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Synthesis of $Ba_{0.6}Sr_{0.4}TiO_3$ Nano Powder Through Slow Rate Sol-Gel Route as a Dielectric Material

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Abstract: $Ba_{0.6}Sr_{0.4}TiO_3$ was prepared through slow rate sol-gel route, characterized and investigated to determine the suitability as a dielectric material in the capacitor of a DRAM cell. X-ray diffractometer results show that single phase formation occurred at 800°C. The crystalline size of $Ba_{0.6}Sr_{0.4}TiO_3$ was found to be in the range of 74.21 nm to 98.76 nm. Scanning electron microscopy analysis shows that the particles are spherical in nature and in the sample calcined at 800°C do not agglomerate. The dielectric constant range ranges from 408 to 1042 and the dielectric loss ranges (measured at 1 kHz) from 0.065 to 0.232.

Key words: Barium strontium titanate · Sol-gel · High-k material · Surface morphology · Dielectric characteristics

INTRODUCTION

$Ba_{0.6}Sr_{0.4}TiO_3$ is one of the metal oxide materials which can be used as dielectric material in the capacitor of a DRAM cell. A DRAM cell consists of a capacitor which is used to store charge and a transistor as a switching device. Since most of the physical space of the cell is occupied by the capacitor, there is a need to reduce the physical size of the capacitor in order to achieve overall dimensions of the DRAM cell. According to the International Technology Roadmap for Semiconductors (ITRS), the feature size of a DRAM cell is expected to be 32 nm by the year 2013 [1]. Among the possible alternatives to reduce the capacitor dimensions could be in term of changing the manufacturing methods, device structures/architectures and/or using alternative dielectric materials. Barium Strontium Titanate (BST) has been chosen as it has the following advantages: (1) high dielectric constant, (2) low dielectric loss (3) high charge storage density and (4) low leakage density [2]. BST powders are commonly prepared using solid-state reaction [3], co-precipitation [4] and sol-gel method [5-7]. The synthesis by solid-state reaction takes about 24 hours [3] and required high temperature (1100°C) during synthesis [8]. On the other hand, the precipitation step involves a large number of variables that could complicate the synthesis procedure [4]. In recent years, many researchers used sol-gel method for the preparation of BST powder because of the homogenous distribution of elements on a molecular level with low temperature calcination capability and relatively low capital cost [9]. In addition, the material composition can be easily adjusted for tuning the electrical and dielectrical properties of the material accordingly.

The chosen materials could be prepared by various routes, but the materials synthesized should be pure, nano-sized dielectric material with high dielectric constant and low dielectric loss. In this context, sol-gel method has been adopted in this research because of the advantages of this technique for providing homogenous distribution of elements on a molecular level, relatively low temperature calcination capability and capital cost [10].

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Experimental Procedure: Barium acetate, strontium acetate and titanium (IV) iso-propoxide were used as starting materials for the preparation of the material synthesis. Acetic acid (Glacial) was used as solvent, whilst ethylene glycol ethyl was used to control the stability of the titanium iso-propoxide solution and reduce the particle grain size. All the acids and chemicals were of Analytical Reagent grade. Stochiometric ratios of barium acetate and strontium acetate were dissolved in acetic acid, separately. The two solutions were then mixed and heated slowly just above room temperature with continuous stirring at 200 rpm for 10 minutes. Subsequently, the resultant solution was injected slowly from a dripping system in the form of a syirnge, into a solution containing titanium iso-propoxide mixed with ethylene glycol ethyl. This slow addition enables better control of the reaction to get the transparent gel. The time taken to complete this formation of BST transparent solution was about 27 minutes. The pH value of the solution was maintained in the range of 3.5 to 5 [11]. The as-prepared gel was dried at 70°C overnight by hot plate in air and was subsequently calcined at different temperatures ranging from 600°C to 1100°C for 3 hours by conventional electrical furnace (Carbolite, 11/6).

The powders calcined at different temperatures were characterized by X-ray diffration method (XRD) (X'Pert Pro PW 3040 Panalytical, Holland) with CuKα-radiation (λ = 1.5406 ε) and XRD patterns were recorded in the 2θ range of 20° to 80°. The crystallite size was calculated according to Scherrer's equation ($d = 0.94\lambda/\beta\cos\theta$) [12]. The particle morphology of BST samples were analyzed by Scanning Electron Microscopy (SEM, Leo 1450 VPSEM). The single phased BST powders were prepared in terms of pellets and silver pasted for metal contacts and dielectric characteristics were measured by LCR meter (HP 4284A with text fixture 16451B).

RESULTS AND DISCUSSIONS

BST dried gels calcined at 600°C and 700°C contained unwanted materials such as barium carbonate (ICDD no: 41-373), barium oxide (ICDD no: 85-418) and strontium carbonate (ICDD no: 5-418). These gels were not considered as single phase elements and thus were not sent for sintering and further characterizations. The XRD patterns of BST powders calcined from 800°C to 1100°C are shown in Figure 1. As observed from Figure 1, when the calcination temperature increases, the diffracted peak increases which indicates higher crystallinity. The prepared material $Ba_{0.6}Sr_{0.4}SrTiO_3$ was identified by ICDD no: 34-0411.The Scherrer's formula was used to calculate the crystallite sizes of the $Ba_{0.6}Sr_{0.4}SrTiO_3$ and was found to be 74.21 nm, 83.34 nm, 91.78 nm and 98.76 nm respectively for the samples calcined from 800°C to 1100 °C. It is noted that when the calcination temperature increases, the respective crystallite size increases.

SEM was used to investigate the surface morphology of the prepared BST powder. Figure 2 shows the images of the $Ba_{0.6}Sr_{0.4}TiO_3$, calcined from 800°C to 1100°C. As seen from the SEM images in Figure 2, the crystalline size is in the range of nanometers (nm). The average crystalline sizes for BST calcined at 800, 900, 1000 and 1100°C are 75.18 nm, 84.10 nm, 92.32 nm and 96.02 nm respectively. This result is consistent with the crystalline size calculated from the XRD results using Scherrer's formula. SEM images in Figure 2 shows that the BST powders prepared are spherical in shape and are crystallined with well defined boundaries no agglomeration.

Table 1 shows the atomic percentage of the elements present in the $Ba_{0.6}Sr_{0.4}SrTiO_3$, with the help of Energy Dispersive Analysis (EDAX). The atomic percentage of barium, strontium, titanium and oxygen of the prepared samples matched closely with those of the standard percentage. This verifies the identity of the prepared BST powder as $Ba_{0.6}Sr_{0.4}TiO_3$, in consistence with the identification using XRD results.

Dielectric characterization was carried out on the samples to determine the dielectric properties. The data collected from the dielectric characterization, such as the diameter and thickness of the pellets and their capacitance is used to determine the dielectric constant using the

Table 1: Percentage of elements in $Ba_{0.6}Sr_{0.4}TiO_3$

		Atomic Percentage of Elements (%)			
Sample	Calcination Temperature (°C)	*Barium*	*Strontium*	*Titanium*	*Oxygen*
Standard	-	12	8	20	60
BST800	800	11.87	7.54	18.26	62.33
BST900	900	11.96	7.84	19.23	60.97
BST1000	1000	12.31	8.05	18.75	60.89
BST1100	1100	12.02	8.21	21.03	58.74

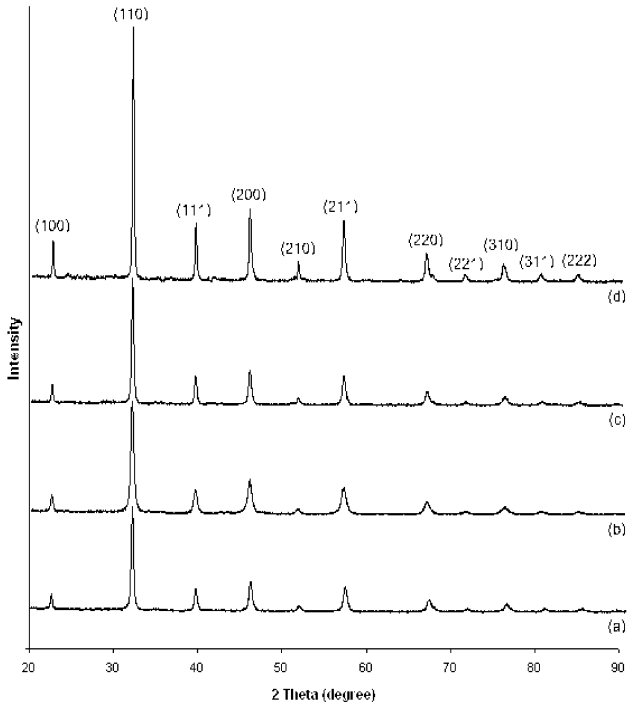

Fig. 1: XRD patterns of $Ba_{0.6}Sr_{0.4}$ calcined at a) 800°C b) 900°C c) 1000 °C and d) 1100 °C

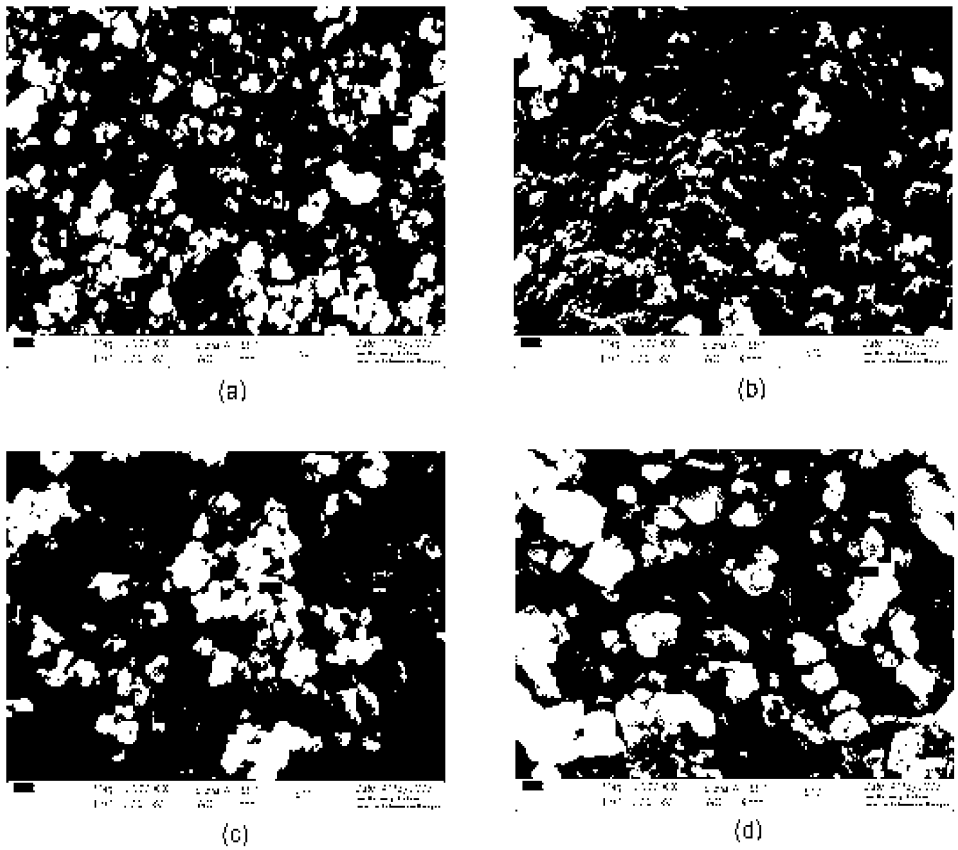

Fig. 2: SEM images of BST at calcined at a) 800 °C b) 900 °C c) 1000 °C and d) 1100 °C

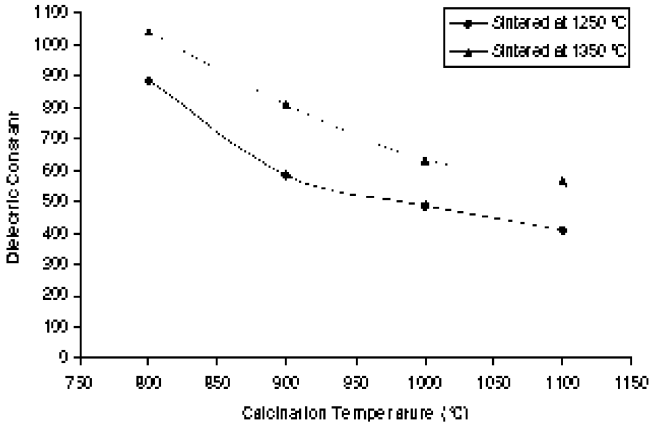

Fig. 3: Effects of calcination temperature on dielectric constant

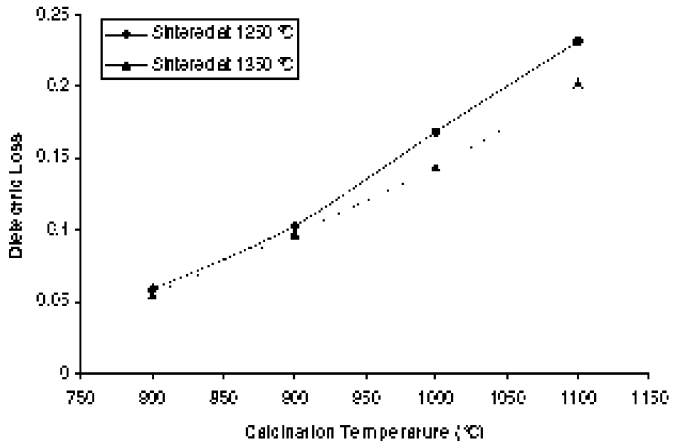

Fig. 4: Effects of calcination temperature on dielectric loss

quation; $C = \frac{k\varepsilon_0 A}{d}$ where C = Capacitance (F), ε_o = Permittivity of free space = 8.854 x 10^{-12} F/m, k = Dielectric constant, A = Area of capacitor (m^2) and d = Thickness of capacitor (m).

Four pellets, calcined from 800°C to 1100°C, were subsequently sintered at 1250°C and 1350°C at a rate of 5°C/minute. The average diameters of pellets sintered were found to be 12 mm and the thickness is 2 mm. The sintered pellets were silver pasted on both sides for metal contact to act as capacitor for measurement of the dielectric constant and dielectric loss.

Figure 3 shows the relationship between the calcination temperature and dielectric constant of the $Ba_{0.6}Sr_{0.4}TiO_3$ samples. The dielectric constant decreases with increasing calcination temperature and the highest value of dielectric constant is 1042 for the pellet sintered at 1350°C. On the other hand, Figure 4 shows the relationship between calcination temperature and dielectric loss of $Ba_{0.6}Sr_{0.4}TiO_3$. The dielectric loss increases with increasing calcination temperature and the lowest value of dielectric loss is 0.065 for the pellet sintered at 1350°C. In summary, dielectric constant becomes larger and dielectric loss become smaller when sintering temperature is increased from 1250 °C to 1350 °C.

CONCLUSIONS

$Ba_{0.6}Sr_{0.4}TiO_3$ was successfully synthesized in this research work using slow rate sol-gel route. The results obtained from the XRD characterization show that $Ba_{0.6}Sr_{0.4}TiO_3$ is of cubic form with lattice parameter a_o of 3.960 Å. This result closely matches with the standard lattice parameters of 3.965 ε. $Ba_{0.6}Sr_{0.4}TiO_3$ only starts to form at calcination temperature of 800 °C. For calcinations temperature below 800°C, impurities such as barium carbonate, strontium carbonate and barium oxide are present in the samples. The crystalline size calculated

from the XRD results shows that the particle size of BST increases as the calcination temperature increases from 800°C. The dielectric constant range from 408 to 1042 and the dielectric loss ranges (measured at 1 kHz) from 0.065 to 0.232. The optimum sample is calcined at 800 °C and sintered at 1350 °C where such combination produces $Ba_{0.6}Sr_{0.4}TiO_3$ with the smallest crystalline size, highest dielectric constant and lowest dielectric loss within the range of parameters studied.

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