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Dielectric Properties of Ti-doped K(Ta,Nb)O_3 Thin Films for Tunable Microwave Applications

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Abstract - Ferroelectric materials have been widely investigated for high density dynamic random access memories, opto-electrics, and tunable microwave devices due to their properties. In this study, we have investigated the dielectric properties of Ti doped K(Ta, Nb)O_3 thin films. By doping Ti into the K(Ta,Nb)O_3 system, Ti with a valence value of +4 will substitute Ta or Nb ions with a valence value of +5. This substitution will introduce an acceptor state. Therefore, this introduced acceptor state will reduce dielectric loss by trapping electrons. Using 3% Ti-doped K(Ta,Nb)O_3 targets, K(Ta,Nb)O_3:Ti films were grown in MgO(001) crystals using pulsed laser deposition. First, growth conditions were optimized. A reduction in the loss tangent was observed for Ti-doped K(Ta,Nb)O_3 relative to undoped films, although a reduction in tunability is also seen. The crystallinity, morphology, and tunability of K(Ta,Nb)O_3:Ti films are reported.

Keywords: Acceptor doping, Dielectric, KTaNbO3, Tunable Microwave

1. Introduction

Perovskite materials have been intensively studied for application in high density dynamic random access memories, large scale integrated capacitors, phase shifters, band-pass filters, and frequency triplers [1-5]. For tunable microwave device applications, low dielectric loss, and high tunability under small bias voltage are required [6-8]. Among the perovskite materials considered, $Ba_xSr_{1-x}TiO_3$ [1-5, 9] has received the most attention as a tunable ferroelectric material. However, $KTa_{1-x}Nb_xO_3$ (KTN) is also an attractive paraelectric / ferroelectric for microwave applications. As with (Ba,Sr)TiO_3, $KTa_{1-x}Nb_xO_3$ (KTN) forms a solid solution for all composition ranges of x [10]. When x is 0, $KTaO_3$ is quantum ferroelectric, consisting of a cubic structure with a lattice parameter of 3.9885Å. By increasing x, the curie temperature, Tc, of KTN is increased and KTN becomes a ferroelectric [11]. When x is 1, $KNbO_3$ undergoes a ferroelectric phase transition at 704K, changing from cubic (a=4.022Å) to tetragonal (a=b=3.997 Å, c=4.063 Å). Additional structural transitions include orthorhombic (a=4.035 Å, b=3.973 Å, and c=4.035 Å) at 498K and rhombohedral (a=b=c=4.016 Å) at 265K [12]. There have been multiple studies of the dielectric properties of KTN bulk [13, 14], thin films [15, 16], and superlattices of $KTaO_3/KNbO_3$ [17, 18]. In addition, some activities have addressed modification of the dielectric response by means of chemical doping. For example, in an effort to enhance ferroelectricity, the properties of KTN or KT single crystals doped with Ca or Li have been investigated [19-21]. In the present study, the effect of Ti doping on the dielectric response of KTN films is investigated. The ionic radius of Ti^{4+} is 0.605 Å with a coordination number of six. This radius was similar to Ta^{5+} (0.64 Å) and Nb^{5+} (0.64 Å). The most stable valence state for Ti is +4, which provides a potential acceptor state, when substituted on the Nb/Ta site. An acceptor state associated with the Ti ion substituted for the Ta or Nb ion at the B site should reduce losses. The dielectric properties of KTN:Ti thin films were studied for materials synthesized using a range of the growth conditions.

For tunable dielectrics, a key issue is dielectric loss. While high dielectric tunability has been demonstrated for both (Ba,Sr)TiO_3 and K(Ta,Nb)O_3 thin films, the accompanying losses are relatively high. A significant fraction of the dielectric loss for these materials is likely associated with donor states due to vacancies on the oxygen sub-lattice. It is well known that oxygen vacancies in these perovskite materials yield donor states resulting in high loss, or even dc conductive materials, if the defect densities are sufficiently high. One approach to reducing losses previously demonstrated in (Ba,Sr)TiO_3 is acceptor doping [22-24]. For (Ba,Sr)TiO_3 materials, doping with various +2 and +3 valence state cations on the perovskite B-site yields compensating acceptor states. This can lead to a reduction in the loss as electrons are trapped on the acceptor sites.

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2. Experimental Methods

The epitaxial Ti-doped $K(Ta,Nb)O_3$ films were grown using pulse d laser deposition. The dielectric properties of the films were measured for materials synthesized over a range of growth conditions. The chosen solid solution was $KTa_{0.524}Nb_{0.446}Ti_{0.03}O_3$. The bulk ferroelectric transition temperature for a solid solution with an equivalent Ta/Nb ratio ($KTa_{0.54}Nb_{0.46}O_3$) is 70°C. With this compound, the dielectric response both below and above the Curie temperature of the equivalent material with no Ti could be investigated.

$KTa_{0.524}Nb_{0.446}Ti_{0.03}O_3$ (KTN:Ti) ablation targets were made by solid state synthesis. The starting materials were puratonic grades of K_2CO_3, Ta_2O_5, Nb_2O_5, and TiO_2. These powders were measured to meet desired composition and then uniformly mixed in a methanol base using the conventional method. The powders were reacted in air at 900°C for 4 hrs to form KTN:Ti phases. KTN:Ti phases of calcined powders were confirmed by x-ray diffraction method. Then these powders were reground, pressed, and sintered at 1150°C for an additional 20 hrs.

$KTa_{0.524}Nb_{0.446}Ti_{0.03}O_3$ films were grown on single crystal (001)-oriented MgO substrates. The substrates were ultrasonically cleaned with trichloroethylene, acetone, and methanol, and blown dry with compressed N_2. In order to compensate for K loss during in-situ film growth, segmented KTN:Ti/KNO_3 ablation targets were used. Deposition temperatures ranging from 650°C – 750°C were investigated. A KrF (248nm) laser was used as the ablation source. The laser repetition rate was 1Hz with an energy density of 5J/cm^2. Target to substrate distance was fixed at 4cm. Prior to growth, the ablation target was cleaned by pre-ablating 2000 shots. KTN:Ti films were deposited at various oxygen pressures. Film thickness was measured with a step profilometer. For this study, film thickness was maintained at approximately 250nm. After KTN:Ti film growth, Al/Cr interdigitated electrodes were deposited via RF sputtering. The electrode pattern was defined using lift off photolithography. The length of each electrode finger was 1mm and the finger width was 10μm. Distance between the fingers was 10μm. The KTN:Ti films were characterized by x-ray diffraction (XRD), atomic force microscopy (AFM), and capacitance measurements. The capacitance measurements included the application of a DC bias voltage in order to probe dielectric tunability. The measurements using HP 4284A LCR meter were performed in air at 1MHz over a temperature range of 20–260°C.

3. Results and Discussion

First, $KTa_{0.524}Nb_{0.446}Ti_{0.03}O_3$ (KTN:Ti) films were grown on (001) oriented MgO single crystals in 100mTorr of oxygen ambient with different growth temperatures ranging from 550°C – 750°C. The crystallinity of KTN:Ti films grown on (001) MgO was investigated using x-ray diffraction shown in Fig. 1, which utilized a wavelength of 1.5405Å of Cu Kα with 40kV and 20mA. KTN:Ti films grown below 650°C were amorphous. The (001) and (002) peaks of KTN:Ti film appeared from a growth temperature of 700°C. The high intensity peaks of KTN:Ti films were observed in the KTN:Ti film grown at 750°C with 100mTorr of oxygen ambient.

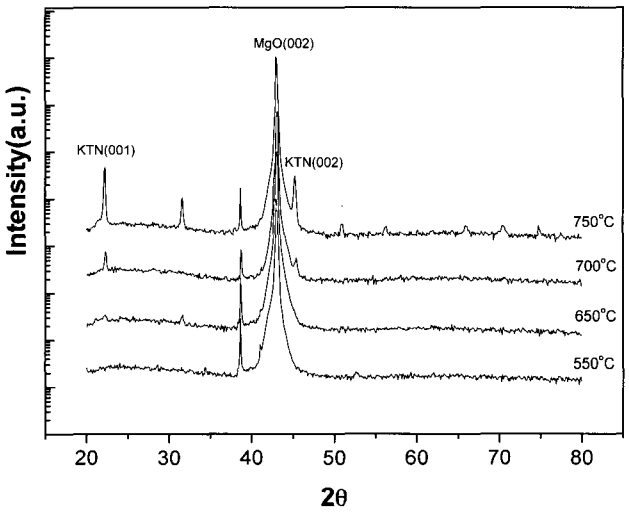

Fig. 1 XRD results of KTN:Ti films grown at different growth temperatures with 100mTorr of oxygen atmosphere and 1Hz of frequencies.

Epitaxial growth of $KTa_{0.524}Nb_{0.446}Ti_{0.03}O_3$ (KTN:Ti) thin films was achieved at a growth temperature of 750°C in background pressures ranging from 0.01-150 mTorr.

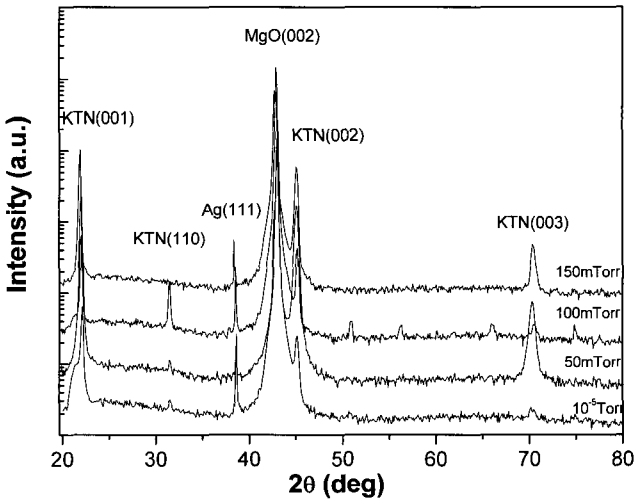

Fig. 2 XRD results of KTN:Ti films grown at different oxygen pressures with deposition temperature 750°C.

Fig. 2 shows the results from θ-2θ x-ray diffraction (XRD) measurements for KTN:Ti films grown on (001) MgO at different oxygen pressures. The deposition temperature was 750°C for all films considered in Fig. 2. The XRD results indicate good crystallinity for all of the KTN:Ti films grown at these conditions. The films are mostly (001) oriented, with only a small KTN (110) peak observed in the diffraction pattern. The Ag peak is from the Ag paint used in mounting the substrates on the heater platen. The intensity of the diffraction peaks are somewhat less for the film grown in vacuum (0.01 mTorr). Note that there is a measurable reduction in c-axis lattice spacing with increasing oxygen pressure during growth. From the θ-2θ plots, the lattice spacing shifts from 4.0155 Å for films grown in vacuum to 4.0004 Å for films grown in 150 mTorr of oxygen. Larger lattice spacing in oxides often reflects the presence of oxygen vacancies.

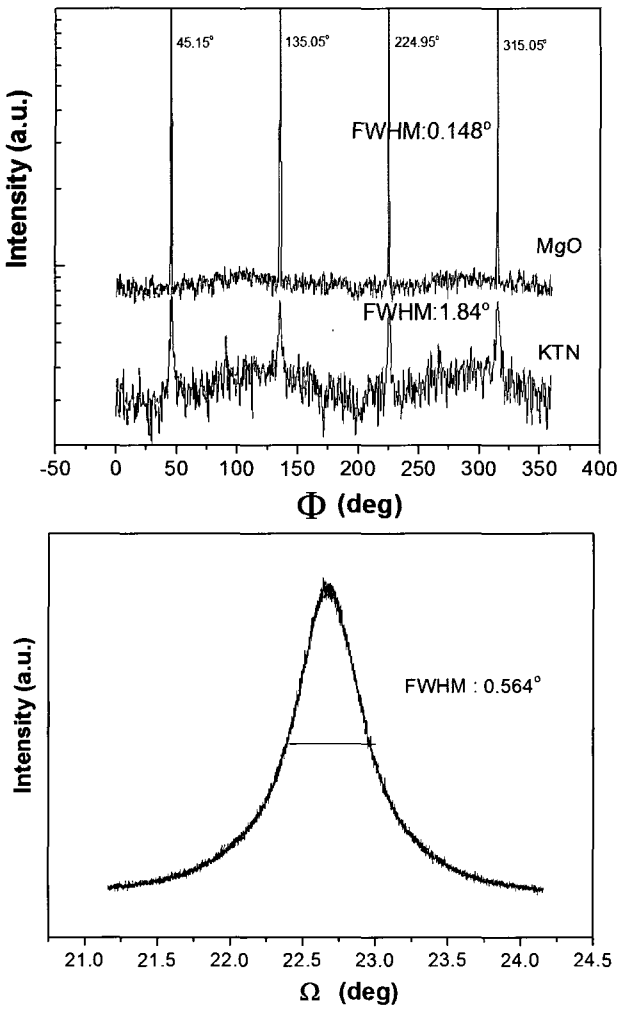

Fig. 3 Four circle XRD results of KTN:Ti films grown at 100mTorr oxygen pressure with deposition temperature 750°C. (a) phi scan for the (111) reflection of KTN:Ti and MgO, and (b) the rocking curve of (200) KTN:Ti film: FWHM is 0.564°.

The epitaxial relationship of the Ti-doped KTN films on the (001) MgO substrate was investigated using four-circle XRD. Fig. 3 demonstrates an in-plane ϕ-scan through the KTN:Ti (111) peaks for a film grown at 750°C in 100 mTorr O_2. The full-width half-maximum of the ϕ peak is 1.84°. Despite the lattice mismatch between the KTN film and MgO substrate, the ϕ-scan indicates cube-on-cube in-plane alignment of the KTN:Ti film on the MgO substrate. Also indicated in Fig. 5-3 is the rocking curve for the KTN:Ti (002) peak. The full-width half-maximum (FWHM) of the KTN:Ti (002) peak is 0.56°.

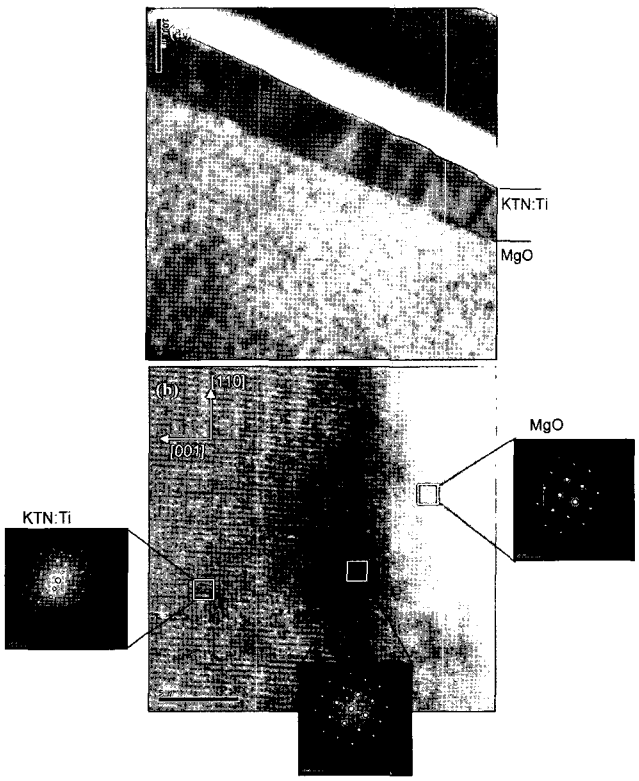

Fig. 4 TEM images of KTN:Ti films grown on MgO single crystals at 750oC of growth pressure, and 100mTorr of oxygen atmosphere.

Fig. 4 presents the HRTEM images and diffraction patterns at the MgO, the KTN:Ti film and the interface between the MgO substrate and the KTN:Ti film. KTN:Ti film was grown on the (001) MgO substrate at growth pressure of 750°C, and oxygen atmosphere of 100mTorr. The sharp interface between the KTN film and the MgO substrates is observed. And there are no secondary phases at the interface or in the KTN:Ti film.

Fig. 5 shows the atomic force microscopy (AFM) images of KTN:Ti films grown at different oxygen pressures with deposition temperature of 750°C. The grain size for all oxygen pressures is on the order of 400-500 nm. It should be noted that micro-cracks were observed due to stress in KTN:Ti films on MgO more than 3000Å of

thickness. These films were easily peeled off due to residual stress in the film after film growth.

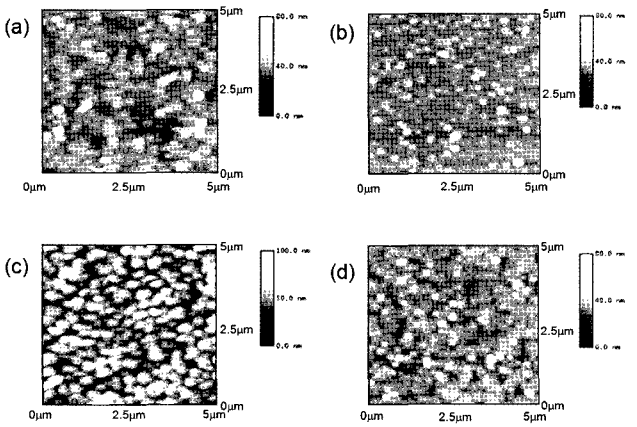

Fig. 5 AFM images of KTN:Ti films grown at different oxygen pressures with deposition temperature 750oC : (a) vacuum, (b) 50mTorr (c) 100mTorr and (d) 150mTorr.

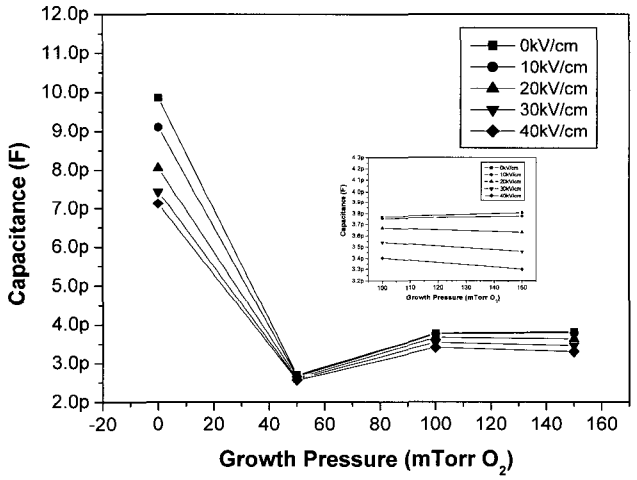

Fig. 6 Results of capacitance of KTN:Ti films on MgO single crystals as a function of oxygen growth pressure under 0, 10,20, 35, and 40V dc bias voltage measured at 30oC, and frequency of 1MHz .

The dielectric response of the films was measured using the interdigitated electrodes. Fig. 6 shows the measured capacitance for KTN:Ti films on MgO single crystals grown in various oxygen pressures at a growth temperature of 750°C. Also, film thicknesses of all grown films were fixed around 250nm. Therefore, the measured capacitance values could be used to compare the KTN:Ti films grown at different oxygen pressures. Capacitance measurements were made for an applied bias voltage ranging from 0 to 40 volts and were performed at 30°C with a measurement frequency of 1MHz. With the exception of the film grown at 10^{-5} Torr, the capacitance for films grown at oxygen pressures ranging from 50-150 mTorr was constant. A reduction in dielectric constant with acceptor doping has also been observed in $(Ba,Sr)TiO_3$ thin films. Note that the high capacitance for KTN:Ti films grown at 10^{-5} Torr reflects the high loss tangent of this film due to a high density of oxygen vacancies. Also note that the KTN:Ti films grown at $P(O_2) \geq 50$ mTorr show or moderate voltage tunability as will be discussed later.

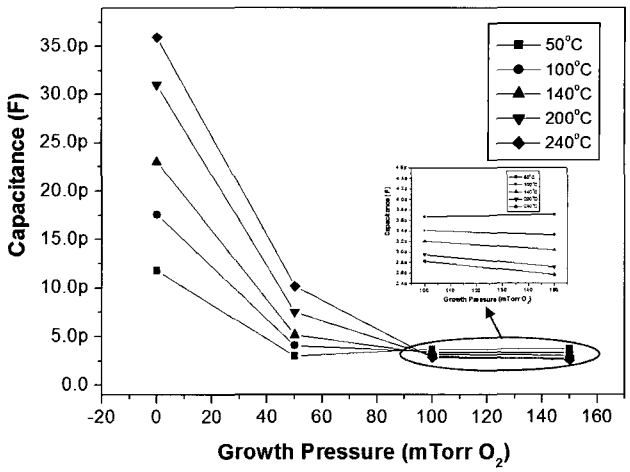

Fig. 7 Oxygen pressure dependence of capacitance for KTN:Ti films on MgO single crystals under temperatures in the range of 50 – 240oC at dc bias of 10V, and frequency of 1MHz.

The capacitance of the titanium-doped films was then measured at various temperatures. The temperature dependence of the dielectric properties for films grown at 750°C in various oxygen pressures was also measured as indicated in Fig. 7. Measurements were made at temperatures ranging from 50–240°C at a fixed dc bias of 10V and a measurement frequency of 1MHz. For films grown at $P(O_2) \leq$ 50mTorr, the measured capacitance significantly increases as the measurement temperature increases. Again, this reflects the activation of a high density of donor defects in films grown under these conditions. These defects were electrically active at higher temperatures. This is also reflected in the dielectric loss measurements discussed later. However, for films grown at oxygen pressures equal to or greater than 100mTorr, the capacitance slightly decreases as temperature increases. This is the expected behavior for temperature biasing a ferroelectric material deeper into the paraelectric regime above T_c.

The motivation for investigating titanium doping is to potentially reduce the losses due to defect donor states. The dielectric loss behavior for KTN:Ti films grown at various oxygen pressures is shown in Fig. 8. Dielectric loss measurements were carried out at 30°C, at a frequency of 1MHz under an electric field in the range of 0–

40kV/cm. For KTN:Ti films grown in vacuum, the dielectric loss is high and is quite sensitive to applied bias voltage. Again, this reflects a high density of oxygen vacancies for films grown in vacuum. However, the loss tangent for KTN:Ti films grown with oxygen pressure greater than 50mTorr is quite low. From the dielectric loss data, the loss tangent for these films is estimated to be less than 0.02. This is 50% lower than that found for Ti-free KTN films grown under the same conditions.

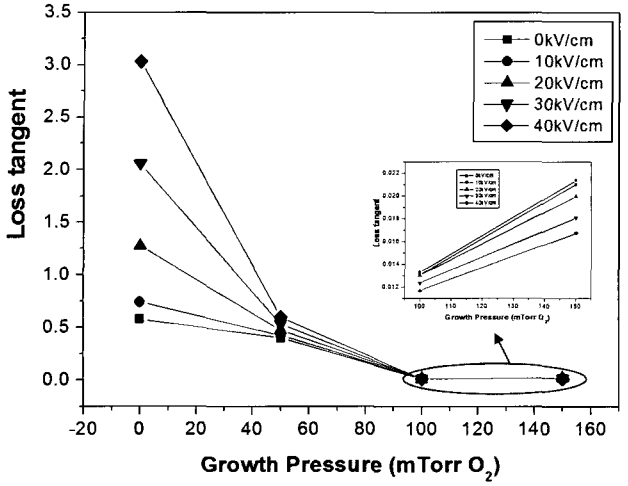

Fig. 8 Oxygen pressure dependence of loss tangent for KTN:Ti film on MgO single crystal under dc bias in the range of 0 – 40kV/cm at temperature of 30oC, and frequency of 1MHz.

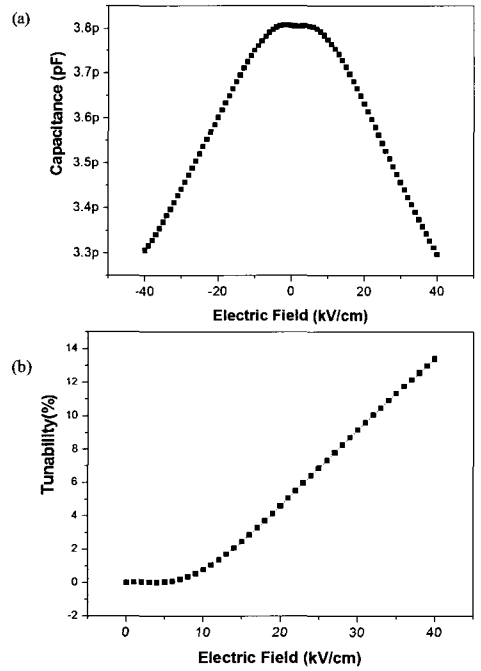

Fig. 9 DC bias voltage dependence of (a) capacitance and (b) tunability for KTN:Ti film on MgO at room temperature at 1MHz frequency. KTN:Ti film was grown at 150mTorr of oxygen with deposition temperature 750oC.

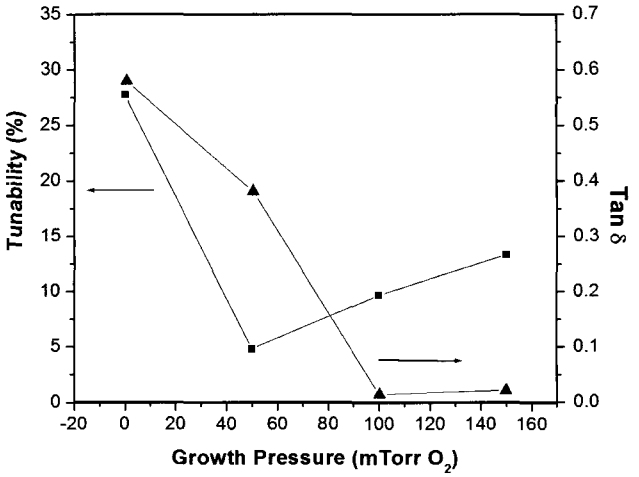

Fig. 10 Tunability (=(C(E0)-C(Emax))/C(E0)x100) and loss tangent of KTN:Ti film grown on (001) MgO at different growth pressures with deposition temperature 750oC.

The tunability in dielectric response was measured for the films grown under all conditions, with particular interest in those films grown at oxygen pressures greater than or equal to 50mTorr, as these exhibit reasonably low losses. Fig. 9 presents the electric field dependent of capacitance and calculated tunability of the dielectric response for a KTN:Ti film grown at $P(O_2)$=150 mTorr. Measurements were made at room temperature and a frequency of 1MHz. The films exhibit a tunability of 14% for an applied electric field of 40kV/cm. This is somewhat smaller than that observed for KTN films that do not contain Ti, where the tunability can exceed 40%. A reduction in tunability with acceptor doping has also been observed in (Ba,Sr)TiO_3 thin films. Fig. 10 gives tunability (=$(C(E_0)-C(E_{max}))/C(E_0)$x100) and loss tangent of KTN:Ti films grown on (001) MgO at different growth pressures with deposition temperature of 750°C. Capacitance was measured at 20°C, 1MHz. Tunability of KTN:Ti films decreased as $P(O_2)$ increased. Films grown at $P(O_2) \geq$ 100mTorr exhibit a tunability on the order of 10%. However, loss tangent of films grown at $P(O_2) \geq$ 100mTorr are most relevant as these have low losses.

Fig. 11 shows the Fig. of Merit, which is also known as K-factor for indication of the performance for tunable microwave devices. FOM is calculated by means of dividing tunability by maximum loss tangent. The highest FOM is observed in KTN:Ti film grown at 750°C and 100mTorr oxygen atmosphere because FOM is dominated by lower loss tangent.

Fig. 12 shows capacitance and calculated tunability of KTN:Ti films as a function of measurement temperature. KTN:Ti film was grown on (001) MgO at deposition temperature of 750°C, and oxygen atmosphere of 150mTorr. Capacitance decreases as measurement temperature

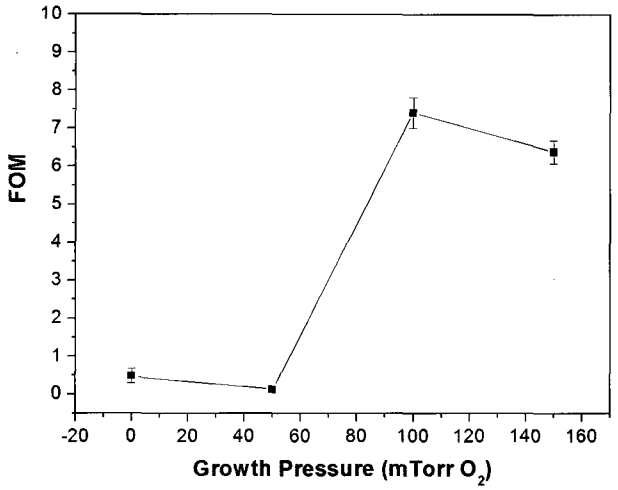

Fig. 11 Figure of merit (FOM=tunability/loss tangent) of KTN:Ti film grown on (001) MgO at different growth pressures with deposition temperature 750oC.

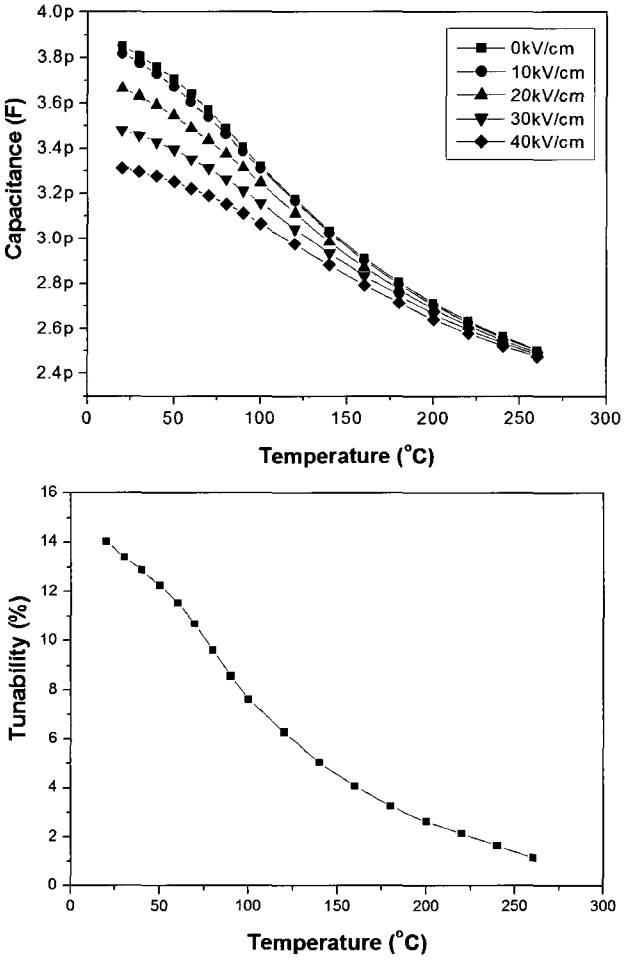

Fig. 12 Capacitance and tunability of KTN:Ti film as a function of measurement temperature. KTN:Ti film was grown on (001) MgO at deposition temperature 750oC, and 150mTorr of oxygen atmosphere.

increases. Also, tunability declines as measurement temperature rises. This occurs with paraelectric behavior in the deeper region as a result of curie temperature. The highest tunability is observed at room temperature. From these results, we can assume that curie temperature, T_c, of KTN:Ti film is lower than room temperature.

Loss tangents of undoped KTN and KTN:Ti are compared in Fig. 13. Both films were prepared under identical conditions. The loss tangent of undoped KTN increased as measurement temperature increased. However, the loss tangent of Ti doped KTN had no significant change along with the measurement temperatures. This result proves that Ti ions, which were doped as acceptor ions, effectively trap electron charges even at high temperatures.

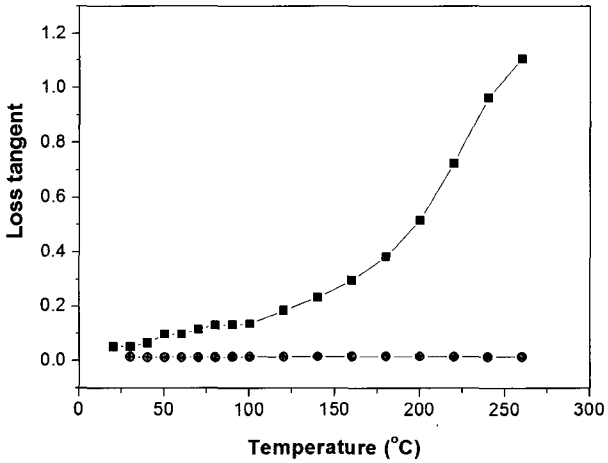

Fig. 13 Comparison of loss tangent of undoped KTN and KTN:Ti film as a function of measurement temperature. Both films were grown on (001) MgO at 750oC of deposition temperature, and 100mTorr of oxygen atmosphere for 1hr. (■: loss tangent of KTN, ●: loss tangent of KTN:Ti films).

4. Conclusion

The dielectric properties of Ti doped KTN films were studied. The growth conditions of KTN:Ti films are a major factor in determining dielectric properties. KTN:Ti film grown without oxygen showed high dielectric constant but with high loss tangent due to oxygen vacancies in KTN:Ti film. Tunability of KTN:Ti films grown at above oxygen pressures of 100mTorr was approximately 10–14% with loss tangent around 0.02. Tunability and loss were reduced by Ti doping.

References

[1] J.F. Scott, Ferroelectr. Rev. 1. 1 (1998); S.R. Summerfelt, in Ferroelectric Thin Films, edited by R.

Ramesh (Kluwer Academic, Netherlands, 1997), Chap. 1, pp. 1.
[2] J. Im, O. Auciello, P.K. Baumann, S.K. Streiffer, D.Y. Kaufmann, and A.R. Krauss, Appl. Phys. Lett. 76, 625 (2000).
[3] Y. Gim, T. Hudson, Y. Fan, C. Kwon, A.T. Findikoglu, B.J. Gibbons, B.H. Park, and Q.X. Jia, Appl. Phys. Lett. 77, 1200 (2000).
[4] P. Padmini, T.R. Taylor, M.J. Lefevre, A.S. Nagra, R.A. York, and J.S. Speck, Appl. Phys. Lett. 75, 3186 (1999).
[5] Ikufumi Katayama, Masanobu Shirai, and Koichiro Tanaka, Journal of Luminescence, 102-103, pp. 54-59 (2003).
[6] R.W. Babbitt, T.E. Koscica, and W.C. Drach, Microwave Journal, pp. 63, June (1992).
[7] L.C. Sengupta and S. Sengupta, IEEE Trans. On Ultrasonics, Ferroelectrics, and Frequency Control 44, 792 (1997).
[8] G.V. Belokopytov, I.V. Ivanov, S.I. Katanov, N.N. Moiseev, and P.P. Syrnikov, Sov. Phys. Solid State 24(6) (1982).
[9] Adriaan C. Carter, James S. Horwitz, Douglas B. Chrisey, Jeffrey M. Pond, Steven W. Kirchoefer, and Wontae Chang, Integrated Ferroelectrics, Vol. 17, pp. 273-285, (1997).
[10] S. Triebwasser, Physical Review, Vol. 114 No. 1, pp. 63, (1959).
[11] D. Rytz, A. Chatelain, and U.T. Hochli, Phys. Rev. B 27, 6830, (1983).
[12] M.D. Fontana, G. Metrat, J.L. Servoin, and F.Gervais, J. Phys. C: Solid State Phys., 16, pp. 483-514, (1984).
[13] J. Toulouse, X.M. Wang, and L.A. Boatner, Phys. Rev. B, Vol. 43, No. 10, pp. 8297, (1991).
[14] P. Dubernet, J. Ravez, and A. Pigram, Phys. Stat. Sol. (a) 152, pp. 555, (1995).
[15] Hans-Martin Christen, D.P. Norton, L.A. Gea, and L.A. Boatner, Thin Solid Films, 312, pp.156-159, (1998).
[16] S. Yilmaz, T.Venkatesan, and R. Gerhard-Multhaupt, Appl. Phys. Lett. 58, 2479, (1991).
[17] H.-M. Christen, L.A. Boatner, J.D. Budai, M.F. Chisholm, L.A. Gea, P.J. Marrero, and D.P. Norton, Appl. Phys. Lett. 68, 1488 (1996).
[18] H.-M. Christen, E.D. Specht, D.P. Norton, M.F. Chisholm, and L.A. Boatner, Appl. Phys. Lett. Vol. 72, No. 20, 2535, (1998).
[19] M. W. Cole, P. C. Joshi, and M. H. Ervin, J. Appl. Phys. 89, 6336 (2001).
[20] M. Jain, S. B. Majumder, R. S. Katiyar, F. A. Miranda, and F. W. Van Keuls, Appl. Phys. Lett. 82, 1911 (2003).
[21] H. S. Kim, M.H. Lim, H.G.Kim, and H.D. Kim, Electrochem. Solid State Lett. 7, J1 (2004).
[22] G.A. Samara, L.A. Boatner, Physical Review B. Vol. 61, No. 6. pp. 3889, (1999).
[23] Gabriel Bitton, Yuri Feldman, and Aharon J. Agranat, Journal of Non-Crystalline Solids, 305, 362-367, (2002).
[24] R.K. Pattnaik, J. Toulouse, Journal of Physics and Chemistry of Solids, 61, 251-259, (2000).

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