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Performance Enhanced Complex Oxide Thin Films for Temperature Stable Tunable Device Applications: A Materials Design and Process Science Prospective

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1. Introduction

The recent growth in the wireless communications area has incurred a large demand for high data rates, broad bandwidth, reliable, and low cost RF tunable microwave devices. Traditional materials, both ferrites and semiconductors, have been exploited for these devices. Unfortunately, semiconductor devices are expensive and have high losses at microwave frequencies while ferrites are not frequency agile and offer slow tuning speeds. Such performance drawbacks have cultivated strong interest in developing new materials, namely perovskite oxide thin films. Recently, barium strontium titanate, $Ba_xSr_{1-x}TiO_3$ (BST), a perovskite oxide solid- solution, has captured the attention of microwave engineers as a candidate material to promote a new generation of passive tunable microwave devices. The intense interest in BST thin films is largely due to the fact that these materials possess the ability to change their dielectric constants as well as their dielectric loss in response to an externally applied field. This feature makes BST thin films ideally suited for electronically tunable microwave devices such as resonators, filters, oscillators and phase shifters (Kalkur et al., 2009). Furthermore BST thin films have several major advantages compared to their conventional ferrite and semiconductor counterparts; they offer fast tuning speeds, low power consumption, and low cost due to affordable fabrication and process science methodologies. Additionally, for microwave applications, the development and implementation of BST materials in thin film form is critical for enabling miniaturization of microwave components and promoting integration with semiconductor microelectronic circuits. Finally, enhanced material performance in concert with scale-up, affordability, integration, and small size are critical metrics for communications systems whether it be a planar phased array antenna system or hand held devices incorporating tunable circuits.

Over the last decade, the growth and process science of uniform composition BST have been investigated intensively for tunable device applications (Weiss et al., 2008, Podpirka et al., 2008); Joshi & Cole, 2000). To achieve optimum device performance, it is critical to fabricate

a material with high dielectric tunability, low microwave losses, and a low temperature dependence of the capacitance/ dielectric constants (i.e., good temperature stability) in the device's operational frequency and temperature ranges. Such properties are critical and are required for optimum performance and long-term reliability. The technical literature is laden with experimental and theoretical investigations focused on optimizing uniform composition BST thin film growth, and process science protocols (achieved via doping, thickness variations, buffer layers, stoichiometry, stress modification, annealing procedures, etc.), in order to develop thin films which possess low dielectric loss and high tunability. Although much success has been achieved in optimizing these two material properties, less attention has been devoted to optimizing material temperature stability.

There is significant concern that in practical applications of such tunable devices, in particular, in BST-based phase shifters for electronically scanned antennas (ESAs), the phase shifter performance will be compromised due to the temperature dependence of the device capacitance. The same temperature instability issues are also relevant to tunable filters/preselectos used in small tactical radio systems and handheld communication devices. Specifically, the capacitance of the BST-based device (phase shifter and/or tunable filter) is strongly influenced by temperature changes because the dielectric permittivity (K), or the relative dielectric constant (ε_r)of a single composition paraelectric BST film (e.g., $Ba_{0.5}Sr_{0.5}TiO_3$) follows the Curie-Weiss law,

$$K = C/(T - \theta) \tag{1}$$

where C is the Curie constant, T is the temperature, and θ is the Curie Weiss temperature (Oates et al., 1997). In field applications, communications systems (antenna and/or radio systems) are exposed to a broad range of harsh operational environments, i.e., variable ambient temperatures, and spurious changes in the device capacitance that stem from ambient temperature fluctuations. These will disrupt the phase shifter performance via device-to-device phase shift and/or insertion loss variations, leading to beam pointing errors and ultimately communication disruption and/or failure in the ability to receive and transmit the information. The same is true for BST-based tunable filters where the susceptibility of the capacitance to temperature changes results in the alteration of the band pass window sharpness (window narrows or broadens), or the entire band pass window may shift to higher or lower frequency and/or insertion loss may be degraded. Such poor temperature stability of the capacitance would result in the carrier signal drifting in and out on hot and cold days. Thus, to ensure device performance consistency and reliability, temperature stable devices are essential for the next generation communications systems, ESA's, radios and hand-held communications devices.

This Chapter discusses the temperature stability issues and puts forward a summary of innovative materials designs, and novel process science solutions which serve to help mitigate this temperature sensitivity and render BST thin films more useful and device-relevant for the next-generation RF-microwave devices/systems. Particular emphasis is concentrated on tunable phase shifters and filters to enable phased array antennas, radars and other advanced communications devices. Advances in wireless communications applications are highly dependent upon improvements in microwave materials in concert with achieving balanced property-optimization. Thus, the critical review put forward in this Chapter holds promises to provide the foundation and spawn new materials research solutions to further enable the development of BST thin films for applications in microwave device arena.

2. Temperature instability of BST materials

It is well known that for single crystal and polycrystalline bulk BST ceramics, the dielectric permittivities are strongly temperature dependent, with a sharp dielectric anomaly at the ferroelectric to paraelectric phase transition, *Tc* (Lemanov et al., 1996). Moreover, due to the functional dependence of the dielectric permittivity with temperature, the resonant frequency of a fabricated microwave device also becomes strongly temperature dependent resulting in carrier signal drift in an ambient surrounding (Cava, 2001). The temperature dependent drift of resonant frequency poses serious problems in using bulk ceramic BST for practical device applications, that must be addressed. Initially, BST in thin film form was considered as a first order solution towards realizing temperature stability. Compared to bulk ceramic BST, thin film BST (of the same composition) does not possess such a pronounced dielectric anomaly (Fig 1). For example, Fig. 1 compares the temperature
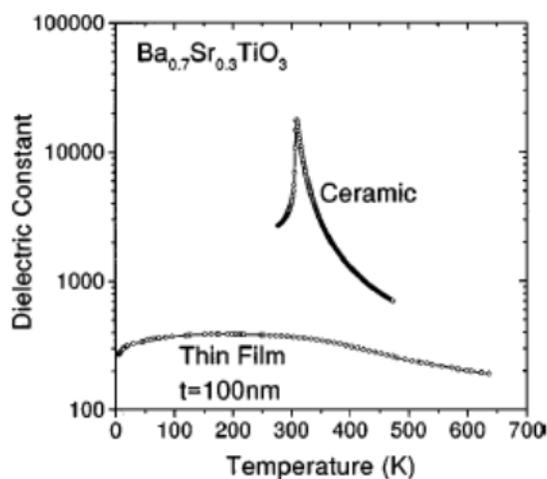

Fig. 1. Variation of the dielectric constant of a bulk ceramic and a film as a function of temperature. [From: Shaw et al. 1999. Copyright 1999, American Institute of Physics.]
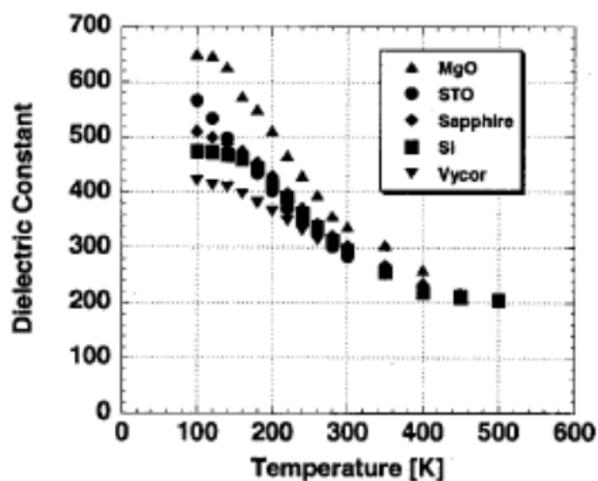

Fig. 2. Dielectric constant as a function of temperature for BST/Pt/substrate structures. From: Taylor et al., 2002. Copyright 2002, American Institute of Physics.]

dependent dielectric constant of a bulk ceramic $Ba_{0.7}Sr_{0.3}TiO_3$/BST70/30 to that of a thin film of the same composition (Shaw et al., 1999). For the BST thin film, not only is the dielectric constant much lower, it also does not have a sharp peak as a function of temperature. This broad dielectric anomaly, indicative of a diffuse phase transition has been attributed to the finer grain sizes, residual strains, composition heterogeneities inherent to synthesis (Kim et al., 2000, Zhang et al., 2010, Mantese et al., 1995). This observed flattening of the dielectric-temperature peak in thin film BST with respect to that of bulk ceramic BST has led many to incorrectly conclude that BST in thin film form is temperature stable. Unfortunately, this is not the case. When compared to bulk ceramics, thin film BST exhibits less temperature sensitivity, (i.e., it has a smaller temperature coefficient of capacitance/TCC). However, it is not temperature stable. Fig. 2 illustrates this temperature instability whereby Taylor and co-workers (Taylor et al.,2002) experimentally explored the dielectric response as a function of temperature for five BST75/25 thin films on a variety of substrates with different thermal expansion coefficients (TECs). This work confirms that there is indeed a temperature dependent dielectric response for thin film BST. However, BST films grown on substrates with smaller TECs (i.e., larger tensile in-plane thermal strain) display a reduced dielectric permittivity and a smaller (although still quite pronounced), temperature dependence of the dielectric response. Therefore, the capacitance of any device based on such a film would be highly temperature dependent, making its use difficult to accommodate in circuit design. Thus, it is important to compensate for the temperature coefficient of the dielectric constant (TCK) and the commensurate TCC. The challenge here is to accomplish this without degrading the other device critical properties, i.e., without decreasing the tunability or increasing the dielectric loss. This notable temperature dependence of the dielectric response is a potential point of concern for the utilization of BST thin film in microwave devices. As such, solutions, whether via engineering or material design must be critically reviewed and considered.

3. Traditional temperature stability solutions

Traditional approaches to address the issue of device (phase shifter and/or tunable filter) temperature instability have focused on employing hermetic or robust packaging, where the package serves to protect the tunable device from the harsh environmental extremes. Although this approach is successful, hermetic/robust packaging would add significant cost, size, and weight to both ESA and radio systems. Other concepts to achieve temperature stability compliance involve the use of system heat sinks and/or cooling apparatuses such as mini-fans, temperature compensation circuits, and/or mini-ovens. Such thermal management solutions may be utilized with ESAs or radios; however, they will add extra weight, size, and cost to the overall system and, as such, are deemed unacceptable. Temperature compensation can also be achieved using either a curve fit or a look-up table approach. The curve fit methodology centers on the formulation of a temperature dependent mathematical expression, which represents the drift of each BST tunable device. A microprocessor utilizes this equation and the ambient temperature data (obtained from a thermocouple mounted on the printed circuit board) to calculate the tuning voltage. The look-up table approach, as its name implies, involves using a look-up table. In order to obtain the relevant coefficients, the phase shifter/filter characteristics must be measured at discrete temperatures. Then the BST bias voltage is manually adjusted to maintain the phase shifter/filter specifications. In the worst-case scenario, one would have to obtain a set of

points for each temperature (i.e., 23oC, 24oC etc). Typically, one would expect to have a small subset of temperature/bias points for each bias line. The exact number of points is, of course, dependent on the BST devices, the other phase shifter/filter components, and the phase/filter topology. Unfortunately, both the curve fit and look-up table approaches are quite complex as there is usually not a one-size-fits-all solution. The calibrations are also labor and time intensive and are useful if only a limited number of ESAs, radio, and communication devices are to be fielded.

In contrast to the above described engineering methodologies, there are also viable novel materials science approaches. Conventional materials science methodology for reducing the temperature dependence of an active material involve the selection of the temperature interval of operation well above the temperature corresponding to the active material's permittivity maximum. Unfortunately, this approach results in reduced material tunability and the TCC is still too high for practical military/commercial communication system applications. More useful materials science methods for achieving material/device temperature stability are based on utilization of artificial structures which generally involve the synthesis of BST multilayers or compositionally graded BST structures. Such BST heterostructures were shown to possess unique and desirable dielectric properties, i.e., a low dependence of capacitance on temperature, high permittivities, and high tunabilities (Zhu et al., 2003, Lu et al., 2003, Tian et al., 2003, Zhang et al., 2006). Although these experimental and theoretical studies have produced very promising results, most of the work focused on compositionally graded/multilayer BST films fabricated by techniques that are non-industry standard such as pulsed laser deposition (PLD). Additionally, many of these graded films were deposited on ceramic small-area expensive substrates, utilized "designer" nonstandard electrodes or asymmetric electrodes, and employed high annealing temperatures which are not compliant with conventional silicon integrated circuit (IC) processing protocols. Specifically, the use of small-area ceramic substrates and designer electrodes is not practical from a scale-up, manufacture, and affordability point of view and high annealing temperatures would deteriorate the quality of the films due to the strong diffusion between films and substrates. In the case of the metal-insulator-metal (MIM) design, heating the film above 800 °C would damage the structure of the bottom electrode which will degrade the dielectric loss, leakage characteristics, and tunability of the device. Furthermore, most of the published results in the relevant literature are incomplete in that there is a lack of systematic experimental data which determine and compare the dielectric properties (loss, tunability, and permittivity) to those of uniform composition BST prepared using the same fabrication technique and post-deposition anneal process protocol. Additionally, there are relatively few investigations which evaluate the temperature dependence of dielectric response at microwave (MW) frequencies. Nonetheless, these studies contain important ideas and methodologies for temperature compensation and it is important to summarize these results and populate a materials data base so that future work can benefit from this knowledge and perhaps spawn innovative industry standard and frequency relevant materials solutions to resolve the temperature stability dilemma.

4. Temperature stability via materials solutions

Since the concept of compositionally graded materials was originally proposed for reducing the thermal stresses associated with dissimilar materials research in this area has been greatly expanded from structural materials to functional materials and ultimately to thin

film electronic materials. Since the late 1990's extensive interest in frequency agile materials for electronics has been cultivated within the materials science community. This interest has encouraged materials research to address performance issues, via hybrid material designs including multilayer and compositionally graded perovskite oxide thin film materials (e.g., BST and other ferroelectrics).   It should be noted that compositionally graded or multilayer ferroelectric thin films exhibit properties not previously observed in conventional monolithic ferroelectric materials. There have been many noteworthy publications which have provided experimental data concentrated on the dielectric performance of tunable devices using graded/multilayer BST thin films. The common thread of this body of literature is focused on the thesis that it is necessary to grow BST thin films with a low temperature dependence of dielectric constant to realize temperature stable/reliable tunable device applications. Furthermore, such results have introduced a variety of functionally graded/multilayer material designs which serve to demonstrate that the low temperature coefficient of the dielectric response can be achieved by producing BST films with graded compositions through the deposition of layers of BST with different Ba/Sr ratios. In order to critically evaluate this technical area and to hone in on a practical materials solution to mitigate the temperature sensitivity of BST in frequency agile communications devices, we summarize here the relevant work, highlighting the technical concepts, results, and solution shortfalls.

4.1 Summary of the relevant literature: non-standard process science

It is well established that the capacitance of any ferroelectric/BST-based device will be highly temperature dependent, making its use difficult to accommodate in circuit design. It is therefore important to compensate for the temperature coefficient of the dielectric constant without decreasing the dielectric tunability and/or increasing the dielectric loss. To maintain such a trade-off, a simple and effective way is to prepare compositionally graded BST films by depositing successive layers with different Ba/Sr ratios. Thus, the graded films are essentially composed of multiphase compositions with different phase transition temperatures, where a high dielectric constant and a relatively smaller TCC and/or TCK values are maintained, making such graded materials highly preferable in applications where the capacitance of a device should be only weakly dependent on temperature.

For microwave device applications, epitaxially grown films are often utilized because of their high dielectric constants and large tunabilities (Lin et al., 2008). Since the pulsed laser deposition (PLD) method of film fabrication is particularly adapted to the growth of stoichiometric epitaxial films with single and multiphase compositions many studies utilize this method for growth of BST graded films. While PLD is a wonderful research tool to study and demonstrate complex film compositions (e.g., compositionally graded/multilayer BST films) it must be kept in mind that this growth technique is not scalable or industry standard for foundry friendly device manufacture (Cole et al., 2002b, Cole et al., 2005). Nevertheless, for research demonstrations, the PLD method of preparing compositionally graded/multilayer BST films has provided some very useful results. In particular Zhu et al., (2003) have grown epitaxial compositionally graded BST with $0.0 \leq x \leq 0.25$ thin films on (100) LaAlO$_3$ (LAO) substrates using La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) bottom electrodes. This study was focused on 2 distinct compositionally graded structures: (1) Down-Graded Films: films with with Ba/Sr ratio varied from BaTiO$_3$ (BTO) at the film/substrate interface to BST 75/25 at the film surface and (2) Up-Graded Films: films with Ba/Sr ratio varied from BST75/25 at the film/substrate interface to BTO at the film surface. The temperature dependence of the

dielectric properties measured between -20ºC and +130ºC as a function of frequency between 1 kHz and 1 MHz is displayed in Fig. 3   which shows that that the dielectric constants and the dissipation factors vary only slightly with frequency. The values of ε_r and the loss tangent (tan δ) at 100 kHz were 380 and 0.013 for the up-graded films, and 650 and 0.010 for the down-graded films, respectively. It can be seen that dielectric behavior was enhanced in the down-graded BST film. The enhanced dielectric behavior observed in the down-graded films was attributed the fact that since the bottom layer (BTO) is under compressive strain in the $b-c$ plane and elongated along the a-axis; such compressive strain would increase the ionic displacement and promote the polarization of electric dipoles along the electric field parallel to the a-axis. Therefore, the enhanced dielectric behavior (larger dielectric response) observed in the down-graded films could be ascribed to the pure BTO layer in the down-graded BST films not only serving as a bottom layer but also acting as an excellent seeding layer to enhance the subsequent film growth, resulting in higher film crystallinity and larger grain sizes in the down-graded films.
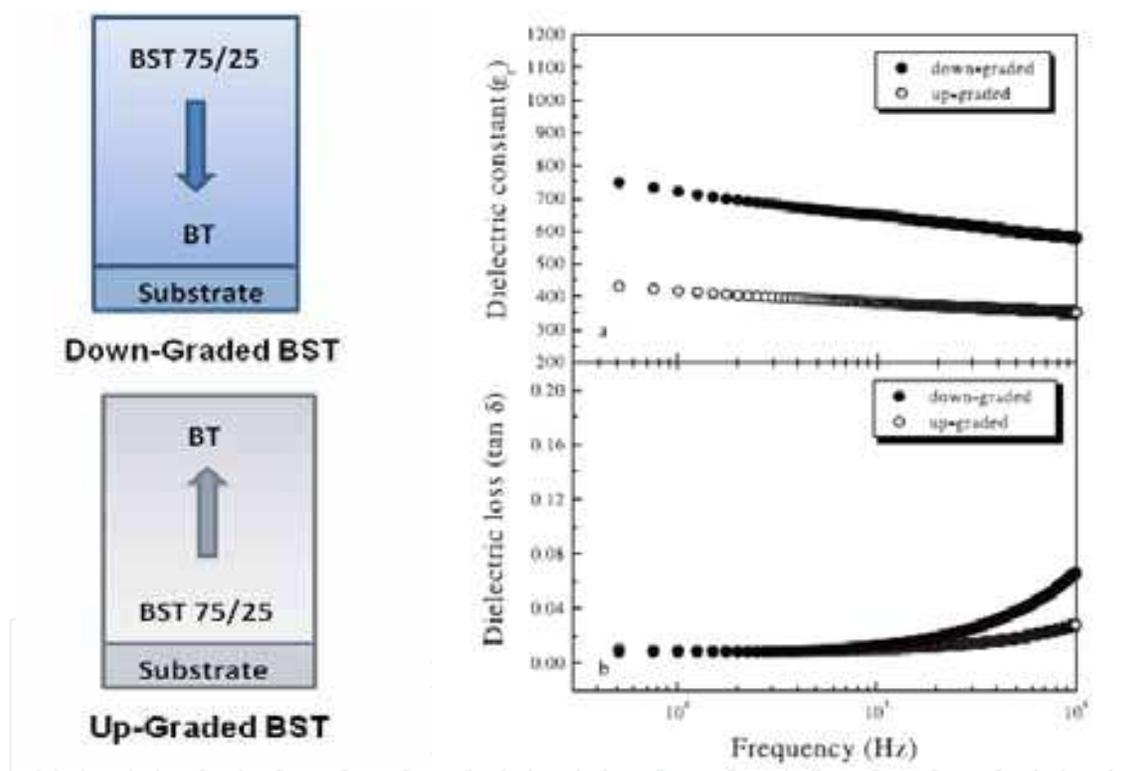

Fig. 3. Schematic drawings of the up-graded and down-graded materials designs (left side). Dielectric constant and dissipation factor of the up-graded and down-graded BST films as a function of measured frequency (right-side). [From Zhu et al. 2003. Copyright 2000.]

The temperature dependence of the dielectric properties of the down-graded BST films is shown in Fig. 4. Fig. 4(a) shows the broadened and flattened transition peak (tetragonal–cubic phase transition) to be at about 90ºC. The authors suggest that the flat profile of the dielectric constant versus temperature for the down-graded BST thin films is explained by the presence of compositional and/or residual strain gradients in the epitaxial graded film. The local variation of the composition and/or the strain leads to local changes in the permittivity, which broadens the peak in the dielectric constant as a function of temperature.

Furthermore, similar to relaxor ferroelectrics, the Curie maximum temperature T_C shifts towards higher temperatures with increasing frequency. Fig. 4(b) compares TCC of down-graded BST with homogeneous BTO. This plot demonstrates that T_C of the monolithic BTO is about 120°C, and that such an isotropic thin film exhibits a narrow plateau region around the dielectric constant maximum compared with the down-graded films, whereas the graded capacitor has a low temperature coefficient for the capacitance and high dielectric permittivity for a wide range of temperature. This work demonstrates that the broad-flat profile of the dielectric constant versus temperature relationship (low TCC) observed in the graded films is paramount and is useful for building dielectric thin-film capacitors having a capacitance which has a low temperature dependence over a broad temperature regime.

(a)   (b)
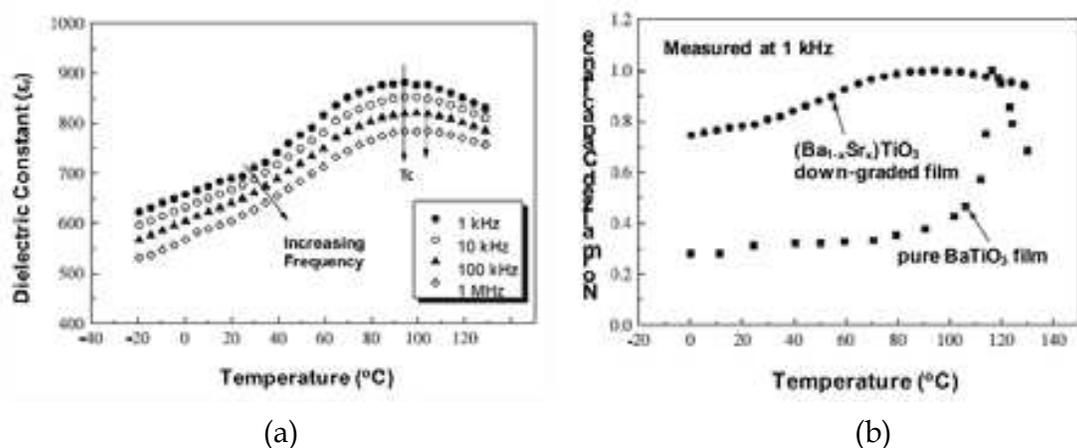
Fig. 4. Temperature dependence of the dielectric response for the down-graded BST films; (a) The dielectric constant vs. temperature as a function of frequency. A comparison of the temperature dependence of the capacitance between the down-graded BST film and pure $BaTiO_3$ film deposited in the same system is shown in (b). [From: Zhu et al. 2003. Copyright, 2000.]
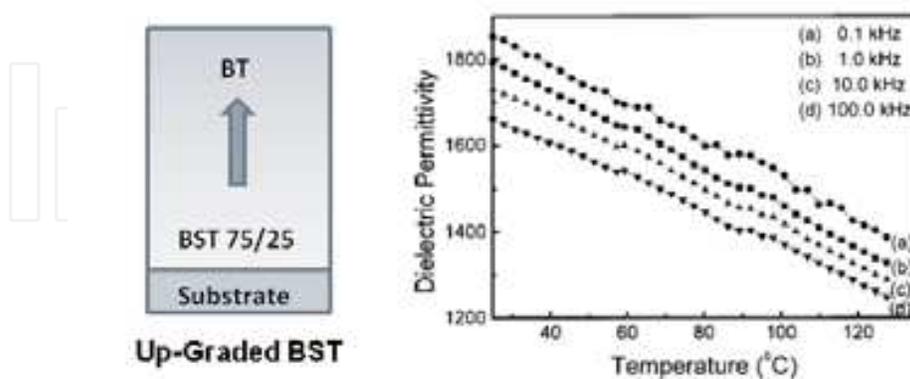

Fig. 5. Temperature relationship of dielectric permittivity for PLD fabricated upgraded BST films on $LaAlO_3$ (001) substrates with $(La_{0.7}Sr_{0.3})MnO_3$ (LSMO) bottom electrodes. [From Lu et al., 2003. Copyright 2003.American Institute of Physics.]

Similar work to promote temperature stable BST films was performed by Lu et al., (2003). However, in this study the authors focused on the up-graded BST thin film structure i.e.,

LAO substrate – $(La_{0.7}Sr_{0.3})MnO_3$ bottom electrode – BST 75/25 – BST 80/20 – BST 90/10 – BTO In this case, considering that the gradient in the film is in an ideal situation, and neglecting the effect of interlayer interactions at the interfaces between the layers, the whole film can be regarded as an ensemble containing a graded distribution of Ba^{2+} and Sr^{2+} ions normal to the growth surface. For this up-graded structure, when the temperature decreases from a temperature higher than 120°C, the phase transition will occur from the top layer to the bottom layer one by one. Because of the induction of polarization, the ''layer'' with a higher permittivity will dominate the permittivity–temperature characteristics (Jeon et al., 2001).

The temperature dependence of permittivity over the range of 25-130°C and for frequencies of 0.1, 1, 10 and 100 kHz is displayed in Fig. 5. Similar to the work of Zhu et al., (2003) (down- graded BST films), the films exhibit a broad and flat variation profile of the dielectric constant over a wide range of temperature, where there was no Curie–Weiss law behavior observed. However, two broad anomalous peaks were seen, indicating some change associated with the broadened phase transition process. These two peaks occurred at about 59°C and 92°C, near the phase transition temperatures of BST 80/20 (57°C) and BST 90/10 (89°C), respectively. It was suggested that these two broadened peaks might be the result of incomplete diffusion of Ba^{2+} and Sr^{2+} ions, resulting in the trace of BST 90/10 and BST 80/20 compositions within the graded film structure. In addition, over the same temperature intervals (25 - 130°C) Lu et al., (2003) up-graded films of possessed enhanced dielectric constant (~1650 - 1250/upgraded films at 100 kHz/negative slope) with respect to Zhu and co-workers (Zhu et al., (2003) down-graded films (690-850/down-grade at 100 kHz/positive slope). While the absolute values of the permittivities differed between these two studies (Zhu et al., 2003, and Lu et al., 2003) the per cent change in permittivity as the temperature was elevated from 20 to 120°C was similar, i.e. the permittivity of Lu et al., (2003) up- graded film decreased by 25% and Zhu et al., (2003) down-graded films' permittivity increased by 23 % over this temperature interval. The loss tangents of the two films displayed similar trends, i.e., broadened peaks over the entire temperature range from 20-130°C; however, the room temperature dielectric loss was much higher for Lu et al., (2003) 0.05 vs. that of Zhu et al., (2003) 0.010-0.013. Furthermore, the high dielectric permittivity and broad temperature characteristics were obtained in conjunction with a very high tunability of over 70% (at 1 MHz,) which is higher than that of monolithic BST 75/25 with the same compositions and applied fields (~60%). Such results suggest that compositionally graded BST films sustain temperature stability with enhanced performance of high tunability and low loss.

Xia et al., (2006) investigated doping BST to modulate T_C and achieved temperature independent tunability over a broad temperature range. A method to vary the T_C is by chemical substitution in such BST films. Sun et al., (2004) reported that the doping of PbO to BST 70/30 thin films derived by sol-gel method enhanced T_C. Moreover, it is also known that adding more kinds of cations to the A site in the ABO_3 perovskite structure usually results in a diffuse phase transition, which can broaden the transition peak and induce low temperature dependence. In order to investigate the temperature stability of the enhanced tunable properties of BST, Xia and co-authors (Xia et al., 2006) leveraged these concepts and fabricated PLD BST films with Ba partially substituted by Pb, i.e., $(Ba_{0.25}Pb_{0.25})Sr_{0.5}TiO_3$ (BPST) on Pt/Si substrates. For comparison BST50/50 films with the same thickness and processing protocols as the BPST films were produced. This study shows that the dielectric

constant of BPST exhibits a maximum at the temperature of 7°C, whereas, in the case of BST, the maximum occurs at −79°C. The temperature corresponding to this peak of dielectric constant is considered to be T_C. As is known, BST is a continuous solid solution between BTO and SrTiO₃ (STO). PbTiO₃ (PTO) has a higher T_C (485°C) than that of BTO (120°C). That is why with the addition of PTO into the BST system, the T_C of the solid solution BPST could be adjusted to shift to higher temperatures.

It is well known that varying the Ba/Sr ratio can also result in a T_C around room temperature (RT) such as in BST 75/25, but it also produces a sharp dielectric peak and a commensurate strong temperature dependence. For BPST films, the addition of Pb cations to the A site in perovskite structure, gives rise to an enhanced relaxor behavior and a diffuse phase transition. This study observed that there was a significant broadening of the transition peak with respect to that of the monolithic BST50/50, and that there was a notable increase of peak temperature with increasing frequency from 100 kHz to 1 MHz. This is indicative of a typical relaxor behavior that is not present in the undoped BST50/50 films. It is well known that the relaxor behavior is related to the heterogeneity of the nanoscale composition. Thus, adding Pb ions into the A site of perovskite structure of BST system could be responsible for the relaxor behavior of BPST films. Specifically, the regions with A site rich in Pb²⁺ would display some PTO-like behavior and become polar at RT, whereas other regions could have a tendency to remain non-polarized since BST with 0.25<x<1 is indeed paraelectric at RT. The existence of nanopolar regions in a paraelectric environment results in the distribution of T_C in BPST films, giving rise to the broadening of the transition peak and low temperature-dependent dielectric constant. This result is similar to the performance of the graded multilayer BST films reported by Lu et al., (2003) and Zhu and co-workers (Zhu et al., 2003, Zhu et al., 2002a). Evaluation of the 1 MHz ε -V characteristics determined that the tunability of BPST is about 60% at the applied voltage of 5 V (160 kV/cm), which is much larger than the value of 34% for monolithic BST films. Furthermore, such enhanced tunability may also be related to the existence of nanopolar regions in BPST films, since such regions may induce ferroelectricity in the paraelectric matrix due to the internal electrostatic fields that are formed because of the polarization mismatch across the interfaces. The analysis of the temperature dependence of the tunability at 5 V indicates that in the temperature ranging from 25 to 100°C, the BPST films still exhibits relatively high tunability from 60% to 54%. In addition, it was speculated that this wide variation of tunability with regard to temperature could be attributed to the broadened dielectric constant peak caused by the diffuse phase transition. Since the dielectric constant decreases slowly with the increasing temperature, a relatively stable tunability can be obtained. Thus, this study demonstrated that the addition of Pb to BST resulted in a relaxor behavior and a diffuse phase transition, which broadened the dielectric peak. Hence, the tunability of BPST films displayed good stability against the temperature. Although this temperature stability of high tunability bodes well for tunable devices made of BPST films which would be operated at environment with different temperatures, the authors did not investigate the behavior of dielectric loss with respect to the Pb addition and/or temperature stability. In addition, no microwave (MW) frequency analyses were presented. However, as a first approximation, these results show promise toward providing a feasible and simple approach for realizing simultaneously high tunability and good temperature stability of BST based thin films.

4.2 Summary of the relevant literature: industry standard process science

Although these experimental studies highlighted above show very promising results, most of the studies focused on compositional graded BST films fabricated by techniques that are non-industry standard such as pulsed laser deposition (PLD). Additionally, many of these graded films were deposited on ceramic small-area expensive substrates (LAO), utilized "designer" non-standard electrodes or asymmetric electrodes, and employed high annealing temperatures which are not compliant with conventional silicon IC processing protocols.

There has been only a limited quantity of published studies focused on graded BST films whereby the film fabrication method employed was either a sol-gel or metal organic solution deposition (MOSD) method, both of which are industry standard growth techniques. As such, these are scalable and thus promote affordable manufacture/scale-up. The work of Tian et al., (2003) focused on fabricating BST thin films on Si substrates with artificial gradients in composition normal to the growth surface via   sol-gel deposition. Specifically, the graded BST thin films were composed of BST 70/30 – BST 80/20 – BST 90/10 layers which were annealed via a special 4-step heating procedure to form the compositional gradient from BST 70/30 to BST 90/10,   similar to the up-graded structure devised by Lu et al., (2003) and Zhu et al., (2003) for PLD films, differing slightly in the strength of the composition gradient (a slightly lower strength). In addition, Tian et al., (2003) up-graded structure was unintentionally capped (artifact of film processing) at the top and bottom by narrow surface layers which were off-stoichiometric compositions (Fig. 6). Auger electron spectroscopy (AES) depth profiling determined that composition gradients of Ba and Sr were gradual and uniform without obvious interfaces between the different layers, i.e. no step variation in Ba and Sr concentration. For comparison, the authors also prepared BST thin films with uniform composition, e.g., BST 70/30, employing the same processing method. The low frequency (10-100 kHz) dielectric properties of the graded BST thin films and the uniform composition BST films (BST 70/30, BST 80/20, BST 90/10) were measured in the metal-insulator-metal (MIM) capacitor configuration (Fig. 7). The maximum of the capacitance was 271 pF (corresponding to a dielectric constant about 300) and loss factor around 0.02 for the graded BST thin film. The tunability of the dielectric constant was calculated in terms of dielectric constant (capacitance) variation rate: $\Delta C / C_0$, where ΔC is the change in capacitance relative to zero bias capacitance C_0. The tunability of the graded BST thin film was ~ 35% while the tunabilities of the uniform composition BST films were around 23–25% obtained at an applied electric field of 240 kV cm^{-1} (Fig. 7). This tunability value of 35 % is significantly lower than that achieved for up-graded BST films by Lu et al., (2003) (~70 %). Although both films were in an up-graded material design, the broader compositional strength (BST75/25 – BTO vs. BST 70/30 – BST90/10; i.e., 25% broader compositional strength) of Lu and co-workers study (Lu et al., 2003) may be the reason for the higher tunability with respect to that of Tian et al., (2003). The enhanced tunabilities for the graded BST films suggest that these films are promising candidates as tunable microwave elements and integrated capacitors. Unfortunately this work did not report results related to the temperature dependence of the dielectric response, hence there no conclusions regarding temperature stability of these films can be inferred.

Zhang and co-workers (Zhang et al., 2006) also investigated compositionally up-graded BST thin films fabricated on Pt/Si substrates by the sol-gel technique. However, in this work the compositional gradient was broadened compared to the studies of Tian et al., (2003), Lu et al. (2003), and Zhu et al., (2003) to span from BST 60/40 to BTO. The results demonstrated the dielectric constant and dielectric loss measured at 200 kHz to be 335 and 0.045,
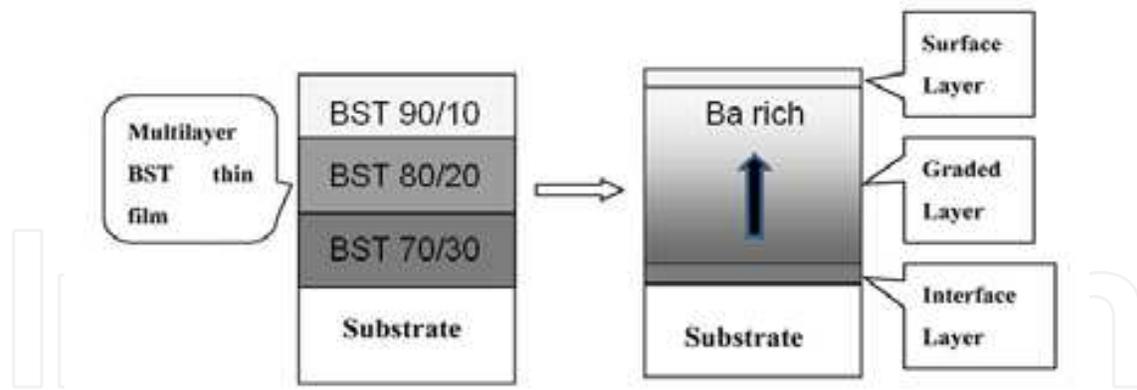
Fig. 6. Schematic of the BST graded thin film. The as-deposited thin film structure (left) and configuration model after heat treatment (right). [Modified Diagram from Tian et al., 2003. Copyright 2003, Elsevier.]
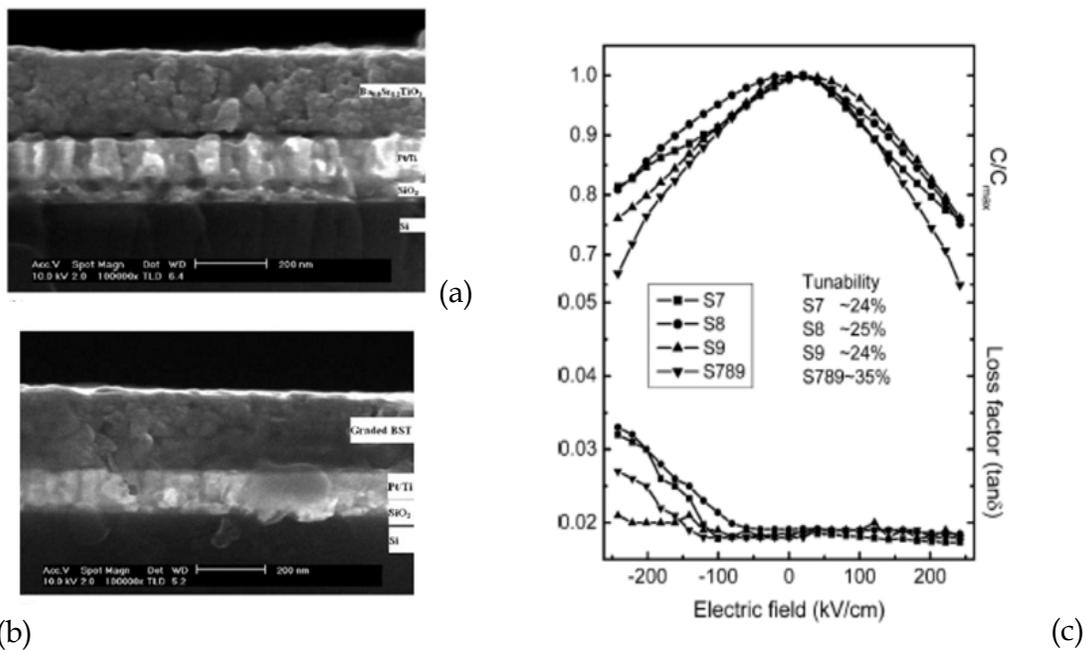

Fig. 7. SEM images of the (a) uniform composition and (b) graded BST films. The field dependence of capacitance (dielectric constant) and dielectric loss at room temperature (100 kHz) is shown in (c). [From Tian et al., 2003. Copyright 2003, Elsevier.]

respectively, and a tunability of 42.3% at an applied field of 250 kV/cm. Unfortunately, this study like that of Tian et al., (2003) did not report the temperature dependence of dielectric response data. The research group of Wang et al., (2008) published an interesting compositionally graded BST study whereby they combined a broad compositional gradient (BST 60/40 to BTO) with a yttria stabilized zirconia (YSZ) buffer layer sandwiched between the film and the Pt bottom electrode on Si substrates. The compositionally graded films were prepared on Pt/Si substrates with and without a buffer layer of YSZ via the sol-gel technique. The results showed that the YSZ buffer layer served to improve the dielectric properties of the graded films, i.e., lower losses (tan δ = 0.026 vs. 0.065), enhanced

permittivity (ε_r=339 vs. 318) and improved leakage current characteristics (3.1 x 10^{-9} A/cm^2 vs. 1.7 x10^{-6} A/cm^2 at 4V). The improved materials properties of the graded films with the YSZ buffer layer was attributed to the fact that the buffer layer serves as an excellent seeding layer which enhanced BST growth and mitigated the interfacial dead layer, i.e., the parasitic, in the MIM capacitor structure. As with the studies discussed above there was no data reporting the temperature dependence of the dielectric response.
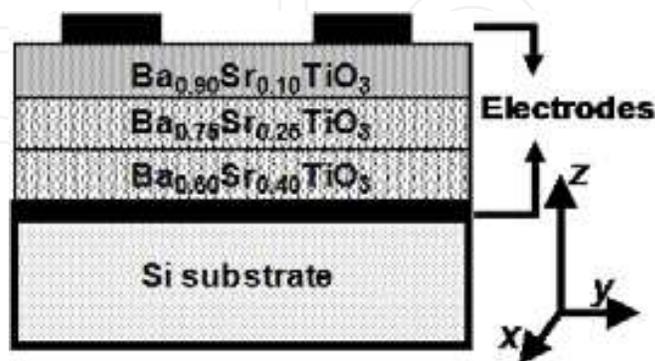
Fig. 8. Schematic diagram of the thin film multilayered material design.[From Cole et al., 2007, Copyright 2007. American Institute of Physics.]

Recently, the collaborative research activities between the U.S. Army Research Laboratory (ARL) and the University of Connecticut (UConn) has resulted in a series of publications focused on the dielectric response and temperature stability of MOSD fabricated compositionally stratified/multilayered BST (BST60/40 – BST75/25 – BST90/10) thin films on Pt-Si substrates (Cole et al., 2007, Zhong et al., 2007, Cole et al., 2008a, Cole et al., 2008b). This series of papers evaluated the dielectric response for both RT material/device performance as well as temperature stability at 100 kHz and microwave (10 GHz) frequencies. The results of this research determined that the effect of the of BST compositional layering, i.e., the "*quasi-up-graded*" film design (Fig. 8) was significant in terms of materials performance with respect to that of uniform composition BST 60/40 prepared by the same MOSD film fabrication method. Specifically, at 100 kHz the multilayer film exhibited a higher permittivity (ε_r=360) and lower dissipation factor (tan δ=0.012) with respect to that of the uniform composition BST film (ε_r=176, tan δ=0.024). The higher permittivity is expected in the multilayered BST films due to the presence of the ferroelectric BST 75/25 and BST 90/10 layers, which possess higher permittivities (and higher tunabilities) with respect to uniform composition paraelectric BST60/40. The dielectric response can be further improved by electrostatic interactions between layers (Roytburd et al., 2005). It has been reported and experimentally demonstrated that permittivity, hence tunability, for single layer uniform composition BST increases with increasing Ba/Sr content (Lu et al., 2003). As discussed earlier in this section, others have reported elevated dielectric constants, 426 to 1650, for compositionally graded BST films prepared via PLD (Lu et al., 2003, Zhu et al., 2003, Zhu et al., 2002a, Zhu et al., 2002b, Zhu et al., 2002c) and 300–320 for graded films prepared by sol-gel methods (Jain et al., 2003, Tian et al., 2003, Zhang et al., 2006). Unfortunately, the literature reports for dielectric loss of compositionally modified (graded and/or layered) films are not as consistent as the reported values for permittivity. Low frequency (100 kHz – 1 MHz) RT dielectric losses have been reported to be as low as 0.007 (Zhu et al., 2002a) for PLD compositionally graded BST (BTO – BST 90/10 – BST 80/20

– BST 75/25) films on MgO substrates to extremely high values of 0.05 (Zhang et al., 2006) for compositionally graded BST sol-gel films (BST 60/40 – BST 70/30 – BST 80/20 – BST 90/10 – BaTiO$_3$) on Pt/Si substrates. However, several research groups have reported dielectric losses which cluster between values of ~ 0.02–0.03 (Lu et al., 2003, Tain et al., 2003, Zhu et al., 2002c). The dielectric loss value, tan δ =0.012, which the ARL-UConn group obtained for their compositionally multilayered BST thin film, was quite low with respect to the reported literature values for graded BST films. Additionally, the fact that these multilayered films also possessed lower loss than the monolithic BST60/40 films prepared by the same method on the same substrate is quite surprising. The reasons for this are not well understood, however, the authors speculated that the lower loss of the compositionally multilayered BST films with respect to both uniform and continuously graded composition BST films may have resulted from the fact that the defects within the film were no longer mobile and were trapped at the compositionally distinct interfaces to compensate for the polarization difference between the layers (Roytburd et al., 2005, Zhong et al., 2006). Such defect trapping at the compositional interfaces may have immobilized the defects such that they were not able to reach the electrodes, thereby allowing the film to possess an improved dielectric loss over films without this interface trapping mechanism, i.e., films which are compositionally uniform and/or continuously graded. Thus, interlayer interfaces appear to promote enhanced material dielectric properties.

The ARL-UConn's researchers also presented experimental data focused on the temperature dependence of the dielectric response for both their quasi-up-graded multilayered BST film and for a homogenous uniform composition BST60/40 film fabricated via the same processing method (Fig. 9). Figure 9(a) demonstrates that the permittivity and dissipation factor of the multilayered film exhibited minimal dispersion as a function of temperature ranging from 90 to −10°C. Lu et al., (2003) also reported a flat variation of dielectric permittivity for compositionally upgraded (BST 75/25 – BST 80/20 – BST 90/10) PLD deposited BST films over a wide temperature range (20−130°C), although there are two peaks at 59 and 92°C, near the phase transition temperatures of BST 80/20 (59°C) and BST 90/10 (89°C), respectively. However, the ARL-UConn results did not show did not display peaks corresponding to the (bulk) phase transition temperatures of the constituents of the multilayered film. Compared to the monolithic paraelectric BST60/40 films (Fig. 9b), the multilayered film possesses a broader, more flat, diffuse dielectric response as a function of temperature. Specifically, the effective change in TCC with respect to uniform BST is significant; i.e., from 20 to 90°C, TCC was lowered by 70% with respect to the uniform composition BST corresponding to an ~3:1 change. Similarly from 20 to −10 °C the TCC value of the multilayered BST film was lowered by 15% with respect to the uniform composition BST film. From Fig. 9 it is also important to note that the dielectric loss exhibits negligible dispersion over the measured temperature range. This is important, since in phase shifter devices the loss must be consistent or predictable to ensure antenna performance consistency and reliability with respect to variable temperature.

In order fully appreciate the BST material property temperature stability enhancements achieved by the ARL-UConn group and that of other researchers, it is important to compare the literature values for both uniform composition BST and compositionally stratified BST thin films. Table I summarizes literature derived dielectric properties, evaluated at 20°C, for monolithic BST films fabricated via sputtering (Taylor et al., 2002), PLD (Lookman et al., 2004), and sol-gel techniques (Jain et al., 2003). In addition, reported literature results for

proposed temperature stable material designs, namely, compositionally graded BST of Lu et al., (2003), BST/MgO layered film structures Jain et al., 2003), are also listed in Table I. The TCC was calculated for the literature studies using the published plots of the capacitance C_F (or ε_r) versus temperature from −10 to 20°C via the equation:
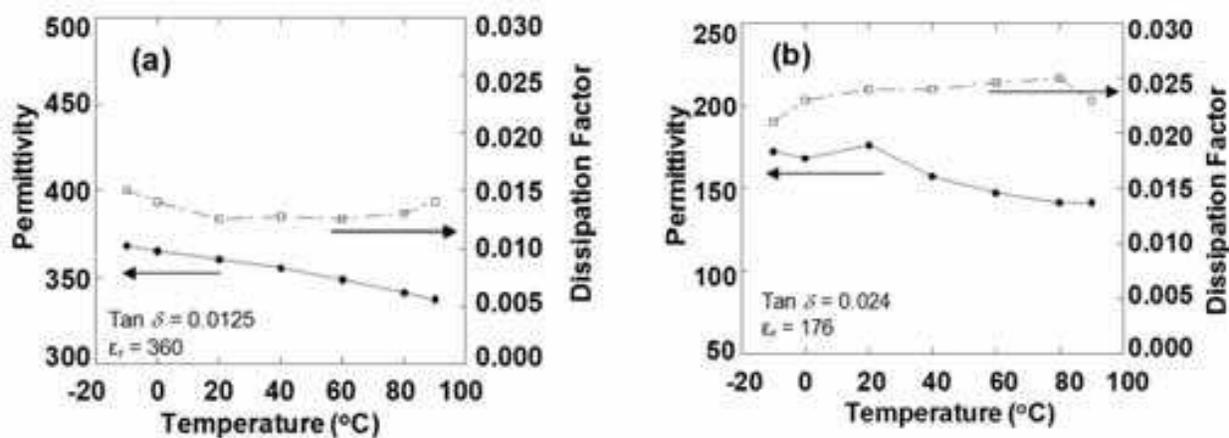

Fig. 9. The temperature dependence of the dielectric response for (a) the post deposition annealed multilayered BST film and (b) homogenous uniform composition paraelectric (BST60/40) BST film measured at 1 MHz. [From Cole et al., 2007. Copyright 2007, American Institute of Physics.]

$$TCC = \Delta C/(C_0 \Delta T), \qquad (2)$$

where ΔC is the change in capacitance with respect to reference capacitance C_0 at 20°C and ΔT is the change in temperature relative to 20°C. TCC values reported in Table 1 show that the magnitude of the TCC for homogenous uniform composition BST thin films is quite high, which is indicative of the large temperature dependence of capacitance/permittivity for these films. Specifically, the decrease in the permittivity as the temperature is raised from 20 to 90°C for paraelectric uniform BST films ranged from 20% to 60% (Taylor et al., 2002). For these same films, the permittivity increase ranged from 6.2% (Taylor et al., 2002) to 35% (Jain et al., 2003) as the temperature was lowered from 20 to −10°C. Thus, the largest change in C_F/ε_r occurred for the high end of the temperature spectrum. The uniform composition BST film, fabricated in the ARL-UConn study, possessed a much lower TCC value than the other literature results (Lu et al., 2003, Lookman et al., 2004, Jain et al., 2003).
Table 1 also displays the TCC results from three heterogeneous material designs: a thin film multilayered BST/MgO heterostructure (Jain et al., 2003) and two compositionally graded BST thin film material designs (Lu et al., 2003, Zhu et al., 2002a) that attempt to lower the TCC, i.e., to broaden the dielectric anomaly over a wide temperature range. Compared to uniform composition BST, the heterogeneous material designs were quite successful in lowering the TCC for over the temperature range of −10 to 90°C. The dielectric response of such compositionally graded ferroelectrics as a function of temperature exhibits characteristics of a diffuse phase transformation, which is reflected by a low TCC value, and is inherently linked, with the distribution of the phase transformation temperature resulting from the composition gradient across the ferroelectric (Ban et al., 2003a, Ban et al., 2003b). It is important to note that the TCC results, of the ARL-UConn's BST multilayered compositional design, was significantly improved over the three heterogeneous material designs represented in Table I. Specifically, this heterostructure exhibited a 6.4% decrease in

permittivity as the temperature was elevated from 20 to 90°C and only a 2.1 increase in permittivity as the temperature was lowered from 20 to −10°C. This very small change in permittivity and low TCC value suggest that the compositional multilayered BST design is temperature insensitive over the temperature range of −10 to 90°C.

Composition Substrate/deposition Method	ε_r (20° C)	Tanδ (20°C)	TCC$_{20\text{-}90}$ (ppt/°C)	$\Delta \varepsilon_r$ (20-90 %)	TCC$_{20(\text{-}10)}$ (ppt/°C)	$\Delta \varepsilon_r$ (20-(-10)%)
$Ba_{0.50}Sr_{0.50}TiO_3$ LSCO/MgO(PLD-210 nm) (Taylor et al., 2003)	410	0.021	-7.32	51 dec	-4.1	12.2 inc
Ba0.24Sr0.76TiO3 PtSi (Sputer-100 nm) (Pervez et al. 2004)	320	--	-4.0	20 dec	-2.1	6.2 inc
Ba0.50Sr0.50TiO LAO (Sol-gel-600 nm) (Lookman et al., 2004)	2934	0.01	-8.52	60 dec	-11.52	35 inc
$Ba_{0.60}Sr_{0.40}TiO_3$ PtSi (MOSD-240nm) (Cole et al., 2007)	176	0.024	-2.9	20 dec	0.83	3 dec
$Ba_{0.50}Sr_{0.50}TiO_3$/MgO-layer LAO (Sol-gel-600 nm) (Lookman et al., 2004)	1932	0.005	-6.89	52 dec	-14.3	43 inc
UG (75/25-80/20-90/10-BT)LSMO/LAO (PLD-800 nm) (Lu et al., 2003)	1650	0.225	-2.16	15 dec	--	--
DG (BT-90/10-80/20-75/25) MgO (PLD-450nm) (Zhu et al., 2002a)	475	--	6.66	44.7 inc	2.25	25 inc
UG (60/40-75/25-90/10) PtSi (MOSD-270 nm) (Cole et al., 2007)	360	0.122	-0921	6.4 dec	-0.716	2.1 inc
UG (60/40-75/25-90/10)+Mg 5 mol%, PtSi (MOSD-270 nm) (Cole et al., 2008a)	316	0.018	-0.94	6.6 dec	-1.14	3.4 inc

Table 1. A comparison of the dielectric properties, TCC, and the percent change of permittivity with respect to 20 °C for heterogenous and uniform composition BST thin films. (Note: UG, up-graded; DG, down-graded; dec, decrease; inc,, increase.) [Modified table from Cole et al., 2007. Copyright 2007, American Institute. of Physics.]

In order to understand why the data for the ARL-UConn group was improved over that of Lu et al,. (2003) and Zhu et al., (2002a) is explained by theoretical models based on a thermodynamic analysis of graded ferroelectric materials and multilayered heterostructures
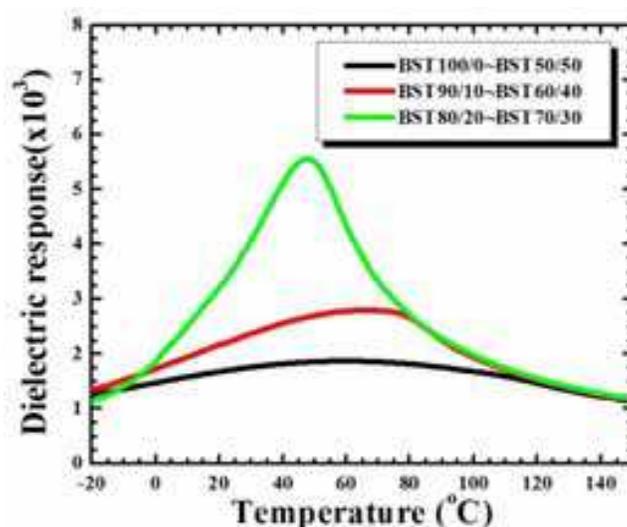
Fig. 10. The theoretical average dielectric response as a function of temperature for three compositionally graded $Ba_xSr_{1-x}TiO_3$ systems with the same nominal average composition. [From   Cole et al., 2007. Copyright 2007, American Institute of Physics.]
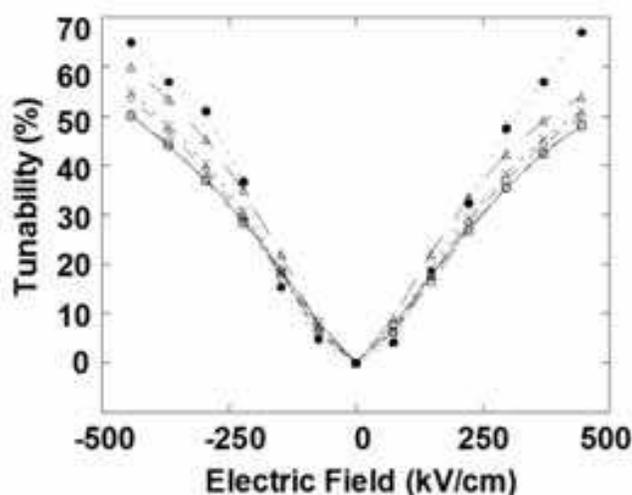

Fig. 11. The temperature dependence of the dielectric tunability for the multilayered BST film from 90 to −10 °C. The symbols on the plot represent the following temperatures: 90 °C (open circles), 80 °C (open squares), 60 °C (open diamonds), 40 °C (crosses), 20 °C (filled circles), and −10 °C (open triangles). [From   Cole et al., 2007. Copyright 2007, American Institute of Physics].

(Ban et al., 2003a, Ban et al., 2003b). Very briefly, this formalism considers a single-crystal compositionally graded ferroelectric bar. It basically integrates free energies of individual layers, taking into consideration the energy due to the polarization (spontaneous and induced), electrostatic coupling between layers due to the polarization difference, and the elastic interaction between layers that make up the graded heterostructure. The mechanical interaction arises from the electrostrictive coupling between the polarization and the self-strain and consists of two components: the biaxial elastic energy due to the variation of the self-strain along the thickness and the energy associated with the bending of the ferroelectric due to the inhomogeneous elastic deformation. Based on this approach, the temperature

dependence of average dielectric response of compositional BST with the same nominal composition (BST75/25) can be calculated using average thermodynamic expansion coefficients and elastic constants available in the literature (Mitsui et al., 1981), as shown in Fig. 10. In comparison with a sharp peak of the dielectric permittivity at T_C for bulk homogenous ferroelectrics, a diffused dielectric response with the temperature can be expected for compositionally graded ferroelectrics as a result of the polarization grading and interlayer interactions. It should be noted that this model is developed for bulk compositionally graded ferroelectrics. However, it is possible to extend it to thin films by incorporating the internal stresses due to thermal strains as well as the clamping effect of the substrate (Roytburd et al., 2005). While these factors tend to decrease the overall dielectric response compared to bulk graded structures, the temperature dependence of the dielectric permittivity displays the same trend (Ban & Alpay, 2003). The maximum in the dielectric permittivity is broadened over a wide range of temperature depending on the strength of the composition gradient, as shown in Fig.10. A steeper composition gradient will give rise to a broader maximum. Thus, since the ARL-UConn multilayered compositional design BST (BST 60/40 –BST 75/25 – BST 90/10) has a steeper compositional gradient compared to that of Lu et al., 2003 (BST 75/25 – BST 80/20 – BST 90/10) and (Zhu et al., 2002a, Zhu et al., 2003) (BST 90/10 – BST 80/20 –BST 75/25) based on these theoretical results, one would expect the ARL-UConn multilayered film to possess a flatter/broader dielectric anomaly, hence a lower TCC, with respect to that of Lu et al., (2003) and Zhu et al., (2002a).

The ARL-UConn researchers also evaluated the temperature dependence of the dielectric tunability for their multilayered BST film (Fig. 11). From Fig. 11 it is clear that over the temperature range of −10 to 90°C, the tunability was not significantly degraded. The bias tunability trends are temperature independent; however, the absolute value of tunability is slightly modified. Thus, this multilayered BST design will allow the antenna phase shift to be temperature stable over the ambient temperature range of −10 to 90°C. This result is significant, as microwave voltage tunable phase shifter devices are expected to be operated in environments with different ambient temperatures with excellent reliability and accuracy. The fact that this multilayered BST material design possesses outstanding dielectric properties and that both tunability and dielectric loss are stable over a broad temperature range bodes well for its utilization in the next generation temperature stable microwave telecommunication devices.

Although excellent temperature stability results have been achieved via compositional grading of BST, there is still need to further reduce the dielectric loss of these new materials. It is well known that acceptor doping of BST is an excellent method to reduce dielectric loss. It has been shown that losses in BST can be reduced via acceptor doping. Dopants (such as Ni^{2+}, Al^{2+}, Ga^{3+}, $Mn^{2+,3+}$, $Fe^{2+,3+}$, Mg^{2+}, etc.) typically occupy the B site of the ABO_3 perovskite structure, substituting for Ti^{4+} ions. The charge difference between the dopant and Ti^{4+} can effectively compensate for oxygen vacancies and thereby have been shown to decrease dielectric losses (Cole et al., 2001). Thus, it is well known that doping of BST with Mg is an excellent avenue to reduce dielectric losses in monolithic BST films especially with low Sr content, although the addition of MgO causes a reduction in dielectric response and its tunability (Cole et al., 2003). Dielectric constant, loss tangent, and tunability (at 237 kV/cm) of BST 60/40 and 5 mol % MgO doped BST 60/40 thin films were reported as 720, 0.1, and 28% and 334, 0.007, and 17.2%, respectively. Thus, acceptor doping combined with compositional grading of BST presents an intriguing opportunity to develop new materials for tunable device applications with stringent demands focused on low dielectric losses and

temperature insensitivity, while still maintaining moderate/good tunabilities. The ARL-UConn researchers extended this idea to a proof-of-concept study. Specifically, they leveraged prior work on Mg-doped BST(Cole et al., 2000, Cole et al., 2002a) to reduce the dielectric loss and blended this acceptor doping approach with their MOSD fabricated quasi-upgraded compositional multilayer design (BST60/40 – BST 70/30 – BST 90/10 – Pt/Si). Both Mg-doped (5 mol%) and undoped quasi-up graded BST films were fabricated via MOSD technique on Pt/Si substrates (Cole et al., 2008a).

The temperature dependence of dielectric constant and loss tangent of thin films are shown in Fig. 12. At a constant temperature, a higher dielectric constant was measured for both doped and undoped multilayered thin films than the uniform BST60/40 film. This can be attributed mostly to the BST 75/25 layer for which T_C is close to RT and, thus, has a significantly higher dielectric response in monolithic form. It is evident that the dielectric constant was somewhat lowered upon MgO doping which also resulted in a decrease in T_C (Cole et al., 2007). These findings, together with the volumetric expansion with the addition of MgO to BST in the ARL-Uconn films, seem to suggest an effective suppression of ferroelectricity with increased MgO doping due to the substitution of Ti (the displacement of which results in a permanent dipole and, thus, ferroelectric behavior) in the perovskite lattice with Mg cations. TCC was evaluated as the variation of capacitance with temperature relative to the capacitance value at 20°C. Both MgO-doped and undoped multilayered BST films exhibited a lower dielectric dispersion in the range of −10 to 90°C than monolithic BST 60/40 thin films. As the temperature was elevated from 20 to 90°C, 6.6% (TCC=−0.94 ppt/°C), 6.4% (TCC=−0.92 ppt/°C), and 13% (TCC=−1.8 ppt/ °C) decrease in permittivity was observed for doped multilayered, undoped multilayered, and monolithic BST films, respectively. In the case of lowering temperature from 20 to −10°C, 3.4% (TCC=1.14 ppt/°C), 2% (TCC =0.67 ppt/°C), and 4.5% (TCC=1.5 ppt/°C) increase in permittivity were noticed for doped multilayered, undoped multilayered, and monolithic BST films, respectively. Additionally, dielectric loss tangent of MgO-doped films was the lowest one among the samples produced in Cole et al. (2008a). From Fig. 12, it can be seen that, on the average, dielectric loss tangents were 0.009, 0.013, and 0.024 for doped multilayered, undoped multilayered, and uniform BST 60/40 thin films, respectively. This fairly "flat," i.e., temperature insensitive, and low loss tangent makes it feasible for such MgO doped multilayered BST films to be employed in tunable devices operating over a broad temperature range.

The variation of tunability in MgO-doped BST films at various temperatures is given in Fig. 13. A slight increase in tunability was observed with increasing temperature. At low electric field strengths (~250 kV/cm), dispersion in tunability with temperature was quite negligible. However, the tunability of doped multilayered films was lower than both undoped and uniform BST thin films reported earlier by Cole et al., (2007). For example at RT and at an electric field strength of 444 kV/cm, tunability was measured as 65.5%, 42%, and 29% for undoped upgraded, uniform, and doped upgraded BST films, respectively. The results achieved in this body of work are important, as the tailoring of BST material design and composition (grading and Mg-doping) is a promising tool to achieve desired material properties. However, it is important to marry this materials performance with the proper/specific tunable device applications. In other words, actual selection and implementation of a specific materials design (Mg-doped vs. undoped graded or uniform composition BST) must be considered in terms of system requirements. For example, for

phase shifters, one would require a large tunability. In this case, undoped multilayered or compositionally graded BST films would be an appropriate choice. On the other hand, for frequency-agile filters operating in the microwave regime, low dielectric losses are a premium. Therefore, acceptor doping combined with compositional grading would yield significantly better loss properties with a reasonable dielectric tunability. It is important to state that such a materials design, Mg-doped quasi-up-graded multilayer BST films, are promising materials for tunable device applications which advocate stringent demands of reduced dielectric loss and temperature stability while maintaining moderate tunability.
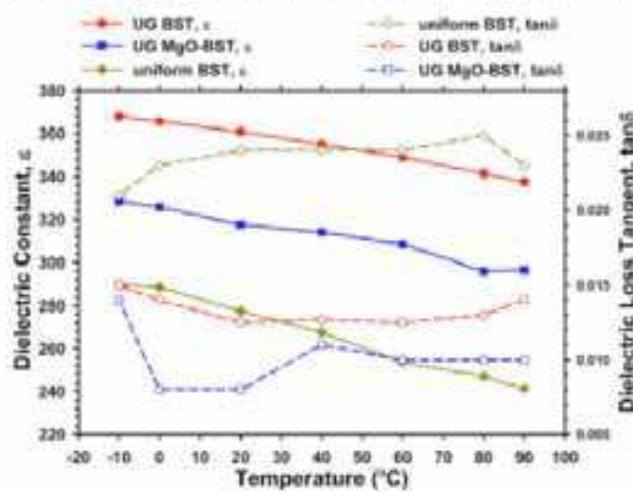
Fig. 12. Temperature dependence of dielectric constant and dielectric loss tangent of MgO-doped multilayered, undoped multilayered, and uniform BST films. [From Cole et al., 2008a. Copyright 2008. American Institute of Physics.]
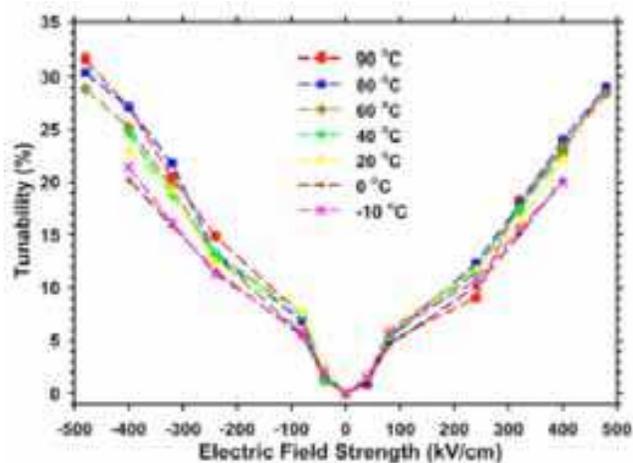
Fig. 13. Variation of tunability of MgO-doped multilayered BST thin film at various temperatures. [From Cole et al., 2008a. Copyright 2008, American Institute of Physics.]

4.3 Summary of the relevant literature: microwave frequency studies
The research summary presented above has discussed the dielectric response/temperature dependence results only within the low frequency (<300 MHz) domain. Since tunable devices for telecommunications are operated in the microwave range (300 MHz to 300 GHz),

it is important to evaluate the dielectric properties of these compositionally stratified BST thin films materials at higher frequencies. Unfortunately, there are relatively few published results that have considered microwave characterization of these complex BST thin film materials designs. One of the more comprehensive studies that focuses on the microwave performance of up- and down-graded BST films is that of Lee et al., (2003). Similar to the low frequency studies of Zhu et al., (2003) and Lu et al. (2003) the films were fabricated via PLD; however, the support substrate was MgO (not LAO) and the strength of the compositional gradient was extremely steep. Specifically, compositionally graded BST $(Ba_xSr_{1-x})TiO_3$ (x=0, 0.2, 0.4, 0.6, 0.8, and 1.0) films were deposited in both the up-graded (STO – BTO) and down-graded (BTO – STO) configurations. The microwave performance (8 to 12 GHz) of the graded BST thin films were investigated with coplanar waveguide (CPW) meander-line phase shifters as a function of the direction of the composition gradient at RT.
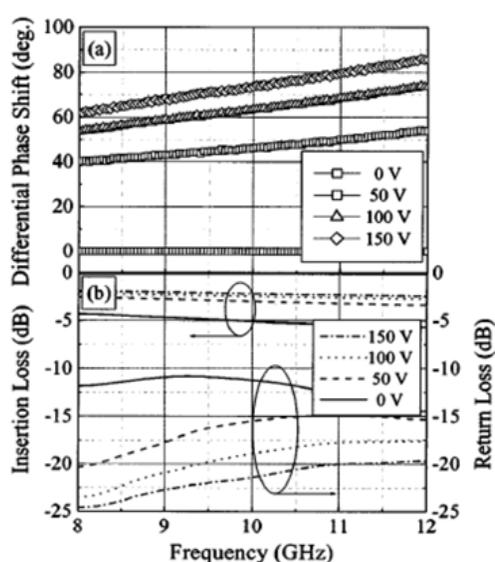

Fig. 14. (a) Differential phase shift and (b) s-parameters of the phase shifter using the graded BTO/STO film. [From Lee et al., 2003. Copyright 2003, American Inst. of Physics.] 2003, American Institute of Physics.]

Fig. 14 shows the measured microwave properties of the CPW meander-line phase shifter based on the down-graded (BTO – STO) thin film. The results in Fig. 14(a) show that as the frequency increased from 8 to 12 GHz, the differential phase shift (at all dc bias values evaluated) also increased. A phase shift of 73° was obtained at 10 GHz with a dc bias of 150 V. Fig. 14 (b) shows the insertion loss (S_{21}) and return loss (S_{22}) as a function of frequency and applied bias voltages. The insertion loss (S_{21}) decreased with an increasing frequency and improved with bias voltage, which is a typical trend of ferroelectric CPW phase shifters. The measured insertion loss at 10 GHz ranged from 5.0 to -2.1 dB with 0 and 150 V, respectively. The return loss (S_{22}) was less than -11 dB over all phase states. The figure of merit of a phase shifter is defined by the differential phase shift divided by the maximum insertion loss for a zero voltage state, which was 14.6 °/dB at 10 GHz. Similar microwave characterization was performed on the up-graded (STO to BTO) BST film (Fig. 15). In this case the differential phase shift was much lower than that of the down-grade BST film, i.e., 22° at 10 GHz with a dc bias of 150 V. The insertion loss (S_{21}) measured at 10 GHz ranged

from -2.2 to -1.7 with 0 and 150 V, respectively. The return loss (S_{22}) of the phase shifter was less than -21 dB with good impedance matching over all phase states. The figure of merit at 10 GHz and 150 V was about 10 °/dB.

The differential phase shift for the graded films was analysed as a function of applied dc bias voltages up to 150 V at 10 GHz. The measured differential phase shifts were 73° and 22° for the down-graded and upgraded BST film, respectively. The down-graded BTO – STO film showed a larger phase tuning and insertion loss than the up-graded STO – BTO thin film. Thus the microwave response is strongly related to the direction of the composition gradient of the graded BST thin films. The down-graded materials design has larger phase tuning and higher insertion loss with respect to the up-graded film. However, in terms of figure of merit (FOM =phase shift/insertion loss) at 10 GHz, the up-graded film has the best overall microwave performance (14.6°/dB down-graded vs. 10°/dB up-graded).
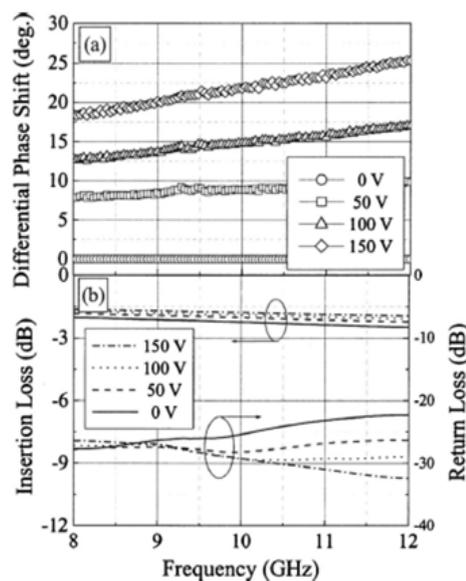
Fig. 15. (a) Differential phase shift and (b) *s* parameters of the phase shifter with graded BTO/STO film. [From Lee et al., 2003. Copyright 2003, American Inst. of Physics.]

The ARL-UConn group has also contributed to the body of knowledge focused on microwave performance of compositionally graded BST films. Specifically, the dielectric properties of their Mg-doped and undoped quasi-up-graded multilayer BST heterostructures at GHz frequencies were reported whereby they achieved high dielectric tunability (15%–25% at 1778 kV/cm) and low losses (0.04–0.08) (Cole et al., 2008b). The microwave characterization of both BST materials designs were carried out at frequencies ranging from 0.5 to 10 GHz using a coplanar inter-digitated capacitor (IDC) device configuration.

Fig. 16 displays a plot showing the microwave dielectric loss as a function of applied electric field at 0.5, 5, and 10 GHz for the up-graded and the Mg-doped up-graded BST films. As expected, the frequency increases, the loss increases. It should be noted that at each frequency the loss is lower at each frequency for the Mg doped up-graded vs. the undoped up-graded film. For example, the loss at 10 GHz in the undoped film is 0.078 compared to 0.039 in the Mg-doped heterostructure at the same frequency. While both values are

significantly larger than the loss at 100 kHz (0.008) (Cole et al., 2008a), these still are within acceptable tolerances for tunable devices. The increase in the dielectric losses in the microwave frequency range can be due to a number of reasons, both of intrinsic (due to the interaction of the ac field phonons, including quasi-Debye losses) and of extrinsic (e.g., mobile charged defects, such as oxygen vacancies) nature.

Fig. 17 shows the dielectric tunability as a function of the applied electric field at 0.5, 5, and 10 GHz for the same two samples. In the undoped up-graded BST, the tunability displays little frequency dependence and is ~25% at 1778 kV/cm for all the test frequencies. In the Mg-doped films, the tunability at 1778 kV/cm decreases from 23% at 0.5 GHz to 15% at 10 GHz. This was also observed at 100 kHz in identical samples; 65% vs. 29% at 444 kV/cm for graded and Mg doped graded films, respectively (Cole et al., 2008a). This reduction in tunability for the Mg-doped up-graded BST film was accompanied by a significant reduction in the dielectric response, (i.e., permittivity). For example, at 10 GHz, the dielectric response of up-graded BST was 261, whereas it was 189 in Mg-doped BST. This is expected as Mg additions are known to lower the ferroelectric transformation temperature, as discussed above. Furthermore, a smaller grain size might also lower the dielectric response (Potrepka et al., 2006).

A comparison of the MW tunability results to that of the 100 kHz performance shows that there is a notable decline in dielectric tunability at the GHz frequencies (Cole et al., 2008a). This behavior may not be entirely intrinsic. It is well known that one can expect a precipitous fall in the dielectric response (and hence its tunability) at higher frequencies for materials where the significant portion of the polarization is due to ionic displacements and/or molecular rearrangement in the presence of an external field. However, the decrease in the tunability noted in comparing the GHz and 100 kHz ARL-UConn studies may also be related to completely different device geometries. The low frequency measurements were acquired in the MIM device configuration, while the GHz measurements were obtained in a co-planar IDC device configuration. Since the device geometry is coplanar, the tunability that is reported for GHz frequencies is actually the lower limit since only a portion (typically less than 50%) of the field is confined within the film (Acikel, 2002). In other words, MIM/parallel plate varactor structures offer higher tunability compared to the coplanar IDC structures since the electric fields are fully confined within the film, as compared to IDCs where there is a large fringing field in the air.

A practical approach to obtaining temperature stabilization of BST varactors was proposed by Gevorgian et al., (2001). The fundamental concept centers on a capacitor which is composed of two ferroelectrics with different Curie temperatures. One of the ferroelectrics is in a paraelectric phase, while and the other is in the ferroelectric state in the temperature interval between T_1 and T_2 (Fig. 18). In the temperature interval between the peaks, the permittivity of the ferroelectric phase increases with increasing temperature, while the permittivity of the paraelectric phase decreases. In a capacitor, the two thin film materials are "connected in parallel;" hence, the decreased permittivity of the paraelectric phase is compensated by the increased permittivity of ferroelectric phase. This concept was experimentally validated using a co-planar capacitor/varactor composed of PLD fabricated epitaxial BST 25/75 and BST 70/25 thin films inter-layered with a MgO seed and a MgO barrier layer (Fig. 19). Here, the lower "seed" layer serves as a strain mitigator and the middle MgO layer serves as a diffusion barrier to ensure that the two ferroelectric layers do not form intermediate phases via diffusion during synthesis.
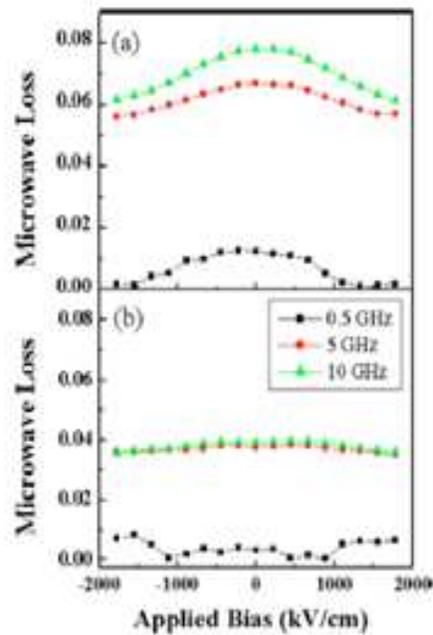
Fig. 16. Microwave loss as a function of the applied bias at 0.5, 5, and 10 GHz for (a) undoped UG-BST and (b) Mg-doped UG-BST. [From   Cole et al., 2008b. Copyright 2008 American Institute of Physics.]
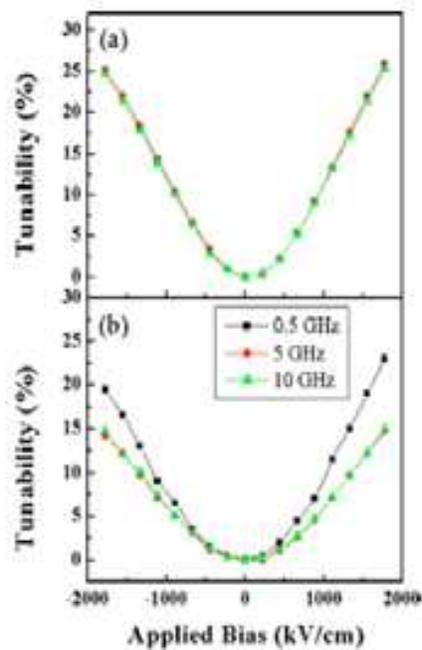

Fig. 17. High frequency tunability as a function of applied bias at 0.5, 5, and 10 GHz for (a) undoped UG-BST and (b) Mg-doped UG-BST. [From Cole et al., 2008b. Copyright 2008, American Institute of Physics.]
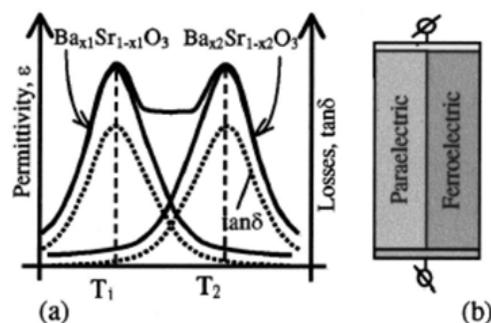
Fig. 18. Temperature dependencies of permittivity and loss (a) and a capacitor (b) with ferroelectrics connected "in parallel". [From Gevorgian et al., 2001. Copyright 2001, Ameer. Inst. of Physics.]
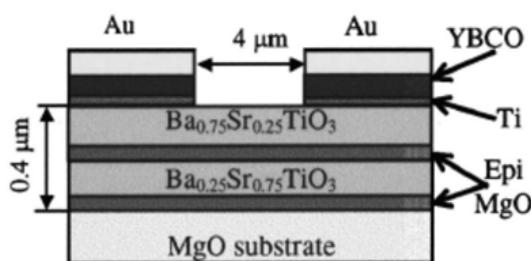
Fig. 19. Cross section of the varactor. Top layer $Ba_{0.75}Sr_{0.25}TiO_3$:0.2mm, bottom layer Ba0.25Sr0.75TiO3 :0.2mm, middle MgO. [From Gevorgian et al., 2001. Copyright 2001, American Institute of Physics.]

The RT frequency dependence of the loss tangent and capacitance was evaluated and the results are displayed in Fig 21. Two relaxation frequencies were observed at 2.15 and 4.61 GHz. The authors suggested that the mechanism for the relaxation may be associated with the interfaces (f_r <1.0 GHz) of BST 25/75 and BST 75/25 films, including electrodes (Sayer et al., 1992). Aside from these relaxation anomalies; it should be noted that tan δ is quite high (~0.1 at 10 GHz). The temperature dependencies of the capacitance and the Q factor (Q=1/($r\omega C$=1/ tan δ) of the varactor at 1 MHz is shown in Fig. 21. The capacitance is almost independent of temperature in a rather wide temperature interval (120 -300 K). The TCC is less than 2 x10^{-4} in the temperature range 150–250 K, which is comparable with the TCC of commercial non-tunable capacitors. However, it is noteworthy to mention that at temperatures above 300K the capacitance is no longer temperature independent and increases dramatically which is a major drawback of this material design. On a positive note, due to the overlapping "tails" of the temperature dependencies of the permittivities of the top and bottom ferroelectric films, the tunability of such a varactor is expected to be larger than if the varactor was composed of only uniform composition BST 25/75 or BST 75/25 films. Although the quality factor of the varactor is highest over same temperature interval where the capacitance is temperature stable, the 1MHz Q-value is somewhat low, Q ~36,/ tan δ~0.028, (Q~ 10/ tan δ~0.1 at 10 GHz) with respect to the that obtained for the graded films and multilayer quasi graded films (Cole et al., 2008b).
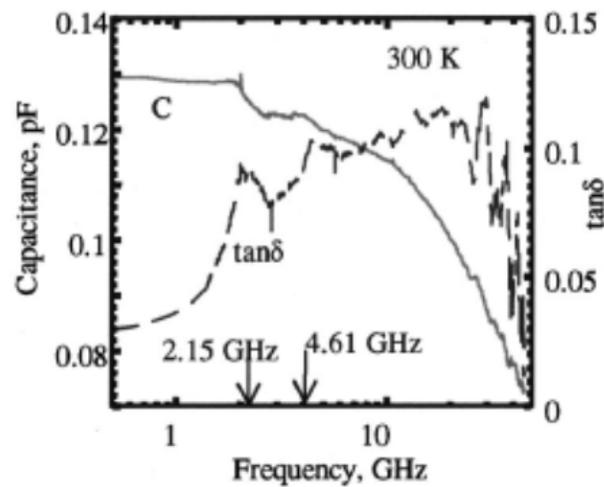
Fig. 20. Frequency dependence of the capacitance and losses at zero dc bias. [From Gevorgian et al., 2001. Copyright 2001, American Institute of Physics.]
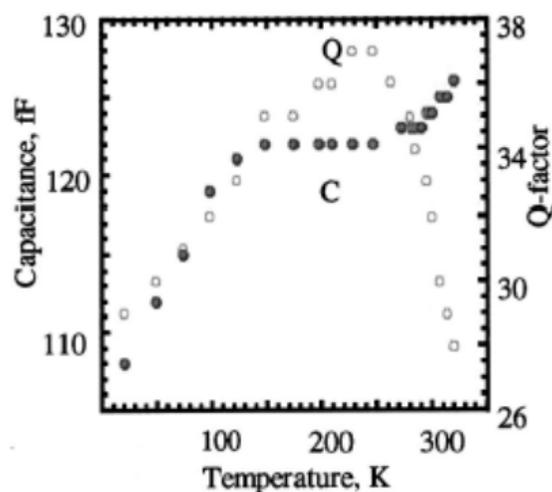

Fig. 21. Experimental dependencies of capacitance and quality factor at 1.0 MHz. [From Gevorgian et al., 2001. Copyright 2001, American Institute of Physics.]

5. Conclusions

This Chapter presented a critical review of the relevant literature pertaining to optimization of BST-based thin film for temperature stable tunable RF-devices. Although, traditional engineering solutions serve to promote material/device temperature stability these add significant cost, size, and weight and/or violate the affordability criteria associated with the systems requirements. Hence, as an alternative to the engineering solutions the material design, approach for eliminating temperature sensitivity was summarized and discussed. Novel material designs, via compositional layering and grading were shown to be effective for achieving dielectric properties with low temperature dependence over a broad temperature regime. While the proof-of-concept of such material designs appears promising, further optimizations are still required to effectively insert these novel designs into practical device applications. In particular there is a need to continue material research

solutions with emphasis on systematic studies employing industry standard film growth techniques and process science protocols, large area low cost device relevant substrates, and industry standard electrode metallizations. Additionally, if such novel material designs are to be useful and device-relevant for the next-generation RF-microwave devices/systems, it is critical to evaluate these material designs at microwave frequencies and operational environments. Finally, the temperature stability criteria must be attained considering the trade-offs of material property balance. In other words, materials temperature stability must be accomplished in concert with achieving balanced property-optimization, i.e., high tunability, low dielectric loss and reduced leakage characteristics.

6. Acknowledgements

7. References

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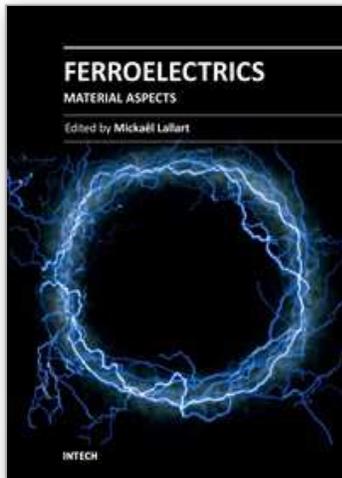
Ferroelectrics - Material Aspects
Edited by Dr. Mickaël Lallart

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on ways to obtain high-quality materials exhibiting large ferroelectric activity. The book covers the aspect of material synthesis and growth, doping and composites, lead-free devices, and thin film synthesis. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric materials, allowing a deep understanding of the material aspects of ferroelectricity.

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