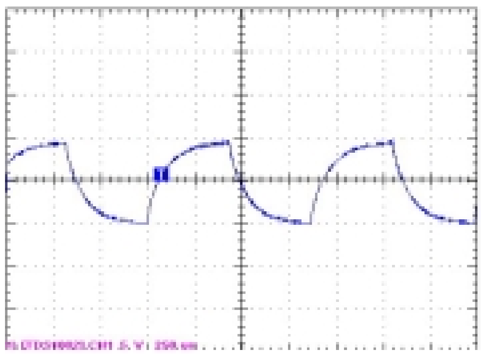
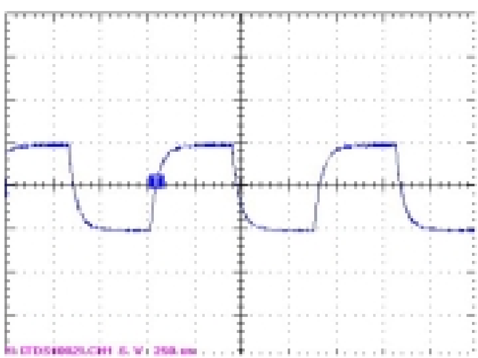


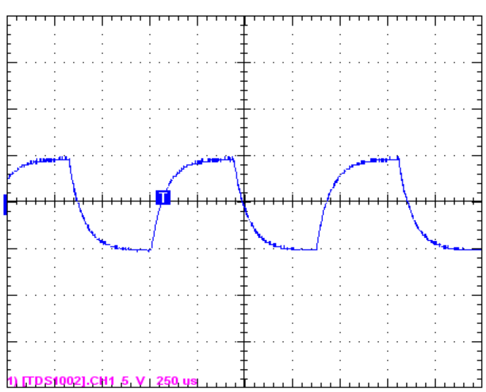

**Fig. 3**. Circuit for the experimental set up for analyzed of dielectric constant.



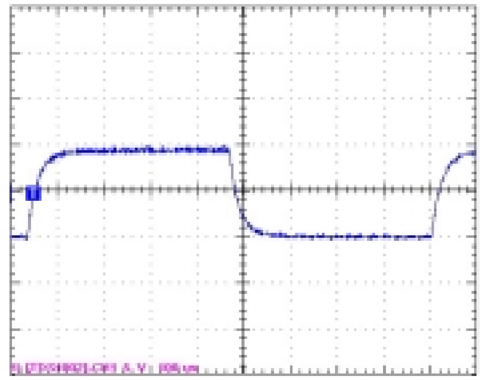
(a)



(b)



(c)



(d)

**Fig. 4.** The oscilloscope output is used to determine the dielectric constant, (a) Capacitor curve for pure BST, (b) Capacitor curve for BFST 5%, (c) Capacitor curve for BFST 10%, (d) Capacitor curve for BFST 15%.

From Fig. 4 and using C = ε εo A/d equation, we carry out the dielectric constant value for pure BST (0%) and BFST (5%, 10% and 15%) (Table 1). From Table 1 below it can be seen that the dielectric constant will increase if ferric doping is added. This is caused by ferric doping increases the negative carrier that causes increases in negative charge carrier which causes the electrical field in the depletion region to increases so that the dielectric molecules increases. This is also caused by the increase of thin film depth due to ferric addition. The highest dielectric constant is achieved for ferric doped BST of 15% namely 83.1. This is merely caused by the depth increase which is higher for 15% BFST than pure BST or those doped with only 5% and 10%.

**Table 1.** Dielectric constant value for pure BST (0%) and BFST (5%, 10% and 15%).

| Thin film | Dielectric constant |
|---|---|
| Pure BST | 6.89 |
| BFST 5% | 11.1 |
| BFST 10% | 41.63 |
| BFST 15% | 83.1 |

Analysis on the p-n junction formed by the thin film and substrate shows that the n-type has free negative charge and static positive ion whereas the substrate has free positive charge and static negative ion. In the junction region and surroundings, free charge diffusion occurs and leaves only static charges, namely ions from donor and acceptor atoms. This junction area is called the depletion region and contains positive static charge in one side and negative in the other one. This electric field is produced at the depletion region and this phenomenon can be seen as pararell slabs [14,15]. Beside, because the hole in p-type has higher concentration than that in n-type, the current diffuses from p to n region. Similar character also occurs for electron although it is not diffuse continuously. If the hole leaves the p-type region to the n-type an acceptor will be ionzised to be negative and produced negative p-type region.

Similar phenomenon occurs for the electrons that leave the positive charges in n-type area, which will produces electric field starting in the positive region and ending in negative region. The electric field will hold the hole diffusion from p to n type region as well as electrons diffusion from n to p type region [14,16].

### X-Ray diffraction characteristics

The structure of the grown film was analyzed by x-ray diffraction (XRD). The XRD spectra were recorded on a Diano type 2100E diffractometer using $CuK_{\alpha}$ radiation at 30 KV and 30 mA (900 watt). Figure 5 shows XRD spectra 0%, 5%, 10%, 15% of ferric oxide doped BST thin film tetragonal phase on the Si (100) substrate. The presence of intense diffraction peak corresponding to (200) plane if compared with diffraction peaks from of (110), (220), (311) planes implied that the ferric oxide doped BST thin film assessed a strong preferential orientation. This indicates that the grown film has good crystallinity for high deposition temperature (850$^{o}$C). The calculate lattice constant of 15% of ferric oxide doped BST using Cohen's and Cramer's method, we carried out the lattice constant were $a = b =$ 4,203 Å; $c$ = 4,214 Å; $c/a$ ratio = 1.003. These values are in good agreement with those observed by other researcher ($a = b =$ 3.977 Å; c = 3.988 Å) [17].

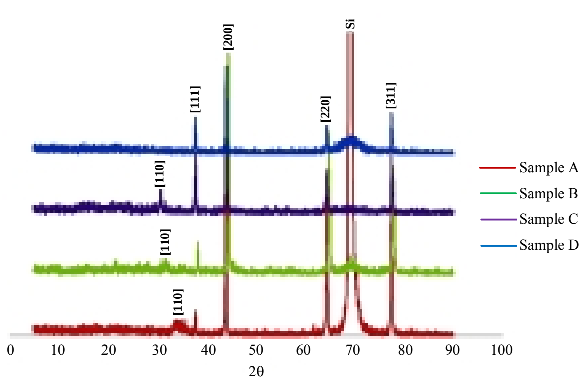



**Fig. 5.** XRD spectra BST thin film (sample A), 5% of ferric oxide doped BST thin film (sample B), 10% of ferric oxide doped BST thin film (sample C), 15% of ferric oxide doped BST thin film (sample D) tetragonal phase on the Si (100) substrate.

## CONCLUSION

Base on the experimental results it can be concluded that the depth of BST and BFST will increase if more ferric doping is added. The doping will decrease the knee voltage for each thin film. Meanwhile, dielectric constant will increase along with addition of more ferric doping. From the current-voltage characteristic curve, BST and BFST thin film possess photodiode properties.

## ACKNOWLEDGEMENTS

This work was supported by Program Penelitian Strategis Nasional 2010, DIPA IPB, The Republic of Indonesia under contract no. 2/I3.24.4/SPK/PSN/2010 and Program Penelitian Antar Lembaga dan Perguruan Tinggi 2011, DIPA IPB, The Republic of Indonesia under contract no. 52/I3.24.4/SPP/PL/2011.

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