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Synthesis and characterization of BaSrTiO3 Perovskite Thin Films Prepared by Sol Gel Technique

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Abstract: Barium strontium Titanate (BST) is a solid solution consist of BaTiO3 and SrTiO3 that mixed with suitable ratio. Barium strontium Titanate oxide (Ba0.8Sr0.2TiO3) thin films prepared by sol gel technique. Barium strontium Titanate thin films deposited on Si substrate and annealing at 400,500, 600 and 700 ºC. The characterization of BST film investigated by a different technique, the XRD and SEM revealed the phases, crystal structure and surface topography of the film. XRD pattern shows tetragonal phase for perovskite structure Ba0.8Sr0.2TiO3 with many peaks for different plans. The films annealed at the different temperature that indicated intermediate phases on perovskite structure of Ba0.8Sr0.2TiO3.

Keywords: BST, perovskite structure, dielectric constant, dielectric loss.

1 Introduction

Thin films of barium strontium titanate are currently attracting much attention because of their useful properties such as high dielectric constant, low dielectric loss, low leakage current, tunable dielectric constant at a wide range of frequencies [1].

Barium Strontium Titanate (BaxSr1-xTi03) is a solid solution of Barium Titanate (BaTi03) and Strontium Titanate (SrTi03). $BaTiO_3$ is a ferroelectric material with Curie temperature (Tc) of 120° C, while SrTi03 is a paraelectric material with no ferroelectric phase transition [2].

The Curie point of BaTi03 is found to decrease linearly with solid solution of Sr^{2+}in place of Ba^{2+} at the rate of 3.7°C/ % of mole. Bulk $Ba_xSr_{1-x}TiO_3$ is ferroelectric and tetragonal phase at room temperature for x= 0.7 to 1.0 (Ba-content). All remain compounds are paraelectric and cubic. The Curie temperature of bulk BST varies from -232 to 127ºC depending upon the Ba/Sr ratio [3,4].

"Here all the strong points of BST as the most suitable material for DRAMs are belonged to some features such as high dielectric constant (ϵ_r> 200), Low leakage current, Low-temperature coefficient of electrical properties, small dielectric loss, lack of fatigue or aging problem, High compatibility with device processes, linear relation of eclectic field and polarization, low Curie temperature (Tc)"[5].

BST thin films can be deposited by a variety of techniques. The commonly used techniques for depositing dielectric thin films are rf- sputtering [6], ion beam sputtering, pulsed laser ablation [7], metallorganic chemical vapour deposition (MOCVD), metallorganic deposition (MOD) [8], and sol-gel. Each technique has its merits and demerits.
For device applications, whatever be the method of production of thin films, it must be economical, and films of good homogeneity and purity must be prepared [9]. Sol-gel is a novel technique in this regard as it offers some practical advantages over the other processing methods.
The sol-gel process offers the following advantages over the conventional methods: films of high purity can be obtained, films have good compositional homogeneity [10]. Processing is carried out at a lower temperature, dopants can be easily introduced for desired electrical and physical properties, Thickness of the film can be controlled by modifying the solute concentration and by varying the no of coatings, It is easier and low-cost method compared to other methods like CVD, sputtering etc[11,12]. However, it has some disadvantages, Long processing time, Residual fine pores after drying and annealing, large shrinkage in films during heating and annealing, which cause crack formation in the film [13].

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In this paper, preparation and characterization of $Ba_{0.8}Sr_{0.2}TiO_3$ thin films with different annealing temperature.

2 Experimental Dilates

For the preparation of BST sol, Ba-acetate is taken as the Ba source Sr-acetate as the Sr-source and Ti-isoproxide as the Ti source. In the sol-gel processing of BST thin films precursors generally used are barium acetate [Ba(CH3C00)2], strontium acetate [Sr(CH3COO)i,2H20] dissolved in heated acetic acid, and titanium isoproxide [Ti(OC4Hg)4] dissolved in 2-methoxy ethanol.
Acetic acid and 2-methoxyethanol are used as the solvent.

At first 1.9434 gms of Ba-acetate and 0.5679 gms of Sr-acetate are weighed to dissolve in acetic acid and stirring 30 min at 60 ºC, separately. The mixed solution were taken and put in a three necked flask containing and refluxed 2 hrs at 110ºC. 2-methoxyethanol is added to Ti- isoproxide and the solution is kept on stirring for another 30 min at room temperature. The mixture of solution Ba, Sr add slow drop by drop then kept for stirring for 30 minutes on hotplate stirrer. The mixture solution is refluxed 2 hrs at 110 ºC. In this way a clear white colored BST sol is obtained.

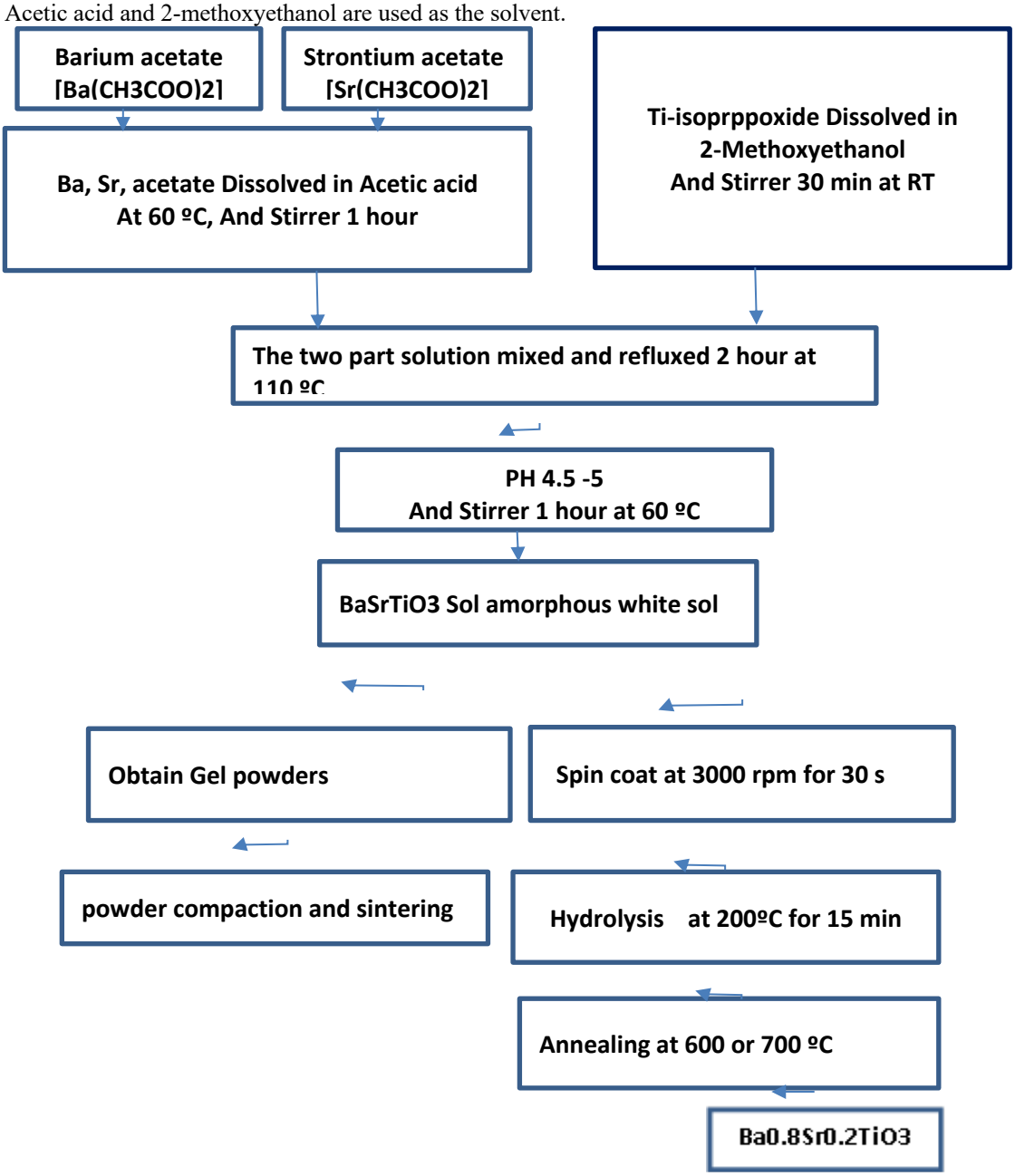

Fig. 1: Flow chart for preparation of $Ba_{0.8}Sr_{0.2}TiO_3$.

Thin films of $Ba_{0.8}Sr_{0.2}TiO_3$ were prepared by the sol-gel processes. The concentration of the starting sol was 0.2M. The sol was coated on to the substrate by spin coating technique. Spin coating technique involves simple fluid flow and evaporation behaviors that generally give uniform coating The substrate was fixed at the center of the rotating vacuum chuck. This chuck has a small hole (2 mm diameter) in its center which is connected to a vacuum pump. The required vacuum is created at the hole and the substrate is held firmly on the chuck. A dropper was used to drop 0.05 ml sol onto the substrate during the initial few seconds of spinning. The sol immediately spreads on the substrate and a gel film is produced. The photoresist spinner was typically operated at 3000 rpm for 30 seconds

After each coating the film was dried in the furnace at 150°C for 15 minutes. After the final coating and drying treatment, the film was annealed at400, 500, 600° and 700°C for one hour in a furnace. After drying, it forms an amorphous coating which after annealing gives a polycrystalline thin film.

Heat treatment of the films deposited on substrate film contains large amounts of organics. Large shrinkage occurs during the heat treatment due to removal of the organics. Crystallization may start before the organics arc completely removed, and sintering and crystallization process may also overlap. Since the material content of the film is extremely small, the signal bottomed is often beyond the detection limits of these techniques.

The films were examined by XRD and SEM. The films were crack-free and crystallized into tetragonal perovskite phase. SEM pictures showed that the films might be porous in nature. The dielectric measurements show the films have a low dielectric constant and high loss (at low frequencies). These can be related to the micro porosity and organic residues present in the film.

3 Results and Discussion

X-ray diffraction is carried out on the gel-powder and thin films samples at different temperatures in order to get information about the phases present and formed during the course of heating to higher temperatures for crystallization. Figure 2 shows the XRD patterns of the gel powder made from a sol containing 2-methoxyethanol and pattern of thin films at different temperature.

The XRD pattern of $Ba_{0.8}Sr_{0.2}TiO_3$ phase has many peaks which related to the tetragonal perovskite phase along the (100), (101), (111), (200), (201), (211), (202), (221), (301) planes. The peak positions matched well with the PDF card no. (96-151-2121). Furthermore, this phase exhibited the P4mm space group with (a=3.9890 Å, c= 3.9950 Å) . The XRD pattern of a tetragonal phase as characterized by the splitting of the (100) and (200) peaks.

"The x-ray peak for $BaCO_3$ is expected at 29 = 24.68 and for oxycarbonate is at 27.0º.

The high intensity broad hump at theta =20-30 º after 400 C treatment is indicates the presence of a carbonate/oxycarbonate phase. A broad peak at 24.5° superimposed on this hump appears at 450°C. At 500 ºC the hump height decreases, the carbonate peak disappears and many peaks correspond to BST appear. On heating to 500°C the BST peaks get sharpened but a peak at 23.98° remained which does not match with either $BaCO_3$ or oxycarbonate peak. They attributed to an unidentified intermediate phase, possibly $(Ba_2Sr)TiO_2CO_3$. Further heating to 500,600, 700°c reduce the intensity of this peak (around 24°) and BST peaks get stronger. After heating to 700°c only the peaks corresponding to the perovskite of BST are present"[7].

Fig. 3 shows the SEM images of the films taken at different magnifications. The sample annealed at temperatures 600°C.

The variations of the dielectric constant with frequency for the samples are shown in Fig. 4 at different annealing temperatures. As seen from these curves the dielectric constant increases with increase in annealing temperature in all the three samples. The dielectric constant is high at low frequencies and decreases as the frequency increases. In case of sample which annealing at 700°C increased the dielectric constant significantly compared to the other two samples, the reason of this behavior belongs to effect temperature on grain crystal size of film with increased temperature and porosity of film.

There is not much regular change in dissipation factor values with annealing temperature. The variation of average dissipation factor as function of temperature are plotted in Fig. 5. It is seen in all the cases that at low temperature the dissipation factor is low and increased with increasing temperature that belong to vibration in atoms around equilibrium position in lattice. The value of dissipation factor in 600 ºC sample less than of remain samples.

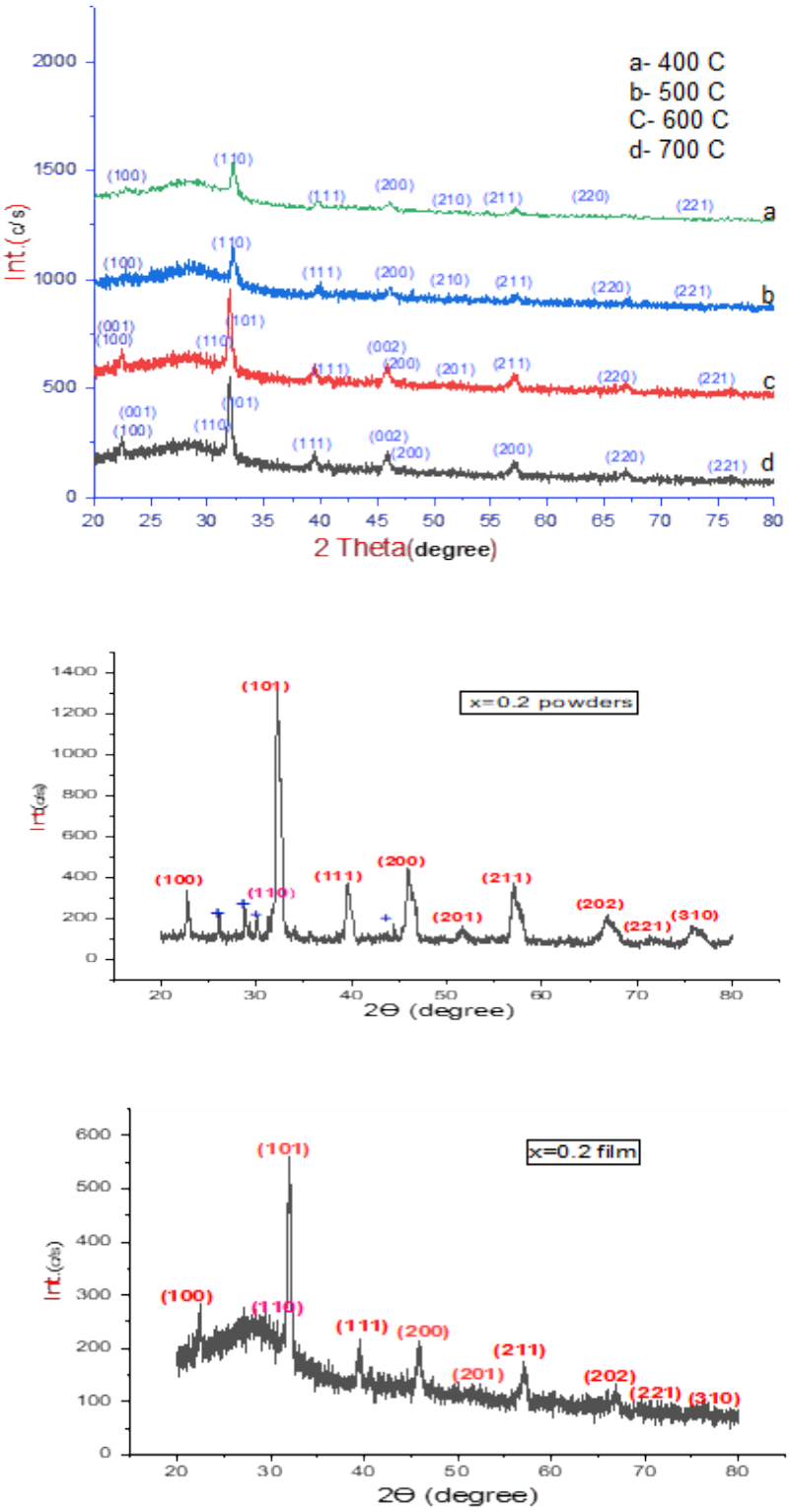

Fig. 2: XRD plots of powder and films annealed at different temperatures.

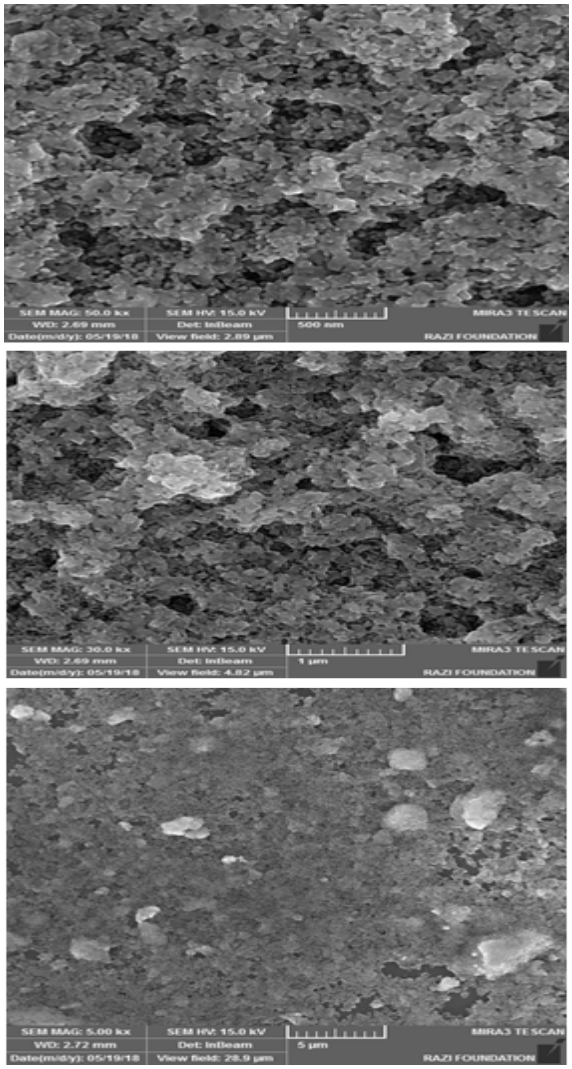

Fig. 3: SEM images of the films with different magnification.

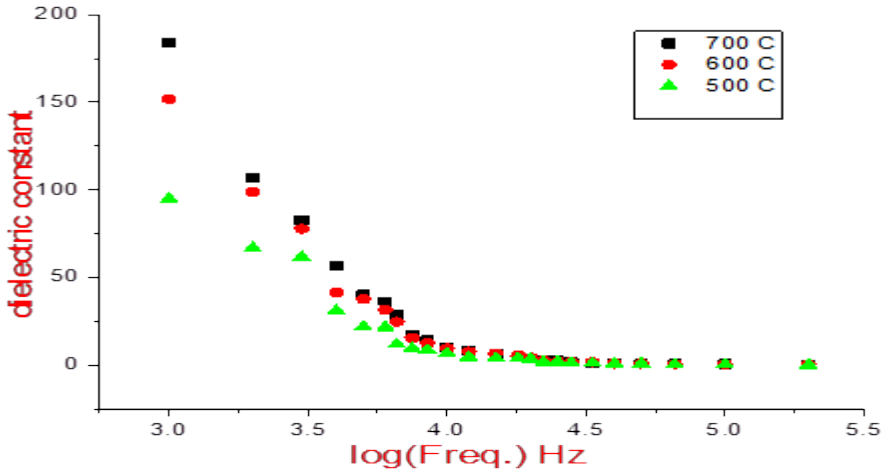

Fig. 4: Dielectric constant Vs frequency plot at different temperature for films.

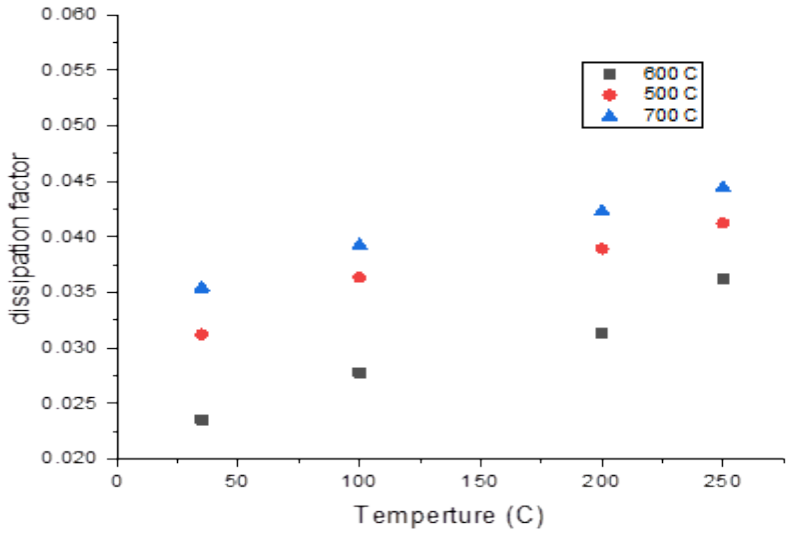

Fig.5: Dissipation Factor Vs Temperature plot at different temperature of film.

4 Conclusions

$Ba_{0.8}Sr_{0.2}TiO_3$ powders prepared by sol gel method that used Ba-acetate, Sr-acetate and Ti- isopropoxide as a source for metals and acetic acid, 2-methoxy ethanol as solvent. $Ba_{0.8}Sr_{0.2}TiO_3$ thin films were prepared with annealing temperature by a sol–gel process. The annealing temperature strongly affected the structure, porosity and dielectric properties of the films. The films prepared at 700 ºC showed tetragonal perovskite phase and high dielectric constant.

Conflict of interest: The authors declare no competing financial interest.

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