SURFACE ROUGHNESS AND GRAIN SIZE CHARACTERIZATION OF ANNEALING TEMPERATURE EFFECT FOR GROWTH GALLIUM AND TANTALUM DOPED $Ba_{0.5}Sr_{0.5}TiO_3$ THIN FILM

Irzaman[1*], H. Darmasetiawan[1], H. Hardhienata[1], M. Hikam[2], P. Arifin[3], S. N. Jusoh[4], S. Taking[4], Z. Jamal[4], M. A. Idris[5]

[1]Department of Physics, FMIPA Bogor Agricultural Unversity (BAU),
BAU Campus Darmaga Gedung Wing S Bogor, Indonesia – 16680
[2]Department of Physics, FMIPA UI, UI Campus Depok, Indonesia – 17000
[3]Department of Physics, FMIPA ITB, Jalan Ganesa 10 Bandung, Indonesia – 40132
[4]School of Microelectronic Engineering, Universiti Malaysia Perlis,
Jalan Bukit Lagi, 01000 Kangar Perlis, Malaysia.
[5]School of Material Engineering, Universiti Malaysia Perlis,
Jalan Bukit Lagi, 01000 Kangar Perlis, Malaysia.

ABSTRACT

SURFACE ROUGHNESS AND GRAIN SIZE CHARACTERIZATION OF ANNEALING TEMPERATURE EFFECT FOR GROWTH GALLIUM AND TANTALUM DOPED $Ba_{0.5}Sr_{0.5}TiO_3$ THIN FILM. Thin films 10 % gallium oxide doped barium strontium titanate (BGST) and 10 % tantalum oxide doped barium strontium titanate (BTST) were prepared on p-type Si (100) substrates using chemical solution deposition (CSD) method with 1.00 M precursor. The films were deposited by spin coating method with spinning speed at 3000 rpm for 30 seconds. The post deposition annealing of the films were carried out in a furnace at 200^oC, 240^oC, 280^oC (low temperature) for 1 hour in oxygen gas atmosphere. The surface roughness and grain size analysis of the grown thin films are described by atomic force microscope (AFM) method at 5000 nm x 5000 nm area. The rms surface roughness BGST thin films at 5000 nm x 5000 nm area are 0.632 nm, 0.564 nm, 0.487 nm for temperature 200^oC, 240^oC, 280^oC, respectively, whereas the grain size (mean diameter) are 238.4 nm, 219.0 nm, 185.1 nm for temperature 200^oC, 240^oC, 280^oC, respectively. In fact, to increase annealing temperature from 200^oC to 280^oC would result in decreasing the rms roughness and grain size. Therefore, rms roughness and grain size would have the strong correlation annealing temperature.

Keywords: BGST, BTST, thin films, CSD method, AFM, roughness, grain size.

INTRODUCTION

Thin $BaTiO_3$ (BT) and $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) is a well known dielectric material and has been attractive for the applications such as capacitors and high density dynamic random access memory (DRAM) due to its high dielectric constant and high capacity of charge storage [1,2] and solar cell [3].

---

* Corresponding author.
E-mail addresses: irzaman@yahoo.com (Irzaman)

BT and BST films can be formed by various methods, such as chemical solution deposition (CSD) [1,2,4], metal organic chemical vapor deposition (MOCVD) [5-7], rf sputtering [8-13] and Pulsed Laser Ablation Deposition (PLAD) [14]. CSD Method is of particular interest because of its good control of stoichiometry, ease of fabrication and low temperature synthesis. It is relatively new and requires a greater understanding to optimize film quality. Crystallization mechanisms in CSD-derived thin films are different from phenomena associated with vapor phase epitaxy. It was reported that CSD derived thermodinamically stable.

Gallium oxide doped barium strontium titanate and tantalum oxide doped barium titanate have been of immense interest in the use of ferroelectric solar cell (FSC) [3]. The roughness and grain size properties of the materials can be tailored by varying the concentration of the dopant and annealing temperature. Since the sensor performance significantly depends on these properties, the FSC performance can then be optimized.

The surface roughness and grain size analysis of the grown thin films are analysed by atomic force microscope (AFM) method at nanoscale area. Instead of tunneling current, an AFM detects interatomic forces that occur between a cantilever probe tip and a sample. Normal imaging forces are in the 1 - 50 nanonewton range and cantilever deflections of less than 0.1 nm can be detected (nanoscale) [15–21].

In this paper we report on the fabrication of 10 % gallium oxide doped barium strontium titanate and 10 % tantalum oxide doped barium strontium titanate thin films by CSD with 1.00 M precursor. Using 10 % gallium oxide and 10 % tantalum oxide doped barium strontium titanate thin films by CSD, can be increase the homogeneous performance of The roughness and grain size. The roughness and grain size properties of the grown films related to the dopant gallium oxide, tantalum oxide and annealing temperature are described.

MATERIALS AND METHODS

Procedural BGST thin films were fabricated by CSD methods using 0.160 g barium acetic [$Ba(CH_3COO)_2$, 99 % purity] + 0.131 g strontium acetic [$Sr(CH_3COO)_2$, 99 % purity] + 0.355 g titanium isopropoxide [$Ti(C_{12}O_4H_{28})$, 99.999 % purity] + 0.060 g gallium oxide as precursor in 1.25 ml 2-methoxyethanol [$H_3COOCH_2CH_2OH$, 99.9 %] and using 0.160 g barium acetic [$Ba(CH_3COO)_2$, 99 % purity] + 0.131 g strontium acetic [$Sr(CH_3COO)_2$, 99 % purity] + 0.355 g titanium isopropoxide [$Ti(C_{12}O_4H_{28})$, 99.999 % purity] + 0.060 g tantalum oxide as precursor in 1.25 ml 2-methoxyethanol [$H_3COOCH_2CH_2OH$, 99.9 %] were used as solvent was introduced under mixing by Ultrasonic at 2 hours. A clear liquid resulted. After 20 minutes of standing at room temperature, this solution acquired a milky appearance. The cloudy appearance disappeared. It contained

equivalent 1.00 M BGST 10% and BTST 10%. After 2 hours of aging, that solution was spin coated on 10 mm x 10 mm *p*-type Si (100) substrates, with spinning speed at 3000 rpm for 30 seconds. The post deposition annealing of the films was carried out in a Furnace Model Nabertherm Type 27 at 200°C, 240°C, 280°C (low temperature) for 1 hour in an oxygen atmosphere. The surface roughness and grain size analysis of the grown thin films are described by atomic force microscope (AFM) method at 5000 nm x 5000 nm area at room temperature in School of Microelectronic Engineering, Universiti Malaysia Perlis, Jalan Bukit Lagi, 01000 Kangar Perlis, Malaysia.

RESULTS AND DISCUSSION

The effect of growth temperature, gallium and tantalum dopant concentration on the surface morphology were carried out by using AFM images, respectively. Figure 1 - 9 shows surface analysis, grain size, 3 dimension using AFM method for annealing temperature at 200°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films varying annealing temperature (200°C, 240°C, 280°C). Whereas, Figure 10 – 12 shows surface roughness, mean grain size, grain diameter varying annealing temperature, dopant gallium and tantalum. The rms surface roughness for BST thin films at 5000 nm x 5000 nm area are 10.50 nm, 0.6324 nm, 0.2202 nm for temperature 200°C, 240°C, 280°C, respectively, whereas the grain size (mean diameter) are   1,046 nm, 238.4 nm, 141.3 nm for temperature 200°C, 240°C, respectively. The rms surface roughness for BGST thin films at 5000 nm x 5000 nm area are 0.632 nm, 0.564 nm, 0.487 nm for temperature 200°C, 240°C, 280°C, respectively, whereas the grain size (mean diameter) are 238.4 nm, 219.0 nm, 185.1 nm for temperature 200°C, 240°C, 280°C, respectively. The rms surface roughness for BTST thin films at 5000 nm x 5000 nm area are 1.087 nm, 0.4870 nm, 0.2317 nm for temperature 200°C, 240°C, 280°C, respectively, whereas the grain size (mean diameter) are   158.7 nm, 291.1 nm, 396.7 nm for temperature 200°C, 240°C, 280°C, respectively. In fact, to increase annealing temperature from 200°C to 280°C dominant would result in decreasing the rms roughness and grain size. Therefore, rms roughness and grain size would have the strong correlation annealing temperature. This suggests the primary mechanism for the decay of thermodynamically unstable BST compound in gallium or tantalum desorption and phase rearrangement of the surface in the absence of reactive oxygen environment during annealing temperature. This thermodynamic tendency for oxygen vacancy formation would lead to structural degradation of the films. By changing the temperature to the optimum growth temperature (280°C), the spots began to shrink indicating that the formation of second phase precipitate can be suppressed at this growth temperature (Figures 3, 6, 9, 10, 11, 12).
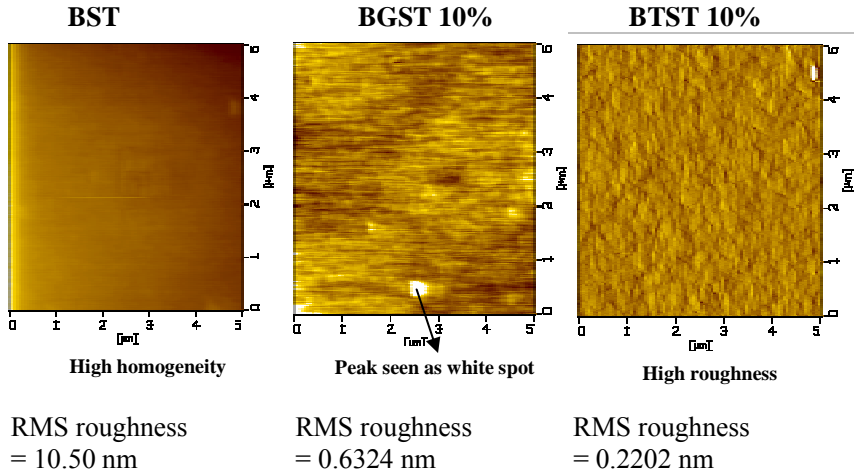
BST	BGST 10%	BTST 10%

High homogeneity	Peak seen as white spot	High roughness

RMS roughness = 10.50 nm	RMS roughness = 0.6324 nm	RMS roughness = 0.2202 nm

Figure 1. Surface analysis using AFM method at 200°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

BST	BGST 10%	BTST 10%

High altidude /thickness (red) Low altitude/ thickness (blue)	Position of peak	Red and blue area mix, showing clear case of roughness

Mean size = 858600 nm^2 Mean diameter= 1046 nm	Mean size = 44650 nm^2 Mean diameter = 238.4 nm	Mean size = 15680 nm^2 Mean diameter= 141.3 nm
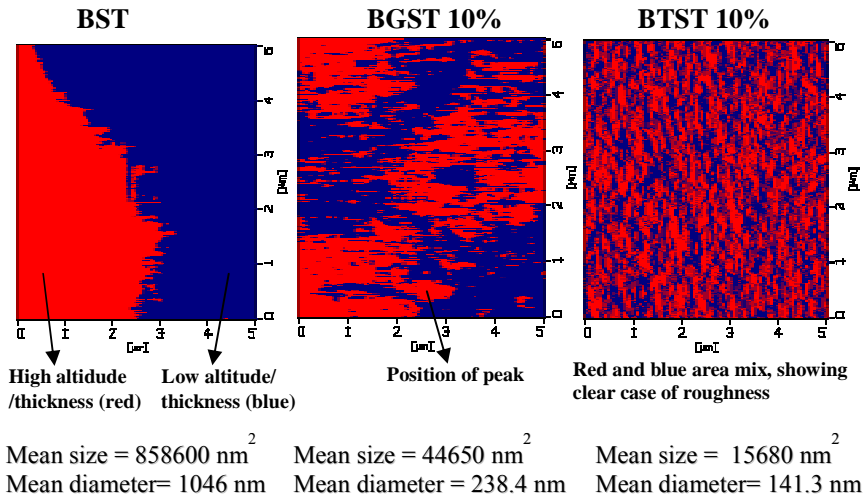
Figure 2. Grain analysis using AFM method at 200°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

60

BST	BGST 10%	BTST 10%

Peak (white color)

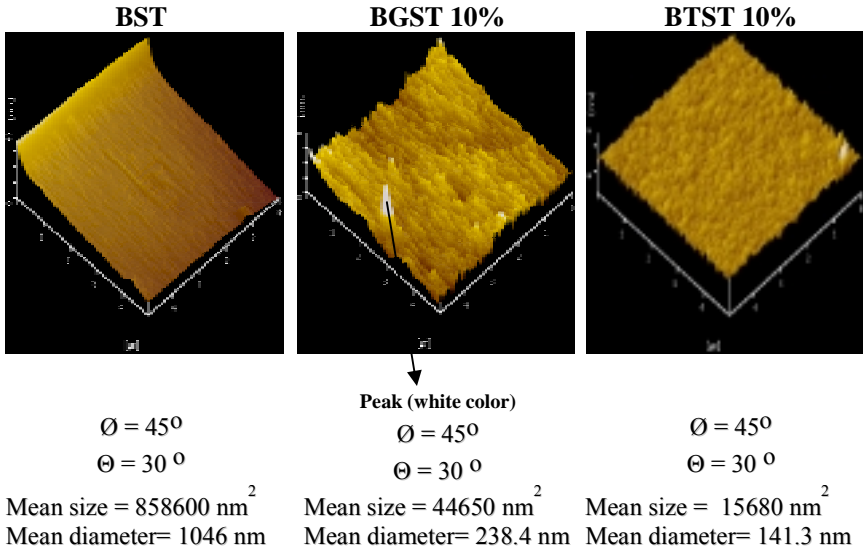| $\emptyset = 45^O$	$\emptyset = 45^O$	$\emptyset = 45^O$
$\Theta = 30^O$	$\Theta = 30^O$	$\Theta = 30^O$
Mean size = 858600 nm^2	Mean size = 44650 nm^2	Mean size = 15680 nm^2
Mean diameter= 1046 nm	Mean diameter= 238.4 nm	Mean diameter= 141.3 nm

Figure 3. The 3 dimension analysis using AFM method at 200°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

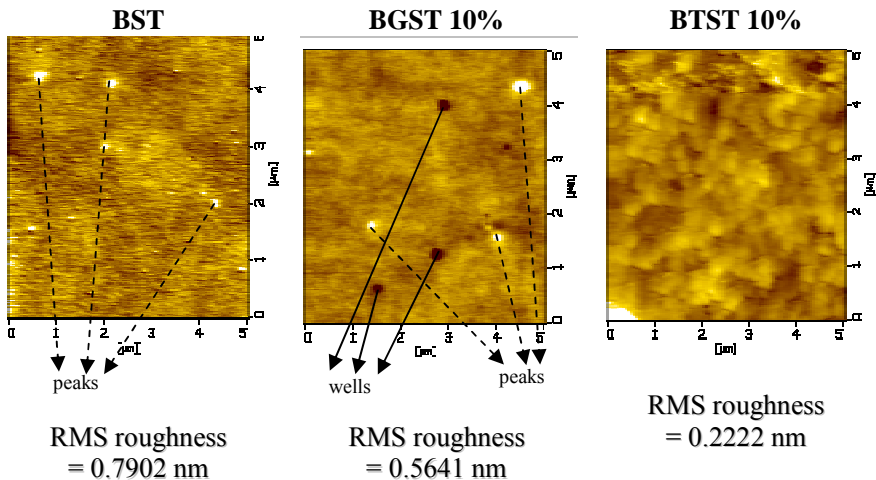| BST	BGST 10%	BTST 10%

peaks

wells   peaks

RMS roughness = 0.7902 nm	RMS roughness = 0.5641 nm	RMS roughness = 0.2222 nm

Figure 4. Surface analysis using AFM method at 240°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

BST   **BGST 10%**   **BTST 10%**

| **Mixing of red and blue areas, blurred distribution** | **Mixing of red and blue areas, less grouped** | **Mixing of red and blue areas, but more grouped** |

Mean size = 19780 nm^2 Mean size = 256410 nm^2 Mean size = 123600 nm^2
Mean diameter= 158.7 nm   Mean diameter= 291.1 nm   Mean diameter= 396.7 nm
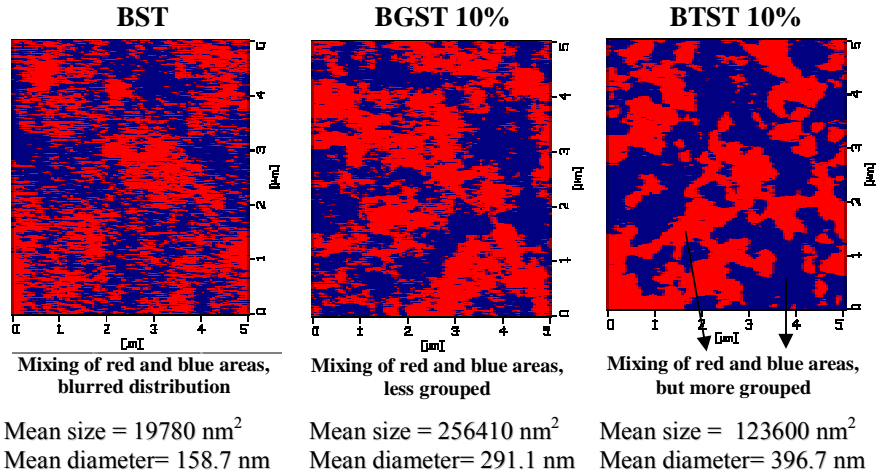
Figure 5. Grain analysis using AFM method at 240°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

BST   **BGST 10%**   **BTST 10%**

Peaks (white spot)   **Peaks (white spot) and holes (dark spot)**   **No peaks nor holes**

$\emptyset = 45^o$ $\emptyset = 45^o$ $\emptyset = 45^o$
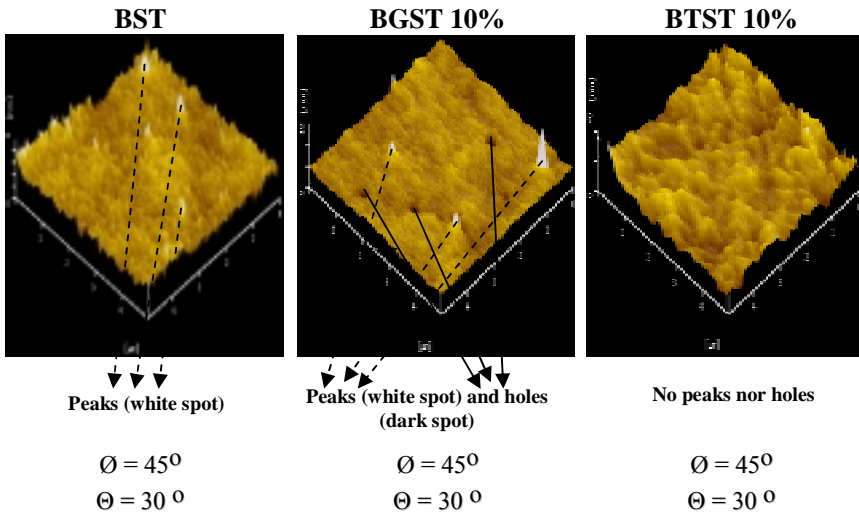$\Theta = 30^o$ $\Theta = 30^o$ $\Theta = 30^o$

Figure 6. The 3 dimension analysis using AFM method at 240°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.
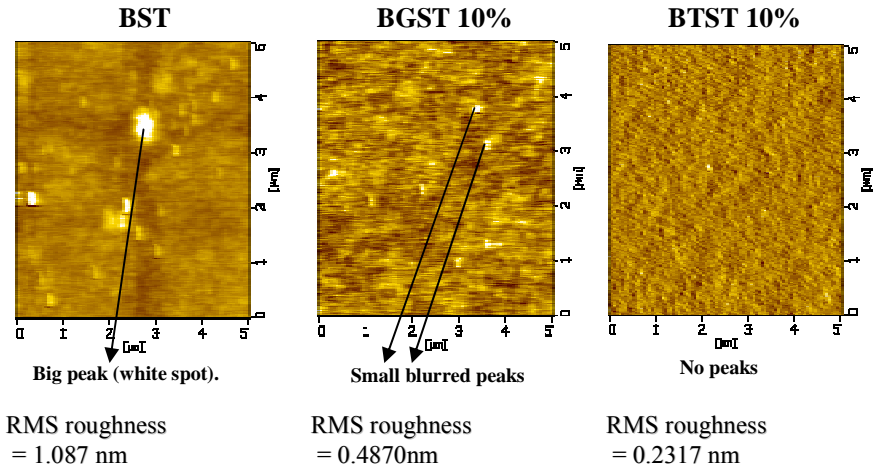
BST	**BGST 10%**	**BTST 10%**

Big peak (white spot).   **Small blurred peaks**   **No peaks**

RMS roughness
 = 1.087 nm

RMS roughness
 = 0.4870nm

RMS roughness
 = 0.2317 nm

Figure 7. Surface analysis using AFM method at 280°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

BST	**BGST 10%**	**BTST 10%**

Big peak (red).   **Smooth mixture between red and blue area**

Mean size = 19780 nm^{2} Mean size = 256410 nm^{2} Mean size = 123600 nm^{2}
Mean diameter= 158.7 nm   Mean diameter= 291.1 nm   Mean diameter= 396.7 nm

Figure 8. Grain analysis using AFM method at 280°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

BST	**BGST 10%**	**BTST 10%**

Big peak   **Peaks and higher roughness**   **Smooth mixing roughness (no single peaks)**

$\emptyset = 45°$ $\emptyset = 45°$ $\emptyset = 45°$

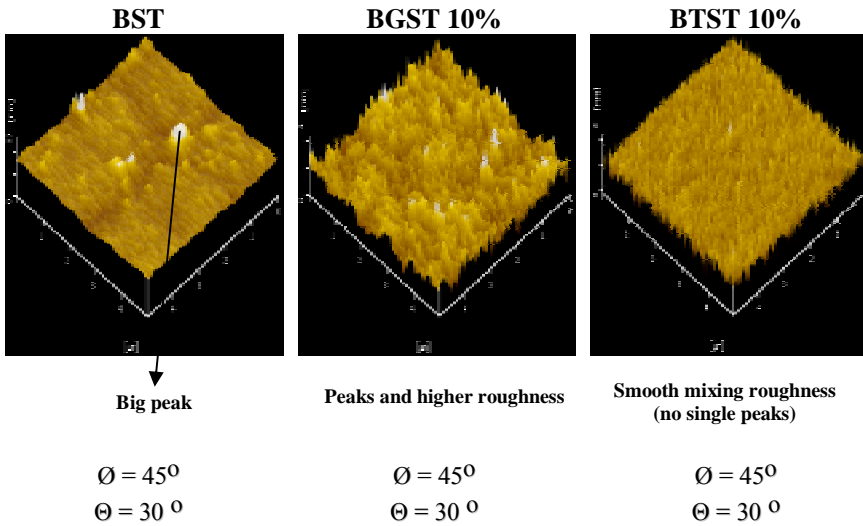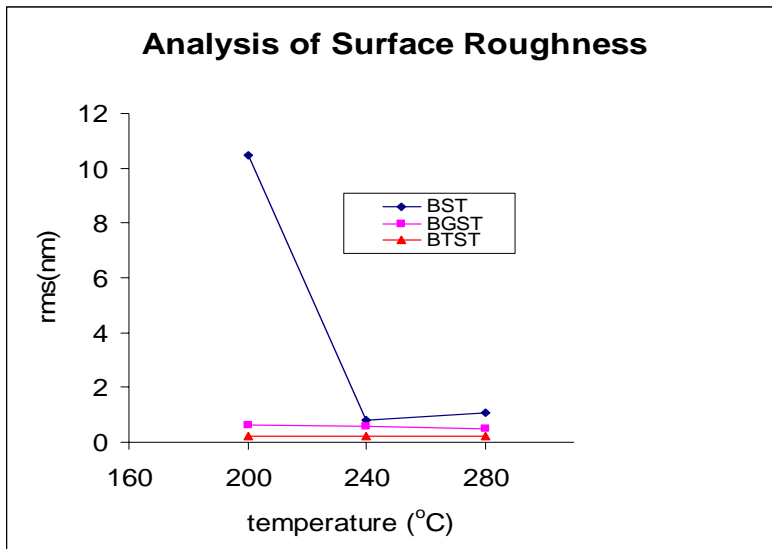$\Theta = 30°$ $\Theta = 30°$ $\Theta = 30°$

Figure 9. The 3 dimension analysis using AFM method at 280°C of 5000 nm x 5000 nm area for BST, BGST, BTST thin films.

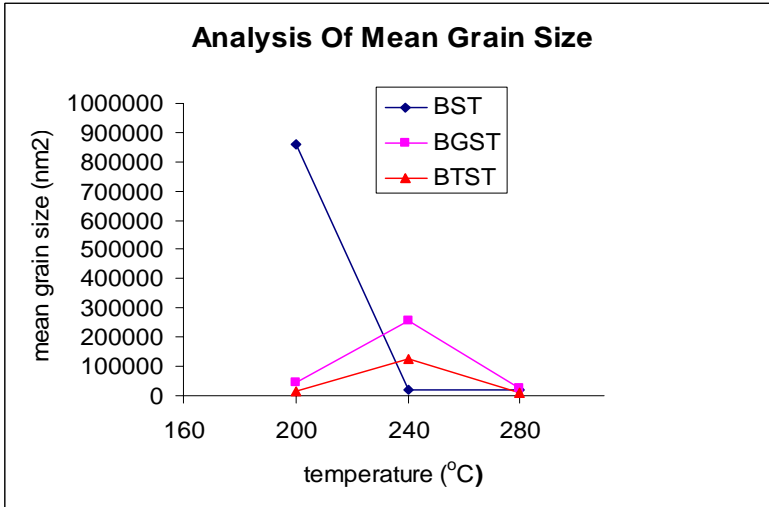Figure 10. Graph of surface roughness varying annealing temperature.

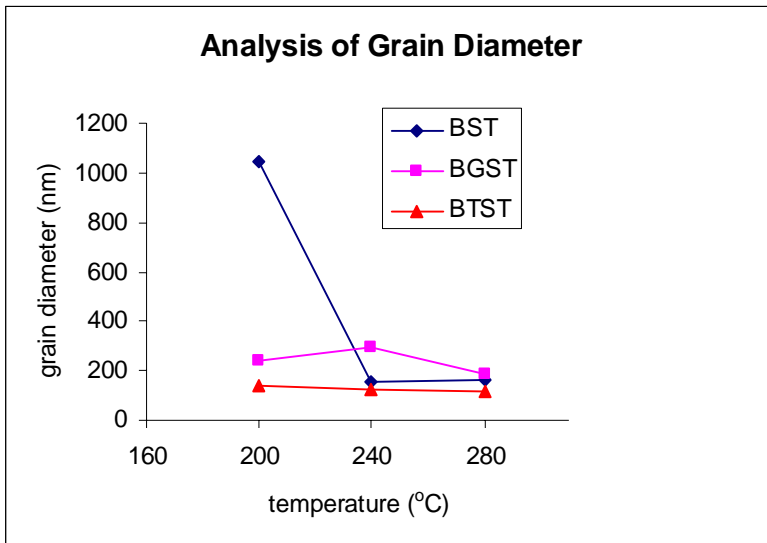Figure 11. Graph of mean grain size varying annealing temperature.

Figure 12. Graph of grain diameter varying annealing temperature.

In ferroelectric fenomenon, acceptor doping gallium oxide doped barium strontium titanate is more likely very effective for generating movable dipoles and domain pinning, since the oxygen ions are still movable even below the Curie temperature (e.g. at room temperature), because the oxygen and vacancy adjacent (only 2.8 Å) and hopping easily occurs, on the other hand donor doping tantalum oxide doped barium strontium titanate is not more likely very effective for generating movable dipoles and domain pinning, since the Ba ion or Sr ion cannot easily hop to an adjacent A-site vacancy due to the close oxygen (O) surroundings [22].

CONCLUSION

We have investigated the annealing temperature of BST, BGST and BTST thin films deposited by the chemical solution deposition (CSD) method with spinning speed at 3000 rpm for 30 seconds. The post annealing at $200^{o}C$, $240^{o}C$, $280^{o}C$ for 1 hour were carried out to each deposited film. In fact, to increase annealing temperature from $200^{o}C$ to $280^{o}C$ would result in decreasing the rms roughness and grain size. Therefore, rms roughness and grain size would have the strong correlation annealing temperature.

ACKNOWLEDGEMENTS

REFERENCES

1. B.A. BAUMERT, L.H. CHANG, A.T. MATSUDA and C.J. TRACY., *J. Mater. Res.,* **13** (1) 197 (1998).

2. F. WANG, A. UUSIMAKI, S. LEPPAVUORI, S.F. KARMANENKO, A.I. DEDYK, V.I. SAKHAROV, I.T. SERENKOV., *J. Mater. Res.,* **13** (5) 1243 (1998).

3. J.G. CHENG, J.TANG, J.H. CHU, A.J. ZHANG., *Appl. Phys. Lett.,* **77,** (7) (2000) 1035.

4. M.A. ITSKOVSKY., *Jpn. J. Appl. Phys.,* **38** (8) 4812 (1999).

5. E.S. CHOI, J.C. LEE, J.S. HWANG, S.G. YOON., *Jpn. J. Appl. Phys.,* **38** (9B) 5317 (1999).

6.   Y. GAO, S. HE, M. ENGELHARD, A.S. LEA, J. FINDER, B. MELNICK, R.L. HANCE., *J. Appl. Phys.,* **87** (1) 124 (2000).

7.   S. MOMOSE, T. NAKAMURA, K. TACHIBANA. *Jpn. J. Appl. Phys.,* **39** (9B) 5384 (2000).

8.   M. IZUHA, K. ADE, M. KOIKE, S. TAKENO, N. FUKUSHIMA., *Appl. Phys. Lett.,* **70** (11) 1405 (1997).

9.   T. KAWAKUBO, K. ABE, S. KOMATSU, K. SANO, N. YANASE, H. MOCHIZUKI., *IEEE Electron Device Letters,* **18** (11) 529 (1997).

10. S.Y. CHA, B.T. JANG, H.C. LEE., *Jpn. J. Appl. Phys.,* **38** (1A) L49 (1999).

11. B.T. LEE, W.D. KIM, K.H. LEE, H.J. LIM., *Journal of Electronic Materials,* **28** (4) L9 (1999).

12. J.C. SHIN, J. PARK, C.S. HWANG, H.J. KIM. *J. Appl. Phys.,* **86** (1) 506 (1999).

13. J.S. LEE, J.S. PARK, J.S. KIM, J.H. LEE, Y.H. LEE, S.R. HAHN., *Jpn. J. Appl. Phys.,* **38** (5B) L574 (1999).

14. S. KIM, T.S. KANG, J.H. JE., *J. Mater. Res.,* **14** (7) 2905 (1999).

15. I. RATERA, J. CHEN1, A MURPHY, D.F. OGLETREE1, J.M.J. FR´ECHET and M. SALMERON., *Nanotechnology*, **16,** S235 (2005).

16. D. DIETZEL, M. FAUCHER, A. IAIA, J. PAIM´E, S. MARSAUDON, A. M. BONNOT, V. BOUCHIAT AND G. COUTURIER.,. *Nanotechnology*, **16,** S73 (2005).

17. B.A. LONG, S.H.U. JIAN, S.U.N. PING, L.U. ZU-HONG., *Chin. Phys. Lett.*, **20** (4) 465 (2003).

18. N.S. TAMBE and B. BHUSHAN., *J. Phys. D: Appl. Phys.*, **38,** 764–773 (2005).

19. M. ABE, Y. SUGIMOTO, O. CUSTANCE and SEIZO MORITA., *Nanotechnology,* **16,** 3029–3034 (2005).

20. A.W. SPARKS and S.R. MANALIS., *Nanotechnology* **17,** 1574–1579 (2006).

21. P.D. SAWANT, and D V NICOLAU., *Smart Mater. Struct*. **15**, S99–S103 (2006).

22. K. UCHINO., :"Ferroelectric Devices", Marcel Dekker, Inc. New York, 131 (2000).