EFFECT OF CHANGE IN Ba CONCENTRATION ON CRYSTALLINTIY AND DIELECTRIC CONSTANT OF THE SOL-GEL DEPOSITED BARIUM STRONTIUM TITANTE (BST) FILMS ON N-TYPE Si WAFER

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Thin (Ba_x*, *Sr_{1-x}*)*TiO_3* (BST) films of different chemical compositions (*$x = 0.3$* 0.5 & 0.7) were prepared by the sol-gel process using barium acetate, strontium acetate and titanium isopropoxide as metal alkoxides. The titanium isopropoxide was dissolved in acetyl acetone (chelating agent) and mixing the resultant solution with barium and strontium acetate dissolved in acetic acid solution. The alkoxide group in titanium isopropoxide was replaced by acetate ligand and after hydrolysis and condensation process a complex solution was obtained. This solution was deposited on n-type (*111*) Si wafers by spin coating and after drying at *350 °C* the samples were annealed at *700 °C* in oxygen ambient. The precise control of composition of different species is important for producing good quality films having high crystallinity and dielectric constant. The crystallinity of the film was found to increase with the increase of Ba concentration as found from X-ray diffraction. The calculated value of dielectric constant from CV measurements revealed that the film of (*$Ba_{0.7}$*, *$Sr_{0.3}$*) *TiO_3* had the maximum dielectric constant as *463* and the surface was examined by SEM.*

***Keywords:** (*Ba_x*, *Sr_{1-x}*)TiO, SOL-GEL PORCESS, DIELECTRIC CONSTANT, XRD, CV-MEASUREMENT.*

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1. INTRODUCTION

BST films are polycrystalline. Their properties mainly depend upon composition, stoichiometry, microstructure, thickness and homogeneity of the film. A variety of techniques such as sputtering, metal organic chemical vapor deposition (MOCVD), pulsed laser ablation [1] and sol-gel processing have been used to deposit BST thin films. The sol-gel method is one of the most important approaches as this helps in forming the films of uniform composition and non vacuum processing. The solution preparation of perovskite materials generally involves the metal alkoxide compounds $M(OR)_n$ where M is metal and R is alkyl radical (CH_3, C_2H_5, etc.). They are

highly reactive towards hydrolysis and condensation and may lead to uncontrolled precipitates and hence they have to be slowed down. The titanium alkoxide (Ti) and titanium isopropoxide [Ti(OPr)$_4$] are modified by a strong chelating agent i.e. acetyl acetone. It reacts with acetyl acetone to form Ti(OPr)$_3$acac in which one of the isopropoxide ligand has been substituted by acetylacetone, (acac) thus chelating the Ti(OPr). The new molecular precursor has reduced reactivity towards hydrolysis. The molar ratio of acetyl acetone/ Ti isopropoxide is = 1 to 2. If the amount of acetyl acetone is increased then the more complex structures are obtained and the final thickness of the film during coating increases [2]. For Ba and Sr precursors, usually Ba and Sr acetates may be taken and dissolved in acetic acid because acetic acid is a good solvent and also acts as a chelating agent. These acetates are less sensitive to hydrolysis and hence can be much more easily handled in air. This acetate solution is dropped into Ti isopropoxide solution modified by acetyl acetone. Ti(OPr)$_4$ also reacts with acetic acid in one to one ratio giving oligomers of Ti(OPr)$_3$(OAc)$_n$ where n = 2 or 3 in which acetate group behaves as a bridging ligand. Acetic acid reacts with alcohol (2-methoxy ethanol) and librates water into the solution through esterfication. Esterfication is a good method of introducing water into the solution − as this leads to slow hydrolysis of alkoxides [3]. The intermediate species of metal hydroxides (Ti(OH)OAc) are unstable and polycon densification reaction takes place by elimination of water/alcohol and they begin to connect and intervene with each other by forming the chain of stable Ti-O-Ti bonds. The condensation generally gives rise to gel and the viscosity of the solution increases. Ba and Sr ions are also incorporated in the frame work of sol-gel network to form Ba-TiO$_6$ clusters. Impurities in the form of metal carbonates are also present depending upon the solvents used .The solution is applied on the substrate by spin coating during which the trapped volatile material (water/alcohol) is driven off and the network shrinks and further condensation may take place and the gel has now the three dimensional matrix. During the heat treatment (350 °C), the liquid phase is removed from the gel and this forms a porous material. The film is amorphous in nature and contains (Ba, Sr) CO$_3$ and TiO$_2$. Then during annealing, at higher temperature ≥ 700 °C, the intermediate phases as oxy-carbonates (Ba, Sr)$_2$Ti$_2$O$_5$CO$_3$ decomposes to form polycrystalline (Ba, Sr)TiO$_3$ film and CO$_2$ is liberated [4, 6]. The crystallization of the film occurs by the nucleation and growth process. The characteristics of nucleation and growth process will define the final microstructure of the film and those films where the nucleation occurs not only at the interface but throughout the film − are typically polycrystalline in nature with random orientation.BST films are sensitive to oxygen vacancies and hence annealed in oxygen ambient to reduce the concentration of oxygen vacancies and to improve the dielectric properties of the film. [5].

In the present approach BST film of various compositions have been prepared by sol-gel process and deposited on n-type Si substrate by spin coating. X-ray diffraction (XRD) and C-V measurements (using MIS structure) were used to analyze the film. We report the effect of variation of Ba composition on dielectric and structural properties of BST thin films.

2. EXPERIMENTAL

The $(Ba_x, Sr_{1-x})TiO_3$ film of different chemical compositions ($x = 0.3, 0.5, 0.7$ & 0.9) designated as BST-1, BST-2, BST-3 and BST-4 were prepared using the sol-gel process. Barium acetate (1.0 gr.) was dissolved in 10 cc of acetic acid (CH_3COOH) by heating the solution at 90 °C and with constant stirring (using ultrasonic bath). Similarly strontium acetate (1.87 gr.) was dissolved in 10 cc of acetic acid. Both the solutions were mixed by heating them at 90 °C with constant stirring for half an hour so as to get a clear homogeneous mixture. The amount of titanium isopropoxide $\{(Ti(OCH(CH_3)_2)_4\}$ is also important for controlling the electrical properties of BST film. The amount of titanium isopropoxide or $Ti(OPr)_4$ was taken such that $(Ba + Sr)/Ti$ was ≈ 1. Therefore the 2.87 cc of titanium isopropoxide was dissolved in 2.0 cc of acetyl acetone ($CH_3\ COCH_2\ COCH_3$) by heating at 90 °C with constant stirring to obtain a clear yellow solution. The acetyl acetone is a very strong chelating agent and also stabilizes the reaction. This solution was mixed with acetate solution drop wise with constant stirring. The mixture was heated (90 °C) for half an hour and stirred thoroughly so that all the parts of the solution were properly mixed. Then 2-methoxy ethanol ($CH_3\ OCH_2\ CH_2\ OH$) was added to the final solution and this solution was heated at 90°C with constant stirring to promote the reaction between the different constituents of the solution [5]. This complex solution was cooled to room temperature, filtered to remove the residual particles and stored in closed bottle. The film was deposited on cleaned n-type Si (111) wafers with 30-40 Ω resistivities by spin coating at 4000 rpm for 30 seconds. The film was dried on a hot plate at 350 °C for half an hour to remove the volatile organics. Spin coating and drying was repeated again so as to increase the thickness of the film. The film was finally annealed at 700 °C for one hour in oxygen ambient to get the crystalline structure. Similarly for BST-2 $(Ba_{0.5}, Sr_{0.5})TiO_3$ with $x = 0.5$ & BST-3 $(Ba_{0.7}, Sr_{0.3})TiO_3$ with $x = 0.7$ were prepared using the stoichiometric ratio. The phase identification of the BST films was determined by X-Ray diffraction (XRD) using Cu radiation ($\lambda_{K\alpha1} = 1.5406$ Å) at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh .The dielectric constant of different films was studied using metal-insulator-semiconductor (MIS) structure [7]. In this structure for top electrode aluminium dots of 0.4 mm diameter were fabricated on BST films by Al evaporation followed by standard photolithography and chemical etching technique. For bottom electrode also, Al was deposited on silicon by vacuum evaporation followed by annealing at 400 °C for 15 minute in nitrogen ambient. Al forms an ohmic contact with rough surfaces and hence Si wafer with semi-polished on backside were used. The C-V measurements were done using Keithley model 82 at Electronic Science Department, Kurukshetra University, Kurukshetra.

3. RESULT AND DISCUSSION

The crystallization of the film occurs by the nucleation and growth process. The characteristics of nucleation and growth process will define the final microstructure of the film and those films where the nucleation occurs not only at the interface but throughout the films − are typically polycrystalline

in nature with random orientation. BST films are sensitive to oxygen vacancies and hence were annealed in oxygen ambient to reduce the concentration of oxygen vacancies and to improve the dielectric properties of the film. [6]. Fig. 1 shows XRD results for different BST films (BST-1 to 4). XRD pattern indicates the films are polycrystalline in nature. For example the BST-3 film have peaks (100), (110) , (111), (200), (210), (211) at angle 2θ values of 22.55°, 32.06°, 39.48°, 45.88°, 51.80° & 57.05° respectively. The lattice parameters for BST sample were calculated from XRD data and using software "Powder 3D". The as deposited films were characterized as tetragonal and the lattice parameters for BST-3 ($x = 0.7$) were calculated as $a = 3.9472$ Å, $c = 3.9654$ Å and $c/a = 1.0046$ Å which is quiet similar to that exist in literature on similar BST films [8, 9]. As the Ba conc. increases in the sample, the values of lattice parameters a and c increase from 3.920016 Å to 3.947274 Å and 3.92005574 Å to 3.96544236 Å respectively, lattice spacing decreases in the $BaSrTiO_3$ lattice. These values are good agreement with literature [10]. In present investigation lattice spacing changes from 3.12208 to 2.94340. The change in the lattice spacing is due to the size difference of Ba and Sr ions. The intermediate phase of oxycarbonate with typical broad reflections at $2\theta = 24.5°$ and 30.5° have been observed as reported in literature [11]. The carbonates are highly stable even at more than 727 °C. The Fig. 1 shows the dominant formation of this phase and is present in all the composition of the BST films probably due to some impurities. It has been reported in the literature [12] that the single phased, crystalline precursor of BST5 is observed when initially subjected at 600 °C for 20 h followed by heat treatment of 800 °C for 3h. However, in the present investigations, the annealing time is significantly low therefore improved thermal budget. The increase in XRD peaks of various reflections with the increase of Ba concentration in the film, increases the crystallinity of the film. This is in accordance with other investigators [13, 14].
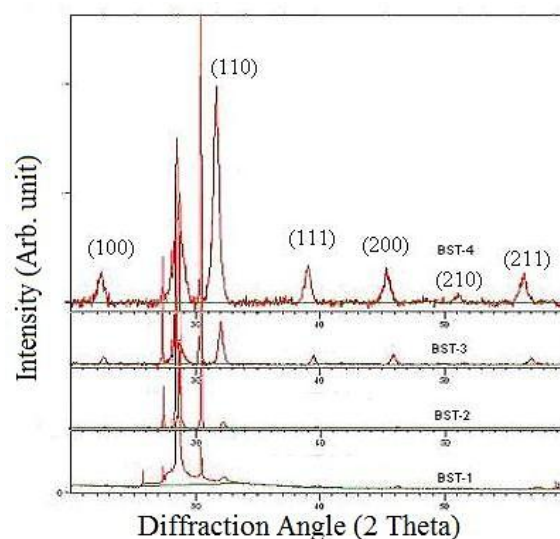

Fig. 1 − XRD pattern of different BST films (1 to 4) deposited on n-type Silicon

From XRD pattern the grain size of the BST films was calculated using Scherrer's formula as follows:

$$T = 0.9\lambda/\beta\cos\theta \tag{1}$$

Where T is mean crystallite size, λ is X-ray wave length (1.54060 Å), β is line broadening at full width half maxima (FWHM) in radians and θ is Bragg's angle. The grain size of BST films, calculated from the (110) peak broadening (Fig. 1) is shown in Table 1.The calculated grain size for BST-1 and BST-2 films are approximately 20.5 nm whereas BST-3 films resulted grain size of 24.6 nm. This is slightly greater than the BST-1 and 2 films. It was observed that with the increases of grain size, dielectric constant increases. The following equation tells the influence of grain size distribution on the curie temperature of BaTiO3 [10]. (Uchino et al 1989)

$$T_c = 128 - 700/(D - 110) \tag{2}$$

Where D is grain size (nm). It shows that with the increase of crystal diameter the Curie temperature is gradually increased and so dielectric constant increases. Horikawa et al. [15] have reported the relationship between the dielectric constant and broadness of an X-ray diffraction in $Ba_{0.65}Sr_{0.35})TiO_3$ thin films deposited at substrate temperature of 500-700 °C. Dielectric constant of these films ranges from 190-700 at room temperature. According to their results, the deposited film with grain size of 45nm had a dielectric constant smaller than 200, while the films with grain size of 200 nm showed a dielectric constant larger than 700. Lee et al. [16] have reported the microstructure dependence of the electrical properties of BST thin films deposited on $Pt/SiO_2/Si$ using SEM, TEM and Diffraction. It was observed that the dielectric constant increased from 348-758 when the grain size increased from 32-82 nm in the 600 °C deposited BST films [17]. Therefore variation in results for present case is also due to the change in grain size. The average grain size of 32 nm has been reported in literature [18]. The grain size of the BST film prepared using modified polymeric precursor method has been reported as 25-30 nm [12]. The reduced grain size of BST film in our case compared to literature is due to different concentration of the precursor solution and the low annealing temperature.
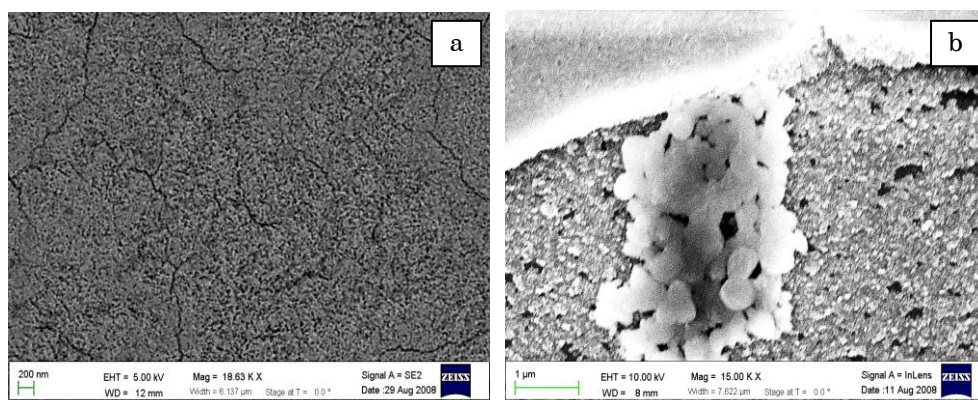

Fig. 2 – SEM picture of BST-3 (a) and BST-4 films (b)

Fig. 2(a) and 2(b) shows the Scanning Electron Microscopy (SEM) image of BST-3and BST-4 films. The uniform structure with a few micro cracks increases with increased Ba concentration in BST-4 films. Actually when films are subjected to heat treatment, the film shrinkage take place and this result in high stress in the films, and cracks formation occurs when the films strength cannot withstand the stress.
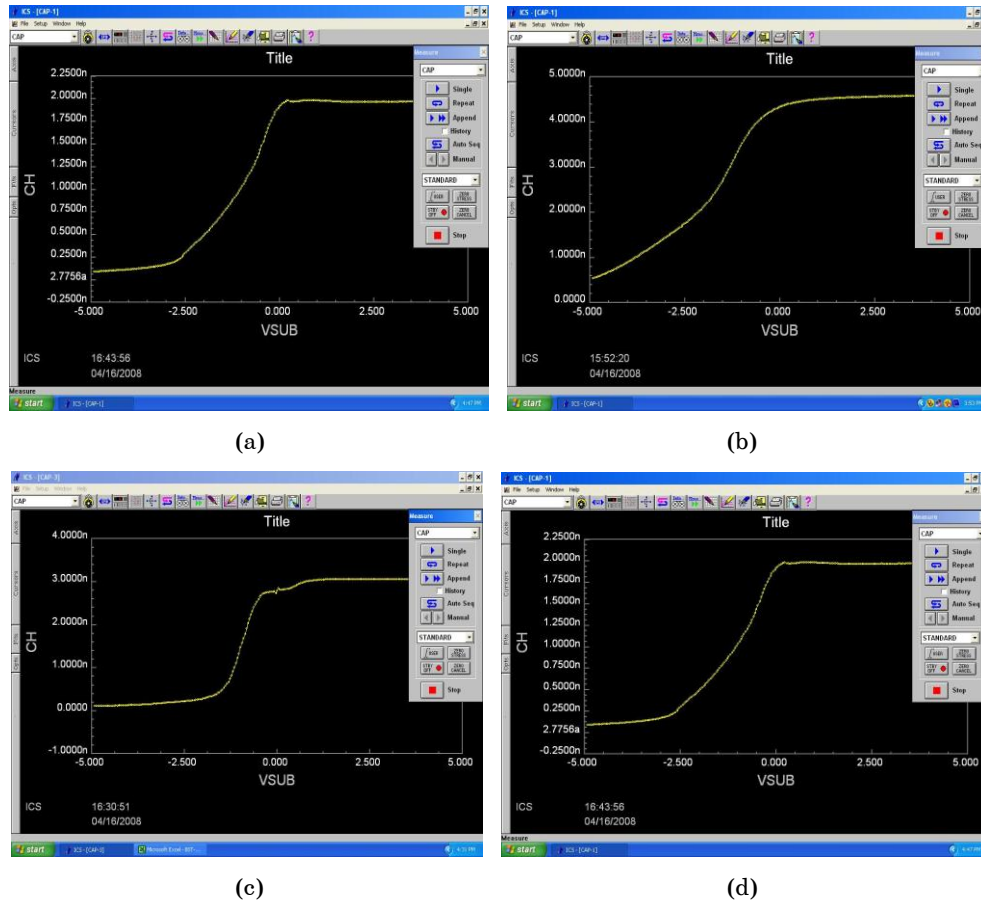

(a)

(b)

(c)

(d)

Fig. 3 − *Capacitance vs. Voltage curve for the films (BST-1 to 4) (a)-(d)*

Fig. 3 (a), (b), (c) and (d) shows capacitance vs. voltage curves obtained for different BST films (1 to 4). The distortion of C-V curves along Voltage-axis indicates that some trapped charges are present at Si/BST interface and are responsible for the leakage current in the film. The capacitance value, C of BST films at 2 V (accumulation region where majority carriers accumulate near the semiconductor surface and capacitance is maximum) was found from CV curves. The relative dielectric constant K, has been calculated using the parallel plate capacitor equation:

$$K = Cd/(\varepsilon_0 A) \tag{3}$$

Where C is the capacitance, d is the thickness of the film, ε_0 is the permittivity of free space (8.85×10^{-12} F/m), A is the area of top electrode (12.56×10^{-8}/m^2). The film thickness (d) was determined using Profilometer. The different results of BST film from 1 to 4 have been summarized in Table 1.

Table 1 − *BST films with their corresponding results of Capacitance, Thickness, Dielectric constant and Grain size*

Film	Capacitance (nF)	Thickness (nm)	Grain Size	Dielectric Constant
BST-1	1.96	112	20.5	197
BST-2	3.05	115	20.5	315
BST-3	4.60	116	24.6	463
BST-4	1.06	117	24.6	133

From Table 1 it can be concluded that increase of Ba concentration in the film increases the dielectric constant and becomes maximum for BST-3 ($x = 0.7$). These values are comparable with the results reported in the literature [6]. The reason for maximum dielectric constant in case of $Ba_{0.7}Sr_{0.3}TiO_3$ may be due to the paraelectric-to-ferroelectric transition, near Curie temperature, T_c reported in literature [19]. But compositions in which $x < 0.7$, wide difference was found between room temperature and T_c. At these compositions films showed the paraelectric nature and low dielectric constant value. S.U. Adikary has analyzed [19] the BST thin films as a function of film composition. Thin films were fabricated by a modified Sol-gel method on a Pt/SiO$_2$/Si substrate. It was observed that dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ was 778.3 for the film thickness of 280 nm, measured at 100 kHz. In present case the dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ films were observed as 463 for a films thickness 116 nm. But however for BST-4 ($x = 0.9$) the dielectric constant decreases abruptly which may be ascribed to the large voids as observed in the SEM study. Variation in dielectric constant in present case is expected due to variation in the grain size of the as-prepared BST films.

4. CONCLUSION

The sol-gel method was successfully employed for the preparation of BST films of various compositions. X-ray diffraction pattern of these films showed that they were poly crystalline in nature and their crystallinity increases with the increase of Ba content. It was found that, with increase of Ba concentration, lattice parameter of the thin film increases slowly, accordingly grain size also increases. The dielectric constant increases with increasing Ba concentration in the film. BST-3 film i.e. $(Ba_{0.7},Sr_{0.3})TiO_3$ was characterized having tetragonal phase with $c/a = 1.0046$ and this has maximum value of dielectric constant which may be due to the paraelectric-to-ferroelectric transition, near Curie temperature, T_c (close to room temperature). The as grown BST films have potential applications in memory chips and microwave devices.

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