Journal of Engineering and Applied Sciences 12 (14): 3678-3681, 2017
ISSN: 1816-949X

Sol-Gel Processed Barium Strontium Titanate Thin Films for Microelectronic Applications

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Abstract: The sol-gel chemical preparation method has been applied in producing ($Ba_{0.8}Sr_{0.2}TiO_3$) solution. The main precursor materials are barium acetate and strontium acetate powder. Acetic acid also has been used as a solvent while titanium Isopropoxide and 2-Methoxyethanol are applied as stabilizer. Annealing process has been used for crystallization of thin films ceramic material. These thin films sample are characterized using X-ray Diffraction for crystalline structure and atomic force microscopy and scanning electron microscopy for microstructure analysis.

Key words: Sol-gel method, $Ba_{0.8}Sr_{0.2}TiO_3$, thin films analysis, XRD, microstructure analysis

INTRODUCTION

Now a days, material for electronic as well as microelectronic application has been upgraded and improved in order to satisfy the evolution of high performance devices. The needs of increase storage densities for electronic application such as dynamic random access memory DRAM are famously researched. It is significant with the necessity of high dielectric constant capacitors. The common dielectric materials for these applications is $Ba_xSr_{1-x}TiO_3$. If the curie temperature of this material is discussed it is decreasing linearly with increasing the amount of strontium in $BaTiO_3$ lattice. Furthermore, the strontium content in $Ba_xSr_{1-x}TiO_3$ also will affect the ferroelectric/paraelectric transition (Gust *et al*., 2001).

Traditionally, BST is prepared by ceramic method. This method is shown the barium, strontium and also titanium oxide are calcined at high temperature without the use of solvent. Since, ceramic method is not suitable for high performance of ceramic material because of larger grain size and also non-homogeneous (Verma *et al*., 2012). The homogeneity of the solution needs to be considered in order to produce a good quality of the sample as well as thin films.

There are a lot of methods to produce the thin film $Ba_xSr_{1-x}TiO_3$ such as sputtering (Kawano *et al*., 1993; Abe and Komatsu, 1995; Ichinose and Ogiwara, 1995) pulse laser deposition and wet chemical preparation like a metallorganic chemical vapor deposition (Chern *et al*., 1994) solid state and sol-gel. MOCVD method often used pure argon gas deposition process. This gas is quite dangerous and also expensive. Moreover, the deposition

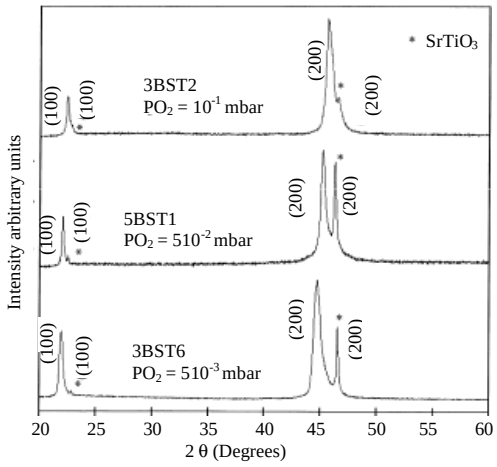

Fig. 1: XRD pattern of pulse laser deposition (Goux *et al*., 2001)

temperature (Fitsilis *et al*., 2001). Figure 1 shows the XRD pattern for the pulsed laser deposition process. From the picture, BST peaks are missing at an angle (101) and (111). This absence peaks indicates that it is highly oriented with (100) peak (Goux *et al*., 2001). Since, PLD is not available in UniMAP there is no possibility to apply this method for current research.

Since, wet chemical preparation is favorable to be applied in UniMAP's laboratory, sol-gel method is chosen. The advantage of sol-gel over other method is low cost of production, better compositional control and also good homogeneity (Czekaj *et al*., 2014). It is also economical because there is no vacuum system applied.

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In this research, the effect of sol-gel method for chemical preparation on microstructure of $Ba_{0.8}Sr_{0.2}TiO_3$ thin film properties is investigated. The crystallization behavior of $Ba_{0.8}Sr_{0.2}TiO_3$ thin films is characterized using X-Ray Diffraction (XRD).

MATERIALS AND METHODS

The sol-gel preparation start by mixing the two main precursor in powder form which are barium acetate and strontium acetate in high purity acetic acid. The amount of barium and strontium acetate is based on the ratio of 80:20. This mixing process uses hotplate to heat the solution at 200°C. The solution is stirred using a mechanical stirrer for 1 h until these two precursor materials is fully dissolved in acetic acid. Then, the Barium strontium solution is refluxed for 1 h and thereafter cooled to room temperature. The next step is mixing titanium (IV) isopropoxide in 2-methoxyetanol for half an hour at room temperature. Then, this solution is dripped into barium strontium solution and stirred for 1 h at 200°C. After that, this solution is refluxed for 1 h until clear and transparent then thereafter cooled to room temperature.

The next step is the sample preparation process which is $Ba_{0.8}Sr_{0.2}TiO_3$ solution is coated on the Pt/Ti/SiO2/Si substrates. A specific amount of this solution is spun onto silicon surface using spinner in order to produce the thin films. Then, the sample is bake using hot plate at 80°C for 20 min. The purpose of this process is to remove the solvent from the film. The coating process is repeated in order to create a multilayer coated thin film. Lastly, samples is annealed at 900°C for 2 h. It is because the crystallization of $Ba_{0.8}Sr_{0.2}TiO_3$ thin films is characterized with X-Ray Diffraction (XRD) while the microstructure are analyzed with Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD): Multilayer coating BST thin films are deposited (or spun on) on Pt/Ti/SiO2/Si substrates. The sample has approximately the thickness about 850 nm. Silicon is the semiconductor material that is widely used as a thin film substrate. However, the titanium layer that has been sputtered on SiO_2 functions as an adhesive layer for platinum. Platinum is used as a bottom metal/electrode since it can withstand the high anneal temperatures (Fig. 2).

Figure 3 shows the XRD patterns for BST thin films. The crystallization of $Ba_xSr_{1-x}TiO_3$ is determined by X-Ray Diffraction (XRD) with CuKa radiation source (λ = 1.54 Å)

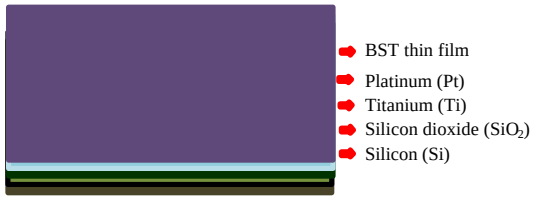

Fig. 2: 3D cross-section of thin films

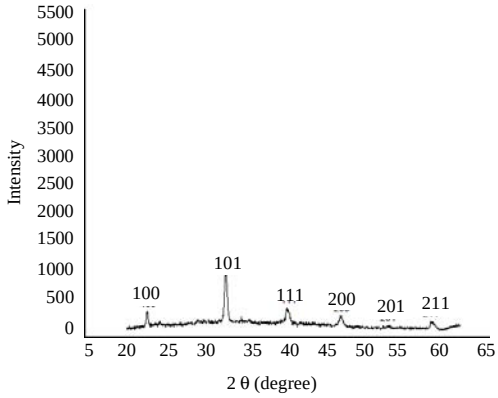

Fig. 3: XRD pattern for BST thin films

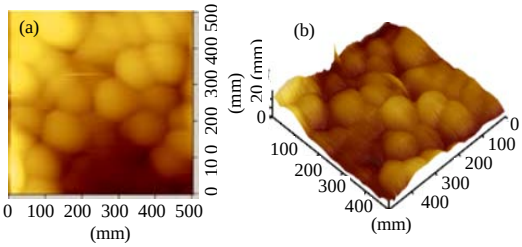

Fig. 4: Image of; a) 3D and b) 2D AFM micrograph with scan area 500×500 nm^2 of thin films

and operated at a voltage of 40 kV and current of 40 mA. As mentioned before, the $Ba_{0.8}Sr_{0.2}TiO_3$ solution was deposited on a Pt/Ti/SiO_2/Si substrate and annealed at 900°C for 2 h. The thickness of film is approximately 850 nm, respectively as determined with a profilometer. Figure 1 shows the XRD pattern for $Ba_{0.8}Sr_{0.2}TiO_3$. It is observed that the peak from (100) until (211) are within the 2θ range of 20-60°.

The strong peak at (101) is determined as platinum peak overlap with $Ba_{0.8}Sr_{0.2}TiO_3$. The compositional is assumed to be cubic since there is no peak splitting in the XRD pattern (Appleby *et al*., 2014).

Atomic Force Microscopy (AFM): Figure 4 shows the image of 3D and 2D AFM micrograph with scan area 500×500 nm^2. The micrograph indicates that the quality of BST thin films is good with crack free surface.

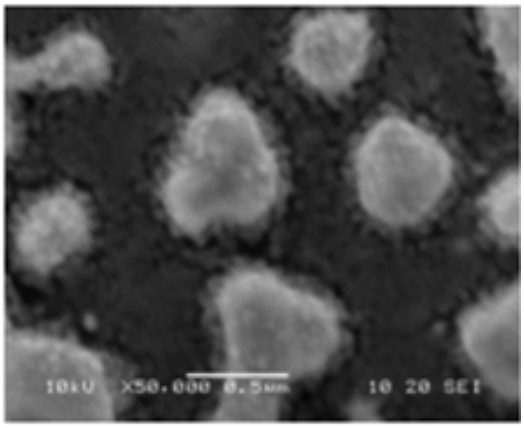

Fig. 5: Surface topography image of BST thin film

The multilayer coated is has an acceptable uniformity. The grain size of the thin film is 110.4 nm while Root Mean Square (RMS) grain size value is 3.64 nm. The grain size is manually calculated from the AFM result. The x-axis and y-axis are plotted through the result image using AFM analysis. The average value of the plotted grain is calculated and taken as a result. On the other hand, RMS value signed with the content of Ba in terms of grain size. Larger RMS value shows the high content of the Ba and increase the size of grain (Alae and Poopalan, 2010). On the other hand, roughness value which is Ra is about 89.3 nm. The roughness of the surface also affect the RMS value and also size of grain. The lower the roughness the better the result. Then, P-V which is peak to valley value is about 12.79 nm. This value means as the measurement highest grain at bright spot to the lowest grain on the dark spot. From observation, dark area of the thin film is indicated as the lower part while light area as upper part. This condition occurs due to the low uniformity of thin film. Low uniformity of the film is effective from spin coated process. The uniformity of the thin film can be improved with spin coat the solution using high spin speed. The quality of the solution also may affect. This condition can be explained as the powder based from the precursor material need to fully dissolve in a solvent.

Scanning Electron Microscopy (SEM): Figure 5 shows the image of surface topography with a magnification of 50000 is operated at 10 kV acceleration voltage. Since $Ba_{0.8}Sr_{0.2}TiO_3$ is the dielectric material the operation voltage need to be as low as possible in order to avoid surface charges. The surface charges can affect the quality of surface topography image. From observation the grain distribution is random. This can be explained with the image that show the bright and dark spots. The bright spots consist of the highest peak of grain while dark spots show the lower peak of grain. Even though, the grain is randomly distributed there are no changes of size.

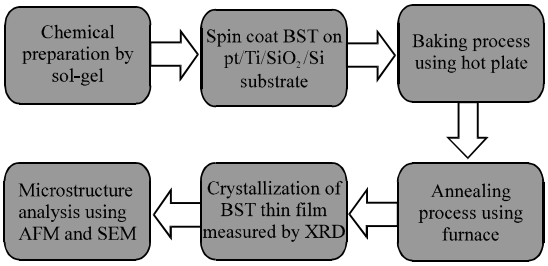

Fig. 6: Block diagram processes of the research project

Figure 6 shows the block diagram of the overall processes in this project. The research begins with the chemical preparation which is sol-gel method. This method taken about 8 h to complete the whole process until the solution is cooled down. Then, BST solution is coated on the $Pt/Ti/SiO_2/Si$ surface. After that the samples are baked using a hotplate in order to remove the solvent material. As mention earlier this process is repeated in order to achieve multilayer coated thin films. Annealing process is taken after multilayer coated thin films are completed. This process utilizes a high temperature split furnace in order to operate at desired temperature. The ramp up and ramp down temperature is critically monitored. It is because, the bonding of crystal structure will be missed match affect from drastically increased or decreased temperature. The crystallized thin films can be achieved after annealing process is completed. Then, samples are characterized using X-Ray Diffraction (XRD) in order to determine the crystallinity and composition of structures. This testing is very important to ensure the correct material's composition and also purity of the solution. Lastly, microstructure of thin films is characterized with the Atomic Force Microscopy (AFM) for its grain and surface characteristics. On the other hand, Scanning Electron Microscopy (SEM) is used in order to obtain the topography image of thin film surface.

CONCLUSION

Based on the experiment result and data analysis, fabrication of $Ba_{0.8}Sr_{0.2}TiO_3$ thin films using the sol-gel method is the best method for chemical preparation. Even though the sol-gel method has a low cost of production, the thin film from this method has a good quality in terms of crack free and smooth surface.

ACKNOWLEDGEMENT

This project is supported by a Fundamental Research Grant Scheme (FRGS) under grant no 9003-00363 from Ministry of High Education Malaysia.

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