

DIELECTRIC AND STRUCTURAL PROPERTIES OF (100) $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ FILMS GROWN ON MgO , LaAlO_3 , AND SrTiO_3 SUBSTRATES BY PULSED LASER DEPOSITION

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ABSTRACT

$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN) thin films (~ 6000 Å) were grown on (100) MgO , (100) LaAlO_3 (LAO), and (100) SrTiO_3 (STO) substrates by pulsed laser deposition (PLD). Deposited films were smooth, single phase and exclusively (100) oriented. KTN films deposited on MgO and LAO substrates were easily cracked after deposition or post deposition heat treatment. The film deformation appeared to be caused by strain due to the lattice mismatch between the film and the substrate. A thin buffer layer of ~ 100 Å was used to eliminate the cracking problem. The high volatility of K at the film deposition temperature required excess K to be added to the ablation target. Sintering of the target and post-deposition annealing of the films were done in a sealed Pt coated stainless steel container. Rutherford backscattering showed the films to have a 1 to 1 atomic ratio of K to Ta + Nb. On top of the KTN films, Ag interdigitated capacitors were deposited. Room temperature measurements of capacitance and dielectric loss as a function of bias electric field (0 - 80 kV/cm) at 1 to 20 GHz were made. Capacitance and dielectric loss measurements were made as a function of temperature and bias electric field at one MHz and as a function of temperature and frequency at 0V DC bias. The results show the strong potential of KTN for use in frequency agile microwave electronics.

INTRODUCTION

Ferroelectrics are a class of non-linear dielectrics which exhibit an electric field dependent dielectric constant. This property is currently being used to develop frequency tunable microwave circuits. $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ is one of the candidate materials for the microelectronic device due to its large electric field dependent dielectric constant and composition dependent Curie temperature. The Curie temperature (T_c), which corresponds to the paraelectric-ferroelectric (PE-FE) transition temperature, varies linearly with composition and ranges from approximately 13 K ($x = 0$) to 708 K ($x = 1$) [1]. The T_c for KTN can be calculated according to the following expression, T_c [K] = $676x + 32$ (for $x \geq 5\%$) [2]. The ability to control the dielectric constant and the Curie temperature will allow device structures to be optimized for maximum dielectric tuning and minimum dielectric loss at the desired frequency and operating temperature.

Thin film ferroelectrics offer a unique advantage over bulk materials for tunable microwave circuits. Using thin films of these materials, the large electric fields (≤ 200 kV/cm) can be achieved using bias voltages of less than 10 V [3]. Electric field effects have already been demonstrated in ferroelectric films deposited by pulsed laser deposition [4]. The critical issues that need to be addressed for tunable microwave devices are the percent change in the dielectric constant and dielectric loss at microwave frequencies. In this investigation, we have grown KTN ($x = 0.4$ and 0.6) thin films by PLD and investigated their structure, morphology, resistivity and dielectric properties from 1 MHz to 20 GHz.

EXPERIMENTAL

KTN targets with $x = 0.4$ and 0.6 were prepared by mixing appropriate amounts of KTaO_3 and KNbO_3 powders compensated with 20 - 40 mol.% excess K by adding KO_2 or KCO_3 powders, pressing 3/4" diameter targets at 15,000 pounds, calcining twice at 500°C and 700°C , grinding and pressing the targets again and then sintering for 12 hours at a temperature of 900°C . KTN targets were calcined and sintered with the same KTN powder inside a Pt coated stainless steel bomb. The PLD system used to grow KTN films has been described previously[5]. A KrF excimer laser (~ 30 ns pulses, ~ 300 mJ/pulse, $\lambda = 248$ nm) was used to ablate the rotating oxide targets. The laser was focused with a 50 cm focal length lens to a spot size of ~ 0.1 cm² to achieve an energy density of 1.5 J/cm² with a repetition frequency of 10 Hz. The vaporized material was deposited onto a heated substrate approximately 3.5 cm away from the target. Typically, for KTN films, the substrate was heated to $725 - 825^\circ\text{C}$ in an oxygen ambient pressure of 300 mTorr. The films were deposited at approximately 2 Å/pulse to a total film thickness of ~ 0.6 μm on MgO, LAO, or buffer layered MgO or LAO substrates and of ~ 7 μm on a STO substrate. The films were then cooled to room temperature in oxygen at $\sim 10^\circ\text{C}/\text{min}$. As a buffer layer, BaTiO_3 (BTO) or STO was deposited to a thickness of less than 100 Å. The KTN films were post-deposition annealed at 800°C in pairs, face-to-face, or singly, open-face in a Pt coated stainless steel bomb which contained the same powder that was used for the deposition target.

Interdigitated capacitors were deposited on top of the KTN films through a PMMA lift off mask by e-beam evaporation of 1 - 2 μm thick Ag and a protective thin layer of Au. The capacitors have gaps that range from 6 to 12 μm . Temperature dependent measurements were performed at 1 MHz with DC bias changes (0 V - 40 V) and at 0 V with frequency changes (500 Hz - 1 MHz) using a HP 4284A or a HP 4285A Precision LCR Meter. The DC resistance measurements at room temperature were carried out using a 1864 Megaohm at 10 - 40 V. One to twenty GHz microwave measurements were made on an HP 8510C network analyzer at room temperature. KTN targets and films were characterized by x-ray diffraction (XRD) and representative films were coated with 500 Å of Au/Pd for scanning electron microscopy (SEM). Compositional analysis of KTN films was determined by Rutherford Backscattering Spectrometry (RBS).

RESULTS AND DISCUSSION

Structural Characterization

The KTN target exhibited a density of about 65% of the theoretical density. The room temperature x-ray diffraction pattern for $\text{K}_{1.4}\text{Ta}_{0.6}\text{Nb}_{0.4}\text{O}_3$ could be indexed as a distorted perovskite structure (tetragonal). The Curie temperature for KTN with $x = 0.4$ is expected at the temperature ~ 302 K and ~ 437 K for $x = 0.6$ [2].

KTN ($x = 0.4$ and 0.6) films were deposited by PLD onto (100) MgO, LAO and STO substrates. As-deposited films grown on oxide substrates were found to be single phase and exclusively oriented in the [001] direction (Fig. 1). The effect of the deposition temperature on the rocking curve width (ω , FWHM) of the (001) peak for KTN ($x = 0.4$) films deposited on

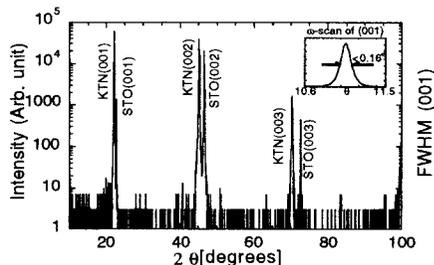


Figure 1 XRD pattern for KTN film(x=0.6) on (100)STO

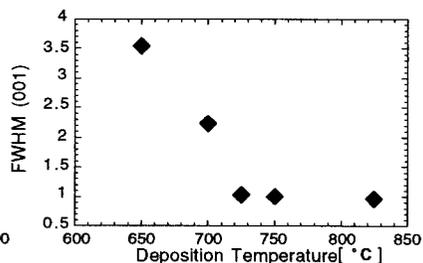


Figure 2 X-ray rocking curve widths for KTN film (x=0.4) on MgO as a function of the deposition temperature

(100)MgO is shown in Fig. 2. At low substrate temperatures, ω is broad. Increasing the substrate temperature leads to a decrease in ω indicating a more highly oriented film. At 725° C, ω reaches a minimum of $\sim 0.9^\circ$. Increasing the substrate temperature higher than 725° C does not lead to a further decrease in ω . Typical FWHM of the ω -scan peaks for the KTN films on (100) MgO and LAO were 0.8° to 1.0° for substrate temperatures over 725° C. Exceptionally well oriented KTN films were deposited onto STO substrates for the same substrate temperatures. The ω widths were at or below the 0.16° resolution limit of the diffractometer for KTN films grown on (100) STO.

KTN films deposited on MgO and LAO substrates at elevated temperatures often cracked on the cooling after deposition or during a post-deposition heat treatment. Fig. 3(a) shows an SEM photomicrograph of $\sim 0.6 \mu\text{m}$ thick KTN films, $x = 0.6$, deposited on (100)MgO substrate. Most KTN films on MgO and LAO exhibited cracking right after deposition or annealing even though some of the KTN films, deposited with a thinner thickness ($< 0.4 \mu\text{m}$) and/or at a higher substrate temperature (825°C), did not show any cracking. The strain in the deposited film can result from several contributions: lattice mismatch between the film and the

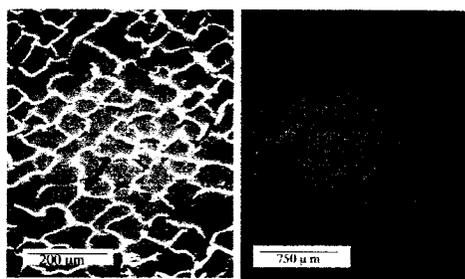


Figure 3 SEM images of (a) KTN film (x=0.6) on (100) MgO and (b) KTN film (x=0.4) deposited onto a thin BTO buffer layer on (100)MgO

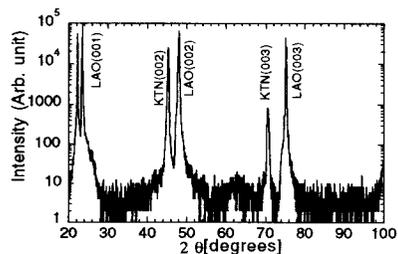


Figure 4 XRD pattern for KTN film (x=0.6) on (100)LAO with a thin BTO buffer layer

substrate, phase transitions in the film and substrate, twinning in the substrate, structural defects in the film, and differences in the thermal expansion coefficient between the film and substrate. The room temperature lattice mismatch for the KTN films are $\sim -4.5\%$ with MgO substrate, which results in a tensile strain in the plane of the substrate-film interface, and $\sim +5.7\%$ with LAO substrate and $\sim +2\%$ with STO substrate, which result in a compressive strain in the interface. To eliminate the cracking problem, we deposited KTN films ($x = 0.4$ and 0.6) on MgO and LAO substrates with a thin buffer layer ($<100 \text{ \AA}$) of STO or BTO. Deposited KTN films on MgO and LAO substrates with the buffer layer were found to be single phase and exclusively oriented in the (100) direction (Fig. 4). These films were stable and did not exhibit any cracking after deposition or annealing (Fig. 3(b)). These KTN films show similar dielectric properties with the un-cracked KTN films without a buffer layer (Fig. 5 and Table 1).

Dielectric Measurement

Previously, we reported the capacitance and dissipation measurements for the KTN film ($x = 0.4$) deposited on (100)MgO substrate as a function of temperature and DC bias voltage [6]. As can be seen in Fig. 5(a), the KTN film showed broad peaks in the temperature dependent measurements of the capacitance and dissipation factor. The Curie temperature is about $\sim 200 \text{ K}$ lower than expected based on the bulk literature [2]. Temperature dependent capacitance and dissipation measurements are shown in Fig. 5. All the temperature dependent dielectric measurements were made as a function of DC bias (0 - 40 V) at 1 MHz except Fig. 5(f), which was measured as a function of frequency (500 Hz - 1 MHz) at 0V DC bias. The dielectric measurements reported here for the KTN films show the same trends in dielectric properties as the previous results.

These results show that KTN films are clearly different from the bulk in terms of the phase transition peak, both the peak position and the peak width [1]. The origin of these differences may be non-uniform strain [7,8], K vacancies [9], and compositional inhomogeneities [10]. Non-uniform strain is believed to arise from the structural defects in the film, such as vacancies and the presence of grains. The KTN film ($x = 0.4$) on (100)MgO, shown in Fig. 5(a), showed a stoichiometry $K_1Ta_{0.64}Nb_{0.36}O_3$ as determined by RBS analysis. Therefore, K deficiency does not seem to be related directly to the broadness of the capacitance peak. Compositional inhomogeneities could arise due to the presence of other phases in the film, structural defects, or intrinsic properties of the thin film. In some films, we observed the presence of the pyrochlore phase in the deposited film. KTN films which exhibit the pyrochlore phase show a K deficiency as determined by RBS. The RBS data also shows a 13 % drop in the Nb/Ta ratio from the deposited films in comparison to the KTN targets that contained a Nb/Ta ratio of 0.66.

Another difference between the thin film and the bulk behavior is that there are two peaks in the dissipation factor for the KTN film; one which is associated with the PE-FE phase transition and a second peak which occurs at a higher temperature. The former peaks located at about 30 - 50 K, which are related to the phase transition, shown in Fig. 5(a), (b) and (e) were characterized based on the dielectric relaxation theory [11,12]. The latter peaks (or shoulders) positioned at about 230 - 250 K, shown in the same figure, were also observed for other system such as $Ba_{1-x}Sr_xTiO_3$. Fig. 5(f) shows the temperature dependent capacitance and dissipation factor as a function of frequency at 0 V DC bias. The shoulder in the dissipation factor shifts to lower temperature (from $\sim 240 \text{ K}$ to $\sim 140 \text{ K}$) with decreasing frequency (from 1 MHz to 500Hz)

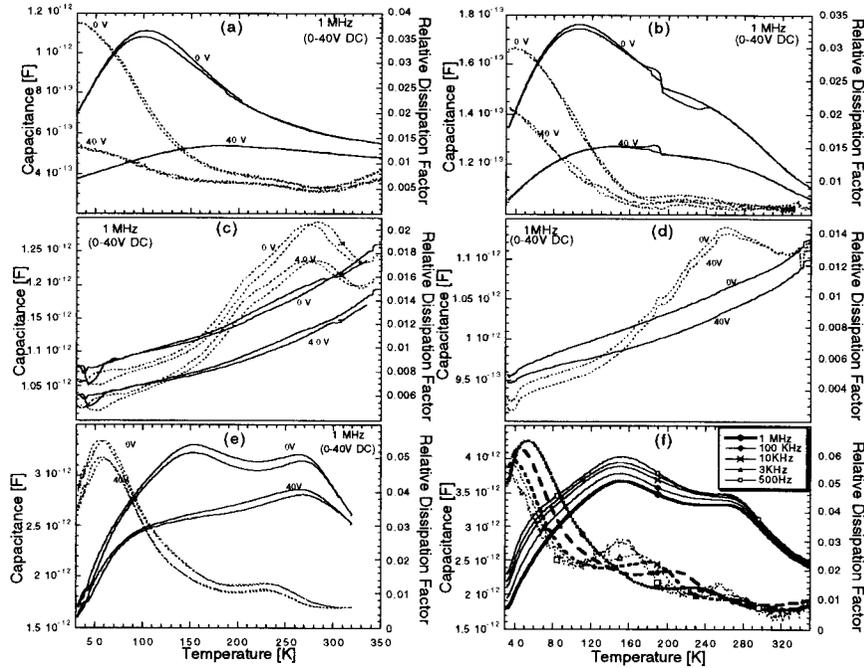


Figure 5 Capacitance (solid line) and dissipation factor (dashed line) versus temperature for (a) KTN film ($x=0.4$)/MgO, (b) KTN film ($x=0.4$)/BTO/MgO, (c) KTN film ($x=0.6$)/MgO, (d) KTN film ($x=0.6$)/BTO/MgO, and (e) and (f) KTN film ($x=0.4$)/STO

and the dissipation factor measured at less than 10 KHz has an additional peak, as one shoulder is followed by the other appearing from the higher temperature side. This shoulder may be related to some conductivity, such as free charge conductivity, ionic conductivity, hopping conductivity of oxygen vacancies, etc. [13,14]. The dielectric loss mechanism associated with this peak in the dissipation may be due to the presence of free charges and oxygen vacancies.

A summary of the dielectric measurements made between 1 and 20 GHz at room temperature and the resistivities are shown Table 1. KTN films ($x = 0.4$) have a lower dielectric Q ($1/\tan\delta$) than KTN films ($x = 0.6$) at room temperature as shown in Fig. 5 and Table 1. The resistance was very stable over the whole bias range (10-40V) and the resistivities, ρ , calculated for this geometry were on the order of $10^9 \Omega \text{ cm}$, which is lower than those for bulk KTN ($\sim 10^{12} \Omega \text{ cm}$ [15]). The KTN films ($x = 0.4$) on MgO with a thin BTO buffer layer are similar to the KTN films deposited on MgO without a buffer layer when measured at high frequencies.

CONCLUSIONS

High quality single phase (100) oriented KTN films were grown by PLD. Film morphology and structure were characterized by SEM and XRD. The data at 1 - 20 GHz

demonstrate the KTN films can be used to fabricate capacitors with up to 34 % tuning and dielectric Q's that ranged from 4 to 55. The temperature dependent measurements at 1 MHz showed that the Curie temperature for the deposited films were significantly lower than expected in bulk KTN. In addition, a second peak was observed in the temperature dependent of the dissipation factor which shifted with frequency. RBS data indicated that the deposited films had a Nb deficiency of ~ 13% which is related partially to the lower T_c in KTN films. Some cracking was observed in KTN films deposited on MgO and LAO which could be removed with the use of a STO or BTO buffer layer.

Table 1. Summary of high frequency dielectric properties and resistivities for $K_{1-y}Ta_{1-x}Nb_xO_3$ films

x	target y, [mol.%]	substrate	Deposition temp. [° C]	# of shots	Anneal temp. [° C]	Anneal time [hr]	tuning [%]	Q	ρ [$\times 10^9 \Omega$ - cm]
0.4	20	MgO	750	1000	Not annealed	-	2	55	
0.4	40	MgO	825	3000	800	12	20	36-40	
0.6	30	MgO	825	3000	Not annealed	-	9	14-16	5.34
0.4	40	STO/MgO	725	3000	800	2	15	22-26	4.79
0.4	40	BTO/MgO	725	3000	800	2	34	20-32	4.70
0.6	40	BTO/MgO	725	3000	800	6	17	11-15	9.34
0.6	30	STO	725	36000	800	2	18	4-6	
0.4	40	STO	725	36000	Not annealed	-	23	37-41	
0.4	40	LAO	725	2000	800	2	23	19-25	7.33
0.6	40	BTO/LAO	725	3000	800	6	24	6-10	4.0

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