Surface Morphological, Topological and Crystallinity Characteristics of Sputtered Barium Strontium Titanate Thin Films on Sapphire Substrates

F.W. Jamaluddin, M. F. Abdul Khalid, M.K.A. Mahmood, M. H. Mamat and A.S.Zoolfakar

***Abstract* — This paper presents the material characterization of barium strontium titanate ($Ba_{0.5}Sr_{0.5}TiO_3$) thin films grown on sapphire substrates. The films were deposited by radio frequency (RF) magnetron sputtering system for 2, 3 and 4 hours on sapphire substrates, achieving film thicknesses of approximately 124 nm, 350 nm and 586 nm respectively. These BST thin films were post-annealed for 2 hours at 900 ºC and then characterized using several analytical techniques including x-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and energy dispersive x-ray (EDX). AFM analysis shows that longer deposition time produces rougher surface due to larger grain size formation. The XRD patterns observed have intense (110) peaks, indicating the preferred orientation of the BST thin films. From the FESEM results, it is observed that the 3-hour deposited sample is dense and uniform compared to the 2-hour deposited sample. However, the 4-hour deposited sample shows a non-uniform film. EDX analysis shows that the composition element of 4-hour deposited sample is the closest to the ideal atomic concentration (at. %) of the BST thin film.**

***Keywords* — RF sputtering, annealing, BST thin film**

I. INTRODUCTION

Over the past few years, ferroelectric materials have been widely considered for advance technology development notably in tunable microwave devices such as phase shifter, oscillators and tunable filter [1]. One of the ferroelectric materials that has attracted immense interests is barium strontium titanate (BST). This is due to their wide variety of applications in electronics technology [2].

At room temperature, BST has high dielectric permittivity, low loss and low leakage current at microwave frequencies[3]. Furthermore, BST films have high power handling capabilities and high tuning speed that makes them very interesting to be used as matching networks[4].

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The rapid development of the BST thin films is due to the demand of lighter weight, small size and low cost tunable circuits[5]. The dielectric properties of BST are mainly dependent on their material compositions, deposition methods, and deposition parameters[4].

Therefore, it is crucial to study the material characteristics of the BST thin films deposited at different deposition conditions for device optimization.

Based on previous studies, the film thickness is one of the considering factors that affect the mechanisms of formation of a film on a substrate which, in turn, determines important structural characteristics, such as the phase composition, crystallite sizes, surface morphology of the film, and quality of transition layers. It is shown that by appropriate selection of film thickness, a high tunability BST thin film varactor can be achieved [6-8].

There are several reviews covering different areas of BST and their material characteristics. In [9], the study was about the effects of both deposition and annealing temperature on the structural properties of BST thin films. The BST films studied in this work were prepared by radio frequency (RF) magnetron sputtering. The film thickness was ~300 nm with tunability, K=2. The deposition was performed on a sapphire substrate (r-cut) with bottom platinum (Pt) electrode. The deposition temperature was increased from 600 to 880 ºC. The results showed that the annealing temperature, being higher than the deposition temperature directly affected the structural properties such as the phase and component compositions of the films.

Recently, there is a study on the effect of working gas pressure on the BST thin films deposited via pulsed laser deposition (PLD) system on magnesium oxide (MgO) substrate [4]. The lower oxygen working pressure (1×10^{-4} mbar) deposited films showed improved crystallinity. The study conducted led to gaining better tunability of 16.5% at 1 GHz in the $Ba_{0.5}Sr_{0.5}TiO_3$ films.

There are some difficulties to access and correlate material properties as most studies on BST that have been reported earlier only focused on determining a single physical property, either on the structural, optical or electrical properties. The measurements of this ferroelectrics thin film properties could be challenging and costly due to their electromechanical properties that change significantly under applied DC bias field

[10-11]. The researchers in [11] studied the impact of deposition pressure, partial oxygen flow, and post-deposition annealing on the film microstructure, surface morphology, refractive index, and dielectric constant of BST films that were deposited at room temperature using RF magnetron sputtering technique. Detailed analysis reported that post-deposition annealing improved crystallinity and the annealed films showed cubic perovskite phase with no sub-phase formation. The electrical dielectric constant and tunability of film increased with deposition pressure upon annealing. Dielectric constant will generally increase with thickness whereas thin films with less than 200 nm thickness are favourable for microwave tunable devices [11].

There was a different sputtering technique used by researchers in [12] where they reported that the structural, dielectric and ferroelectric properties of BST film capacitors that were fabricated using spin-coating technique on platinum/silicon (Pt/Si) substrate and lanthanum nickel oxide buffer layer (LNO/Si) substrates showed dense polycrystalline BST thin films formed without apparent defects or secondary phases. The dielectric constants of BST thin films on both substrates had good frequency stability. The polarisation-electric field (*P-E)* loops and energy storage performance of both films were similar. The dielectric loss at 1 kHz of both films was also very low, <5 %. These properties indicated that BST/LNO thin film can be applied as a cost-effective and environment-friendly capacitor in hybrid/electric vehicles and power supplies [12].

As pointed out earlier, understanding the relationships between the structural characteristics and the electrical properties of deposited BST thin films are important for their extensive use in microwave devices.

Therefore, in this work, the phase and component composition as well as the structural properties of BST were studied under different deposition time to determine the optimum conditions of the material characteristics for microwave applications.

II. Experimental Details

In the preparation of the samples, a 2-inch c-plane sapphire wafer was diced into 2×2 cm^2 substrates and later rinsing them thoroughly with acetone, isopropyl alcohol IPA or methanol and deionized (DI) water. Then, a nitrogen gun was used to blow-dry the samples. To ensure the samples were cleaned and unwanted particles removed, they were checked under a high magnification microscope. Then, the samples were kept in a dry cabinet to prepare for thin film deposition.

In this paper, BST thin films were deposited on 0.43 mm thick sapphire substrates by RF magnetron sputtering system (ULVAC MUE-ECO-C) in an ultrahigh vacuum (UHV) chamber. A stoichiometric 100 mm $Ba_{0.5}Sr_{0.5}TiO_3$ target (purchased from Kurt J Lesker) was used. The distance between the target and substrate was maintained at 70 mm. The deposition parameters such as RF power of 200 W and substrate temperature of 400 ºC were fixed accordingly. The deposition time was varied for 2, 3 and 4 hours. Deposition pressure was set at 5 mTorr, while 100 % Argon was used during the deposition [13-14]**.**

The samples were subsequently annealed in air at 900 ºC for 2 hours [6]. The structural characterization of the thin films was performed by Panalytical X'Pert PRO x-ray diffraction (XRD) and the Fei Quanta FEG 450 field emission scanning electron (FESEM) was used to characterize the morphology of the films. The surface topology of BST was analysed using Park XE-100 atomic force microscopy (AFM) whilst the composition of the film was investigated by using energy dispersive xray (EDX) Zeiss Supra 40 VP.

III. Results and Discussions

A. Surface Topology using AFM

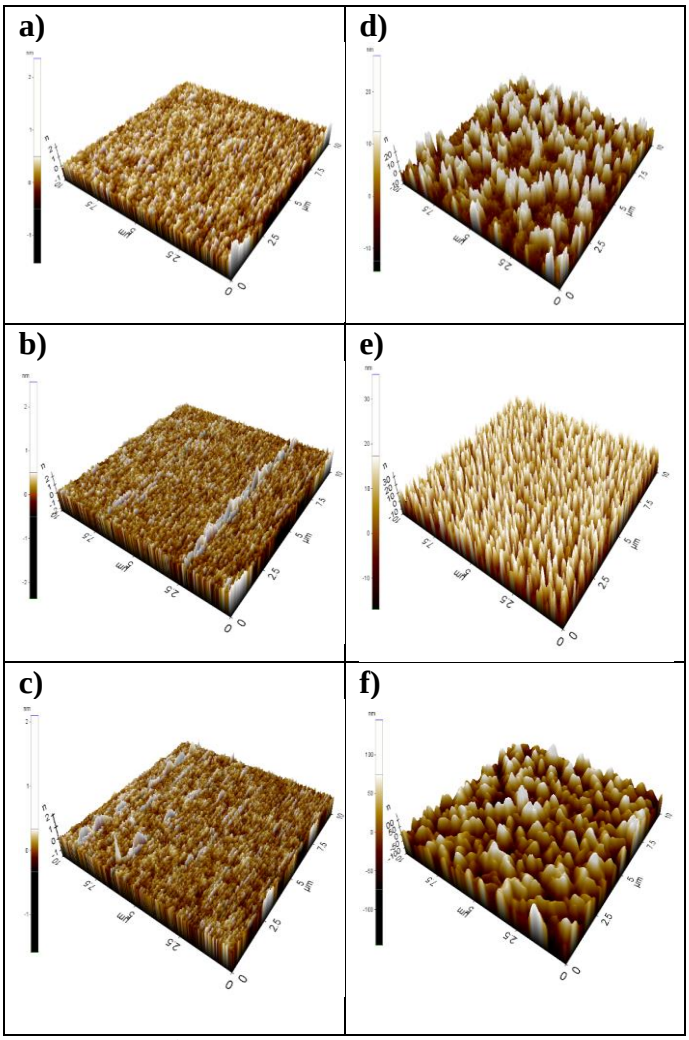

Fig 1. AFM analysis for as-deposited and annealed samples at 2-hour, 3-hour, and 4-hour deposition time. All as deposited thin films (a-c) show smooth surface morphology while deposited thin films (d-f) show rougher surfaces.

The microstructure of BST thin films was investigated using topographic images obtained by AFM in contact mode [15]**.** The surface roughness and grain size of the grown BST

thin films can be analyzed via this method. Fig.1(a-f) show three-dimensional AFM images of the 2-, 3- and 4-hour as-deposited and annealed samples respectively. The surface roughness measured by the root-mean-square (RMS) of the films were achieved at 6.306 nm, 8.806 nm and 37.621 nm respectively. The figures revealed that the surface of the 4-hour deposited sample was significantly rougher than the 2- and 3-hour deposited samples.

It is observed that the 3-hour sample exhibited a uniform and dense microstructure compared to the 2-hour and 4-hour sample.

B. Structural Analysis using XRD

XRD spectra analysis was carried out to investigate the phase composition of the BST thin films [16] and the results are displayed in Fig. 2. As-deposited films were found to be initially amorphous without any preferred orientation. As for the annealed samples, all the major peaks at (100), (110) and (111) were observed in all samples indicating cubic perovskite BST phase with no secondary phase formation.

It is shown that the preferred orientation in all BST annealed samples is at (110). With the increment of deposition time, the dominant XRD peaks became intense and sharp indicating improved crystallinity. It was evident that the baseline of 3-hour deposited sample was reduced and the peaks were more resolved, symmetrical and not as broad. After further investigation, the unknown peak (x) at ~ 26 degrees of angle as depicted in the 4-hour annealed sample is learned to be α-Al_2O_3. As there are no impurities existed, the peak is believed to be indexed at Al_2O_3 (sapphire) which is the substrate of the film. [17-18]

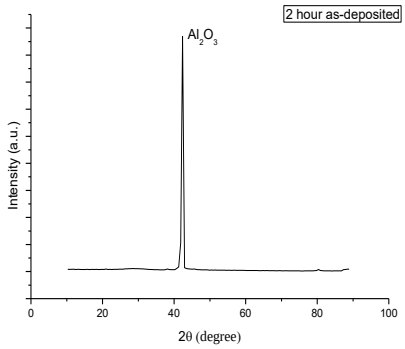

Fig. 2(a). XRD pattern of 2-hour as-deposited sample.

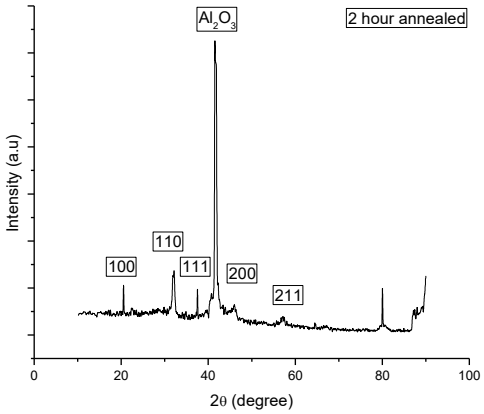

Fig. 2(b). XRD pattern of 2-hour annealed sample.

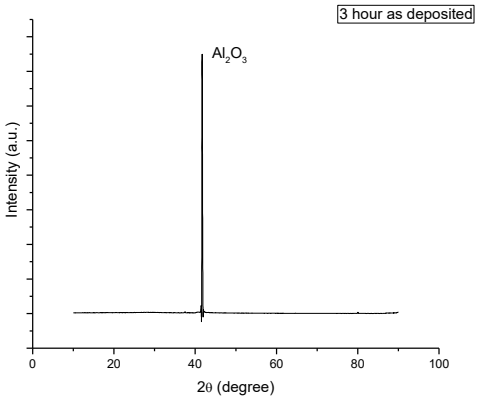

Fig. 2(c). XRD pattern of 3-hour as-deposited sample.

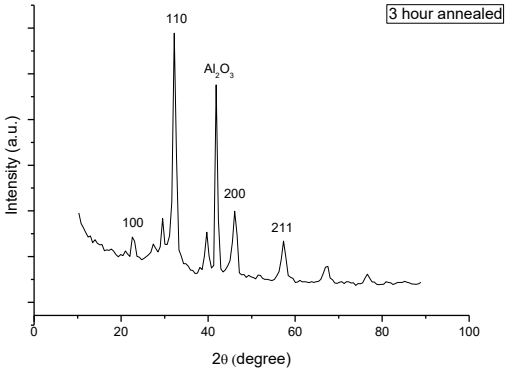

Fig. 2(d). XRD pattern of 3-hour annealed sample.

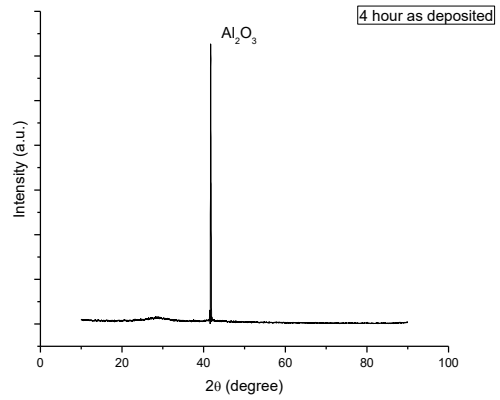

Fig. 2(e). XRD pattern of 4-hour as-deposited sample.

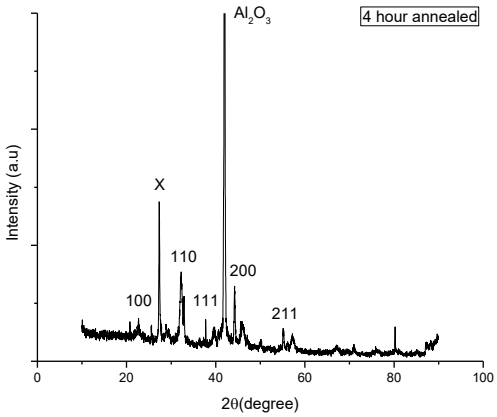

Fig. 2(f). XRD pattern of 4-hour annealed sample.

C. Surface morphology analysis using FESEM

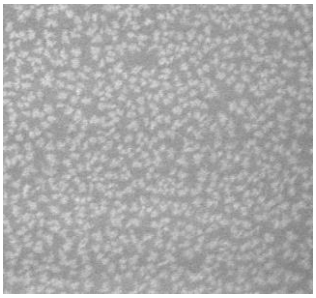

Fig. 3(a). FESEM image of 2-hour deposited sample.

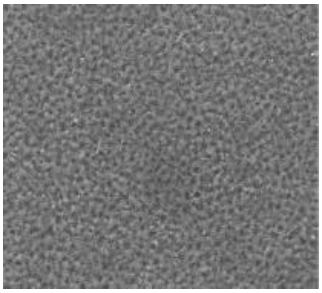

Fig.3(b). FESEM image of 3-hour deposited sample.

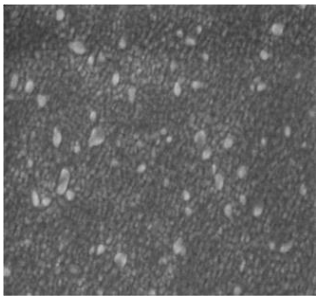

Fig. 3(c). FESEM image of 4-hour deposited sample.

The FESEM images of the annealed BST thin films deposited at different deposition time are shown in Fig. 3. The as-deposited sample is known to be amorphous from the XRD results. The surface morphology of the film for the 2-hour deposition duration had a porous surface with the particles resembled snow flake-shapes. The 3-hour deposited sample was clearly dense, uniform and slightly increased in grain size. It can be observed that the film had granular microstructure consisting of a network of tightly coupled grain leading to a polycrystalline surface. For the 4-hour deposition sample, it can be seen that the film contains some agglomerates and non-uniform areas.

D. Composition Elements using EDX

EDX analysis is used to investigate the composition of the BST thin film [19]**.** The results of the three samples are presented in the Fig. 4 and their respective tables. EDX spectra showed the presence of the main elements (Ba, Sr, Ti). The as-deposited sample should be close to the ideal atomic concentration of 10 at. % Ba, 10 at. % Sr, 20 at. % Ti and 60 at. % O [8]**.**

As shown in Fig.4(a) and Fig.(b) along with their tables (Table 1(a) and Table 1(b) , the at. % of Ba, Sr and Ti had slightly increased and the at. % of O had slightly reduced when the deposition time was longer. This suggested that the samples had increased crystallinity due to the annealing process.

However, the sudden increase in at. % of Ba, Sr and Ti and the substantial reduction in at. % of O in Fig. 4(c) suggested the presence of deformations in the crystal structure of the films. This condition was in good agreement with the previously discussed AFM, XRD and FESEM analyses.

BST is naturally perovskite with the ABO_3 structure and A-to-B site ratio is an important predictor of the defect density and quality of the film structure [20] .From calculations based on Table 1(c), the A-to-B ratio of the 4-hour deposited sample had increased from 0.746 (in the 3-hour deposited sample) to 0.858. This slightly increasing trend of ratio suggested that the 4-hour deposited sample had higher dielectric constant (higher tunability) but with higher loss and lower breakdown field strength compared to the 3-hour deposited sample. There have been many studies on varying the compositions which can affect the dielectric properties. The increased in dielectric constant may be the result from the improved crystallinity and denser structure [21-22].

Table 1(a). Composition elements in 2-hour deposited sample

Elements	Weight (%)	Atomic (%)
O K	34.54	71.61
Ti K	22.86	15.83
Sr L	16.57	6.27
Ba L	26.03	6.29
Total	100.00	

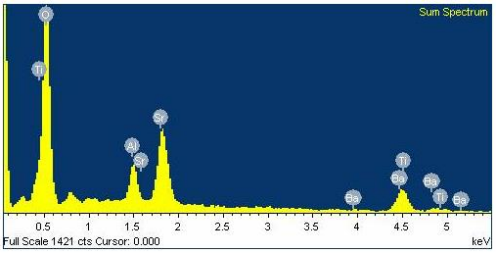

Fig. 4(a).Elements in 2-hour deposited sample.

Table 1(b). Composition elements in 3-hour deposited sample

Elements	Weight (%)	Atomic (%)
O K	31.83	68.78
Ti K	24.77	17.88
Sr L	16.90	6.67
Ba L	26.51	6.67
Total	100.00	

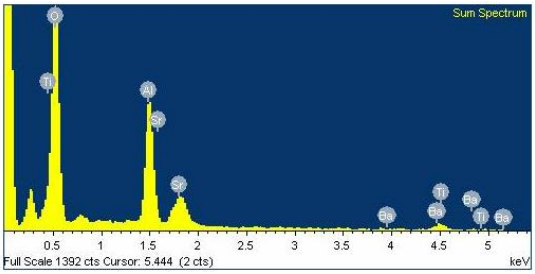

Fig. 4(b). Elements in 3-hour deposited sample.

Table 1(c). Composition elements in 4-hour deposited sample

Elements	Weight (%)	Atomic (%)
O K	30.83	58.11
Ti K	24.65	22.40
Sr L	16.92	9.32
Ba L	27.60	9.90
Total	100.00	

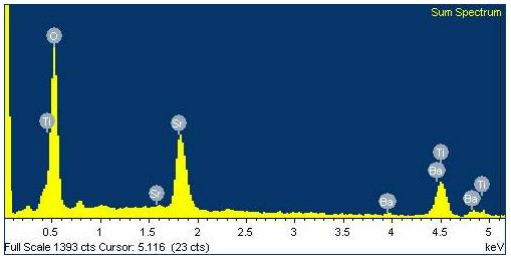

Fig. 4(c). Elements in 4-hour deposited sample

IV. Conclusion

In summary, $Ba_{0.5}Sr_{0.5}TiO_3$ thin films were successfully deposited using RF magnetron sputtering at various deposition times ranging from 2 to 4 hours and their properties were studied. AFM results had shown that larger grain size formation was due to the longer deposition time. It was also found that the BST phase was intensified due to the augmentation of deposition time and all samples showed a preferred (110) orientation. FESEM image appeared to be amorphous in the as-deposited sample and as the deposition time increased, dense and uniform images were observed. The slightly increased ratio in EDX result suggested that the 4-hour deposited sample may have higher dielectric constant but with higher loss. The results indicated that the deposition time may have a strong influence on the material characteristics of BST thin films.

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REFERENCES

[1] M. W. Cole, E.Ngo, C.Hubbard, S.G.Hirsch, M.Ivill, W.L.Sarney *et al* "Enhanced dielectric properties from barium strontium titanate films with strontium titanate buffer layers," vol. 164107, pp. 1–10, 2013.

[2] J. Iskandar, H. Syafutra, J. Juansah, and Irzaman, "Characterizations of Electrical and Optical Properties on Ferroelectric Photodiode of Barium Strontium Titanate (Ba0.5Sr0.5TiO3) Films Based on the Annealing Time Differences and its Development as Light Sensor on Satellite Technology," *Procedia Environ. Sci.*, vol. 24, pp. 324–328, 2015.

[3] H. Yue, D. Brown, G. Subramanyam, K. Leedy, and C. Cerny, "Thin film Barium-Strontium-Titanate Parallel-Plate varactors integrated on low-resistivity silicon and saphhire substrate," *2013 Jt. IEEE Int. Symp. Appl. Ferroelectr. Work. Piezoresponse Force Microsc. ISAF/PFM 2013*, pp. 291–294, 2013.

[4] A. Joseph, "Effect of crystallinity on microwave tunability of pulsed laser deposited Ba0 . 5Sr0 . 5TiO3 thin films," *Thin Solid Films*, vol. 626, no. July, pp. 126–130, 2017.

[5] G. Subramanyam, M.W.Cole, Nian X.Sun, Thottam S. Kalkur, *et al* " Challenges and opportunities for multi-functional oxide thin films for voltage tunable radio frequency," *J. Appl. Phys.*, vol. 114, p. 191301, 2013.

[6] M. Farid A. Khalid, "Investigation of Large-Signal Performance on BST Thin Film Varactors for Microwave Device Applications Investigation of Large-Signal Performance on BST Thin Film Varactors for Microwave Device Applications," 2014.

[7] M. Farid A. Khalid, J. R. Scott, A. S. Holland, and K. Ghorbani, "Progress In Electromagnetics Research C, Vol. 44, 225–238, 2013," vol. 44, no. September, pp. 225–238, 2013.

[8] M. F. Abdul Khalid, A. S. Holland and K. Ghorbani, " Influence of Post Annealing on the Performance of BST Thin Film Varactors," in *Proceeding of Asia Pacific Microwave Conference 2014, 2014.*

[9] A. V. Tumarkin, A. A. Odinets, A. G. Gagarin, A. G. Altynnikov, E. N. Sapego, and O. G. Vendik, "Microwave and structural properties of barium strontium titanate films grown under different technological conditions," in *Proceedings of the 2016 IEEE North West Russia Section Young Researchers in Electrical and Electronic Engineering Conference, EIConRusNW 2016*, 2016.

[10] V. B. Shirokov, V. V Kalinchuk, and P. E. Timoshenko, "Electric- fi eld-dependent mechanical and electrical properties of barium strontium titanate fi lms for tunable device applications," Thin Solid Films, vol. 657, no. October 2017, pp. 8–15, 2018.

[11] T. Bayrak, C. Ozgit-Akgun, and E. Goldenberg, "Structural, optical and electrical characteristics BaSrTiOxthin films: Effect of deposition pressure and annealing," J. Non. Cryst. Solids, vol. 475, no. September, pp. 76–84, 2017

[12] C. Diao, H. Liu, H. Hao, M. Cao, and Z. Yao, "Structure , dielectric properties and energy storage performance of barium strontium titanate thin films prepared by spin-coating technique," pp. 3–6, 2016.

[13] F. W. Jamaluddin *et al.*, "Characterization of Barium Strontium Titanate Thin Films on Sapphire Substrate Prepared via RF Magnetron Sputtering System," vol. 020065, 2018.

[14] F. W. Jamaluddin, M. F. Khalid, and S. Alam, "The Effect of Deposition Time on Sputtered Barium Strontium Titanate Thin Films," no. Micc, pp. 28–30, 2017.

[15] M. Raposo, Q. Ferreira, and P. A. Ribeiro, "A Guide for Atomic Force Microscopy Analysis of Soft- Condensed Matter," pp. 758–769, 2007.

[16] Wagner F."Texture Determination by Using X ray Diffraction," 1999.

[17] R. Prakash, S. Kumar, V. Kumar, R. J. Choudhary, and D. M. Phase, "Optical And X-ray Photoelectron Spectroscopy Studies Of," vol. 050097, pp. 10–13, 2016.

[18] M. P. Nanoparticles, "Highly Dispersed PdNPs/ α -Al 2 O 3 Catalyst for the Selective Hydrogenation of Acetylene Prepared with Monodispersed Pd Nanoparticles," 2017.

[19] J. L. Marshall, "Solderability and Reliability," no. 173, pp. 173–174, 1991.

[20] N. K. Pervez, P. J. Hansen, R. A. York, N. K. Pervez, P. J. Hansen, and R. A. York, "High tunability barium strontium titanate thin films for rf circuit applications," vol. 4451, no. 2004, pp. 17–20, 2008.

[21] R. Gupta, V. Gupta, and M. Tomar, "Structural and dielectric properties of PLD grown BST thin fi lms," *Vacuum*, vol. 159, no. September 2018, pp. 69–75, 2019.

[22] L. Gao, Z. Guan, S. Huang, K. Liang, H. Chen, and J. Zhang, "Enhanced dielectric properties of barium strontium titanate thin films by doping modification," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 14, pp. 12821–12839, 2019.