Characterization of Micro Structure, Morphology and Electrical Properties Barium Titanate (BT) Doping Sr by Chemical Solution Deposition (CSD)

H D Mahmudah, Y Iriani, A H Ramelan
Graduate Physics Departement, Sebelas Maret University, Surakarta, Indonesia
Physics Department, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, Indonesia

E-mail: yopen_2005@yahoo.com

Abstract – Thin films successfully grown on the substrate Pt / Si is thin films BT doping Strontium (BST) by Chemical Solution Deposition (CSD) method. The percentage of doping Sr material are 1%, 3%, and 5%. The BST thin layer was characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and the hysteresis curve testing by Sawyer tower methods. The diffraction angle (2θ) in the XRD curve shifts to the right (bigger) along with increasing doping mol % Sr. Lattice parameters BST using the refinement GSAS program showed that a thin layer of BST has a tetragonal structure. From SEM analysis, along with increasing variation mol % Sr doping does not affect the thickness, but affects the grain size of a thin layer. BST thin layer of a ferroelectric material which has been formed mark a hysteresis curve. The characterization results to show that a thin layer of BST has been deposited on the substrate Pt/Si.

1. Introduction
Barium Titanate (BT) is a type perovskite ferroelectric and piezoelectric material first developed and studied since the 1940’s. It goes through a paraelectric-ferroelectric phase transition from cubic to tetragonal at 130°C [1]. Barium Strontium Titanate (BST) is a material that has response ferroelectric and dielectric [2]. Research on BST originated from studies of barium titanate (BT), which showed that the addition of Sr ion in BT will lower the Curie temperature and change the ferroelectric properties of the BT [3]. So that the material can be used to manufacture BST thin layer which is applied as a FRAM [4].

Barium strontium titanate (BST) is a ferroelectric material. This material is the result of a mixture of Barium Titanate (BaTiO3) with strontium acetate. BST is usually obtained by substituting ions in position A and the perovskite structure ABO3 or Ba in BaTiO3 compound with Sr. The Curie temperature of barium titanate is 130°C and in the presence of doping strontium (Sr). Curie temperature decreased to room temperature and can be used in these devices that require room temperature [5]. Among thin film deposition techniques, such as wet chemical solution deposition, rf sputtering, metal-organic chemical vapor deposition and pulsed laser deposition [6]. CSD method is a process of making a thin layer with a chemical solution deposition on the substrate, and then prepared by spin coating with certain rotational speed [7]. Excellence CSD method with another method is by this method stoikiometry easily controlled properly, easily prepared and carried out at low temperatures [8]. BST Samples were characterized by X-ray diffraction (XRD) to determine the thin film’s microstructure, Scanning Electron Microscopy (SEM) to determine the morphology of thin film, and Sawyer Tower method to determine the hysteresis curve of a thin film.
2. Experimental

BT thin layer deposited by the method of Chemical Solution Deposition (CSD) prepared by spin coating method. BT has created a layer of doped Sr 0.5 M on the substrate Pt/Si. Barium acetate, titanium isopropoxide, used as precursor and acetic acid as a solvent. Ethylene glycol is also used in the manufacture of the BT solution which serves to prevent the occurrence of a crack. Growing thin layer of BT doping strontium (Sr) carried on a substrate Pt/Si with doping Sr mole percent variation is 1%, 3%, and 5%.

The steps in this research are the substrate preparation, preparation of the solution, solution deposition, and characterization. There are three sections in the thin layer deposition method Chemical Solution Deposition (CSD), it is the preparation of the solution, deposition on the substrate using a spin coater a rotation speed of 4000 rpm for 30 seconds. After the spin coating process, the substrate that has been coated with the solution is then heated using a hot plate. Heat treatment is hydrolysis and annealing, annealing performed at a temperature of 800°C; the heating rate is 3°C per minute with a holding time is 3 hours. Characterization is carried out in the study include testing the microstructure of thin layers BT doped Sr using X-Ray Diffraction (XRD), test morphology using SEM and electrical properties using Sawyer tower method.

3. Result and Discussion

The use of XRD equipment produces characterization in the form of a graph of diffraction angle and intensity. Figure 1 showed the peaks assumed that the belong to BT and BST at an angle (110). This indicates that the sample BST made is crystal. From Figure 1 it is showed that there is the shift of the peaks with increasing Sr.

\[
\text{Figure 1. Diffraction Pattern XRD (a) BaTiO}_3 \quad \text{(b) Ba}_{0.99}\text{Sr}_{0.01}\text{TiO}_3, \\
\text{(c) Ba}_{0.97}\text{Sr}_{0.03}\text{TiO}_3, \quad \text{(d) Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3
\]

The data taken from XRD is analyzed by working GSAS, this analyze produce the lattice parameters with each values are \(a=b\neq c\) and \(\alpha=\beta=\gamma=90^\circ\) on 101 orientation, which means the crystal structure is tetragonal. Field (110) is used to calculate the value of FWHM. The value of FWHM affected by a high intensity value for each sample. The higher the intensity, the FWHM values obtained will be smaller, because the smaller the peak width. FWHM value can be used to determine the size of the crystals. Based Scherrer equation which states that the value of FWHM is inversely proportional to the size of the crystals, in order to get a large crystal size for a small FWHM values. Material Sr replace Ba has a radius larger, in order to obtain the greater the number of doping resulted in changes in crystal size greater.

Assumption of the peak that belongs to sample wanted is done by refinement using Rietveld analysis with GSAS program. This method is matching result pattern of raw data XRD with refinement GSAS program. Figure 2 is the result of refinement thin layer of BT and BT doped 1%, 3%, and 5% mol Sr. Figure 2 showed that the doping Sr, BT have entered the compound, as in data processing used occupancy GSAS data that entered in the atom that makes the thin layer BT is appropriate that is Ba, Sr, Ti, and O3.
The processing of GSAS is done by refinement background so obtained approach between theoretical curve (calculated) which the curve experiment (observed) to obtain the chi square ($\chi^2$) value is small to form convergentitas with indicators of success chi square small.

(a)BaTiO$_3$  
(b) Ba$_{0.99}$Sr$_{0.01}$TiO$_3$  
(c)Ba$_{0.97}$Sr$_{0.03}$TiO$_3$  
(d) Ba$_{0.95}$Sr$_{0.05}$TiO$_3$

**Figure 2.** Refinement Result with GSAS

Based on Table 1 it can be seen that there is the shift of angle, theta angle is smaller with the increasing of Sr doping mole percent on the orientation of the field of (110), shifted to the left. Without the addition of Sr on BT that have at peak, diffraction angles 31.21 with the addition of Sr in the (110) the angle shifted to 30.66. From Table 2 it appears that the addition of the composition of the doping Sr caused changes in lattice parameter values. The more doping Sr are added, then the value of the lattice parameter increases. This occurs because the atoms Sr and Barium (Ba) have a radius size of atomic are almost identical so that the atoms Sr$^{2+}$ and Ba$^{2+}$ will occupy the same position in the side of the unit cell diagonal.

**Table 1.** The diffraction angle doping Sr

| Sample          | Diffraction Angle |
|-----------------|-------------------|
| BaTiO$_3$       | 31.21             |
| Ba$_{0.99}$Sr$_{0.01}$TiO$_3$ | 30.66             |
| Ba$_{0.97}$Sr$_{0.03}$TiO$_3$ | 30.76             |
| Ba$_{0.95}$Sr$_{0.05}$TiO$_3$ | 30.81             |
Table 2. Lattice Parameter BST

| Sample         | Lattice Parameter | Parameter | $\lambda^2$ |
|----------------|-------------------|-----------|-------------|
|                | $a$(Å)             | $c$(Å)    | $c/a$       |
| BaTiO$_3$      | 3.995             | 4.035     | 1.010       | 1,683       |
| Ba$_{0.99}$Sr$_{0.01}$TiO$_3$ | 3.958 | 4.006 | 1.011 | 1,632 |
| Ba$_{0.97}$Sr$_{0.03}$TiO$_3$ | 3.858 | 4.114 | 1.066 | 1,732 |
| Ba$_{0.95}$Sr$_{0.05}$TiO$_3$ | 3.806 | 4.168 | 1.096 | 2,230 |

Figure 3. Photo SEM BT and BST Layer with doping Mol Variation

Photo SEM results in Figure 3 for the total sample it doesn’t see happen to crack on the surface morphology of thin layers of BT and BST. It showed a thin layer of BT and BT with a variety of moles Sr doping was deposited well on the substrate Pt/Si with 3 number of layer, the annealing temperature 800°C for 3 hours and heating rate of 3°C/min. Based on the picture, it appears that the morphology of the thin film look homogeneous and the grain size is not visible.

Figure 4 is a cross-sectional SEM images samples of BT and BT with a variety of moles doping Sr. The results of the image are used to determine the thickness of thin layer of BT and BT with a variety of moles doping Sr. It appears that BT and BST thin layer of light-colored and dark beside a substrate Pt/Si. The result of the calculation of film thickness for all samples it appears that the overall thickness of the thin layer of BT and BT with Sr doping mole variations in size tend to have similar thickness is about 350 nanometers. Figure 5 shows the hysteresis curve of a thin layer of BT and Ba$_{1-y}$Sr$_y$TiO$_3$ (BST) with $y$ (mole percent doping) is 1%, 3%, and 5%. Of the four samples, it appears that the hysteresis curve has been fully formed. This indicates that the thin layer formed BT and BST are ferroelectric.
Figure 4. The Thickness Thin Films

Figure 5 showed variations in the number of moles doping 1%, 3%, and 5% respectively show the change on the Y-axis, means that any changes in remanent polarization. The addition of a small amount of doping which has remanent polarization bigger than the number of larger doping. This means that the value of remanent polarization is getting smaller with an increasing number of doping Sr on the base material that is BT. Samples some of doping material Sr 1% had the larger electric field (E) than the material in doping Sr 3% and 5%, which means the addition of the percent number doping caused smaller of the electric field.

Figure 5. Hysteresis Curve
4. Conclusion

The addition of Sr doping on the crystal structure of Barium Titanate caused diffraction angle shift to the right, and the size of the crystal lattice parameter increases, the thickness of the thin layer is almost the same, the smaller caused, the smaller coercive field and remanent polarization.

Reference

[1] Jiangying W, Xiaoying Z, Jingji Z., Huiling L., and Zhengfa L 2012 Science Direct 957-960
[2] Pontes F, Leite E, Varela J, and Longo E 2001 Science Direct 91-98
[3] Dus B W, Czekaj A L, Ortiz T, Adamezyk M, Osinska K, Kozielski L, and Czekaj 2007 Science-Poland 25 3
[4] Seo J Y and Park S W 2004 Journal of Korean Physical Society 45 3 769-772
[5] Remmel Thomas 1999 Characterization of Barium Strontium Titanate Films Using XRD (Mesa, Arizona)
[6] Kim J, Kim S, Kim W, Ha T, Kim I-S and Song J S 2006 Science Direct 2322-2325
[7] Muhammad Hikam, Edy Sarwono dan Irzaman 2004 Makara Sains 8 108-115
[8] Schwartz Robert W 1997 Chemical Solution Deposition of Perovskite Thin Films. Department of Ceramic and Materials Engineering (Clemson: University Clemson South Carolina) 9 11