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$Ba_{0.6}Sr_{0.4}TiO_3$-MgO Thick Films Deposited by Electrophoretic Deposition for Tunable Microwave Device

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Abstract

We report on the structural, dielectric, and optical properties of barium strontium titanate-magnesium oxide composite (BST-MgO) thick films fabricated by the electrophoretic deposition (EPD) technique. The structure and morphology of the films were analyzed by x-ray diffraction and scanning electron microscopy, respectively. The films were optically characterized via FT-Raman spectroscopy. The dielectric measurements were conducted on MIM capacitors using platinum as the top and bottom electrodes. The typical small signal dielectric constants of $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO thick films, measured at an applied frequency of 1 MHz, were 603 and 327, respectively. The corresponding values of dissipation factor were 0.029 and 0.002, respectively. A high dielectric tunability of 17.3% was obtained for $Ba_{0.6}Sr_{0.4}TiO_3$ thick films at an applied electric field of 20 kV/cm. The dielectric properties of the present thick films were comparable to those of the bulk ceramics, suggesting their suitability for high-frequency, wide band voltage tunable device applications.

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1. Introduction

Recently, there has been a significant increase in the need for and applications of microwave circuit technologies. The progress in the communication applications has resulted in a demand for miniaturized components, which are a key factor for low power and integratable microwave devices [1–4]. Ferroelectric films have attracted considerable attention for applications in computer memory elements, frequency agile microwave components, pyroelectric sensors, and voltage tunable capacitors [3–8]. For tunable device applications, the ferroelectric material should possess a Curie temperature that results in low loss, low leakage current, and high voltage tunability [4]. A promising candidate material is $Ba_{1-x}Sr_xTiO_3$ (BST). BST is a continuous solid solution between barium titanate and strontium titanate over the entire range of concentration. The Curie temperature of $Ba_{1-x}Sr_xTiO_3$ decreases linearly with increasing strontium titanate concentration. As a result, the transition temperature and hence the electrical and optical properties of $Ba_{1-x}Sr_xTiO_3$ can be tailored over a broad range to meet the requirements of various electronic applications. The $Ba_{1-x}Sr_xTiO_3$-MgO based bulk composite materials have shown excellent dielectric loss and dielectric tunability characteristics at X-band and K-band frequencies compared to those of pure BST bulk ceramics [7–11]. However, a major drawback of these bulk ceramics for tunable devices, such as phase shifting elements, is the large drive voltages required for phase shifting [3]. Thick and thin films of the optimized bulk ceramic compositions are required to significantly lower the operating voltages. The thick films of these composite materials will offer the additional advantages of lightweight, compactness, and conformal deposition [3, 4, 7]. We report on the fabrication of BST and BST-MgO composite films by the electrophoretic deposition (EPD) technique, which is a simple, cost effective, and conformal method of depositing thick films. The films were characterized in terms of their structural, dielectric, and optical properties, and a comparison was made of the thick film properties with those of the bulk ceramics to establish their suitability for tunable microwave devices.

2. Experimental and Discussion

Figure 1 shows the schematic diagram of the EPD process. The EPD technique is composed of three major process steps: (1) formation of a charged suspension of

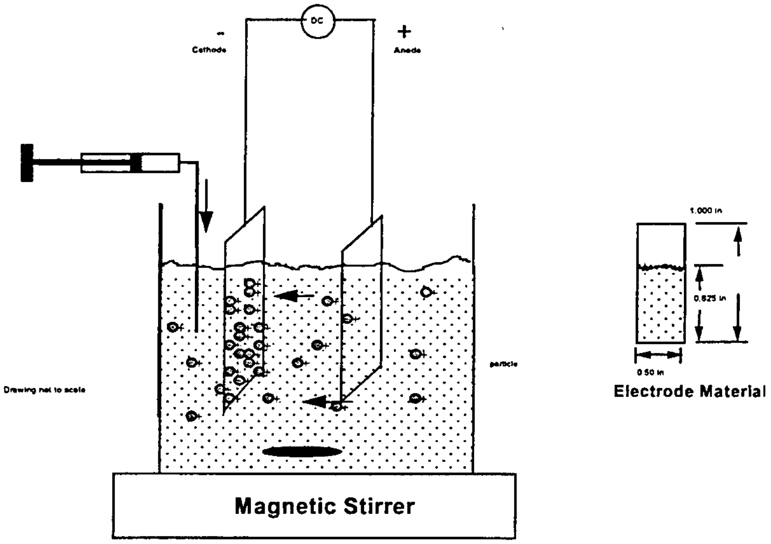

Figure 1. Schematic representation of the electrophoretic deposition technique.

the constituent particles required to achieve the final film composition, (2) application of a *dc* electric field in the suspension medium for deposition of the charged particles on the substrate, and (3) sintering of the deposited film to obtain a dense and crystallized thick film [11-13] The EPD thick films, $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$ - 20 weight-percent MgO, were fabricated using $BaTiO_3$, $SrTiO_3$ and MgO powders (FERRO Corp. Penn Yan, NY). The ceramic powders were processed by the standard solid-state methods. The powder mixture was ball milled in ethanol using an alumnia grinding media for about 24 hr. The mixture was air dried and, subsequently, calcined at 1100 °C for 2 hr. Immediately after calcining, the materials were mixed and ball milled a second time in order to obtain an average particle size of 0.5 µm, which was confirmed by sedigraph particle size analysis. The electrophoretic deposition was performed in acetone base slurry mixed with $C_{20}H_{37}O_7NaS$-surfactant (OTS) as a reactive agent media. Continuous stirring at 150 rpm was employed to prevent particle sedimentation. Two platinum (Pt) substrates were immersed into the solution separated by a gap of 1 cm. The films, 10 and 80 µm thick, were deposited on the Pt substrates for time intervals of 2 and 6 min, respectively. The film quality was strongly influenced by the ratio of acetone to aerosol OT-S surfactant in the EPD dispersive medium. For a BST-acetone solution (no OT-S surfactant) at an applied *dc* bias of 100 V, a negligible amount of film was deposited on the Pt cathode. The addition of an aerosol to the EPD solution was necessary to achieve a measurable film deposition. It was found that even at a low OT-S surfactant concentration level, $Ba_{0.6}Sr_{0.4}TiO_3$ films were easily deposited in a uniform and conformal fashion on the Pt cathodes. The as-deposited films were placed in a saturated acetone bath in order to extend the film drying time. This process step is crucial to avoid microcracks in the as-deposited film.

Any microcracks in the as-deposited green-body films will expand and propagate during film sintering, causing the film to degrade. The films were sintered in air at 1250 °C for 2 hr. The structure of the sintered films was analyzed by BRUKER D5005 x-ray diffractometer using Cu$K\alpha$ radiation at 40 kV. The surface morphology of the films was analyzed by an Amray 1830 scanning electron microscope operated at 20 kV. The electrical measurements were conducted on the films in a metal-insulator-metal (MIM) configuration using platinum as the top and bottom electrode. The MIM capacitors were fabricated by sputtering 0.2-mm Pt dots separated by 0.5-mm spacing through a shadow mask over a 1×1 cm^2 area of the film surface. The dielectric properties were measured with an HP4194A impedance/gain-phase analyzer.

Figure 2 displays the scanning electron microscopy (SEM) micrographs illustrating the conformal nature of the EPD films. Thick films with a dense microstructure and uniform surface morphology were obtained at an optimized acetone to aerosol ratio of 100:1. The film thickness increased rapidly in the first minute of deposition, then decreased, and ultimately stopped after 6 min. The surface morphology and plan-view microstructure of the film was analyzed by SEM. Figure 3 displays the surface morphology of the thick film and the bulk ceramic. The SEM analysis established that the microstructure of the EPD films was notably different from that of bulk ceramic in both grain size and film porosity. The average EPD film grain size was significantly smaller and much more uniform than that of the bulk ceramics. In contrast, the bulk ceramics possessed an extremely dense microstructure with no detectable porosity at the same SEM magnification.

The structure of the films was determined by x-ray diffraction (XRD). The XRD patterns of the EPD thick films and bulk ceramics are displayed in Figure 4. The films exhibited a well-crystallized phase with peaks attributable to cubic $Ba_{0.6}Sr_{0.4}TiO_3$. The XRD results demonstrated that both the EPD films and bulk ceramics possessed a polycrystalline structure. There was no apparent change in peak intensity resultant of the material fabrication process, indicating that both the films and bulk ceramics were well crystallized at their optimized sintering temperatures. FT-Raman spectroscopy results substantiated that the optical properties of the thick films were similar to those of the bulk ceramics. Specifically, the Raman peak shifts for both the bulk and the thick films were at around 2000 cm^{-1} in Figure 5. The Raman results established that no detectable alteration of the ceramic composition occurred as a result of the material processing method.

The dielectric properties of the films were measured in terms of the dielectric constant (ε_r), dissipation factor (tan δ), and dielectric tunability. The following equation was used to calculate the dielectric constant:

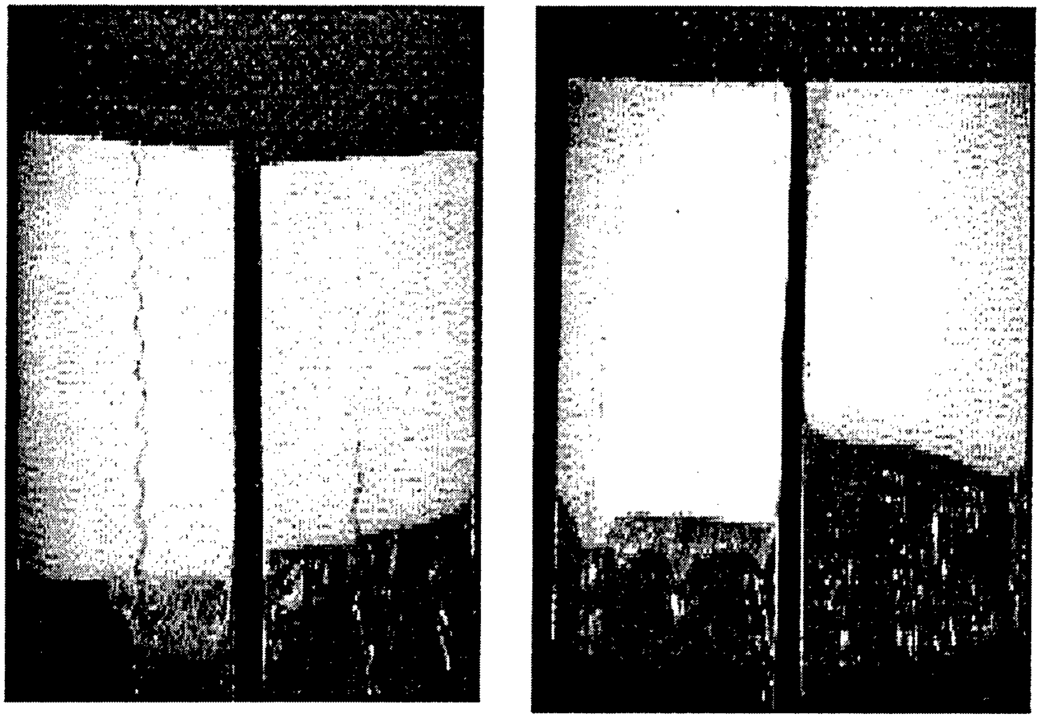

Figure 2. SEM images of electrophoretic deposited $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO thick films showing the conformal nature of the film deposition on (a) the front and (b) the back of the Pt substrate.

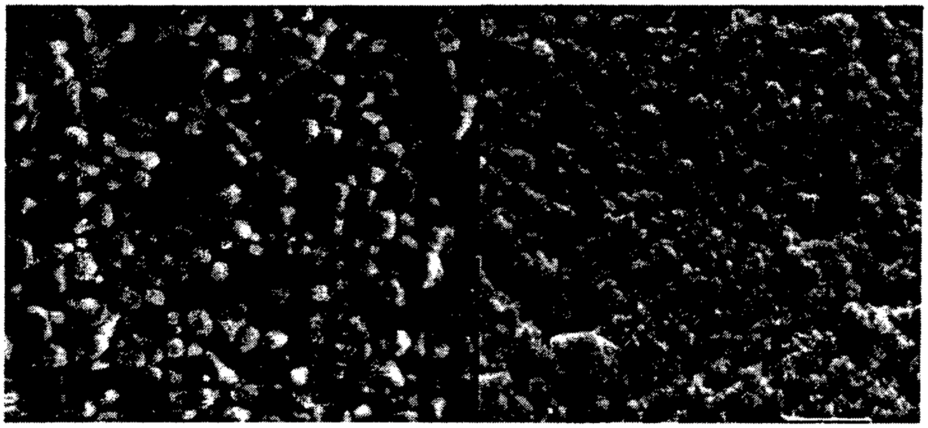

Figure 3. Plan-view SEM micrographs of the $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO (a) bulk ceramic sintered at 1350 °C for 2 hr and (b) the EPD film sintered at 1250 °C for 2 hr.

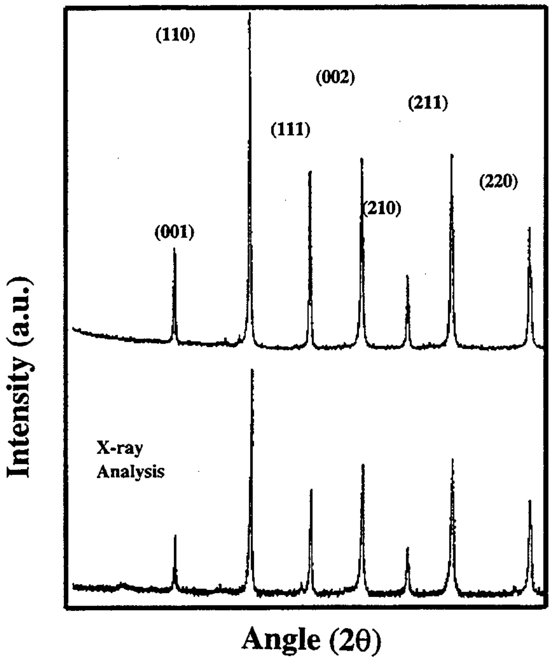

Figure 4. X-ray diffraction patterns of the sintered $Ba_{0.6}Sr_{0.4}TiO_3$ (a) EPD film and (b) the bulk ceramic.

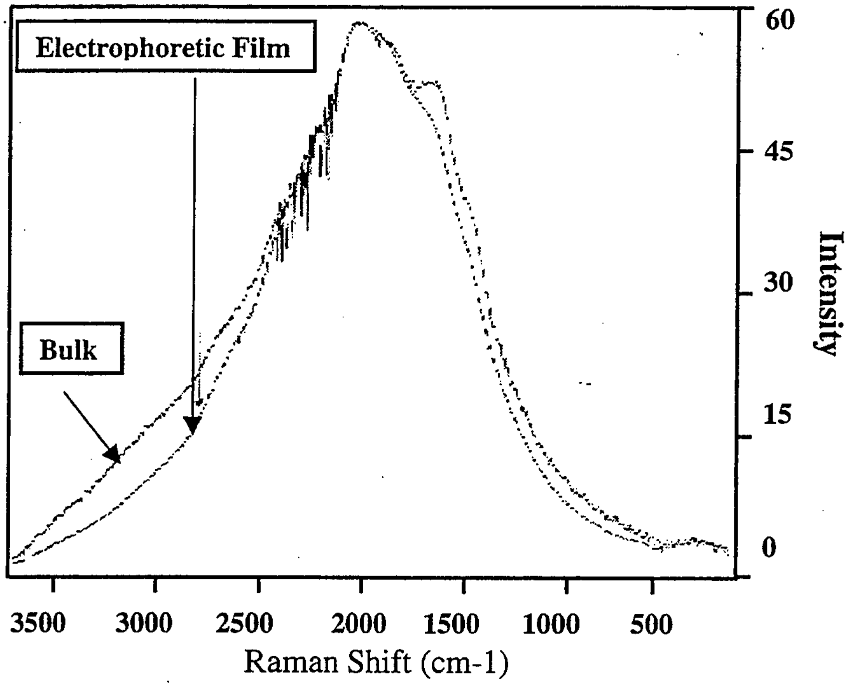

Figure 5. FT-Raman of $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO electrophoretic film and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO bulk shows similar vibration mode confirmed film deposited and powder are the same.

$\varepsilon' = Ct / A\varepsilon_0$,

ε' = dielectric constant of the thick film,

C = capacitance measured at 1 MHz,

t = thickness,

A = area, and

$\varepsilon_0 = 8.8542 \times 10^{-12}$.

The dielectric tunability was calculated from the capacitance-voltage (*C-V*) characteristics. The *C-V* measurements were conducted by applying a small *ac* signal of 10-mV amplitude and 1-MHz frequency across the sample while the *dc* electric field was swept from a negative bias to a positive bias. The tunability of capacitance was measured, at an applied *dc* field of 20 kV/cm, in terms of the parameter $\Delta C/C_o$, where ΔC is the change of capacitance relative to zero-bias capacitance C_o. The dielectric properties of the BST and BST-20 weight-percent MgO films and bulk ceramics are presented in Table 1. The dielectric constant of the EPD films was significantly reduced for both compositions (BST and BST-MgO) compared to that of bulk materials. This reduction in dielectric constant is attributed to the higher porosity and finer grain structure of the films. The effect of the MgO additive on the dielectric properties of the films paralleled the overall trend of the bulk ceramics; that is, a reduced dielectric constant, loss tangent, and tunability was obtained with the MgO additive to BST. The low dielectric loss of the BST-MgO films, comparable to BST-MgO bulk ceramics, indicates good stoichiometry and crystallinity of the EPD deposited films. The tunability of the BST-MgO films was much lower than the bulk value; however, it must be noted that the film tunability displayed in Table 1 is not the maximum obtainable value. Since the EPD films are significantly thinner than the bulk ceramics, the film tunability can be elevated by applying a higher *dc* electric field strength to achieve higher tunability values with an overall lower power consumption compared to bulk ceramics.

Table 1. The dielectric properties for the bulk ceramics and the EPD thick films at a frequency of 1 MHz. The dielectric tunability was measured at E = 2V/μm.

Composition	ε_r		tan δ		Tunability (%)	
	Bulk	Films	Bulk	Films	Bulk	Films
$Ba_{0.6}Sr_{0.4}TiO_3$	5160	603	0.009	0.029	56.7	17.3
$Ba_{0.6}Sr_{0.4}TiO_3$ -20 weight-percent MgO	1068	327	0.002	0.002	15.8	8.0

3. Summary

$Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO thick films were successfully fabricated by the electrophoretic deposition technique. The films exhibited good structural and electrical properties at a lower sintering temperature compared to the bulk ceramics. The $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO composite thick films exhibited a lower dielectric constant than the bulk ceramics due to smaller grain size. The dielectric constant, dissipation factor, and the tunability of the BST films were found to decrease with increasing MgO content. The typical small signal dielectric constants of $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO thick films, measured at an applied frequency of 1 MHz, were 603 and 327, respectively. The corresponding value of dissipation factor was 0.029 and 0.002, respectively. A high dielectric tunability of 17.3% was obtained for $Ba_{0.6}Sr_{0.4}TiO_3$ thick films at an applied electric field of 20 kV/cm. The good structural, dielectric, and tunability of the $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$-20 weight-percent MgO thick films, comparable to the bulk ceramics, suggest their suitability for tunable wide band microwave devices with significantly lower drive voltages.

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