Synthesis and characterization of $Ba_{0.8}Sr_{0.2}TiO_3$ perovskite thin films prepared by Sol Gel Technique

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Abstract

Barium strontium Titanate (BST) is a solid solution consist of $BaTiO_3$ and SrTiO3 that mixed with suitable ratio. Barium strontium Titanate oxide ($Ba_{0.8}Sr_{0.2}TiO_3$) thin films prepared by sol gel technique. Barium strontium Titanate thin films deposited on Si substrate and annealed at [400,500, 600 and 700] ºC. The characterization of BST films investigated by a different technique, the X-Ray Diffraction (XRD) and Scanning Electron Macroscopy (SEM) revealed the phases, crystal structure and surface topography of the films. XRD pattern shows tetragonal phase for $Ba_{0.8}Sr_{0.2}TiO_3$ perovskite structure with many peaks for different plans. The films annealed at the different temperature that indicated intermediate phases on perovskite structure of $Ba_{0.8}Sr_{0.2}TiO_3$.

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 ($Ba_xSr_{1-x}Ti0_3$) 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 Dynamic Random Access Memory (DRAMs) are belonged to some features such as high dielectric constant ($\epsilon r > 200$), 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 spin coating technique. 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 number 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].

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 solution, 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 at 60ºC. The mixture solution is refluxed 2 hrs at 110 ºC with PH of 4.5-5. In this way a clear white colored BST sol is obtained.

Thin films of $Ba_{0.8}Sr_{0.2}TiO_3$ were prepared by the spin coating technique. 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.

3-Results and Discussion

X-ray diffraction is carried out on the gel-powder and thin films samples at different annealing temperatures in order to get information about the phases present and formed during treatment heating to higher temperatures for crystallization. Fig. 1 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 with prefer peaks(101). 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 2Θ at 29.0º and for oxycarbonate is at 27.0º. The high intensity broad hump at theta =20-30 º after 400 ºC 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].

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Table.1 Density of dislocation, and lattice parameters of the thin films with different annealing Temperature

Aneealining Tem. ºC	hkl	Crystallite size D (nm)	Dislocation density($x10^{14}$	Lattice Constant ((Å) a (Å)	c (Å)
400	(101)	24.29	0.71	3.9890	3.9950
500	(101)	25-33	0.85	3.9890	3.9950
600	(101)	31-45	1.12	3.9950	3.9950
700	(101)	41-71	1.32	3.9950	3.9950

Table .2 Structural parameters viz. Miller indices 2θ values, inter-planar spacing, and phase of $Ba_{1-x}Sr_xTiO_3$ powders.

x=0.2									
hkl	100	101	111	200	201	211	202	221	301
d $_{Exp.}$ (Å)	3.9893	2.8232	2.3048	1.9962	1.7840	1.62835	1.4118	1.3301	1.2614
d Stand.$_o$ (Å)	3.9890	2.8228	2.3042	1.9945	1.7839	1.6289	1.4114	1.3299	1.2616
2 theta (Theo.)	22.33	31.77	39.10	45.37	51.12	56.53	66.18	71.00	75.16
2 theta (Exp.)	22.29	31.67	39.06	45.37	51.10	56.44	66.16	70.89	75.15

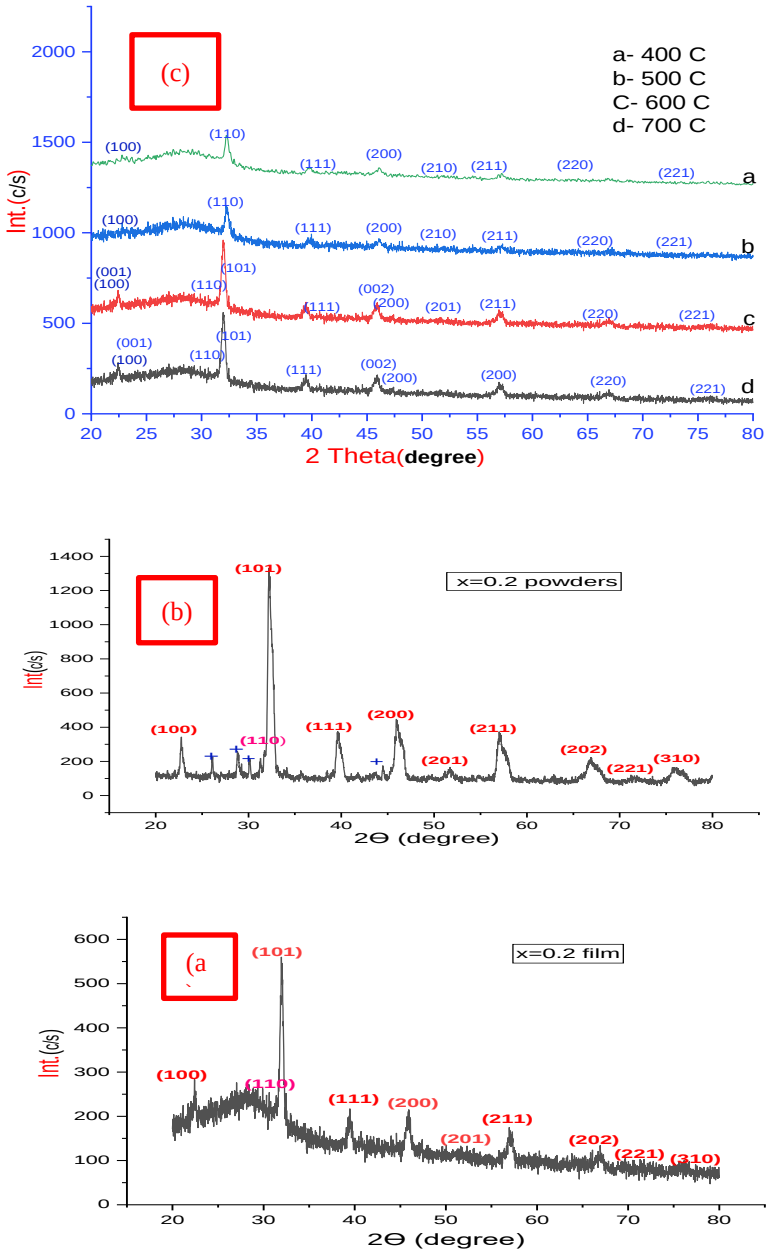

Fig. 1 XRD plots of powder and films annealed at different annealing temperatures
(a)- films (b) powders (c) films with different annealing temperature

As a mention in a Table. 1, and Table. 2 the crystallite size increased with increasing temperature at highest peaks (101). This behavior is due to the effect of the annealing temperature on the size of the object, which in turn leads to the material reaching a complete crystallization at that temperature.

Fig. 2 shows the SEM images of the films taken at different annealing temperature, from the images appeared the morphology surface changes with increased annealing temperature. The smooth surface

shows at 700 ºC that belong to complete crystallization of film at this temperature and the residual organic solvent is removed.

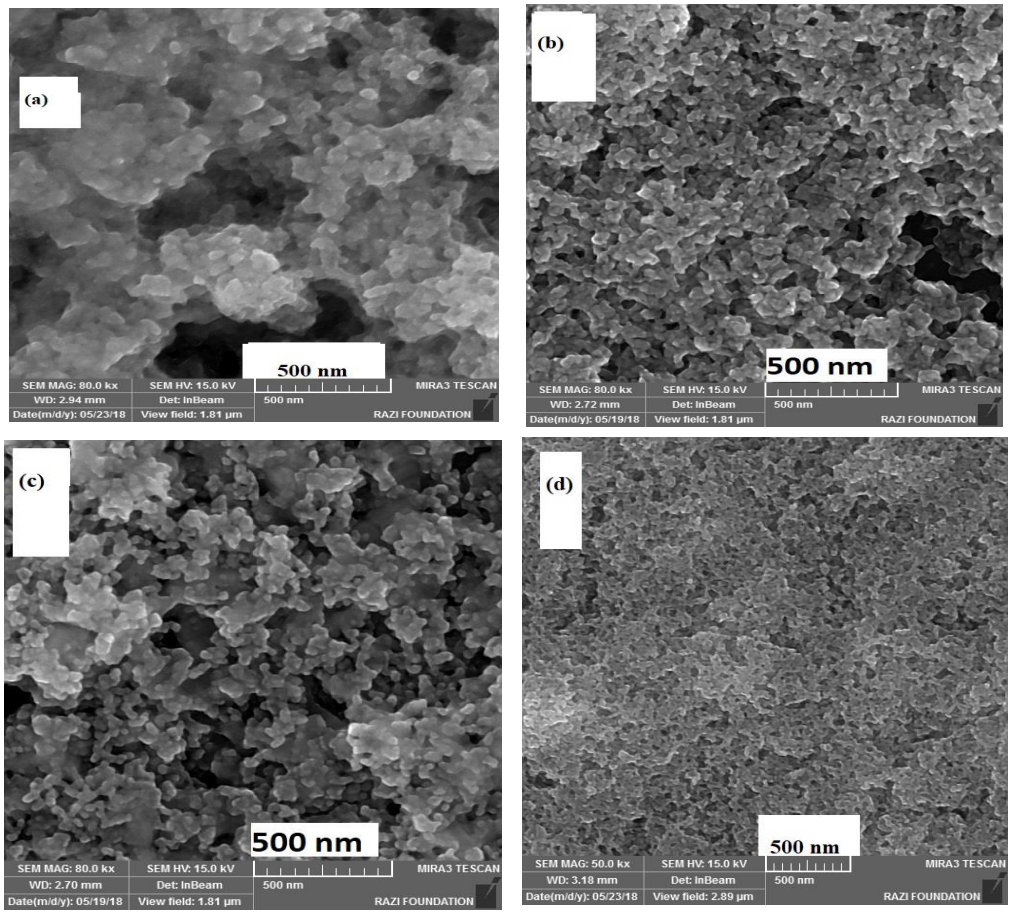

Fig. 2 SEM images of the films with different magnification
a- 400 ºC, b-500 ºC, c- 600 ºC, d- 700 ºC

The variations of the dielectric constant with frequency for the samples are shown in Fig. 3 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 annealing temperature are plotted in Fig. 4. It is seen in all the cases that at low annealing 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.

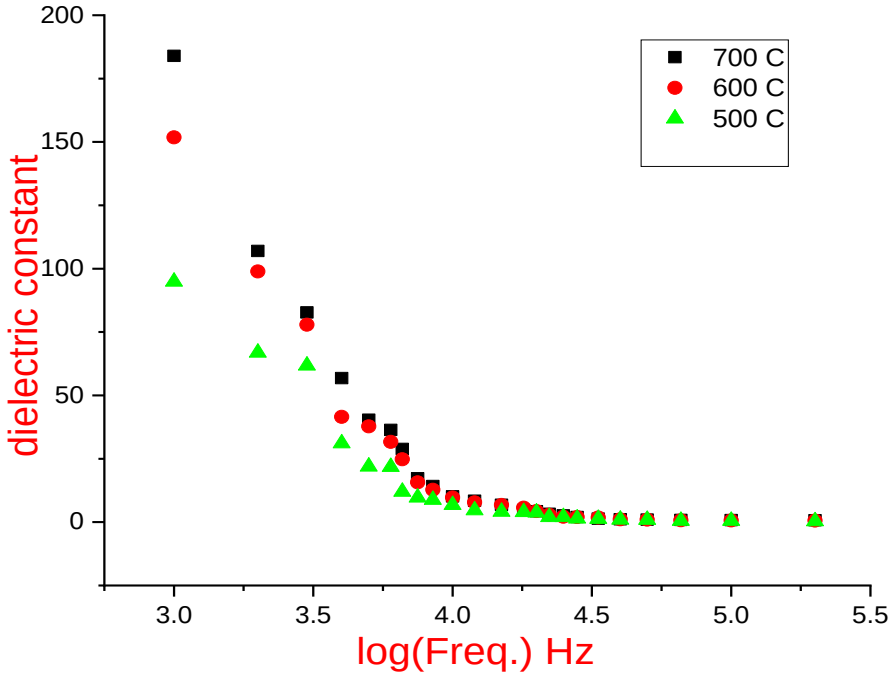

Fig. 3: Dielectric constant Vs frequency plot at different annealing temperature for films

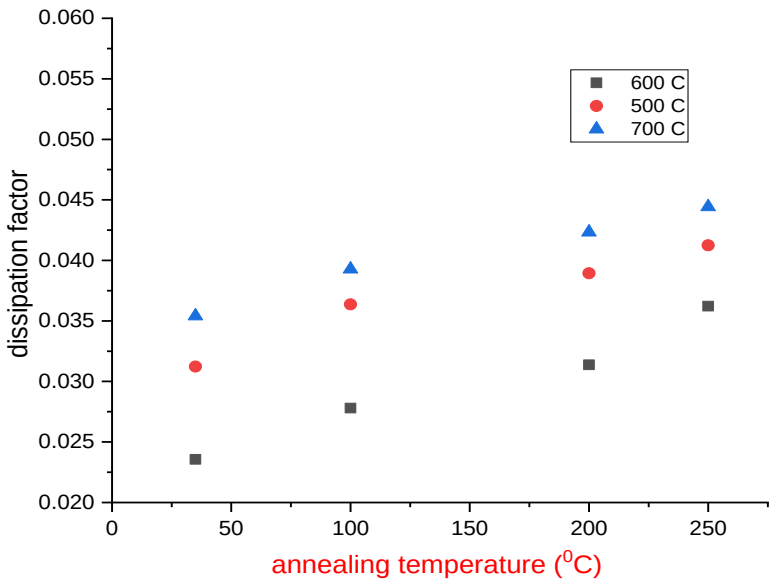

Fig. 4: Dissipation Factor Vs Temperature plot at different annealing temperature of film

4-Conclusion

$Ba_{0.8}Sr_{0.2}TiO_3$ powders prepared by sol gel method successfully. $Ba_{0.8}Sr_{0.2}TiO_3$ thin films were prepared with annealing temperature by spin coating technique. The annealing temperature strongly affected the structure, porosity and dielectric properties of the films. XED patterns show the intensity increased with increasing annealing temperature that belong to complete crystallization degree. SEM revealed the films surface is changing with increased temperature. The dielectric measurement appeared when increased annealing temperature increasing dielectric constant. The films prepared at 700 ºC showed tetragonal perovskite phase and high dielectric constant.

Conflict of interest

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

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