表と図についての情報はありません。
Characterization of Ferroelectric Na$_x$K$_{1-x}$NbO$_3$ System Films Prepared by Pulsed Laser Deposition

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Ferroelectric Na$_x$K$_{1-x}$NbO$_3$ (NKN) films were prepared on quartz and Pt/SrTiO$_3$ (100) substrates by pulsed laser deposition. The effects of composition and preparation conditions on the crystal structure and ferroelectricity of the NKN films were investigated by changing the Na content ($x$), substrate temperature ($T_{\text{sub}}$), oxygen partial pressure ($P_{\text{O}_2}$), target-to-substrate distance ($D_{\text{t-s}}$) and laser energy density ($E_l$). The permittivity values of the NKN films were 390 to 520 at room temperature and 100kHz, showing a maximum at $x = 0.5$. The maximum remnant polarization value was $8.2 \times 10^{-2}$ C m$^{-2}$ at $x = 0.5$. [doi:10.2320/matertrans.MRA2008116]

1. Introduction

The NaNbO$_3$-KNbO$_3$ solid solution system is a promising lead-free ferroelectric and piezoelectric material and thus great effort has been made to increase its ferroelectric and piezoelectric performance.1,2) According to the phase diagram for the solid solution of the Na$_x$K$_{1-x}$NbO$_3$ (NKN) system, a morphotropic phase boundary (MPB) separating two orthorhombic ferroelectric phases exists at $x$ of around 0.5.3,5) Near this MPB composition, the dielectric constant and piezoelectric constant are the highest$^4,5$ with the smallest coercive field ($E_c$).6) Saito et al. reported that Na$_{0.5}$K$_{0.5}$NbO$_3$-based sintered bodies had a large piezoelectric coefficient ($d_{33}$), with a comparable value to that of commercial Pb(Zr, Ti)$_3$O$_7$ (PZT).7,8)

NKN and NKN-based thin films have potential applications for non-volatile ferroelectric random access memories (FRAM) and ferroelectric actuators and devices in micro-electromechanical system (MEMS). Na$_3$K$_{5}$NbO$_9$ films have been prepared by several routes, including pulsed laser deposition (PLD),9,10) magnetron sputtering,11,12) metal-organic chemical vapor deposition (MOCVD)$^{13,14}$ and sol-gel.$^{15,16}$

Pulsed laser deposition has been widely applied for preparation of many kinds of thin films due to several advantages, i.e., stoichiometric transfer of compositions from source to film, growth from a high energy beam resulting in high crystallinity and inherent simplicity for the growth of multilayered structures.$^{17}$ Na$_{0.5}$K$_{0.5}$NbO$_3$ thin films were first prepared by Cho et al. using pulsed laser deposition.$^{18}$ Kim et al. prepared a highly oriented Na$_{0.5}$K$_{0.5}$NbO$_3$ film by pulsed laser deposition, the piezoelectric constant of which was comparable to that of epitaxially grown PZT film by pulsed laser deposition.$^{19}$

However, no study on NKN films with various compositions has been reported. In this work, NKN films were prepared by pulsed laser deposition, and the effects of preparation conditions on the crystal structure and the electrical properties of the films were investigated.

2. Experimental

Starting materials of Na$_2$CO$_3$, K$_2$CO$_3$ and Nb$_2$O$_5$ powders were mixed in the nominal composition of Na$_x$K$_{1-x}$NbO$_3$ with $x$ changing from 0.2 to 0.8, pressed into pellets with diameter ($\Phi$) of 15 mm and height ($H$) of 3 mm and then calcined at 1173 K for 14.4 ks. The pellets were sintered by spark plasma sintering (SPS) at 1323 K for $x = 0.2$ to 0.6 and at 1373 K for $x = 0.8$ for 600 s in a vacuum and then annealed at 1123 K for 36 ks in air.

NKN films were prepared on quartz glass and Pt/SrTiO$_3$ (100) substrates by pulsed laser deposition. Hereafter, various compositions of NKN films are expressed as $x$NKN, where $x$ represents the nominal composition (Na$_x$K$_{1-x}$NbO$_3$) of the targets. A third harmonic wavelength of a Q-switch pulsed Nd:YAG laser (Spectron Laser System SL805, \(\lambda = 355\) nm, pulse duration of 15 ns and repetition of 10 Hz) was used as the laser source. Deposition parameters are summarized in Table 1.

Amorphous quartz plates (12 $\times$ 10 $\times$ 0.5 mm) and SrTiO$_3$(100) single crystal wafers (10 $\times$ 10 $\times$ 0.5 mm) with a Pt bottom electrode were used as substrates. The target and substrate stage were rotated at 12 rpm in converse directions. Films were deposited at a vacuum (10$^{-7}$ Pa) and different oxygen partial pressures ($P_{\text{O}_2}$) ranging from 2.67 to 26.7 Pa.

<table>
<thead>
<tr>
<th>Targets</th>
<th>NKN pellets ((x = 0.2 \text{ to } 0.8, \Phi \text{ 15 mm, } H \text{ 3 mm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Quartz glass, STO (100) single crystal</td>
</tr>
<tr>
<td>Substrate temperature ((T_{\text{sub}}))</td>
<td>723–973 K</td>
</tr>
<tr>
<td>Deposition ambient</td>
<td>Vacuum ((10^{-7} \text{ Pa}))</td>
</tr>
<tr>
<td>Distance between target and substrates ((D_{\text{t-s}}))</td>
<td>40–70 mm</td>
</tr>
<tr>
<td>Laser energy density ((E_l))</td>
<td>2.7–5.8 $\times$ 10$^4$ J m$^{-2}$</td>
</tr>
<tr>
<td>Deposition time</td>
<td>3.6–14.4 ks</td>
</tr>
</tbody>
</table>
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The substrate temperature (Tsub) was changed from 723 to 973 K. The distance between the target and the substrate (Dsub) was changed stepwise from 45 to 70 mm. The power density of the laser output (EL) was controlled in a range from 2 to 7.5 × 104 J m−2.

The crystal structure was examined by X-ray diffraction (Rigaku, RAD-2C). To determine the lattice constants of the targets and the films, X-ray step scanning was employed. The thickness was measured by a profilometer (Taylor-Hobson Talystep). The composition was studied by electron probe microanalysis (EPMA, JEOL JXA-8621MX). The surface morphology was observed by scanning electron microscopy (SEM, Hitachi S-3100H). The dielectric properties were measured in air by an AC impedance analyzer (Hewlett Packard 4194) in a frequency (f) range of 102 to 107 Hz from room temperature to 773 K. The polarization–electric field (P–E) hysteresis loops were measured by a ferroelectric test system (FCE-1, TOYO Corp., Japan) at a frequency (f) of 10kHz at room temperature.

3. Results and Discussion

Figure 1 shows the effect of x on the XRD patterns of NKN films at Psub = 10 Pa, Tsub = 973 K, Dsub = 60 mm and EL = 3.8 × 104 J m−2 for 7.2 ks. Perovskite structures were obtained in NKN films with different compositions, which were the powder diffraction of KNbO3 (JCPDS #32-0822) and NaNbO3 (JCPDS #33-1270). A small amount of second phases of K2Nb5O17 (Orthorhombic, a = 0.783, b = 3.321 and c = 0.646 nm) and K2Nb5O17 (Orthorhombic, a = 1.25, b = 3.75 and c = 0.396 nm) was contained at 0.2NKN and 0.8NKN, respectively. The NaNbO3-KNbO3 system is a pseudo-binary solid solution system in the whole range and all targets were of perovskite structure in a single phase. Second phases observed in the NKN films near the two end members could have been caused by the volatilization of Na and K, which is a common problem encountered in the preparation of compounds containing alkali metal elements.20,21) In addition, slight changes in stoichiometry (both on the Na-rich and the K-rich side) easily lead to the formation of second phases.22)

NKN films with different compositions had similar dense microstructures with particulates, showing little dependence on composition.

The average compositions of NKN films measured by EPMA were almost in agreement with that of the targets. The difference of Na/(Na+K) and (Na+K)/Nb ratios between the NKN films and targets was less than 10%.

The structure of NaNbO3 and KNbO3 crystals is orthorhombic at RT with lattice parameters of a = 0.5568 nm, b = 1.552 nm and c = 0.5504 nm, and a = 0.5695 nm, b = 0.5721 nm and c = 0.3973 nm, respectively. To compare lattice parameters between NKN films and bulk crystals, the lattice parameters were transformed into a pseudo-cubic structure through relations of a = a/√2, b = b/√2 and c = c.23) Figure 2 depicts the pseudo-cubic lattice parameters of the NKN targets and films prepared at Tsub = 973 K and Psub = 10 Pa for 7.2 ks on quartz glass substrates. The lattice parameters of both targets and NKN films decreased with increasing Na content. A transition of slope in lattice parameters occurred at x = 0.4 to 0.6 for both targets and films, owing to the MPB composition of NaNbO3–KNbO3 system. The lattice parameters of the NKN films were smaller than those of the targets, which might have been due to compressive stress generated during the pulsed laser deposition and/or cooling process. Film compressive stress has been reported to arise due to a variety of different mechanisms, including differential thermal contraction, island coalescence, grain growth, grain boundary diffusion, competitive columnar growth and high-energy particle bombardment.24) Since the thermal expansion coefficient of quartz is smaller than that of NKN films, the smaller lattice parameters of NKN films can not be explained by the difference in thermal expansion, but may result from

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Fig. 1. Effect of x on XRD patterns of NKN films deposited on quartz glass at x = 0.2 (a), 0.4 (b), 0.5 (c), 0.6 (d) and 0.8 (e) at Tsub = 973 K, Psub = 10 Pa, Dsub = 60 mm and EL = 3.8 × 104 J m−2 for 7.2 ks.

Fig. 2. Effect of x on the pseudo-cubic lattice parameters a, b, and c of the NKN targets and films (subscript c means pseudo-cubic).
the stress generated during the pulsed laser deposition process. Some stoichiometric deviation or defects in the NKN films may also be associated with the smaller lattice parameters.25)

The effect of deposition parameters, such as \( T_{\text{sub}} \), \( P_{O_2} \), \( D_{\text{t-s}} \) and \( E_L \), on the crystal structure and microstructure of NKN films will be described later, taking \( x = 0.5 \) as an example.

Figure 3 shows the effect of \( T_{\text{sub}} \) on XRD patterns of 0.5NKN films prepared on quartz glass at \( T_{\text{sub}} = 723 \) (a), 873 (b), 923 (c) and 973 K (d) at \( P_{O_2} = 10 \text{ Pa} \), \( D_{\text{t-s}} \) of 50 mm and \( E_L = 3.8 \times 10^4 \text{ J m}^{-2} \) for 3.6 ks.

Figure 4 shows the effect of \( T_{\text{sub}} \) on microstructures of 0.5NKN films prepared on quartz glass at \( T_{\text{sub}} = 723 \) (a) and 973 K (b) at \( P_{O_2} = 10 \text{ Pa} \), \( D_{\text{t-s}} = 50 \text{ mm} \) and \( E_L = 3.8 \times 10^4 \text{ J m}^{-2} \) for 3.6 ks.

Figure 5 shows the effect of \( P_{O_2} \) on XRD patterns of 0.5NKN films prepared on quartz glass at vacuum (a), \( P_{O_2} = 2.67 \) (b), 10 (c) and 26.7 Pa (d) at \( T_{\text{sub}} = 973 \text{ K} \), \( D_{\text{t-s}} = 50 \text{ mm} \) and \( E_L = 3.8 \times 10^4 \text{ J m}^{-2} \) for 3.6 ks.

The second phase of \( K_2\text{Nb}_6\text{O}_{17} \) was detected at \( T_{\text{sub}} = 923 \) and 973 K.

Figure 4 shows the effect of \( T_{\text{sub}} \) on the microstructure of 0.5NKN films. The 0.5NKN film showed a micro-sized particulate microstructure with a relative flat matrix at \( T_{\text{sub}} = 723 \text{ K} \) and a dense particulate microstructure at \( T_{\text{sub}} = 973 \text{ K} \). The stacking density of the particulates increased with increasing \( T_{\text{sub}} \), which was associated with decreasing particulate size. This indicates that the adhesion between the substrate and the ablated species increased at higher \( T_{\text{sub}} \). There was no obvious existence of a second phase at high \( T_{\text{sub}} \) from surface morphology observation.

Figure 5 shows the effect of \( P_{O_2} \) on the XRD patterns of the 0.5NKN films prepared at \( T_{\text{sub}} = 923 \text{ K} \), \( D_{\text{t-s}} = 50 \text{ mm} \)
and $E_L = 3.8 \times 10^4 \text{ J m}^{-2}$ for 3.6 ks. In a vacuum ($P = 10^{-7}$ Pa), a small amount of the second phase of $K_2\text{Nb}_5\text{O}_{17}$ appeared. The peaks of $K_2\text{Nb}_5\text{O}_{17}$ and 0.5NKN films decreased with increasing $P_O$. The intensity ratio of (001) to (011) of 0.5NKN film ($I_{\text{NKN-001}}/I_{\text{NKN-011}}$) increased from 2.1 in a vacuum to 5.3 at $P_O = 26.7$ Pa, while it was 0.67 for the 0.5NKN target. This implies that the (001) orientation of 0.5NKN films is preferred at higher $P_O$. A similar effect of $P_O$ on the preferred orientation of $\text{Na}_0.3\text{K}_{0.5}\text{NbO}_3$ films has been reported for $P_{\text{sub}}/\text{Ir}_2$ and $\text{SiO}_2$/native oxide)/Si(111) substrates by Cho et al.\cite{Cho2009}. In their work, second phases of $K_2\text{Nb}_5\text{O}_{12}$ and $K_2\text{Nb}_5\text{O}_{11}$ were identified at $P_O = 1.33$ Pa. The formation of alkali-poor niobates by pulsed laser deposition at a low $P_O$ may be caused by the high volatility of Na and K. At high $P_O$ ($\sim 53.2$ Pa), the present 0.5NKN films were in a single phase and were highly (001)-oriented ($I_{\text{NKN-001}}/I_{\text{NKN-011}} = 60$), showing a tendency similar to that reported by Cho et al.\cite{Cho2009}

Figure 6 shows the effect of $D_{\text{sub}}$ on the XRD patterns of 0.5NKN films prepared on quartz glass at $D_{\text{sub}} = 50$ (a), 60 (b) and 70 mm (c) at $T_{\text{sub}} = 973$ K, $P_O = 10$ Pa and $E_L = 3.8 \times 10^4 \text{ J m}^{-2}$ for 3.6 ks. The amount of particulates decreased significantly with decreasing $D_{\text{sub}}$. At $E_L < 2.5 \times 10^4 \text{ J m}^{-2}$, a dense microstructure with a grain size of 500 nm and a few particulates were observed. The deposition rates of 0.5NKN films dramatically decreased from about 1.4 to 0.07 $10^{-10}$ m s$^{-1}$ with decreasing $E_L$ from 5 to $2 \times 10^4$ J m$^{-2}$. Moreover, the XRD patterns of 0.5NKN films turned to be amorphous when $E_L$ decreased to $2 \times 10^3$ J m$^{-2}$, partly due to the slow deposition rate. $D_{\text{sub}}$ of 40 mm and $E_L$ of $2.5 \times 10^3$ J m$^{-2}$ were found to be effective to achieve an increase in the deposition rate to $0.6 \times 10^{-10}$ m s$^{-1}$ with clear perovskite XRD peaks and only slight particulate generation, as shown in Fig. 7(d).

Figure 8 shows the temperature dependence of permittivity at 100 kHz for NKN films prepared on a Pt/STO(100) substrate at $T_{\text{sub}} = 973$ K, $P_O = 10$ Pa and $D_{\text{sub}} = 60$ mm for 7.2 ks. The permittivity continuously increased with increasing temperature and exhibited peaks around 680 K. The Curie temperature ($T_C$) slightly increased from 670 to 700 K with decreasing $x$ from 0.8 to 0.2, slightly less than those of sintered bodies reported by Egerton et al.\cite{Egerton1987}. The permittivity peak value of 5000 was obtained for 0.5NKN films, which was larger than those of 1200 and 2500 for $\text{Na}_0.3\text{K}_{0.5}\text{NbO}_3$ films prepared by Khartsev et al. using RF-sputtering and pulsed laser deposition, respectively.\cite{Khartsev2003} The permittivity value of 5000 obtained in the present study is the highest thus far reported in the literature.

Figure 9 shows the hysteresis loops of NKN films prepared on Pt/STO (100) substrates at $T_{\text{sub}} = 973$ K, $P_O = 10$ Pa and $D_{\text{sub}} = 60$ mm for 7.2 ks. Well-saturated hysteresis loops were observed at $f = 10$ kHz under an electrical field of $5 \times 10^4$ V m$^{-1}$ at room temperature. The remnant polarization ($P_r$) reached the highest value of $8.2 \times 10^{-2}$ C m$^{-2}$ for 0.5NKN. The coercive field ($E_c$) of NKN films varied from 1.24 to 1.57 $10^4$ V m$^{-1}$. The value of $E_c$ was the highest at 0.6NKN, with a slight dependence on the composition. These $E_c$ values were smaller than that of $2 \times 10^4$ V m$^{-1}$ of the c-axis-oriented NKN films prepared by Cho et al.\cite{Cho2009}

Figure 10 demonstrates the permittivity ($\varepsilon'$) and remnant polarization ($P_r$) of NKN films as a function of Na content at room temperature. The $\varepsilon'$ of NKN films at $f = 100$ kHz ranged from 390 to 520 and showed the maximum value in 0.5NKN film. The permittivity of NKN films had a compositional dependence similar to that of NKN ceramics. The peak permittivity of NKN ceramics was observed at $x = 0.5$ by Chu et al.\cite{Chu1998} and around $x = 0.4$ to 0.6 by Zhang et al.\cite{Zhang2003} Several groups have reported the permittivity of NKN films. Table 2 summarizes the permittivity of NKN films prepared by various processes, indicating rather small values of 37 by RF magnetron sputtering\cite{Syono1986} and 545 by aerosol deposition.\cite{Khasthurin1999} High permittivity values above 500 have been reported for epitaxial and (001)-oriented 0.5NKN films,\cite{Cho2009, Egerton1987} whereas the non-oriented 0.5NKN film in the present study showed a relatively high value. To date various compositions of NKN films have been prepared, but only the composition of 0.5NKN film has been focused on in the literature. This paper is the first to report the composition dependence of $\varepsilon'$ and $P_r$, and the study herein reported achieved the highest $\varepsilon'$ of NKN film to date.
Fig. 7 Effect of $E_L$ on microstructures of 0.5NKN films prepared on quartz glass at $E_L = 5 \times 10^4 \text{ J m}^{-2}$ and $D_{ts} = 60 \text{ mm}$ for 7.2 ks (a), $3.8 \times 10^4 \text{ J m}^{-2}$ and $D_{ts} = 60 \text{ mm}$ for 3.6 ks (b), $2 \times 10^4 \text{ J m}^{-2}$ and $D_{ts} = 60 \text{ mm}$ for 30.4 ks (c) and $2.5 \times 10^4 \text{ J m}^{-2}$ and $D_{ts} = 40 \text{ mm}$ for 3.6 ks (d), $T_{sub} = 973 \text{ K}$, $P_{O_2} = 10 \text{ Pa}$.

Fig. 8 Temperature dependence of permittivity for NKN films prepared on Pt/STO(100) substrates at $T_{sub} = 973 \text{ K}$, $P_{O_2} = 10 \text{ Pa}$ and $D_{ts} = 60 \text{ mm}$ for 7.2 ks.

Fig. 9 Hysteresis loops of NKN films prepared on Pt/STO(100) substrates at $T_{sub} = 973 \text{ K}$, $P_{O_2} = 10 \text{ Pa}$ and $D_{ts} = 60 \text{ mm}$ for 7.2 ks.
The NKN films had a dense, uniform granular microstructure. Most of the deposited films were smaller than those of the targets. Pulsed laser deposition. The compositions of the films were prepared by aerosol deposition 29), RF magnetron sputtering 28) and magnetron sputtering 11).


table 2 comparison of composition and permittivity values at 100 kHz of NKN films prepared by different methods.

<table>
<thead>
<tr>
<th>Na,K₁₋ₓNbO₃</th>
<th>ε' at R.T.</th>
<th>ε' (Maximum) at Tc</th>
<th>Film deposition method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.5</td>
<td>550</td>
<td>/</td>
<td>Pulsed laser deposition</td>
<td>10)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>200</td>
<td>/</td>
<td>Pulsed laser deposition</td>
<td>10)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>520</td>
<td>/</td>
<td>Magnetron sputtering</td>
<td>11)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>540</td>
<td>/</td>
<td>Sol-gel deposition</td>
<td>16)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>514</td>
<td>2500</td>
<td>Pulsed laser deposition</td>
<td>26)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>530</td>
<td>1200</td>
<td>RF magnetron sputtering</td>
<td>26)</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>37</td>
<td>/</td>
<td>RF magnetron sputtering</td>
<td>28)</td>
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<td>x = 0.5</td>
<td>545</td>
<td>/</td>
<td>Aerosol deposition</td>
<td>29)</td>
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<td>x = 0.5</td>
<td>114</td>
<td>/</td>
<td>Pulsed laser deposition</td>
<td>30)</td>
</tr>
<tr>
<td>x = 0.2–0.8</td>
<td>390–520</td>
<td>5000 (at x = 0.5)</td>
<td>Pulsed laser deposition</td>
<td>This work</td>
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</table>

Fig. 10 Effect of x on permittivity at 100 kHz and remnant polarization at room temperature of NKN films prepared on Pt/STO(100).

4. Conclusions

NKN films with different compositions were prepared by pulsed laser deposition. The compositions of the films were almost as close as those of the targets. The lattice parameters of the deposited films were smaller than those of the targets. The NKN films had a dense, uniform granular microstructure. High T_{sub} and P_{O2} promoted the (001) orientational growth. E_L was the key deposition parameter which controlled the particulate generation on the film surface. Permittivity and remnant polarization showed the maximum values of 520 and 8.2 \times 10^{-5} \text{C.m}^{-2} at 0.5NKN, while the highest permittivity value was 5000 at T_c = 680 K.

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REFERENCES