

STRUCTURE/PROPERTY RELATIONSHIPS IN FERROELECTRIC THIN FILMS FOR FREQUENCY AGILE MICROWAVE ELECTRONICS

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Ferroelectric thin films, deposited by pulsed laser deposition (PLD), are currently being used to develop a new class of tunable microwave circuits based on the electric field dependence of the dielectric constant. Single phase, (100) oriented $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) films have been deposited onto (100) LaAlO_3 , SrTiO_3 , and MgO substrates. Interdigitated capacitors patterned on top of the ferroelectric film have been used to measure the dielectric constant and dissipation factor of these films as a function of DC bias and temperature at 1 MHz and as a function of DC bias and frequency (1 to 20 GHz) at room temperature. The dielectric properties of the ferroelectric film is sensitive to both the deposition and post processing conditions. Optical imaging of the ferroelectric films using confocal scanning optical microscopy (CSOM) shows reproducible polarization fluctuations over sub-micrometer length scales for BST films deposited onto SrTiO_3 which are not observed for films deposited onto MgO . Dielectric loss in the ferroelectric film is reduced through a combination of post deposition processing and donor/acceptor doping of the films. The lowest dielectric loss measured has been $\tan\delta = 0.01 - 0.005$.

Keywords: $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, tunable microwave devices, pulsed laser deposition

INTRODUCTION

Ferroelectric (FE) thin films offer unique opportunities for the development of tunable microwave signal processing devices^[1]. In a ferroelectric, the dielectric

constant can be reduced by more than a factor of 2 in the presence of a DC electric field (~ 20 kV/cm)^[2,3]. The field dependent change of the dielectric can be used to produce a shift in a resonant frequency, time delay or a phase shift in a device. Most tunable RF circuits currently rely on a variable capacitance device e.g., GaAs varactor. These varactors suffer from a number of disadvantages, the most serious being that the devices are inherently lossy, especially at microwave frequencies. GaAs varactor quality factors (Q's) are $\sim 100 - 200$ at 1 GHz and decrease exponentially as frequency increases. To improve the characteristics of tunable oscillators at high frequencies will require the development of a new device technology. Ferroelectric based oscillators offer a new approach and will have a frequency independent Q limited only by the loss tangent of dielectric. Most applications will require a $\tan\delta \leq 10^{-3}$.

The solid solution ferroelectric, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), is well suited for the development of FE based microwave electronics operating at temperatures between 30 K and 400 °C. A large electric field effect has been observed in BST for fields ≤ 200 kV/cm^[2]. At issue in the development of microwave devices based on ferroelectric thin films is the magnitude of the dielectric loss.

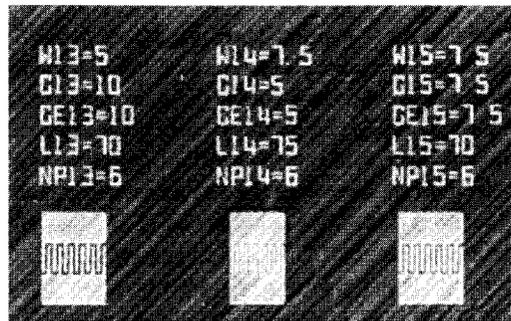


FIGURE 1 Interdigitated capacitor used to measure dielectric properties of ferroelectric thin films.

EXPERIMENTAL

High quality BST thin films (~ 0.5 μm thick) were deposited using pulsed laser deposition (PLD)^[1,4]. The output of a short pulse excimer laser (248 nm, 30 ns FWHM) is focused on the target to an energy density of 1 - 2 J/cm². The BST targets were made from equal molar amounts of BaTiO_3 and SrTiO_3 . The powders were then mixed in a mechanical shaker for 30 minutes and pressed

into the form of a pellet that is one inch in diameter under 2000 pounds for 15 minutes. The pressed pellets were then dried and calcined in Pt foil at 800° C for 4 hours, crushed, repressed and sintered in Pt foil at 1350° C for 6 hours. Chemical analysis of the films was performed by inductively coupled plasma spectroscopy (ICP) and electron-beam microprobe analysis to determine the elemental ratios of Ba, Sr, and Ti.

For annealing temperatures below 1050 °C, BST films were post-deposition annealed in flowing O₂. Films annealed above 1050° C were done in a BST vessel that was wrapped in platinum foil and placed in a alumna tube. The tube was capped at both ends, flushed with O₂ before annealing and maintained at a slight positive pressure of O₂ during the annealing process.

All films were characterized by x-ray diffraction (XRD) and representative films were coated with 500 Å of Au/Pt for scanning electron microscopy (SEM). Interdigitated capacitors, shown in Figure 1, were deposited on top of the FE films through a PMMA lift off mask by e-beam evaporation of 1-2 μm thick Ag and a protective thin layer of Au. Interdigitated capacitors had finger lengths of 10 to 100 μm with gaps that ranged from 5 to 15 μm. Microwave measurements were made on an HP 8510 network analyzer between 1 and 20 GHz at room temperature. Temperature dependent measurements were performed at 1 MHz using a HP 4285A Precision LCR Meter.

1 MHz DIELECTRIC CHARACTERIZATION

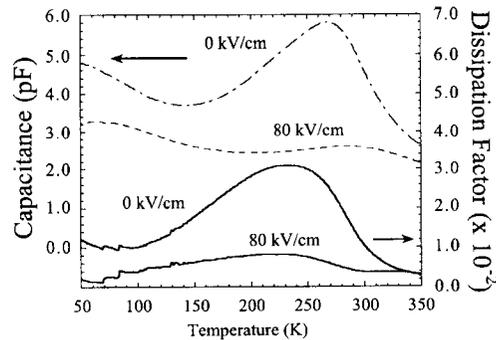


FIGURE 2 Temperature dependence of capacitance and dissipation factor for a Ba_{0.5}Sr_{0.5}TiO₃ thin film capacitor measured at 1 MHz.

The temperature dependence of the capacitance and dissipation factor measured at 1 MHz for an interdigitated ferroelectric capacitor is shown in Figure 2. The peak in the capacitance curve corresponds to the phase transition between the paraelectric and ferroelectric phases, known as the Curie temperature (T_c). The dielectric loss exhibits a temperature dependence reaching a maximum at a temperature slightly lower than T_c . When a DC field is placed across the capacitor, the dielectric constant is reduced. In general, the dielectric properties of the films are different from the corresponding bulk material. The temperature dependence of the dielectric constant and dissipation factor for the film are much broader than the bulk (by about a factor of 6)^[5] and the dielectric constant is lower by about a factor of 5^[6].

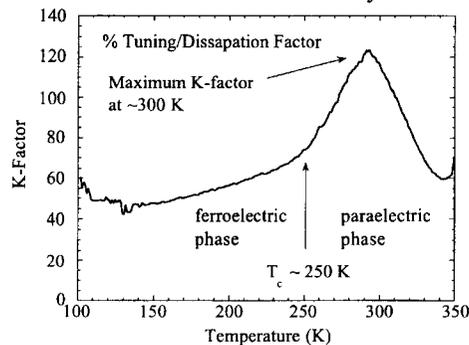


FIGURE 3 Calculated K-factor for 80 kV/cm for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin film capacitor as a function of temperature measured at 1 MHz.

A single figure of merit is often used to measure the quality of the thin film material for microwave tunable applications. A K-factor is defined as the ratio of the % change in the capacitance for a given applied field divided by the dielectric loss. It is shown in Figure 3 for a BST ($x=0.5$) thin film ferroelectric interdigitated capacitor. Large K-factors correspond to a large tuning range and/or low dielectric loss. The K-factor for this BST film is at a maximum just above T_c . The T_c for BST ($x=0.5$) is ~ 250 K. It is therefore necessary to remain just to the paraelectric side of T_c to have a low loss oscillator with a large dynamic range. To achieve intrinsic dielectric loss in BST materials will require materials with a low defect density. Typically, the lowest defect density is observed in single crystals. Only BaTiO_3 and SrTiO_3 are readily available as single crystals. Low dielectric loss BST suitable for room temperature device operation can readily be obtained using single crystal films.

MICROWAVE DIELECTRIC PROPERTIES

The dielectric properties for BST ferroelectric thin films have been measured at room temperature between 1 - 20 GHz. As-deposited films exhibit a large electric field dependence. Capacitance changes as large as 4:1 were observed for fields ≤ 80 kV/cm (Figure 4).

As-deposited films have relatively high dielectric loss. At zero bias, dielectric Q's ($\sim 1/\tan\delta$) of 5 - 20 are typical. The Q is strongly dependent on the electric field and increased as the electric field increased. There are several sources of dielectric loss in the ferroelectric films including stoichiometric deficiencies which create vacancies (cation and anion), film strain (due to the lattice mismatch between the film and the substrate), and the presence of small grains (resulting a large grain boundary/grain ratio). To reduce the dielectric loss, as-deposited films were post-annealed in flowing oxygen. The post-deposition anneal was designed to remove film strain by filling oxygen vacancies and increase the overall grain size of the dielectric film.

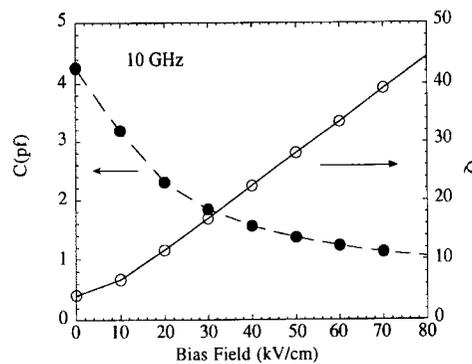


FIGURE 4 Electric field dependence of FE capacitor measured at 298 K at 10 GHz.

POST DEPOSITION PROCESSING OF FE FILMS

Oxygen (anion) vacancies are present in films deposited in a relatively low partial pressure of oxygen (~ 300 mTorr). To remove oxygen vacancies, PLD thin films have been post-annealed in flowing oxygen at temperatures from 900 °C to 1350 °C. After annealing the as-deposited films, significant changes were observed in the structure and dielectric properties. X-ray diffraction of the post-annealed films indicates a decrease in the lattice parameter

(presumably due to filling of oxygen vacancies) and a decrease in non-uniform strain^[7]. The influence of the post-deposition anneal can be seen clearly in several aspects of the capacitance and dissipation factor as a function of temperature. In the capacitance data, we see the temperature dependence of the dielectric constant, approaching more bulk-like behavior. Second, we see a shift in the Curie temperature of the film. The T_c is increased by about 25 K. In general, annealing of the BST films reduces the disparity between bulk and thin film dielectric properties.

As-deposited BST films are smooth and have a grain size of ~ 250 Å as observed by scanning electron microscopy (SEM). After annealing at 900° C for 8 hours, the films were smoother but the surface topology still suggested grain boundaries underneath. Annealing at temperatures above 1000° C in flowing O₂ resulted in surface coarsening such that the films could no longer be patterned for devices. The films became cloudy to the eye and showed what appeared to be erosion at the grain boundaries, revealing a 20 fold increase in grain size from the as deposited films (Figure 5a).

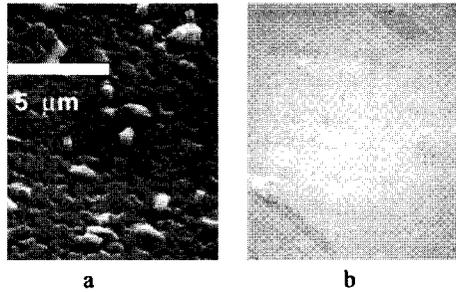


FIGURE 5 SEM photomicrograph of oxygen annealed (a) and bomb annealed (b) BST thin film .

Using a ceramic “bomb” to increase the partial pressure of the volatile elements in the vapor surrounding the film completely stopped the grooving around the grains and allowed annealing^[8] temperatures of 1250° C while the films maintained a smooth surface that revealed no grain boundaries (Figure 5.b). (The bomb is the bulk ceramic target material which surrounds the film during the high temperature, post-deposition anneal).

CSOM

Optical methods are being used to understand the origin of dielectric loss in BST thin films^[9]. A technique based on confocal scanning optical microscopy

(CSOM) has been developed for probing ferroelectric domain structure and dynamics by measuring small polarization-induced changes in the refractive index. The high sensitivity ($\Delta n/n \sim 10^{-7}$) and high spatial resolution of this technique ($< 0.5 \mu\text{m}$) could help to identify factors contributing to dielectric loss.

The CSOM experimental setup is as follows: a linearly polarized Helium-Neon laser ($\lambda = 633 \text{ nm}$) is focused to a diffraction-limited spot ($\sim 470 \text{ nm}$ diameter) on the film surface. A combined dc and ac electric field is applied to the film *via* the interdigitated electrodes on the sample ($E(t) = E_{dc} + E_{ac} \cos(\omega t)$, $\omega/2\pi = 50 \text{ KHz}$). Electric field-induced reflectivity changes in the thin film arise from the linear electro-optic effect, whose coefficient is proportional to the spontaneous ferroelectric polarization P_s . The reflected light intensity r is modulated at the frequency of the driving field, and detected with a lock-in amplifier. This lock-in signal dr/dE is normalized by r to form the CSOM signal. All measurements are performed at ambient room temperature ($\sim 295 \text{ K}$).

Measurements are performed in two modes. In one mode, images of the ferroelectric polarization are obtained by raster-scanning the sample at a fixed dc electric field. In this way, it is possible to track the re-orientation of ferroelectric domains as a function of the applied field. In the second mode, the dc electric field is slowly swept while acquiring data at a fixed point on the sample. These traces yield information about the local hysteretic behavior of the sample.

Fig. 6.a shows a CSOM image of a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ film at zero bias grown on an MgO substrate. Fig. 6.b shows a CSOM image of a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ film grown on SrTiO_3 . Both images show reproducible polarization fluctuations over sub-micrometer length scales, but the film grown on SrTiO_3 exhibits a much larger signal ($\times 50$). The application of a dc bias reveals further differences between the two samples. CSOM images of the same $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ sample as in Fig. 6b, in which E_{dc} is varied from -30 kV/cm to $+30 \text{ kV/cm}$ and back show a large number of micron-sized domains that flip their orientation. The coercive field is comparable to what is observed in bulk BaTiO_3 ($\sim 1\text{-}2 \text{ kV/cm}$). Surprisingly, a number of regions re-orient *opposite* to the applied field. In these samples, one can observe many localized regions of hysteresis. These regions are interspersed with areas which are not hysteretic. No hysteresis was observed for the samples grown on MgO substrates.

DOPING EFFECTS

Improvements in the dielectric properties (i.e., increase in tuning and dielectric Q) of the annealed BST films have been found through the use of two types of dopants, compensation and donor acceptor dopants^[10]. Chemical analysis of deposited films shows they exhibit measurable cation vacancies which are as much as ~6% deficient in Ba and Sr. Increasing the amount of available Ba and Sr was achieved by compensating the targets with excess metal oxides. Initial measurements in which the target was compensated with an additional 2 % Ba and Sr did not show a significant increase of Ba and Sr content of the deposited films, but it did result in ~60% improvement in dielectric loss compared to uncompensated films.

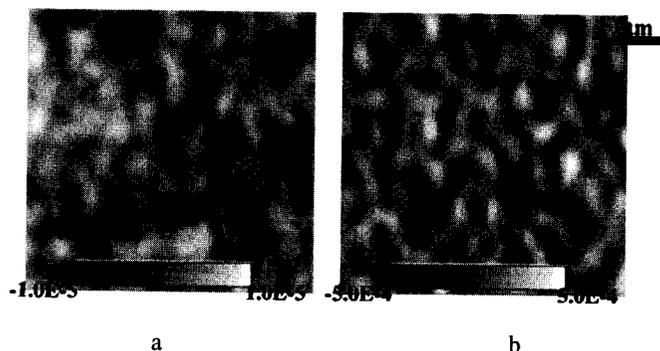


FIGURE 6 CSOM images of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films grown on (a) MgO and (b) SrTiO_3 , taken at zero bias. Image area is $(7\mu\text{m})^2$ for each sample.

It is possible that the stoichiometry of the film may have a fixed deficiency in Ba and Sr due to surface effects at grain boundaries. As-deposited films show columnar structure. Each grain is a column approximately 125 Å in radius. Each unit cell is approximately 4 Å in size. Assuming that the BST grain is coated with a material that is deficient in Ba and Sr. If all the missing Ba and Sr material were at the grain boundary then the boundary layer would consist of pure TiO_2 . Assuming a single unit cell layer of TiO_2 , that gives the grain an inner core of 121 Å and an outer surface layer of 4 Å. That the outer layer represents 7 % of the total volume. This could account entirely for the Ba and Sr deficiency observed in the as-deposited films. To achieve stoichiometric films will require techniques that

can alter the grain size of the as deposited film. To increase the grain size will require greater surface mobility of the arriving vapor atoms at the substrate surface which can be achieved both by raising the substrate deposition temperature and reducing the oxygen deposition temperature.

To compensate for the resultant and perhaps the intrinsic vacancy rate of the Ba and Sr, donor/acceptor dopants are being used to further reduce the dielectric loss. Manganese (Mn) is typically regarded as an acceptor dopant and in high enough concentrations changes the conductivity of the ferroelectric from an insulator to n-type semiconductor. Mn migrates preferentially to the grain boundary. Shown in Figures 7 are the dielectric measurements for a Mn-doped (1-2 atomic percent) $Ba_{0.5}Sr_{0.5}TiO_3$ film which has been bomb annealed. A 30% change in the capacitance is observed for an applied field of 67 kV/cm (40V bias over a 6 μm gap). Dielectric Qs are ~ 100 over the entire frequency range. In addition, the dielectric loss is relatively insensitive to the applied electric field.

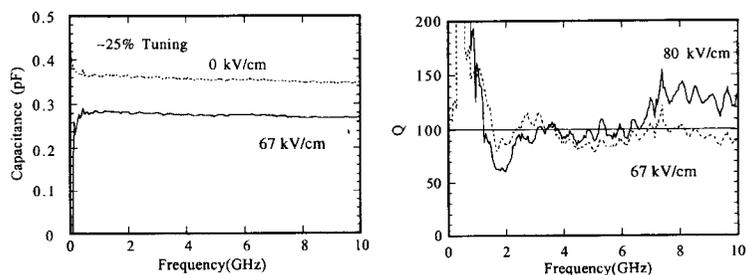


FIGURE 7 Capacitance and dielectric Q for BST ($x=0.5$) film measured from 1 - 10 GHz at room temperature.

The dielectric properties of another BST capacitor is shown in Figure 8. A small ($\ll 1\%$) amount of Fe has been added to the Mn-doped target. Fe preferentially substitutes for Ti and Fe concentrations of $\sim 5\%$ dramatically reduce the dielectric loss but at the same time, eliminate the dielectric tuning. Over the frequency range (1-20 GHz) and modest bias field examined (0 - 67 kV/cm), the deposited film exhibits $\sim 8\%$ tuning, however, the loss tangent is significantly reduced in comparison to the previous film. Dielectric Q's from 100 to 200 are seen up to 20 GHz. These are the largest Q's observed to date in films that exhibit significant tuning.

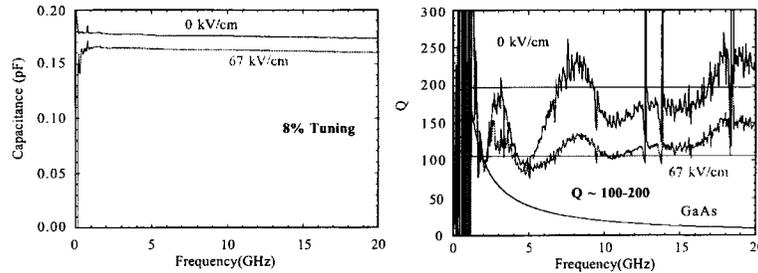


FIGURE 8 Capacitance and dielectric Q for BST film measured from 1 - 10 GHz at room temperature.

CONCLUSION

High quality, single phase, (100) oriented $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films were grown by PLD. Dielectric tuning and loss were measured from 1 - 20 GHz at room temperature and at 1 MHz as a function of temperature. These measurements showed that the dielectric properties could be significantly improved by annealing under the appropriate conditions. Precautions were needed to avoid the volatilization of elements in the films when annealed at temperatures above 1000°C . Bomb annealed films at temperatures as high as 1250°C show an improvement in dielectric behavior. CSOM images indicate electrical inhomogeneities in the deposited films. BST films grown on SrTiO_3 exhibit behavior which is closer to the bulk single crystals, showing higher dielectric constants, a more sharply peaked temperature dependence, and lower dielectric losses, however, the temperature dependence of the phase transition is still sufficiently broad that ferroelectric switching is observed in nominally paraelectric ($x=0.5$) films. The most likely source of the broadened transition temperature is nonuniform stress. The film chemical stoichiometry was also shown to have a profound effect on dielectric properties. The addition of Mn (1-2 atomic %) has a dramatic effect on the dielectric loss. For modest bias fields (67 kV/cm) a ferroelectric thin film with 30% tuning and a dielectric Q of 100 ($\tan\delta - 1 \times 10^{-2}$) at room temperature (1 - 10 GHz) and 8% tuning with Q between 100 and 200 has been obtained. The data show that ferroelectric thin films can be used to make tunable microwave devices that have superior performance characteristics to devices fabricated from semiconducting materials at frequencies above 1 GHz.

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