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Properties of (K,Na)NbO_3-based lead-free piezoelectric films prepared by pulsed laser deposition

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ABSTRACT

To investigate the properties of (K,Na)NbO_3-based lead-free piezoelectric films at the morphotropic phase boundary composition, we fabricated epitaxial [$(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}$] ($Nb_{0.8}Ta_{0.2}$)$O_3$ films on (001), (110) and (111)-oriented single crystal $SrTiO_3$ substrates by pulsed laser deposition. The structure and electrical properties of the films were studied. Dielectric constants of 540, 390 and 300 and remnant polarizations of 4.00, 1.05, and 0.35 μC/cm^2 were observed for the (001), (110) and (111) oriented films, respectively.

1. Introduction

Lead-based piezoelectric materials, such as lead zirconate titanate, are widely used because of their excellent piezoelectric properties near the morphotropic phase boundary (MPB). However, due to environmental concerns associated with lead, alternative lead-free piezoelectric materials have attracted much attention recently.

Solid solution of (K,Na)NbO_3, (K,Na)TaO_3 and $LiTaO_3$ is one of the leading candidates, in which the piezoelectric and dielectric properties were greatly enhanced at the MPB composition [1–5]. Saito et al. have reported that the piezoelectric properties of ($K_{0.44}Na_{0.52}Li_{0.04}$)($Nb_{0.86}Ta_{0.10}Sb_{0.04}$)$O_3$ (KNN-KNT-LS) and [$(K_{0.5}Na_{0.5})_{0.97}Li_{0.03}$] ($Nb_{0.8}Ta_{0.2}$)$O_3$ (KNN-KNT-LT) are comparable to that of the Pb($Zr_{0.52}Ti_{0.48}$)O_3 ceramic (~220 pm/V) [6]. KNN-KNT-LT, which has an MPB separating orthorhombic and tetragonal phases, shows piezoelectric coefficient (d_{33}) of ~230 pm/V whereas the KNN-KNT-LS can reach ~300 pm/V. It has also been reported that the <001> textured polycrystalline samples of KNN-KNT-LT and KNN-KNT-LS show even larger value of ~373 pm/V and ~416 pm/V, respectively. However, a complex texturing process is required to achieve the high piezoresponse [5,6]. For certain applications, it is desirable to use the piezoelectric materials in thin film form. Many have chosen KNN-KNT-LS to study the properties in thin film form. However, the results are not comparable to that of the bulk and they mainly cover the dielectric and ferroelectric properties [7,8]. No study on KNN-KNT-LT film has been reported.

In this letter, we report the fabrication and characterizations of epitaxial KNN-KNT-LT films deposited on (001), (110) and (111)-oriented $SrTiO_3$ substrates. The epitaxial films enable us to study the properties of the KNN-KNT-LT system along different crystallographic directions. The crystal structure and the electrical properties (dielectric, ferroelectric and piezoelectric) are investigated and the structure-property relationship can be established.

2. Experimental details

The KNN-KNT-LT films were prepared by pulsed laser deposition (PLD) using a KrF excimer laser ($\lambda = 248$ nm). A thin $SrRuO_3$ layer was deposited first as the bottom electrode by using a commercially available target (99.9% purity). The KNN-KNT-LT target was synthesized by using the conventional solid state reaction method. Details of the deposition parameters are listed in Table 1. After the deposition of $SrRuO_3$ and KNN-KNT-LT films, oxygen was introduced into the deposition chamber until near ambient pressure (7.0×10^4 Pa) was reached while the sample was kept at the deposition temperature. It was then cooled down slowly at 5 °C/min to room temperature. The thickness of the KNN-KNT-LT and $SrRuO_3$ layers were 1.5 μm and 20 nm, respectively.

The phase purity and structures of the (001), (110) and (111) oriented films were characterized by X-ray diffraction (XRD, PANalytical X'pert PRO MRD). The dielectric, piezoelectric and ferroelectric properties were studied using LCR meter (Agilent, E4980A), piezoelectric force microscopy (PFM, Asylum Research, MFP-3D-SA) and

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Table 1
Optimized deposition parameters for $SrRuO_3$ and KNN-KNT-LT films.

Film	Substrate temperature (°C)	O_2 partial pressure (Pa)	Energy density (J/cm^2)	Laser repetition rate (Hz)
$SrRuO_3$	750	13	1	3
KNN-KNT-LT	725	2.7	1	10

ferroelectric tester (Radiant Technologies, Precision LC), respectively. The Pt top electrodes were sputtered following standard photolithography process and have an area of 2500 μm^2. For the local piezoelectric hysteresis studies, Pt-coated Si tip with force constant of ~42 N/m and resonance frequency of ~320 kHz was used.

3. Results and discussion

Typical XRD θ–2θ scans for KNN-KNT-LT films are shown in Fig. 1. Only (001) and (111) type diffraction peaks were observed for films grown on (001) and (111)-oriented substrates, respectively, in addition to the peaks from $SrTiO_3$. The $SrRuO_3$ peaks overlap with that of the KNN-KNT-LT films. No second phase was observed. However, small (00 l) peaks are observed for the films grown on (110)-oriented substrates. The MPB was reported to occur between orthorhombic and tetragonal phases in bulk KNN-KNT-LT system [5,6]. However, in this study, the as-deposited films with cubic structure could transform into orthorhombic and/or tetragonal phases at the Curie temperature of 323 °C when cooling down from the deposition temperature of 725 °C, due to the effect of the substrate.

The polarization-electric field (P–E) hysteresis loops along the three crystallographic directions were determined using a ferroelectric tester at 1 kHz as shown in Fig. 2(a). The coercive fields (E_c) are 30 kV/cm, 18 kV/cm and 8 kV/cm and the remnant polarizations (P_r) are 4, 1 and 0.3 μC/cm^2 for (001), (110) and (111) oriented films, respectively. The P_r are comparable with reported values in the literature for (001)-oriented KNN-KNT-LS thin film (3.7 μC/cm^2) but smaller than the (001)-oriented Mn-doped KNN-KNT-LS film (10 μC/cm^2) [7,8]. However, compared with the synthesized ceramic target, whose P_r and E_c are ~18 μC/cm^2 and 8.60 kV/cm (not shown), the thin films show much smaller P_r and larger E_c. Furthermore, the P_r along (110) and (111) directions do not correspond to the projections of polarization along (001) direction, suggesting that the films grown on different substrates may have different structures. Thus the spontaneous polarizations lie along different crystallographic directions.

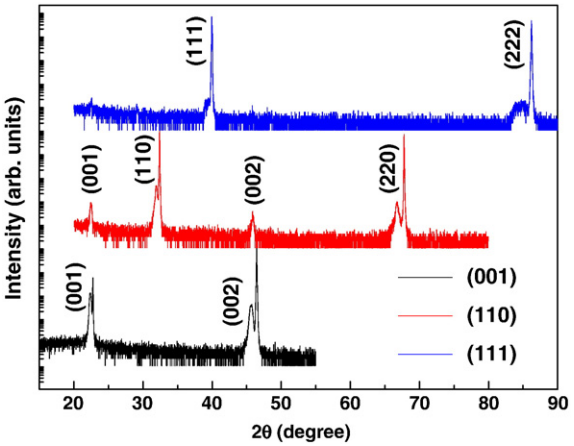

Fig. 1. XRD θ–2θ scans of KNN-KNT-LT films deposited on (001), (110) and (111)-oriented $SrTiO_3$ substrates.

To gain more insight into the properties of the KNN-KNT-LT films, we have also performed small signal dielectric and piezoelectric coefficient measurements. The variation of dielectric constant (ε_r) as a function of DC bias was measured by applying a small AC voltage of 100 mV (peak to peak) at 100 kHz. Fig. 2(b) shows the butterfly-type ε_r–E hysteresis loops with two maxima due to the ferroelectric polarization reversal. However, the peaks almost merge together for the (111) oriented film, consistent with the slim P–E hysteresis loop. The zero-field ε_r are 540, 390 and 300 for the (001), (110) and (111) oriented films, respectively. These values are again smaller than that of the bulk ceramic (~1256) and slightly smaller than the (001)-oriented KNN-KNT-LS film (~640) [5,9]. The out-of-plane piezoelectric hysteresis loops (d_{33}–E) of KNN-KNT-LT films are shown in Fig. 2(c). The quantitative results is obtained by calibrating the PFM response using a sample with known d_{33} (X-cut quartz in this case, d_{11} = 2.3 pm/V). The d_{33} of films are then calculated using $d_{33\text{film}} = (A/A_0)d_{11\text{quartz}}$, where A is the lock-in amplifier reading divided by the AC voltage used to excite sample vibration and A_0 is the corresponding value for quartz. This method has been used by other research groups and proven to be reliable [10]. The d_{33}–E loops are consistent with the P–E hysteresis loops, where no distinct remnant d_{33} is observed for the (110) and (111) oriented films. In perovskite ferroelectric systems, susceptibilities are usually larger along directions different from the spontaneous polarization direction. However, in this case, both ε_r and d_{33} are the largest along (001) oriented film, which shows the largest polarization.

Relatively low leakage current is observed in our samples as shown in Fig. 2(d). The leakage current of Mn-doped KNN-KNT-LS and KNN-KNT-LS films reported in the literatures are two and five order magnitudes higher than our KNN-KNT-LT film, respectively [7,9]. Hence, the defect contributions to the polarization and dielectric constant should be small. The rather small susceptibilities of the epitaxial films can be explained by the fact that the large piezoelectric response observed in bulk is due to the polymorphic phase transition, which consists of substantial contribution from the 18-fold domain variants (12 variants from orthorhombic and 6 from tetragonal phases) [11]. In epitaxial thin film systems with a single preferred orientation, the extrinsic contribution is small [12]. The clamping effect by the substrate also could reduce the susceptibilities.

We have also studied the dielectric constants of the epitaxial films (measured with AC voltage of 100 mV at 100 kHz) at temperatures ranging from 25 °C to 360 °C as shown in Fig. 3(a). From the literature, two dielectric anomalies were observed in the KNN-KNT-LT ceramic [5]. The Curie temperature, at which the dielectric constant attains its maximum value, occurs at 323 °C, while the other at ~70 °C, corresponding to the phase transition of orthorhombic–tetragonal. The orthorhombic–tetragonal transition is a good indicator for the presence of an MPB. However, for the KNN-KNT-LT films, only the paraelectric–ferroelectric transition temperatures were observed and the peaks are broadened. The Curie temperatures are ~260 °C, 220 °C and 270 °C for (001), (110) and (111) oriented films, respectively. These values are lower than that of the bulk. The difference could be due to composition variation of the films or the effect of the substrate.

Fig. 3(b) shows the frequency dependence of dielectric constant and dielectric loss of the KNN-KNT-LT films along different crystallographic directions at room temperature. The trend of the dielectric constant along (001), (110) and (111) oriented films is consistent with the ε_r–E hysteresis loops. Frequency dispersion in dielectric constant increases slightly from (001), (110) to (111) oriented films, and the dielectric losses remain relatively low for all three films up to 1 MHz.