$Ba_{1-x}Sr_xTiO_3$ THIN FILM SPUTTER-GROWTH PROCESSES AND ELECTRICAL PROPERTY RELATIONSHIPS FOR HIGH FREQUENCY DEVICES*

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DISCLAIMER

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ABSTRACT

Precise control of $Ba_{1-x}Sr_xTiO_3$ (BST) film composition is critical for the production of high-quality BST thin films. Specifically, it is known that nonstoichiometry greatly affects the electrical properties of BST film capacitors. We are investigating the composition-microstructure-electrical property relationships of polycrystalline BST films produced by magnetron sputter-deposition using a single target with a Ba/Sr ratio of 50/50 and a (Ba+Sr)/Ti ratio of 1.0. It was determined that the (Ba+Sr)/Ti ratios of these BST films could be adjusted from 0.73 to 0.98 by changing the total ($Ar+O_2$) process pressure, while the O_2/Ar ratio did not strongly affect the metal ion composition. The crystalline quality as well as the measured dielectric constant, dielectric tunability, and electrical breakdown voltage of BST films have been found to be strongly dependent on the composition of the BST films, especially the (Ba+Sr)/Ti ratio. We discuss the impact of BST film composition control, through film deposition and process parameters, on the electrical properties of BST capacitors for high frequency devices.

INTRODUCTION

Recently $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ (BST) films are investigated as electric-field tunable elements for high frequency devices.[1,2] The high dielectric tunability (dependence of permittivity on electric field), high breakdown field, and relatively low loss tangent of BST at microwave frequencies[3] make it attractive for application in high frequency devices such as varactors, frequency triplers, tunable phase shifters, etc.[1,2]

Radio frequency (RF) magnetron sputter deposition of BST thin films, using a multi-component BST oxide target, is a suitable processing route for the production of high-quality BST thin films. However, it is important to understand the effect of film processing parameters on the composition and microstructure of the BST films in order to achieve optimum properties. It is typically found that sputtering from a single multicomponent stoichiometric oxide target produces a non-stoichiometric oxide thin film. For the BST system, BST targets with various (Ba+Sr)/Ti ratios[4] and Ba/Sr ratios[5] were utilized to produce compositionally-adjusted BST films by physical vapor deposition. In this paper, we report that the (Ba+Sr)/Ti ratios of BST films can be adjusted simply by using a single stoichiometric BST target in conjunction with accurate control of the total process gas ($Ar+O_2$) pressure.

EXPERIMENT

BST thin films were deposited using an Ar-O_2 gas mixture in a RF magnetron sputtering system equipped with a 3" diameter target. The substrate and target (a sintered stoichiometric $Ba_{0.5}Sr_{0.5}TiO_3$ disc provided by Johnson Matthey) were positioned parallel to each other in an on-axis configuration with 10 cm separation. Prior to the initial deposition, the BST target was pre-sputtered for more than 20 hours to stabilize the surface composition. All BST films were deposited at 650°C on Pt(120nm)/SiO_2(300nm)/Si substrates. The thickness of all BST films was approximately 80nm. Capacitors for electrical testing were produced by depositing 100nm Pt top electrodes at 350°C through a shadow mask with circular openings of 100 μm diameter. After top electrode deposition, the samples were annealed in a quartz tube furnace at 550°C for 30 minutes in air in order to improve the top Pt electrode/BST interface.

Rutherford backscattering spectrometry (RBS), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and scanning probe microscopy (SPM) were used to investigate the thickness, composition, crystallographic orientation, microstructure, and roughness of the BST films, respectively. Dielectric properties (relative permittivity ε and dielectric loss $\tan\delta$ as a function of applied electric field) of the Pt/BST/Pt capacitors were measured at 10 kHz and 0.1 Vrms oscillation level using a Hewlett-Packard 4192A impedance analyzer.

RESULTS AND DISCUSSION

Fig. 1 (a) shows the variation of the (Ba+Sr)/Ti and Ba/Sr ratios as a function of the total (Ar+O_2) pressure used to deposit various BST films. The O_2/Ar ratio was fixed at 1/5. The ratio of (Ba+Sr)/Ti changed from 0.73 to 0.98 for a variation in the total gas pressure from 22 to 58 mTorr. In contrast to the (Ba+Sr)/Ti ratio, the Ba/Sr ratio demonstrated a much weaker trend with pressure. The Ba/Sr ratio was 0.73 for BST films deposited in 22 mTorr total process pressure and 0.84 for films grown in 30 mTorr total process pressure; this ratio remained constant for films deposited at pressures higher than 30 mTorr. As expected, the growth rate of the magnetron sputtered BST strongly depends on the total process pressure (Fig. 1 (b)). In separate experiments, the O_2/Ar ratio was varied from 1:1 to 1:5, but no changes were observed in the metals composition of the BST films. These results are consistent with a mechanism based on the pressure dependencies of the individual fluxes of Ba, Sr, and Ti impinging on the substrate (i.e., the different constituents have different, pressure dependent angular scattering distributions in the gas phase, due to their different masses).[6]

BST films with (Ba+Sr)/Ti ratios of 0.9 or higher exhibited a polycrystalline structure characterized by the appearance of (100), (110), and (111) peaks in the XRD spectra (see Fig. 2). Note that the BST (111) peak for these films is not well resolved from the very intense Pt (111), and is therefore not shown in Fig. 2. The BST peaks disappeared as the (Ba+Sr)/Ti ratio is reduced below 0.85 (Fig. 2). The disappearance of the BST- XRD peaks, coupled with the fact that relatively high permittivities are still found for these samples, indicates that the high-Ti BST films are nanocrystalline.

Significant differences were also found in the surface morphology of BST films with various (Ba+Sr)/Ti ratios. As shown in Fig. 3, the root mean square (RMS) roughness measured by SPM over a scan area of 14 μm x 14 μm was approximately 30 Å for BST films with (Ba+Sr)/Ti ratios of 0.9 or higher, for which BST-related XRD peaks are clearly visible. The RMS roughness was reduced to approximately 20 Å for BST films with (Ba+Sr)/Ti ratios less than 0.85, correlating with the structural changes indicated by the XRD spectra (Fig. 2 and Fig. 3).

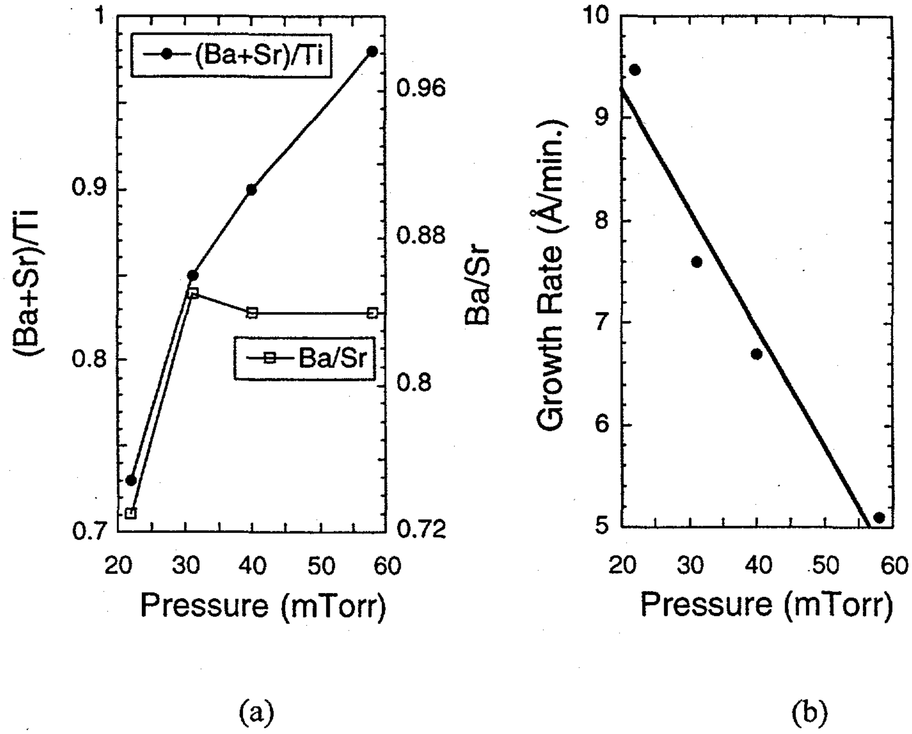


Figure. 1. (a) Variation of (Ba+Sr)/Ti and Ba/Sr ratios for BST films deposited at 650°C from a stoichiometric target with a Ba/Sr ratio of 50/50; and (b) growth rate as a function of the total pressure ($Ar+O_2$) in the magnetron deposition chamber.

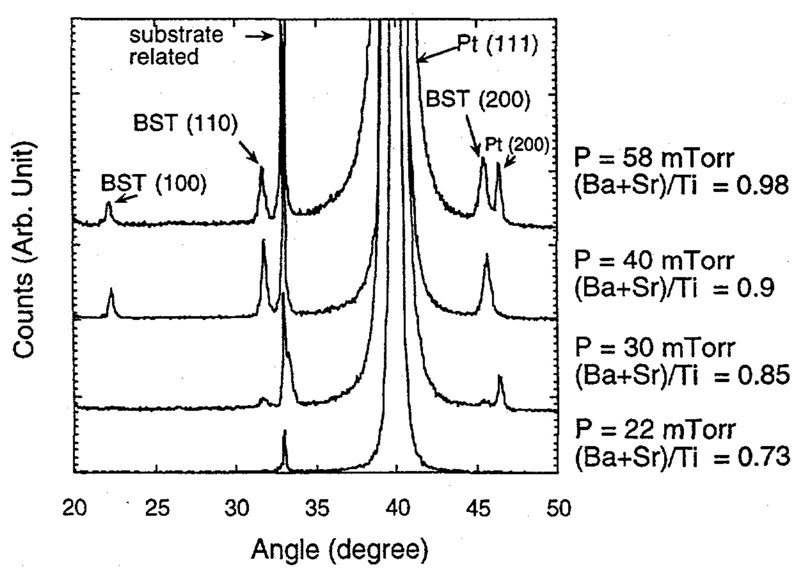


Figure. 2. X-ray diffraction spectra of BST thin films with various (Ba+Sr)/Ti ratio as a function of the total pressure ($Ar+O_2$) in the magnetron deposition chamber.

BST films with (Ba+Sr)/Ti ratios > 0.9 exhibited a dense and granular microstructure (Fig. 4(a)). In contrast, BST films with (Ba+Sr)/Ti ratios < 0.85 exhibited a featureless microstructure given the resolution of the FESEM techniques (Fig. 4 (b)). These surface morphology changes of BST films also support that the high-Ti BST films ((Ba+Sr)/Ti ratios < 0.85) are nanocrystalline. Further work, including TEM studies, is underway to elucidate the nature of these structural changes.

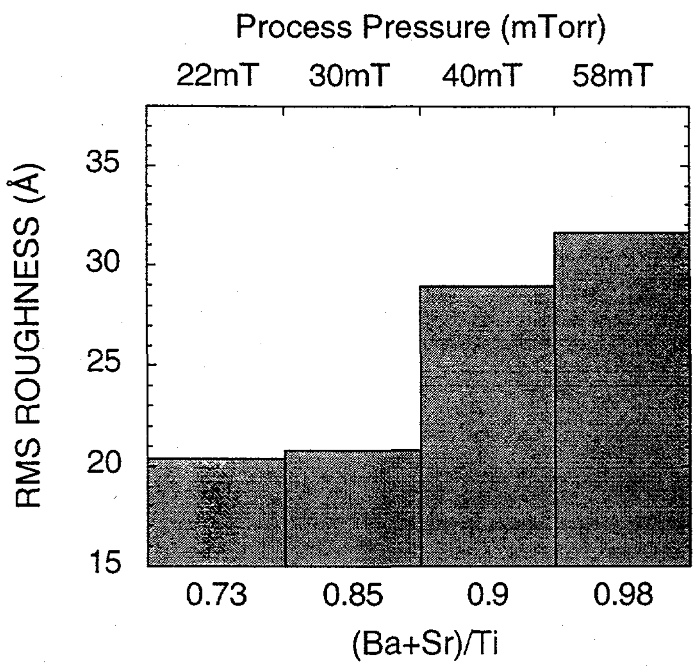
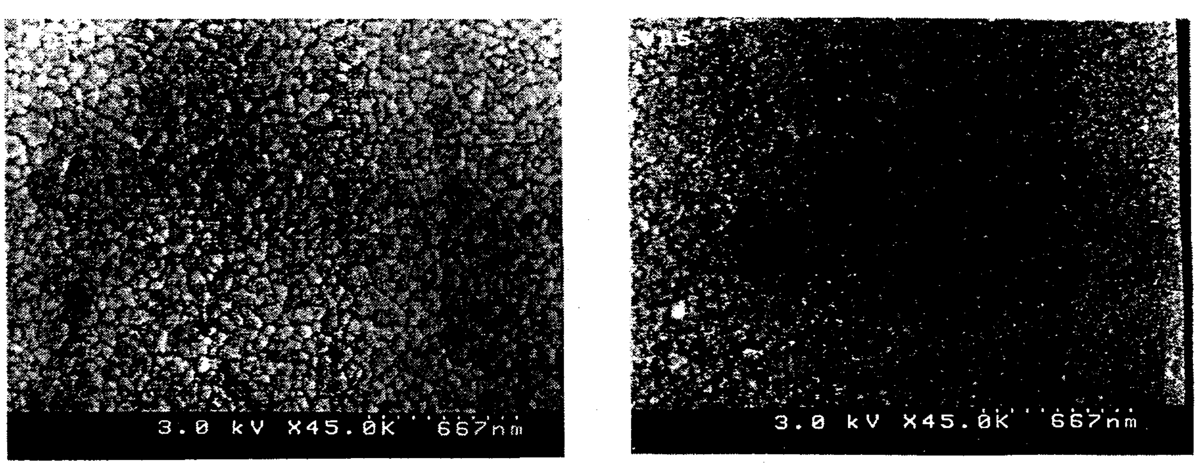


Figure 3. RMS roughness for BST films with various (Ba+Sr)/Ti ratio as a function of the total pressure ($Ar+O_2$) in the magnetron deposition chamber.



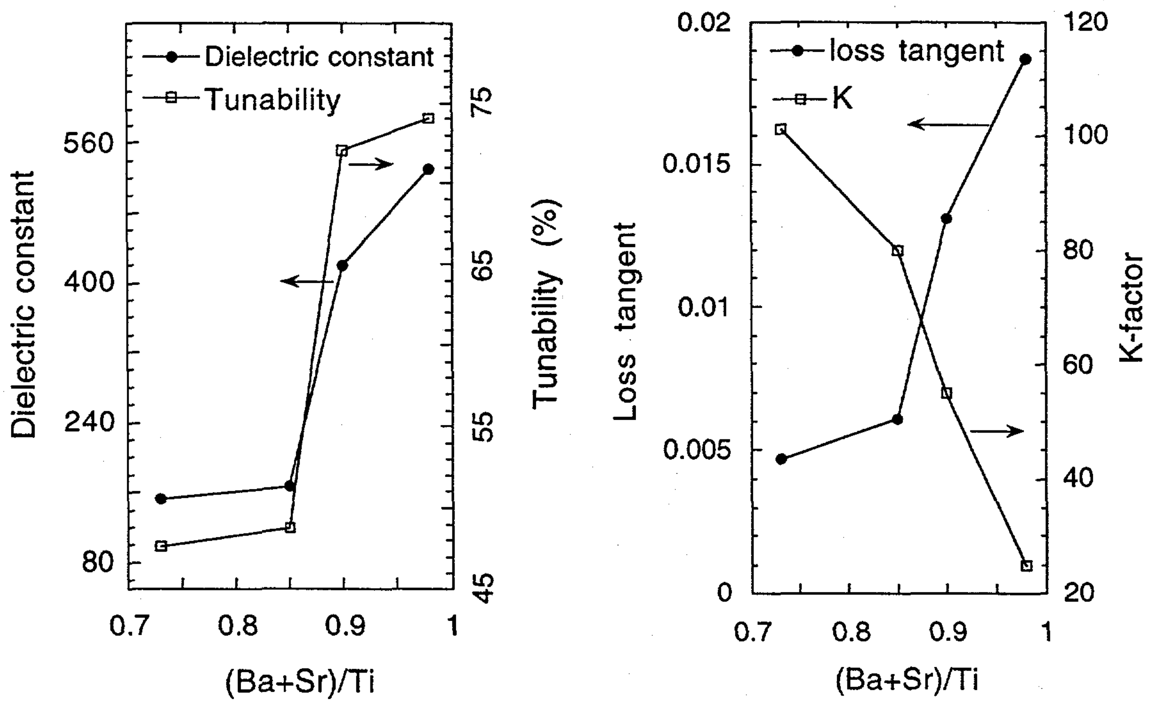
(a) **(b)**

Figure 4. FESEM spectra for BST films with (Ba+Sr)/Ti ratio of (a) 0.9 and (b) 0.85

The dielectric constant, and dielectric loss at zero bias also exhibited a clear dependence on the total process pressure or (Ba+Sr)/Ti ratio[7]. As shown in Fig. 5 (a), the near-stoichiometric BST film ((Ba+Sr)/Ti = 0.98) exhibited the highest dielectric constant as well as the largest tunability (defined as (ε_{max}-ε_{min}/ε_{max}), where ε_{max} and ε_{min} are the maximum and minimum measured permittivity) of approximately 74%. Tunability tracks the general trends in dielectric constant, as shown in Fig. 5 (a). A significant reduction in permittivity and dielectric loss at zero bias was observed for films with (Ba+Sr)/Ti ratio < 0.85 (Fig. 5). The lowest dielectric loss of 0.0047 at zero bias was found for the sample with a (Ba+Sr)/Ti ratio of 0.73. Given the observed correlations between tunability and loss, a figure of merit K is frequently used, and is defined as:

$$K = \text{tunability}/\tan\delta \quad (1)$$

As shown in Fig. 5 (b), the highest K value was found for the sample with a (Ba+Sr)/Ti ratio of 0.73. This demonstrates that the decrease in zero-bias permittivity for the highly nonstoichiometric samples is more than compensated for by their lower losses and higher breakdown fields, such that they may offer superior performance for some applications.



(a) Dielectric Constant and Tunability (b) Loss tangent and K-factor

Figure 5. (a) Dielectric constant, tunability and (b) loss tangent and K-factor measured for BST capacitors with various (Ba+Sr)/Ti ratios, deposited at various total pressures ($Ar+O_2$) in the magnetron deposition chamber.

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CONCLUSIONS

In conclusion, we have shown that BST films with high tunabilities, low losses, and high-dielectric breakdown fields can be grown using magnetron sputter deposition with judiciously chosen process parameters. Specifically, control is demonstrated of the composition (i.e., the (Ba+Sr)/Ti ratio) of BST films grown from a single stoichiometric target by use of tailored target-substrate geometry and deposition pressure. Figures of merit, defined as the ratio of tunability to dielectric loss, of approximately 100 have been obtained under optimized deposition conditions, with among the lowest losses at zero bias (0.0047) reported for physical vapor deposited BST films.

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