

## Metal Organic Chemical Vapor Deposition of Monolithic and Functionally Graded BST Films

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### ABSTRACT

Thin films of barium-strontium-titanate (BST) can serve as the tunable dielectric in a variety of RF and microwave devices. Compositionally graded BST films optimize films for the highest permittivity, highest tunability, maximum temperature stability, and minimum dielectric loss. This paper describes recent work to deposit BST films using a dual injection, metal organic chemical vapor deposition (MOCVD) technique. Injecting two separate precursor solutions (one for Ba-Ti oxide and one for Sr-Ti oxide) provides easy adjustment of the Ba/Sr ratio in the film. The dual injection MOCVD technique can also be extended to a wide range of other complex oxide systems.

**Keywords:** BST, MOCVD, dual injection, thin films, functional grading, tunable dielectric

### INTRODUCTION

Recently, there has been considerable interest to develop tunable dielectric materials for frequency-agile RF and microwave devices, including tunable filters, voltage controlled oscillators, varactors and phase shifters [1–6]. Most of this work has concentrated on barium strontium titanate— $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST), which is a solid solution of  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$ . The ferroelectric to paraelectric transition temperature (Curie temperature) for BST can be adjusted by the Ba/Sr ratio [7]. In order to be most effectively utilized in tunable RF devices, BST films must be simultaneously optimized for highest permittivity, highest tunability, maximum temperature stability and minimum dielectric loss. Difficulties arise, since the highest permittivity and maximum tunability are

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achieved near the Curie temperature, where the dielectric properties are most sensitive to temperature. Thus there is a basic trade-off between tunability and temperature stability, for monolithic composition BST films.

It has previously been recognized that compositionally graded ferroelectric films have unique properties [8–12]. Recent work has shown tunabilities as high as 65% can be achieved for compositionally grading BST films [11,12]. Models have been developed which explain how composition grading improves tunability and temperature stability, based on a thermodynamic analysis which includes the effects of temperature, composition and strain [13,14]. Previous demonstrations of compositional grading in ferroelectric thin films used solution deposition techniques [8,9,11,12] or pulsed laser deposition [10]. Deposition of BST films by MOCVD offers greater flexibility to tailor the film composition profile, since the precursor vapor flux can be continuously adjusted during film growth. Therefore, MOCVD should provide the greatest potential to optimize dielectric properties for BST and other tunable dielectric thin films.

This was the motivation for the current work, to develop MOCVD processes which could be used for both monolithic and compositionally graded BST films. In this paper, we describe MOCVD process development and composition calibration for BST films. Unlike other deposition techniques, film composition for MOCVD deposited films can be significantly different than the source composition. Therefore, an empirical calibration is typically required, of film composition versus source composition, which was the main focus of this work. Once established, we can use this calibration to deposit compositionally graded BST films, with optimized dielectric properties. Future work will utilize these optimized BST films in the development of tunable filters for RF and microwave device applications.

## EXPERIMENTAL

All process development was done work at Structured Materials Industries, using a research scale MOCVD reactor. The reactor consisted of a stainless steel vacuum chamber, with a non-rotating, horizontal-disc substrate configuration. A separate flash evaporator was connected to the MOCVD chamber via heated gas lines. The metal organic precursors were Ba(thd)<sub>2</sub>, Sr(thd)<sub>2</sub> and Ti(i-PrO)<sub>2</sub>(thd)<sub>2</sub> for the barium, strontium and titanium sources respectively. In the above formulae, “thd” = 2,2,6,6-tetramethyl-3,5-heptanedionato and “i-PrO” = iso-propoxide. Since these precursors are solids at room temperature, they were dissolved in solvents for injection into the flash evaporator. The molar concentration of the precursor solutions was 0.02 moles/liter, based on the total metal ion concentration. A variety of solvents were investigated; including toluene, tetrahydrofuran, octane, n-butyl acetate and pentamethyldiethylenetriamine (PMDT). The selection criteria for the solvent was; forms clear and

stable solutions with no precipitation of insoluble components, injects easily into the flash evaporator without clogging, and provides a high deposition efficiency (moles of film deposited per mole of precursor injected). Best results were obtained using either n-butyl acetate or PMDT. However, for the majority of the deposition trials we used n-butyl acetate, to avoid the toxicity issues for PMDT.

The precursor solutions were injected into the flash evaporator using peristaltic pumps, with Teflon tubing. The liquid injection rates were computer controlled, with rates from 0.10 to 1.25 ml/minute done in CW mode, and rates below 0.10 ml/minute done in pulsed mode. Since the film parameter of greatest interest is the Ba/Sr ratio, we used a dual injection technique, with two separate peristaltic pumps. Separate master solutions were prepared for Ba-Ti oxide and Sr-Ti oxide. Using this dual injection technique, we can prepare  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  films with any value of “x”, once we have calibrated the Ba/Ti and Sr/Ti ratios of the master solutions.

The substrates used were single crystal wafers of uncoated (1–102) sapphire and platinum coated (100) silicon. The MOCVD process conditions are listed in Table 1. Preliminary analysis of film composition was done by x-ray fluorescence (XRF). This technique could not accurately determine the Ba content of the films, due to the overlap of the Ba L peaks and Ti K peaks. Therefore, all film composition and thickness results reported below were obtained by Rutherford Back Scattering (RBS), on uncoated sapphire substrates. The RBS analysis was performed by Evans Analytical Group in Sunnyvale, CA.

## RESULTS AND DISCUSSION

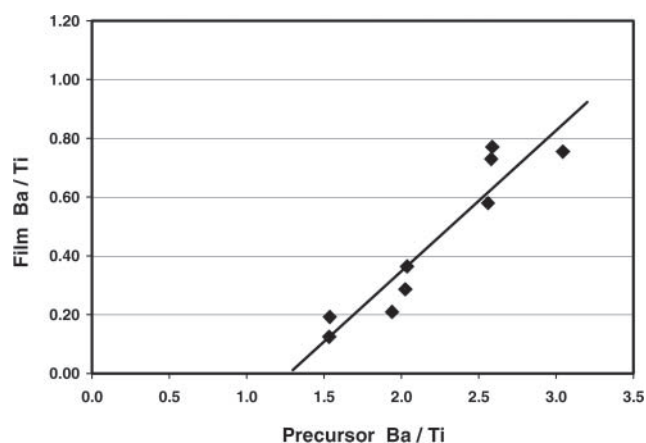
The main objective of this work was to develop a technique to deposit BST films with controlled composition profiles. The substrates of greatest interest

Table 1  
Process conditions for MOCVD of BST films.

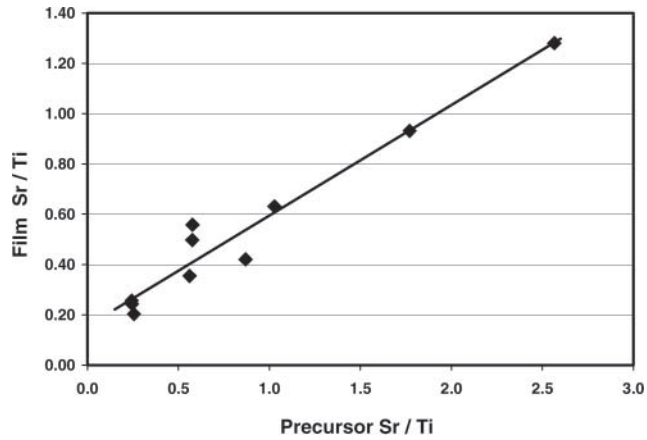
Substrate temperature	760 C
Flash evaporator temperature	240 C
Gas line temperature	270 C to 290 C
Showerhead temperature	290 C to 300 C
Chamber pressure	3.0 Torr
Flash evaporator gas flow	500 sccm Ar
Flash evaporator pressure	40 Torr
Chamber push gas flow	500 sccm Ar
Uniform chamber gas flow	500 sccm O <sub>2</sub>
Film thickness	300 nm to 450 nm

are Pt coated silicon and Pt coated sapphire, since these will be the substrates of choice for ultimate device applications. However, RBS, which was the primary analytical technique employed, could not obtain reliable results on the Pt coated substrates, since Pt and Si interfere with RBS analysis of BST films. Instead, we deposited BST films on uncoated sapphire substrates for the RBS analysis, and assumed that MOCVD on Pt coated substrates, under identical conditions, would result in the same film composition. The justification for this assumption was the XRF analysis. For all deposition trials, we consistently observed identical XRF spectra for BST films deposited on Pt coated silicon and on uncoated sapphire substrates, for MOCVD under similar conditions.

Initially, we prepared a series of monolithic composition BST films on sapphire substrates. We used two separate master precursor solutions, one for Ba-Ti oxide and one for Sr-Ti oxide. We varied the Ba/Ti and Sr/Ti ratios in the master solutions, as well as the relative injection rates of the Ba-Ti oxide and Sr-Ti oxide master solutions. For the composition calibration, we considered the total amount of each precursor (in moles) injected into the flash evaporator, compared to the total amount of material deposited on the substrate. Since we are primarily interested in the relative ratios of the three metal components, we can consider this as two independent calibrations for Ba/Ti and Sr/Ti. The results of these calibrations are shown in Figs. 1 and 2. The observed results are not linear, in that a least squares fit does not pass through the origin of the plot. However, this is not an issue, since there is no *a-priori* reason to assume these plots should be linear. These results can be approximated by a linear relation



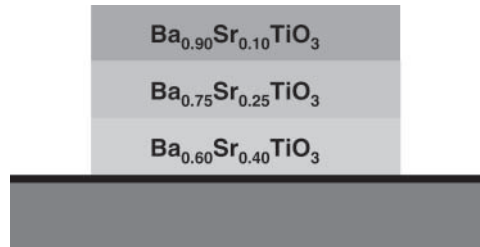
**Figure 1.** Composition calibration results for Ba/Ti, based on RBS analysis of BST films on uncoated sapphire.



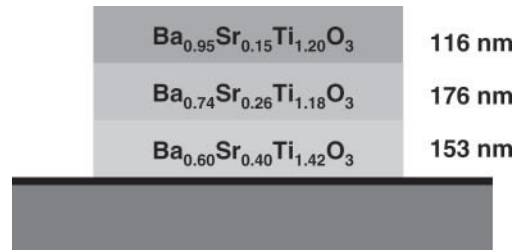
**Figure 2.** Composition calibration results for Sr/Ti, based on RBS analysis of BST films on uncoated sapphire.

near the Film Ba/Ti = 1 and Film Sr/Ti = 1 points, which is the most critical data regions for the calibrations.

Once established, these calibrations were used to prepare compositionally graded BST films. Our initial target was the three layer structure shown in Fig. 3. This composition profile was previously identified as having the optimum trade-off of high tunability and maximum temperature stability [12]. Samples of the three layer structure were prepared by MOCVD, using the dual injection technique. Results of RBS analysis of the three layer film are summarized in Fig. 4. As can be seen, control of the Ba/Sr ratio was very good. The Ti concentration for these films was somewhat high, indicating that composition calibration of the master solutions need to be further refined.



**Figure 3.** Target composition profile for the functionally graded BST film.



**Figure 4.** Actual composition profile for the functionally graded BST film as measured by RBS.

## CONCLUSIONS

MOCVD processes have been developed for BST films with good composition control. The dual injection MOCVD technique has been shown to be a viable means to control the Ba/Sr ratio for both monolithic and compositionally graded BST films. In addition, the dual injection technique avoids potential problems with ligand exchange for Group IIA beta-diketonate metal organic precursors. This technique also provides a convenient means for doping of BST films for tunable dielectric applications. Previous studies have shown that doping BST with acceptor ions can be an effective means to reduce dielectric loss [15]. The dual injection MOCVD technique can provide an easy method of film doping, by adding additional precursors to either of the master precursor solution, or to a third solution. Structured Materials Industries and our development partners are presently using these techniques to produce compositionally graded BST thin films on Pt coated Si and Pt coated sapphire substrates, to develop frequency agile filters for Ka band communication applications.

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