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The effect of spin coating rate on the microstructure, grain size, surface roughness and thickness of $Ba_{0.6}Sr_{0.4}TiO_3$ thin film prepared by the sol-gel process

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The paper reports on the effect of spin coating rate during the sol-gel process on the microstructure, grain size, surface roughness and thickness of barium strontium titanate ($Ba_{0.6}Sr_{0.4}TiO_3$) thin films. Variable coating rates do not influence the microstructure of the films. All films are polycrystalline and single phase, as was found from X-ray diffraction analysis. Changing the spin rates also does not influence the grain sizes of the films. All films have nanometer particle size ranging from 37.2 nm to 30.7 nm. However, roughness and thickness of the film depend on the spin coating rates. The highest spin rates produce the thinnest film with the roughest surface, while the lowest spin rate produced the thickest films with the smoothest surface.

Key words: *barium strontium titanate; sol-gel method; spin coating*

1. Introduction

The sol-gel process allows one to synthesize ceramic materials of high purity and homogeneity. The sol is made of solid particles of diameter of few hundred nm suspended in a liquid phase. Then the particles are condensed in a new phase (gel), in which the solid macromolecule is immersed in a liquid phase (solvent) [1].

$Ba_{1-x}Sr_xTiO_3$ (BST) is currently one of the most interesting ferroelectric materials due to its high dielectric constant and the composition-dependent Curie temperature. The dielectric and ferroelectric properties of the sol-gel derived BST thin films are strongly dependent on the Sr content and the grain size [2]. At room temperature BST is ferroelectric when the Ba content x does not exceed 0.3 and paraelectric when it is in the range $0.3 > x > 1$ [3]. Ferroelectric BST thin films have been widely investigated as potential materials for application in microelectronic devices such as dynamic

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random access memories, infrared detectors, microwave devices, and hydrogen gas sensors [4–7]. In particular, dielectric nonlinearity is one of the most important factors for tunable microwave applications. It is found that tenabilities depend on the microstructures of the thin films, such as the phase, grain size, composition, defects, strain, etc. [8]. BST thin films have been prepared by various methods, such as radio-frequency (r-f) sputtering, ion-beam sputtering, laser ablation, metal-organic chemical, vapour deposition and sol-gel technique. However, sol-gel processing has advantages over other methods in homogeneity, cost, and process control [9, 10].

In this work, $Ba_{0.6}$ $Sr_{0.4}$ TiO_3 thin films have been prepared using the sol-gel method. The as-prepared films were annealed at 700 ºC in order to crystallize the films. The effect of different spin coating rates on the microstructure, grain size, surface roughness and thickness of the film was investigated.

2. Experimental

Barium acetate $Ba(CH_3CO_2)_2$, strontium acetate $Sr(CH_3CO_2)_2$ and titanium(IV) isopropyloxide, $(Ti(OCH(CH_3)_2)_4)$ 99.999% were used as starting materials for the synthesis of precursors for BST thin films. Barium acetate (0.6 mole) and strontium acetate (0.4 mole) were first dissolved in acetic acid containing 20 vol. % of deionized water at room temperature. A clear and transparent solution was obtained. Titanium(IV) isopropyloxide was then added to this solution. In order to improve the stability of the solution, a few drops of acetylacetone were added to the solution precursor during constant stirring. A transparent yellowish solution formed at room temperature. Using a spin coater, the solution was transformed into thin film form. Silicon (boron p-type with impedances 16–24 Ω·cm (625 μm thick) wafers were used as substrates. The coating rates were 3000, 3500 and 4000 r.p.m (hereinafter, the samples will be denoted as A, B and C films, respectively) and the coating time was 30 s for all films. The films were dried at 150 ºC in air for 15 min to evaporate the solvent and heated at 350 ºC in air for 15 min to burn off residual organics. This would form an SiO_2 layer on the substrate surface. Previous papers indicated that BST thin films annealed at temperatures lower than 600 ºC had an amorphous nature, the films annealed at 600 ºC showed inferior crystallinity, suggesting an incomplete perovskite phase formation [11], while those annealed at 700 ºC crystallized [6, 12, 13]. Hence all the investigated films were annealed at 700 ºC for 60 min in oxygen atmosphere. Figure 1 shows the flow chart of the preparation procedure.

The microstructure and grain size of the films were studied using X-ray diffractometer (XRD) model D-5000 Siemens and scanning electron microscope (SEM) model LEO VPSEM 1450, respectively. The surface roughness and thickness of the films were studied using atomic force microscopy (AFM) Burleigh personal model ARIS 3300 and Ellipsometer Rudolf model Auto E1-111, respectively.

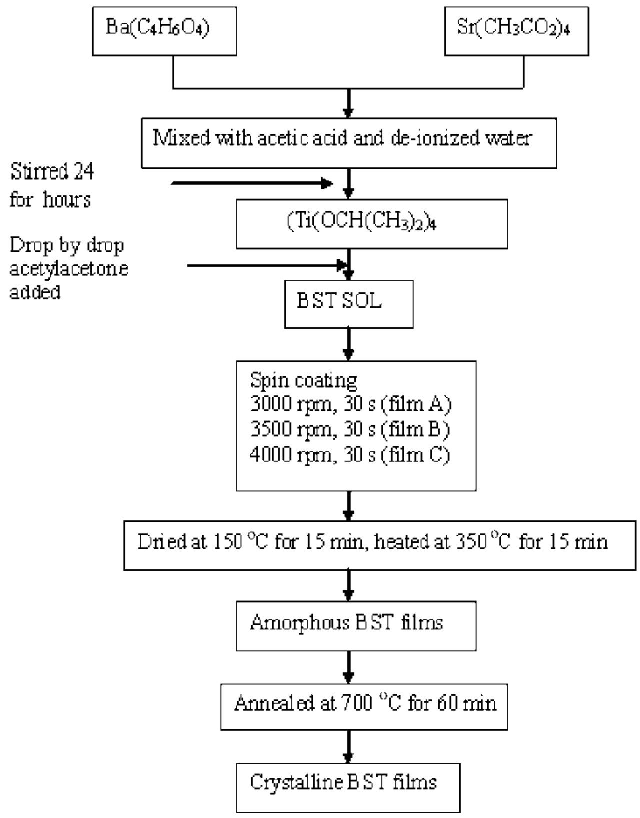


Fig. 1. Flow chart of the procedure of the film preparation

3. Results and discussion

Figure 2 shows the XRD spectra of a bare silicon wafer (a), a silicon wafer with SiO_2 layer produced by heating at 350 ºC (b), and films prepared at various spin coating rates (c–d). After annealing, the intensities of the diffracted peaks further increased showing an increase in the crystallinities of the films. However, different coating rates do not influence the microstructure of the films. The structure was found to be cubic with the lattice constant a = 3.965 Å.

Figure 3 shows the surface morphologies of the films obtained using the AFM. The scan area was 3500 nm×3500 nm. The root mean square (RMS) roughness was 7.85, 15.21 and 23.65 nm for films A, B and C, respectively. This shows that the RMS roughness increased as the spin coating rate increased. Yang et al. [14] and Shim et al. [15] have also reported that the RMS roughness increased as the film thickness decreased.

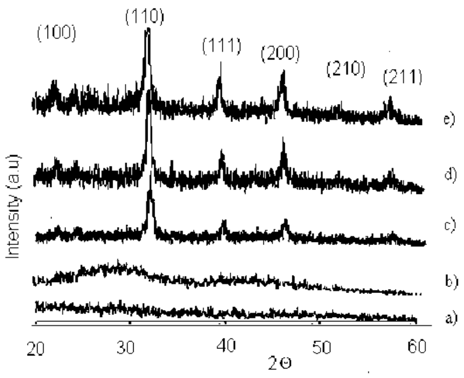


Fig. 2. The XRD patterns of: a) bare silicon wafer, b) silicon wafer with SiO_2 layer on its surface, c) film A, d) film B, e) film C

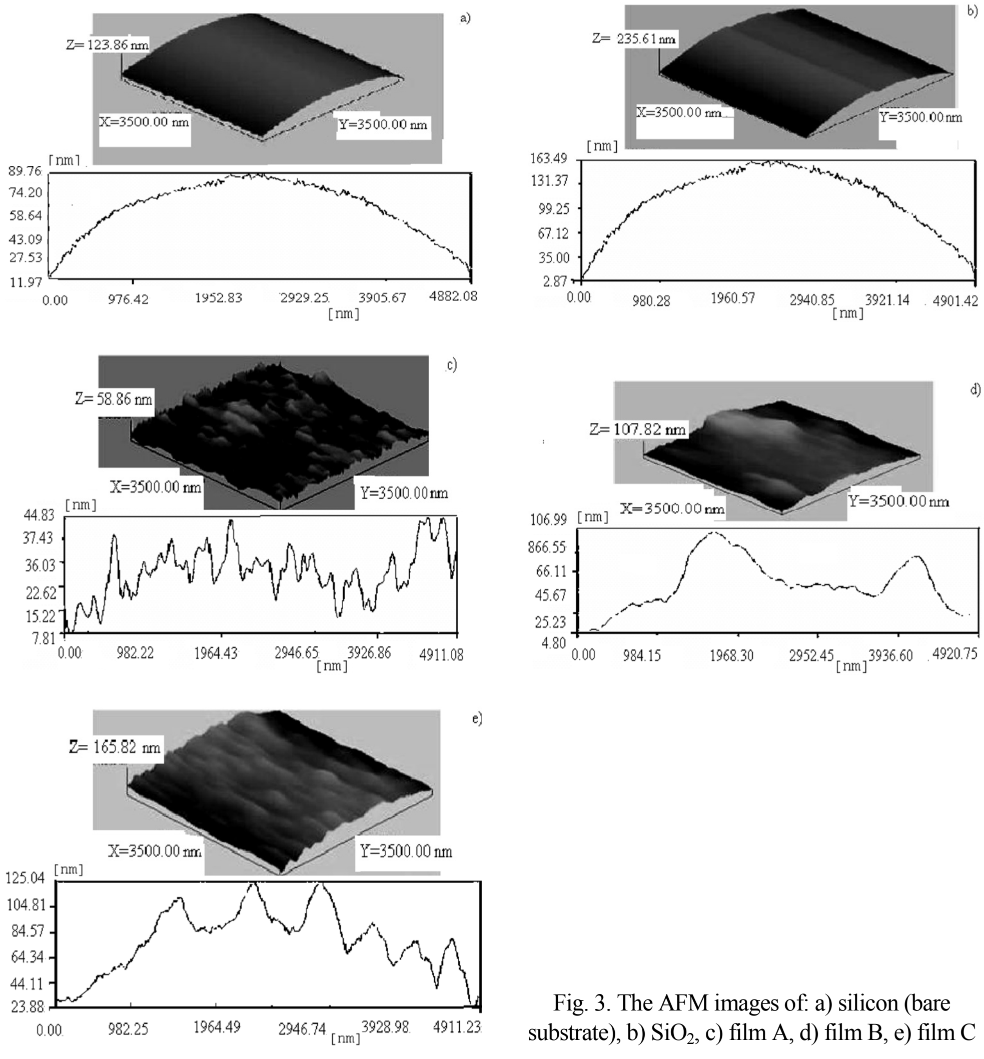
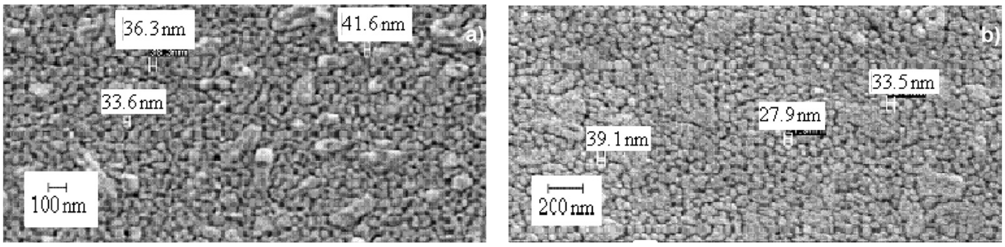


Fig. 3. The AFM images of: a) silicon (bare substrate), b) SiO_2, c) film A, d) film B, e) film C

Figure 4 shows SEM images of all films. The images indicated that the films were in orderly form, fine and homogeneous. The average grain sizes were approximately 37.2 nm for film A, 33.5 nm for film B, and 30.7 nm for film C. All of the films have nanometer size particles and, in general, changing the spin rates does not influence the grain size of the films. The larger particles that can be seen in the micrographs are actually clusters of small particles. Heywang and Thoman (1991) have also reported similar combination of small particles due to high annealing process [16].



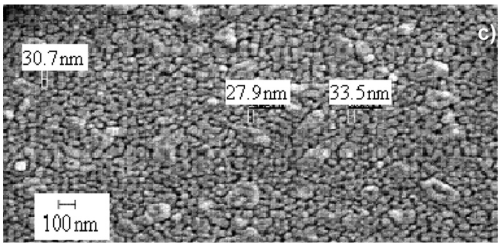


Fig. 4. SEM micrograph of BST thin films showing the nano-grain structure of: a) film A, b) film B, c) film C

The average thicknesses of the films measured using the ellipsometer are 153.5 nm, 96.02 nm and 80.39 nm, for spinning rates of 3000, 3500, and 4000 r.p.m., respectively. The film thickness versus spinning speed is plotted in Fig. 5. As appears in the figure, the higher the spinning speed, the thinner the film. This shows that increasing the spinning speed decreased the film thickness. The relation between film thickness, h, and spin rate, ω, obeys the power law relation of the form $h \propto \omega^{-3/2}$ [1].

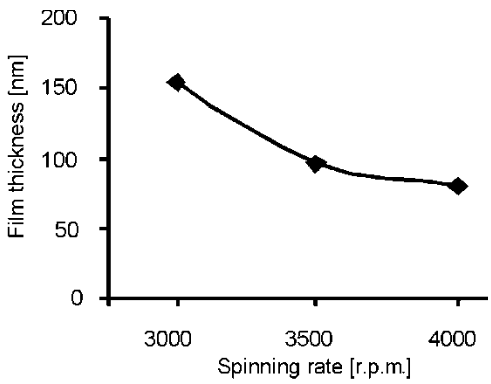


Fig. 5. Film thickness as a function of spinning rate

4. Conclusions

The effects of spin coating rates on the microstructure, grain size, surface roughness and thickness of $Ba_{0.6}Sr_{0.4}TiO_3$ sol-gel films have been investigated. The microstructure and grain sizes of the films are not affected by the coating rates. However, they do influence the roughness and thickness of the film. The highest spin rates produced the thinnest films with the roughest surfaces, while the lowest spin rates produced the thickest films with the smoothest surfaces.

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References

[1] BRINKER C.J., SCHERER G.W., *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York,1990.
[2] ADIKARY S.U., CHAN H.L.W., Thin Solid Films., 424 (2003), 70.
[3] MAJED S.M., NAIK R., J. Mater. Res., 10 (1996), 2588.
[4] CHENG J.G., MENG X.J., TANG I., GUO S.L., CHU J.H., Appl. Phys. A., 70 (2000), 411.
[5] YANG X., YAO X., ZHANG L., J. Ceram. Inter., 30 (2004), 1525.
[6] ZHANG T.J., NI H., J. Mater. Sci., 37 (2002), 4155.
[7] ZHU W., TAN O.K., DING J., J. Mater.Res., 15 (2000), 1291.
[8] FU C., YANG C., CHEN H., HU L., WANG Y., J. Mater. Lett., 59 (2005), 330.
[9] TSUZUKI A., KATO K., KUSUMOTO K.,TORH Y., J. Mater. Sci.,33 (1998), 3055.
[10] WU D., LI A., LING H., YIN X., GE C., WANG M., MING N., J. Appl. Surface Sci., 165 (2000), 309.
[11] HU W., YANG C., ZHANG W., QIU Y., J. Sol-Gel Sci. Tech., 36 (2005), 249.
[12] PAIK D.S., RAO A.V.P., KOMARNENI S., J. Sol-Gel Sci. Tech.,10 (1997), 213.
[13] ZHU H., MIAO J., NODA M., OKUYAMA M., Sensors Act. A, 110 (2004), 371.
[14] YANG.W., LAMBETH D.E., TANG.L., LAUGHLIN D.N., J. Appl. Phys., 81 (1997), 4370.
[15] SHIM J.B., YOSHIMOTO N., YOSHIZAWA M., YOON D.H., J. Cryst. Res. Technol., 36 (2001), 1209.
[16] HEYWANGW., THOMAN H., *Positive temperature coefficient resistors*, [in:] B.C.H. Steele (Ed.), *Electronic Ceramics*, Elsevier, London, 1991, p. 29.

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