

## PULSED LASER DEPOSITION OF FERROELECTRIC THIN FILMS FOR ROOM TEMPERATURE ACTIVE MICROWAVE ELECTRONICS

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Single phase, (100) oriented  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  films have been deposited by pulsed laser deposition (PLD) onto (100)  $\text{LaAlO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{MgO}$  substrates and single crystal (100)  $\text{Ag}$  films. Single phase, (100) oriented  $\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$  films have been grown on (100)  $\text{SrTiO}_3$  and  $\text{MgO}$ . The dielectric properties of these films were measured as a function of DC bias at 1 MHz and 1 to 20 GHz. The 1 MHz measurements were made as a function of temperature between 30 - 350 K and the 1 to 20 GHz measurements were made at room temperature. Dielectric properties were measured using interdigitated and parallel plate capacitors. A 75% change in the capacitance was achieved using a 40 V bias across a 5  $\mu\text{m}$  interdigitated capacitor gap (80 kV/cm). Capacitors with high tuning were always accompanied by low Q's ( $\sim 10$ 's). Conversely, capacitor Q's in excess of 500 were observed but these films had poor tuning. Deposited films were annealed over a temperature range of 900 to 1250 C for 8 to 12 hours. Post annealing the films generally improved both the Q and percent tuning and indicates a direction for further dielectric film improvement.

**Keywords:** ferroelectric thin films, BST, KTN, pulsed laser deposition, microwave devices, tunable capacitor, loss tangent, grain size.

### INTRODUCTION

Ferroelectric (FE) thin films grown by pulsed laser deposition (PLD) are currently being explored as the dielectric medium in tunable capacitors for the development of a low phase noise voltage controlled oscillator (VCO) to operate in the 1.5 to 2.5 GHz range. The device is

to be based on the large electric field dependence of the dielectric constant in FE materials near their ferroelectric-paraelectric (FE/PE) phase transition <sup>[1]</sup>. This effect has already been demonstrated in FE films deposited by PLD <sup>[2]</sup>. The critical issues that need to be addressed for the FE VCO are percent tuning and dielectric loss.

The solid solutions  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) and  $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$  (KTN) are well suited for the development of FE based microwave electronics. The Curie temperature of BST ranges from 0 K to 400 K for  $x = 0$  to 1, and KTN ranges from 0 K to 700 K for  $x = 1$  to 0 <sup>[3]</sup>. Being able to control the phase transition temperature in such a simple way is important because the electric field dependence of the dielectric constant is largest at the phase transition temperature. However, it necessary to remain just to the paraelectric side phase transition of the material to eliminate the losses due to ferroelectric domain wall motion in the ferroelectric phase <sup>[4]</sup>. Thus tuning and loss can be optimized over a wide range of temperatures. KTN has the additional advantage over BST in that it can be processed at much lower temperatures. This is a property that may be necessary for eventual integration of the ceramic materials with semiconductors <sup>[5]</sup>.

We have grown KTN and BST thin films by PLD and investigated their structure, morphology and dielectric properties under a variety of annealing conditions. The dielectric constant, loss tangent and their dependence on DC bias field were measured at 1 MHz as a function of temperature and at 1 to 20 GHz at room temperature.

## EXPERIMENTAL

The ferroelectric films were deposited by PLD. The output of a short pulsed (30 ns FWHM) excimer laser operating with KrF (248 nm) at 5 Hz was focused to a spot size of  $\sim 0.1 \text{ cm}^2$  and an energy density of  $\sim 1.9 \text{ J/cm}^2$  onto the desired targets. During deposition the substrate-target distance was 3.5 cm, the  $\text{O}_2$  pressure was 0.35 Torr, the substrate temperature was  $750^\circ \text{C}$  and the target was rotated at  $\sim 1 \text{ Hz}$  while the focused laser beam spot was rastered over the entire target. BST films were grown using a stoichiometric target, while the KTN films were grown from targets with 20% and 40% excess K by mole fraction.

For interdigitated capacitors, FE films were deposited directly onto single crystal (100)  $\text{SrTiO}_3$  (STO), MgO and  $\text{LaAlO}_3$  (LAO) substrates. For parallel plate capacitors the FE films were deposited onto 3  $\mu\text{m}$  thick single crystal (100) Ag films grown on (100) MgO substrates. The Ag films were grown using a combination of PLD and e-beam evaporation of Ag <sup>[6]</sup>. FE films were deposited on top of a thin MgO buffer layer deposited by PLD onto the (100) Ag. The conditions for MgO buffer layer growth were 400 laser shots at 5 Hz focused to an energy density of  $2.6 \text{ J/cm}^2$  in a  $\sim 0.1 \text{ cm}^2$  spot on a Mg target. Substrate target distance was 7 cm, with an  $\text{O}_2$  pressure of 0.5 Torr,

and a substrate temperature of 690° C. The resulting MgO films were approximately 800 Å thick.

$Ba_xSr_{1-x}TiO_3$  films that were post-deposition annealed at temperatures below 1100° C were done in flowing  $O_2$ ; BST films annealed above 1100° C were done in a BST vessel that was surrounded by a platinum foil (Figure 1). The KTN films were annealed at 800° C in a KTN vessel, enclosed in an air tight Pt coated stainless steel bomb. The KTN vessel was made with 20% excess K, and KTN powder with 20 % excess K was packed between the bomb walls and the KTN vessel. BST films deposited on Ag were annealed in flowing  $O_2$  at 900° C.

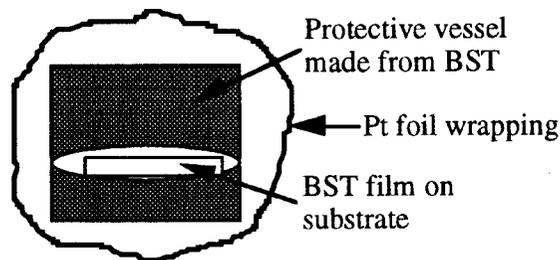


FIGURE 1 Schematic diagram showing the arrangement used during annealing of  $Ba_{0.5}Sr_{0.5}TiO_3$  (BST) films. Both the Pt foil and the BST vessel are there to help create an equilibrium vapor pressure of Ba, Sr, Ti, and O in the immediate vicinity of the BST film.

Interdigitated capacitors were deposited on top of the FE films through a PMMA lift off mask by e-beam evaporation of 1-2  $\mu m$  thick Ag and a protective thin layer of Au. Interdigitated capacitors had finger lengths of 10 to 100  $\mu m$  with gaps that ranged from 5 to 15  $\mu m$ . One to twenty GHz microwave measurements were made on an HP 8753 network analyzer at room temperature. Temperature dependent measurements were performed at 1 MHz using a HP 4285A Precision LCR Meter. 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).

$Ba_xSr_{1-x}TiO_3$  films examined by Rutherford Backscattering Spectrometry (RBS) and electron microprobe for chemical composition showed nearly the same composition as the target. RBS on  $KTa_xNb_{1-x}O_3$  films showed chronic deficiency in K except when the films were grown from a target containing a 40 % excess of K. The

KTN films also always showed about a 13 % drop in the Nb/Ta ratio from KTN targets that contained a Nb/Ta ratio of 0.66.

## RESULTS

### X-Ray Diffraction

All as-deposited BST and KTN films grown on oxide substrates were found to be single phase and exclusively oriented in the (100) direction (Figure 2). Typical FWHM of the  $\omega$ -scan peaks for the ferroelectrics on (100) MgO were 0.6 to 0.9°, and at or below the 0.166° resolution limit of the diffractometer for BST films grown on (100) SrTiO<sub>3</sub> or LaAlO<sub>3</sub> and KTN grown on (100) SrTiO<sub>3</sub>.

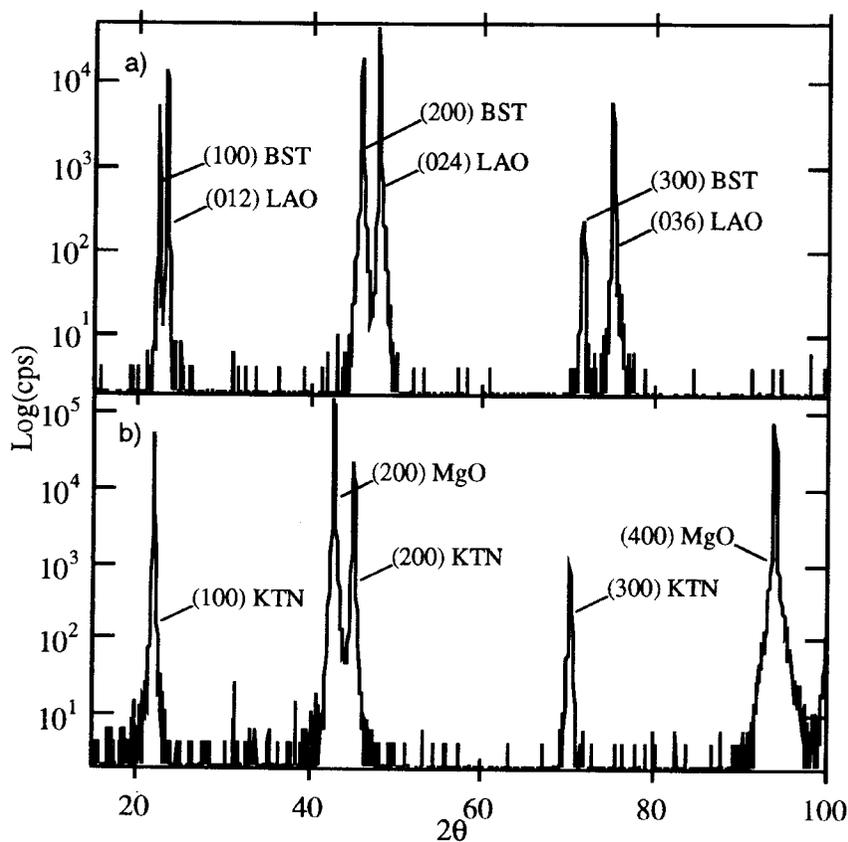


FIGURE 2 Theta/two-theta x-ray diffraction patterns of a)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  on (100)  $\text{LaAlO}_3$ , and b)  $\text{K}_{1.05}\text{Ta}_{0.64}\text{Nb}_{0.36}\text{O}_3$  on (100)  $\text{MgO}$ .

BST films grown on (100) Ag using a buffer layer of MgO were single phase and well oriented (Figure 3). Full width at half maximum of the (200) BST  $\omega$ -scan peaks ranged from  $1.6$  to  $0.9^\circ$ . The quality of the BST films grown, as determined by the ratio of the (100) peak intensity to the intensity of diffraction peaks from other orientations, were sensitive to the deposition conditions of the MgO buffer layer. Figure 4 shows the (200)  $\omega$ -scan peak of a thick MgO buffer layer deposited on a  $3 \mu\text{m}$  thick (100) Ag film on (100) MgO. The sharp central peak is from the MgO substrate, and the wings are from the MgO buffer layer, which has a FWHM  $\sim 1^\circ$ . No other MgO orientations appear in  $2\theta$  scans indicating that the MgO buffer layers grow in the (100) orientation.

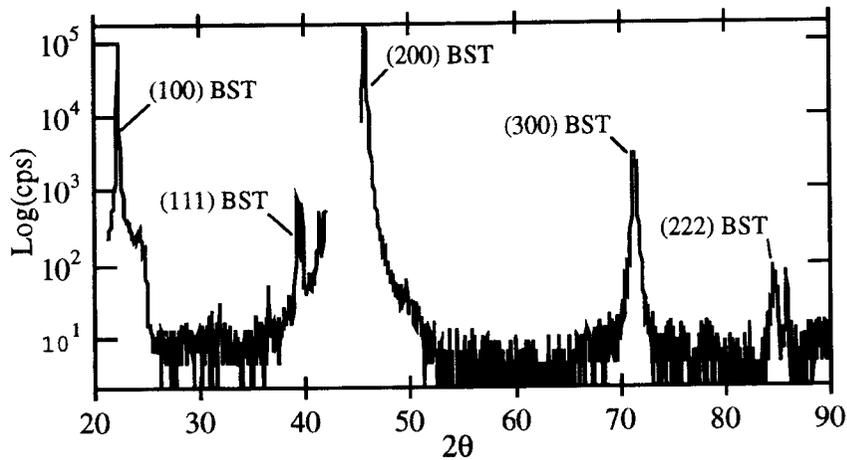


FIGURE 3  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{MgO}/\text{Ag}/(100)\text{MgO}$  x-ray diffraction pattern. The (200) Ag and MgO peaks were excluded from the scan.

#### Effects of Annealing on Film Morphology

As-deposited BST films show mirror like smoothness to the eye but have a rough surface morphology under the SEM. Grain size ranged from  $250$  to  $500 \text{ \AA}$  depending on the deposition temperature and substrate (Figure 5 a). After annealing at  $900^\circ \text{C}$  for 8 hours, the films were smoother but the surface topology still suggests grain boundaries underneath (Figure 5 b)).

Annealing at higher temperatures does not necessarily promote better film morphology. At higher temperatures the environment that the films experience while being annealed becomes important. BST films

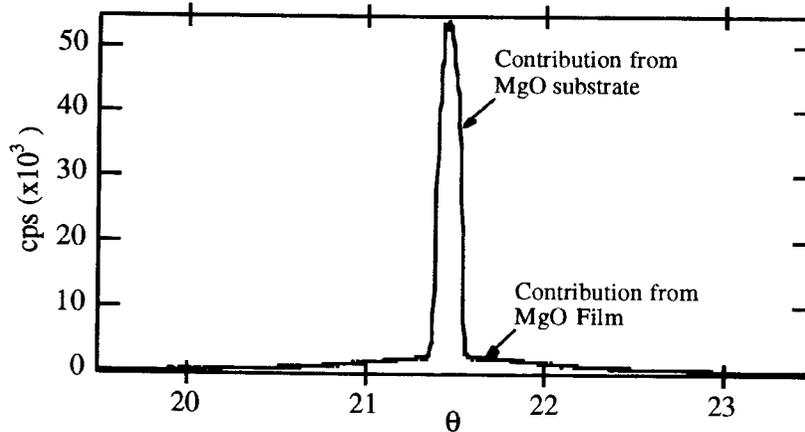


FIGURE 4 MgO/Ag/(100)MgO x-ray  $\omega$ -scan of the (200) MgO diffraction peak. The strong central peak comes from the MgO substrate. The wings come from the MgO film grown on top of the Ag.

showed surface degradation at temperatures above 1000° C in flowing O<sub>2</sub>. 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 5 c)). Using a "bomb" to increase the partial pressure of the films elements in the vapor surrounding the film completely stopped the grooving around the grains and allowed annealing temperatures of 1250° C for BST while the films maintained a smooth surface that revealed no grain boundaries (Figure 5 d).

#### Dielectric Measurements

Dielectric measurements at 1 MHz were made as a function of temperature and DC bias field. Figure 6 shows the capacitance and dissipation curves of interdigitated capacitors with 5  $\mu$ m gaps at 0, 20, and 40 V DC bias for three films that differ mostly by their annealing conditions. Figure 6 a) and b) were measurements made from Ba<sub>0.35</sub>Sr<sub>0.65</sub>TiO<sub>3</sub> films deposited on (100) LAO where the films were measured as deposited and after annealing at 900° C in O<sub>2</sub> for 8 hours, respectively. Figure 6 c) is a measurement made from a Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> film on (100) STO that has been annealed in a BST bomb at 1180° C for 12 hours. All films show peaks in the dissipation factor at  $\sim$  250 K and  $\sim$  50 K, which correspond to the bulk BST FE/PE (cubic-tetragonal), and tetragonal-orthorhombic phase transitions, respectively. The

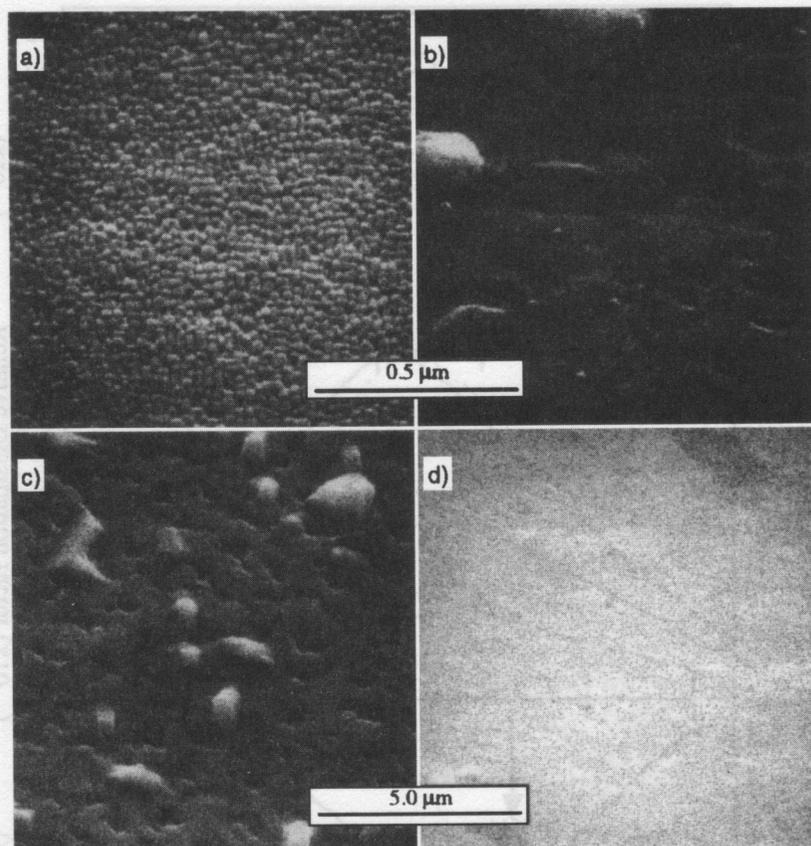


FIGURE 5 Scanning electron micrographs of four  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  films on (100)  $\text{LaAlO}_3$  annealed under different conditions. a) As deposited, b) annealed at  $900^\circ\text{C}$  for 8 hours in flowing  $\text{O}_2$ , c) annealed at  $1140^\circ\text{C}$  for 12 hours in flowing  $\text{O}_2$  and d) annealed at  $1250^\circ\text{C}$  for 12 hours in an environment enclosed by  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  in  $\text{O}_2$ .

capacitance curves all show a peak at  $\sim 250\text{K}$  (FE/PE phase transition), but only Figure 6 c) shows the peak at  $\sim 50\text{K}$  corresponding to the tetragonal-orthorhombic phase transition. The overall increase in capacitance at lower temperatures in Figure 6 c) may also be due to the increasing dielectric constant of the STO substrate. The important features to notice in Figure 6 are that at higher annealing temperatures

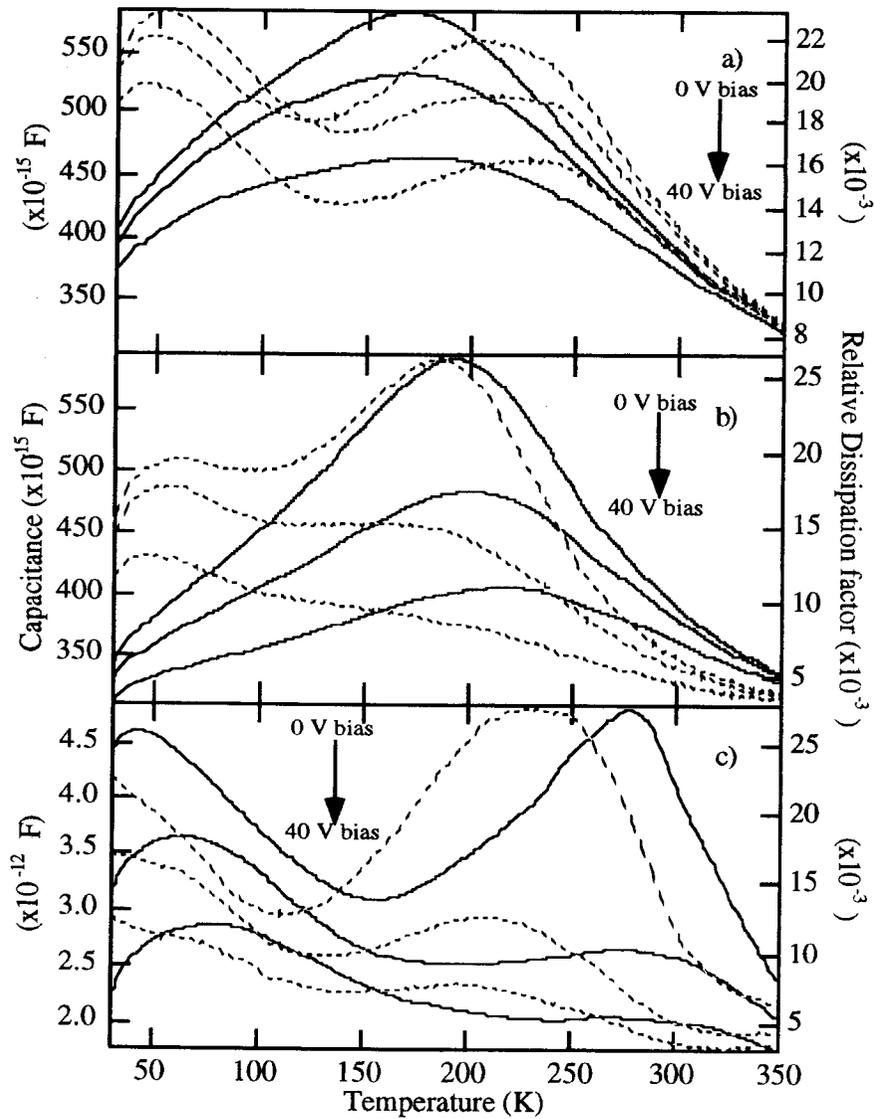


FIGURE 6 Capacitance (solid) and dissipation (dashed) measurements made at 1 MHz with 5  $\mu\text{m}$  gap interdigitated capacitors at 0, 20, and 40 V DC bias as a function of temperature. a) and b) are Ba<sub>0.35</sub>Sr<sub>0.65</sub>TiO<sub>3</sub> on (100) LaAlO<sub>3</sub>, as deposited and annealed at 900°C in O<sub>2</sub> for 8 hours, respectively. c) Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> on (100) STO annealed at 1180°C for 12 hours in an environment enclosed by Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> in O<sub>2</sub>.

the capacitance and dissipation peaks that correspond to the FE/PE phase transition become sharper and the peaks in dissipation shift to lower temperature as compared to their respective peaks in capacitance. The approximate half maximum peak widths of the capacitance versus temperature were 150 K, 120 K, and 90 K for the as deposited, annealed at 900° C, and annealed at 1180° C films, respectively. Likewise, the peak in dissipation shifted from ~ 50 K above the peak in capacitance for the as deposited film, to ~ 50 K below capacitance for the film annealed at 1180° C. In bulk BST, the peak in capacitance versus temperature is much sharper (FWHM ~ 25 K) than in the films [7]. Also, in bulk material the dissipation is always lower in temperature than the peak in capacitance, that is in the ferroelectric phase. As deposited films do not behave like bulk material in these regards and only after annealing do bulk-like properties begin to recover.

The capacitance and dissipation measurements for the  $\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$  film as a function of temperature and DC bias voltage are shown in Figure 7. The film was annealed in the KTN bomb at 800° C, which is a relatively low annealing temperature, but it is ~ 70% of the melting point of  $\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$  ( $m_p \sim 1250$  K).  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  ( $m_p = 1850^\circ\text{C}$ ) shows significant grain growth at 1100° C, which is ~ 65 % of the melting temperature [7]. Therefore, more bulk like properties should be able to be recovered for KTN films at lower annealing temperatures. As can be seen, the peak in dissipation versus temperature is well below the peak in capacitance versus temperature, as it is in bulk material. For bulk  $\text{K}_{1.0}\text{Ta}_{0.64}\text{Nb}_{0.36}\text{O}_3$ , the paraelectric-ferroelectric phase transition should occur ~ 300° C, but for this film with a RBS measured stoichiometry of  $\text{K}_{1.05}\text{Ta}_{0.64}\text{Nb}_{0.36}\text{O}_3$  it appears to be much lower ( $T_c = 100$  K) [8]. The important feature is that in the film there are temperatures where the tuning remains large and dissipation is relatively low, making KTN a good candidate material for making capacitors with high tuning and low loss.

A summary of the dielectric measurements made between 1 and 20 GHz at room temperature are shown in Table 1. The first three rows of Table 1 seem to indicate that there is a trade off between tuning and Q. The film annealed at 1180° C for 12 hours shows only a modest improvement. The  $\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$  film is similar to the BST films in dielectric properties, however our KTN processing techniques have not been fully optimized and there is much room for improvement. The trilayer capacitor is interesting because it exhibited nearly 2 to 1 tuning while only being biased over a 0 to 5 V range as opposed to 0 - 40 V range for the interdigitated capacitors.

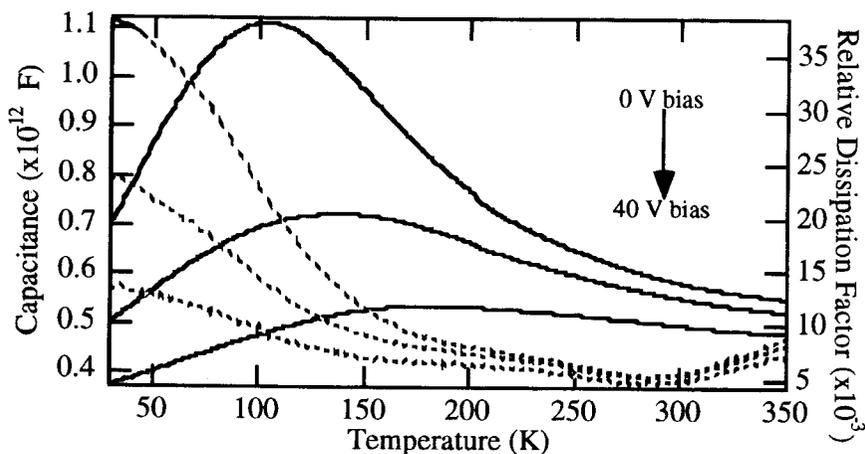


FIGURE 7 Capacitance (solid) and dissipation (dashed) measurements made at 1 MHz at 0, 20, 40 V DC bias as a function of temperature for a 0.6  $\mu\text{m}$  film with a stoichiometry  $\text{K}_{1.05}\text{Ta}_{0.64}\text{Nb}_{0.36}\text{O}_3$ , as measured by Rutherford Backscattering Spectroscopy.

TABLE 1 Summary of 0.5  $\mu\text{m}$  gap interdigitated capacitor properties at 10 GHz (no mark), 2 GHz (\*), and 5 GHz (†) at room temperature.

sample description	Q (0 - 40 V bias)	C (pF) (0 - 40 V bias)	Tuning (0 - 40 V bias)
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	6 - 19	0.97 - 0.43	56 %
0.5 $\mu\text{m}$ thick	4 - 44	4.22 - 1.04	75 %
1000° C annealed			
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	5 - 59	14.7 - 5.05	66 %
5.0 $\mu\text{m}$ thick	†	†	†
1180° C annealed			
$\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$	10 - 15	13.4 - 22.4	40 %
0.5 $\mu\text{m}$ thick	*	*	*
(trilayer capacitor)	(0 - 5 V bias)	(0 - 5 V bias)	(0 - 5 V bias)
$\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$	30 - 64	0.577 - 0.482	16 %
0.5 $\mu\text{m}$ thick			
800° C annealed			

## DISCUSSION

From the data presented here, there is a strong relationship between annealing temperature, grain size and dielectric properties. This has been seen previously in bulk BST and has been reproduced in these films<sup>[7]</sup>. SEM showed as-deposited films to have small grain size (~250 Å) while capacitance measurements showed dielectric properties very different from the large grained and single crystal FE material<sup>[7, 8]</sup>. Temperature dependent measurements of the as deposited film showed broad peaks in the capacitance and dissipation factor as a function of temperature. Large tuning in this film was only observed at temperatures where the dielectric loss was high. As films were annealed in O<sub>2</sub>, the grain size increased and bulk-like dielectric properties began to emerge. The capacitance and dissipation curves as a function of temperature sharpened, and the peak in dissipation shifted to below the T<sub>c</sub> for the film. At 1 to 20 GHz the measurements indicate that annealing only provides small improvements in the dielectric loss, but temperature dependent measurements of the annealed films made at 1 MHz show potential for significant improvement at high frequencies if more bulk properties can be recovered by higher temperature anneals.

Despite the recovery of some of the bulk behavior by annealing, the capacitance peak widths for the films (FWHM ~ 100 K) are still much broader than in the bulk (FWHM ~ 25). The broadening of the capacitance versus temperature curve in the films is due to a broadening of the temperature dependence of the FE/PE phase transition. It is speculated that the phase transition broadening is both homogeneous and inhomogeneous. Possible homogeneous effects would be those that might "frustrate" each grain equally, such as grain boundary effects, finite grain size effects, and nonstoichiometry. Inhomogeneous effects would cause different grains to go through the phase transition at different temperatures and these effects might include strain due to lattice mismatch at the substrate, strain due to neighboring particles, or grain size effects on a distribution of grain sizes. It is unlikely that different grains have different stoichiometry so it is not included as a possible inhomogeneous effect.

Annealing affects all of these possible sources of phase transition broadening. Annealing reduces film strain, promotes grain growth which reduces grain size and grain boundary effects, and it decreases oxygen deficiencies. As the films recover bulk properties by annealing at higher temperatures, they are brought into a regime where they can begin to be compared to the wealth of literature on bulk ferroelectrics. This lays the ground work for future studies of loss mechanisms in thin film ferroelectrics.

The volatility of the elements in the films being annealed becomes important at higher annealing temperatures. The vapor pressure of the

elements in BST are low, but surface smoothness is crucial for device patterning, thus a small losses of material results in severe sample degradation. The problem is much worse for materials with more volatile components like the K in KTN. "Bomb" annealing eliminates this problem by increasing the partial pressure of the elements in the materials being annealed. This technique allows higher annealing temperatures for BST films and the processing of K compensated KTN targets for PLD of KTN into high quality films, which is otherwise difficult.

Preliminary results show that KTN competes well with BST for microwave applications. In addition, the lower processing temperatures required for KTN make it more desirable for integration with semiconductors. The lower processing temperatures will also allow the KTN to be deposited on Ag films and be annealed above the sintering temperature of KTN. The Ag films can withstand 900° C for prolonged periods of time, allowing the KTN to sinter in the parallel plate configuration.

## CONCLUSION

High quality single phase (100) oriented BST and KTN films were grown by PLD. Film morphology and structure were characterized by SEM and XRD. Dielectric properties were measured from 1 - 20 GHz at room temperature and at 1 MHz as a function of temperature. The GHz measurements demonstrated FE based capacitors with up to 4 to 1 tuning ranges and Q's that ranged from 10 to 50. The temperature dependent measurements at 1 MHz on annealed films showed that the dielectric properties could be significantly improved by annealing above 1100° C. Precautions needed to be taken to avoid the volatilization of elements in the films when annealed at higher temperatures.

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## References

- [1.] V. K. Varadan, D. K. Gohdagaonkar, V. V. Varadan, J. F. Kelly, P. Glikerdas, *Microwave Journal*, **35**, 116, (1992).
- [2.] K. R. Carroll, J. M. Pond, D. B. Chrisey, J. S. Horwitz, R. E. Leuchtner, K. S. Grabowski, *Applied Physics Letters*, **62**, 1845-7, (1993).
- [3.] M. E. Lines, A. M. Glass, *Principles and Applications of Ferroelectirc and Related Materials* (Clarendon Press, Oxford, 1977), p. 242, 244, 246, 252.

- [4.] M. E. Lines, A. M. Glass, *Principles and Applications of Ferroelectric and Related Materials* (Clarendon Press, Oxford, 1977), p. 139.
- [5.] P. D. Garn, S. S. Flaschen, *Analytical Chemistry*, **29**, 275, (1957)
- [6.] A. C. Carter et al., in progress.
- [7.] U. Kumar, S. F. Wang, S. Varanasi, J. P. Dougherty, ISAF '92 Proceedings of the Eighth IEEE International Symposium on Applications of Ferroelectrics, 55-8, (1992)
- [8.] S. Triebwasser, *Physical Review*, **114**, (1959).