

## MOCVD Growth of Compositionally Graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ Thin Films

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*This paper describes an MOCVD technique for producing both monolithic and compositionally graded  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) thin films for tunable RF device applications. Specifically, we describe a “multiple injection flash evaporation” technique, which can easily produce BST thin films with a wide variety of compositional grading and dopant profiles. Preliminary results show the films to have excellent voltage standoff properties and tunability of dielectric permittivity. These materials are presently being used in the development of tunable RF filters for communication and radar applications.*

**Keywords** BST; Ferroelectric; MOCVD; Thin Films; Compositional Grading; RF Filters

### Introduction

Recently, there has been considerable interest to develop tunable dielectric materials for frequency-agile RF and microwave devices, including tunable filters, oscillators, and phase shifters [1–5]. The development of materials for tunable RF device applications has mainly focused on the perovskite oxides. The material of greatest technological interest is barium strontium titanate (BST). Presently, there are two main obstacles to implementing tunable dielectric materials in commercial applications, high dielectric losses and poor temperature stability. High dielectric losses result in a large fraction of the RF signal being lost to heat, which has several undesirable consequences including shorter battery life and increased thermal management issues for the device. Poor temperature stability is a particularly challenging problem, since the highest dielectric constant and greatest tunability are achieved near the Curie temperature, which coincides with the greatest temperature sensitivity of the material’s dielectric properties.

Recent work has shown that both issues can be effectively addressed by composition modification of the BST films. Compositional grading has been shown to reduce the temperature dependence of the dielectric properties for BST films, both through theoretical

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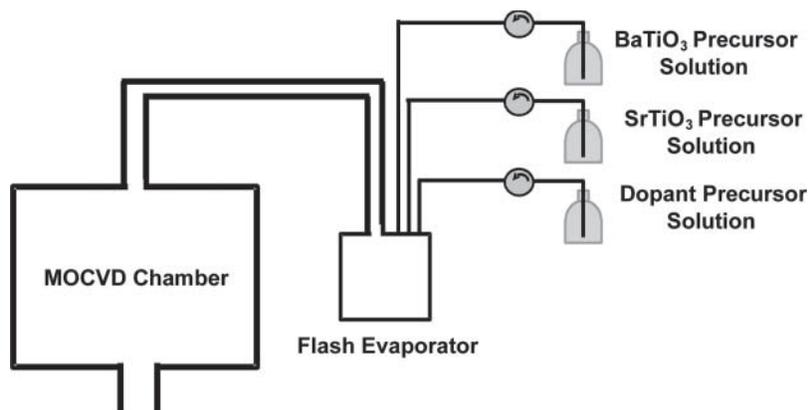
modeling [6, 7] and experimentally using metal organic solution deposited (MOSD) thin films [8, 9]. Other studies have shown compositional modifications to be an effective means to reduce dielectric losses in BST films, both through uniform doping of the film [10, 11] or through control of the interface chemistry [12]. To date, most of this development work has been done using BST films deposited by MOSD, sputtering, or pulsed laser deposition (PLD). While these techniques are well suited to produce monolithic composition films, they do not provide an easy means for compositional grading, or to investigate doping over a range of concentrations. This paper describes a metal organic chemical vapor deposition (MOCVD) process for BST films. MOCVD is particularly well suited to produce compositionally graded films. MOCVD allows for easy and direct control of film composition continuously during film growth. MOCVD also provides an easy and direct means to add dopants to the growing film, and to deposit controlled composition interface layers.

## Experimental

The substrates used in this work were single crystal wafers of r-plane sapphire, either uncoated or with a Pt/TiO<sub>2</sub> bottom electrode structure. To fabricate the bottom electrode, we first deposited 30 nm of titanium by DC magnetron sputtering, followed by a 30 minute anneal at 800°C in oxygen. We then deposited 200 nm of platinum by DC magnetron sputtering, followed by another 30 minute anneal at 800°C in oxygen. All BST film depositions were performed in a research scale MOCVD reactor, which includes a stainless steel high vacuum chamber and a temperature controlled showerhead for uniform reactant vapor delivery. Separate gas injection is provided for inert and oxidizing gas delivery.

The metal organic precursors used were Ba(thd)<sub>2</sub>, Sr(thd)<sub>2</sub>, and Ti(i-PrO)<sub>2</sub>(thd)<sub>2</sub> for the BST films, and La(thd)<sub>2</sub> and Mg(thd)<sub>3</sub> for the dopants. In these designations, “thd” = 2,2,6,6-tetramethyl-3,5-heptanedionato and “i-PrO” = iso-propoxide. Precise quantities of these precursors were weighed out in a nitrogen purged glove box and dissolved in a mixture of tetrahydrofuran plus 10% tetraethylene glycol dimethyl ether. The precursor solutions were sealed in glass bottles and connected to the MOCVD system without exposure to ambient atmosphere.

For MOCVD of compositionally graded Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> films, we use a multiple injection flash evaporation technique, illustrated schematically in Fig. 1. The liquid precursor solutions are injected into the flash evaporator at controlled rates. The flash evaporator is maintained at a temperature above the evaporation temperature of the precursors, but below their decomposition temperature. We use separate master solutions for barium titanate and strontium titanate, which are injected into the flash evaporator using separate peristaltic pumps. The peristaltic pumps run under computer control in either continuous or pulsed mode, with the lowest flow rates (>0.10 ml/min) achieved using pulsed mode. By adjusting the relative pump speeds, we can continuously adjust the Ba/Sr ratio in the film throughout the MOCVD run. The system also has additional injection lines and pumps for dopants. Using this multiple injection flash evaporation technique, we can produce a wide range of composition profiles for our MOCVD BST films. The MOCVD process conditions are listed in Table I. The only process conditions that were varied were the precursor solution compositions and their injection rates into the flash evaporator. After the MOCVD process, the BST film samples were slow cooled under an oxygen back pressure. All films received a post deposition anneal at 800°C in air for 60 minutes, followed by a slow cool to room temperature.



**Figure 1.** Schematic illustration of the multiple injection flash evaporation technique for MOCVD of compositionally graded BST films.

## Results and Discussion

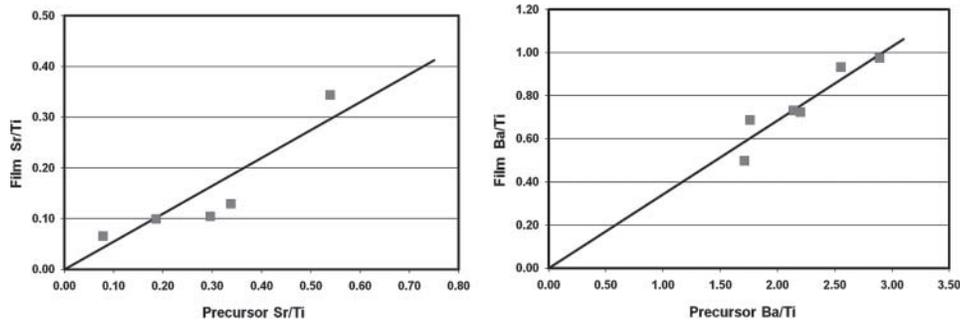
Unlike many other film deposition techniques, MOCVD requires an empirical calibration of source composition to achieve the desired film composition. For this calibration, we prepared a series of monolithic composition BST films with nominal compositions in the range of  $\text{Ba}_{0.60}\text{Sr}_{0.40}\text{TiO}_3$  to  $\text{Ba}_{0.90}\text{Sr}_{0.10}\text{TiO}_3$  on uncoated sapphire substrates. The actual film compositions were determined by Rutherford Backscattering Spectroscopy (RBS) performed by Evans Analytical Group in Sunnyvale, CA. We used uncoated sapphire substrates for this calibration, since platinum interferes with RBS analysis of BST films. Since we are only interested in the relative amounts of the metal components Ba + Sr + Ti, we need only consider two primary variables: the Ba/Ti and Sr/Ti ratios.

Figure 2 shows results for the composition calibration. In these calibrations, the precursor composition is the molar ratio of Ba/Ti or Sr/Ti atoms injected into the flash evaporator, as calculated from the precursor solution compositions and their injection rates. The film composition is the actual metal atom ratios in the BST films, as determined by RBS. Figure 3 shows the results of calibrating the BST film thickness, as determined by RBS, to the total moles of metal atoms injected into the flash evaporator.

With the calibration data of Figs. 2 and 3, we have all information necessary to produce BST films of nearly any composition profile. We need only program the process control

**Table 1**  
MOCVD Process Parameters.

Susceptor temperature	700 C
Flash evaporator temperature	240 C
Gas line temperatures	270 C to 290 C
Showerhead temperature	300 C to 320 C
Chamber pressure	3.0 Torr
Flash evaporator push gas flow	300 sccm Ar
Chamber push gas flow	250 sccm Ar
Uniform chamber flow	500 sccm O <sub>2</sub>

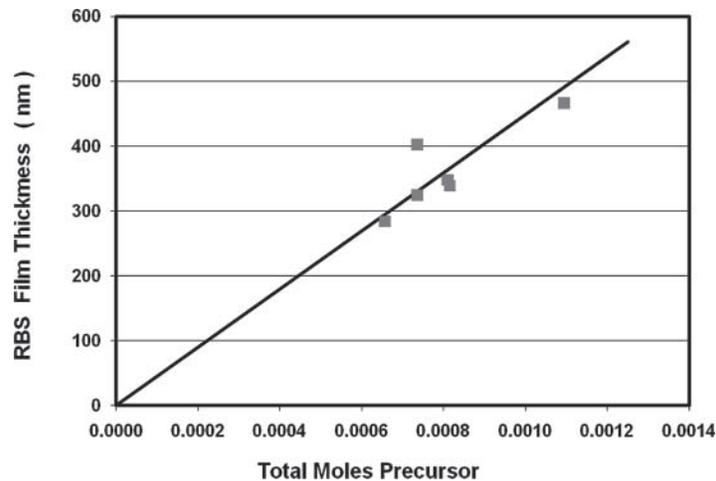


**Figure 2.** Calibration of film composition versus precursor vapor flux composition, for BST films deposited on uncoated sapphire substrates using the multiple injection flash evaporation technique.

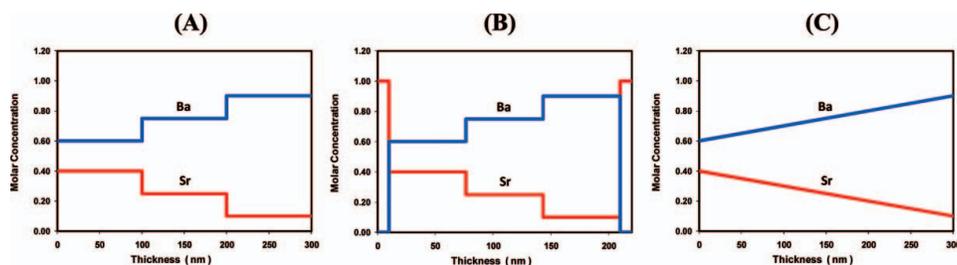
computer to adjust the precursor solution injection rates as a function of time during the MOCVD run. For the majority of our BST film samples, we prepared a 3-layer structure with equal thickness layers of:

$\text{Ba}_{0.90}\text{Sr}_{0.10}\text{TiO}$  – top layer,  
 $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$  – middle layer,  
 $\text{Ba}_{0.60}\text{Sr}_{0.40}\text{TiO}_3$  – bottom layer,

as illustrated in Fig. 4A. This structure was predicted to provide optimized temperature stability in earlier theoretical work [6, 7]. As an additional demonstration of the technique, we also produced several other composition profiles, including the 5-layer structure with 10 nm layers of  $\text{SrTiO}_3$  at each interface (as shown in Fig. 4B) and a continuously graded BST film (as shown in Fig. 4C). We also produced several series of compositionally graded BST films doped with lanthanum or magnesium. We used separate dopant solutions with



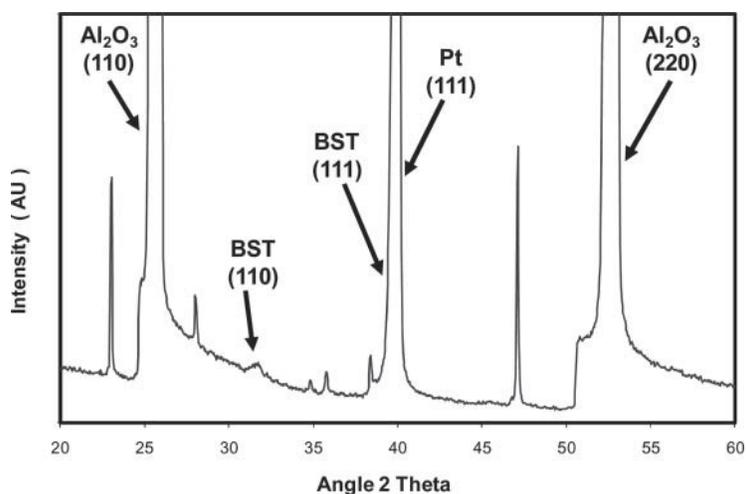
**Figure 3.** Calibration of BST film thickness versus the total moles of metal atoms injected into the flash evaporator.



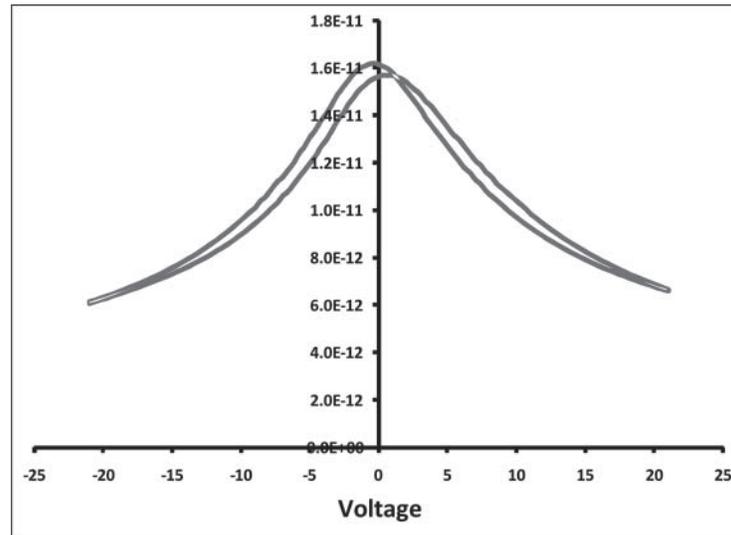
**Figure 4.** Composition profiles for MOVD BST films produced using the multiple injection flash evaporation technique. (A) 3-layer structure. (B) 5-layer structure. (C) continuously graded BST film.

La(thd)<sub>2</sub> or Mg(thd)<sub>3</sub>, and varied the dopant concentration by adjusting the relative injection rate of the dopant solution.

The resulting BST films were smooth and glassy, as observed by optical microscopy. X-ray diffraction (XRD) shows the BST films to be (111) oriented, as shown in Fig. 5. The bottom electrode platinum layer for these samples is also strongly (111) oriented, and the BST(111) and the Pt(111) peaks nearly overlap. In many cases, we also see a small BST(110) peak, as Fig. 5 indicates. For the electrical characterizations, we deposited an upper electrode structure by DC magnetron sputtering of platinum. The upper electrode layers were patterned to form parallel plate capacitor structures, using standard photolithography and ion milling. The resulting BST capacitors were characterized by capacitance-voltage (C-V) scans at 1.0 MHz. The results consistently show tunabilities over 60%, as shown in Fig. 6. The measured Dissipation Factor at 0 volts ranged from about 1% in the best case to about 5% in the worst case.



**Figure 5.** Typical XRD results for a 3-layer compositionally graded BST film prepared by MOCVD on a Pt coated sapphire substrate.



**Figure 6.** Capacitance versus voltage scan results at 1.0 MHz for a 200 nm thick 3-layer BST film prepared by MOCVD on a Pt coated sapphire substrate, showing tunability over 60%.

## Conclusions

MOCVD techniques have been developed for both monolithic and compositionally graded BST films. The multiple injection flash evaporation technique can produce compositionally graded BST films with a wide range of composition and doping profiles. Electrical characterization shows the films to have excellent tunability and voltage standoff properties. Compositionally graded BST films prepared at Structured Materials Industries are presently being used in prototype RF filter development. Preliminary results of this development work are reported elsewhere in these proceedings.

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