Deposition of orientation-controlled thick (K,Na)NbO₃ films on metal substrates by repeated hydrothermal deposition technique

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(K,Na)NbO₃ thick films were grown at 240°C on Ni-based metal substrates by repeated hydrothermal method. The metal substrates were covered with two types of buffer layers; SrRuO₃/LaNiO₃ and SrRuO₃. Film thickness monotonically increased with increasing number of deposition cycles. The 27 μm-thick film was obtained on the metal substrate with SrRuO₃/LaNiO₃ by four cycles. The obtained films tended to show {100}, orientation and their degree of orientation increased with increasing number of deposition cycles. Films deposited on SrRuO₃/LaNiO₃-covered metal substrates showed more highly {100}, orientation compared with those on SrRuO₃-covered metal substrates. Remnant polarization and coercive field measured at 5 kHz were 12 μC/cm² and 70 kV/cm, while their effective values of piezoelectric coefficient (d₃₃) was 35–40 pm/V for both films. These properties remained unchanged irrespective of a number of deposition cycles despite the orientation change of films. These results show that repeated hydrothermal deposition technique is one of the effective ways to prepare thick (K,Na)NbO₃ films on metal substrates.

Key-words: Hydrothermal synthesize, Lead-free (K,Na)NbO₃ film, Orientation control, Metal substrate, Ferroelectric and piezoelectric properties

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1. Introduction

Piezoelectric films have been widely used for sensors, actuators, and energy harvester devices.¹⁻⁴ These devices require films with various thicknesses from sub-millimeter to several-ten-nanometer order depending on the applications.⁵ Some applications including energy harvesters and sensors for the human body require piezoelectric films deposited on the flexible substrates, for example, metal and polymer substrates.⁶⁻⁸ Therefore, there is a requirement for the deposition of piezoelectric films with a wide variety of thickness on the flexible substrates.

Among various piezoelectric materials, (K,Na)NbO₃-based materials have been expected as the alternative to lead-based piezoelectric materials such as Pb(Zr,Ti)O₃ in the form of not only the sintered bodies but also thin films. This is because (K,Na)NbO₃-based materials show relatively good piezoelectric properties and high Curie temperature compared with other lead-free piezoelectric materials.⁹⁻¹¹

Hydrothermal method is a wet process and can deposit (K,Na)NbO₃-based films at a relatively low temperature below 250°C. In fact, epitaxial (K,Na)NbO₃ films were grown on single crystal substrates at 240°C.¹²⁻¹³ In addition, we have succeeded the growth of (K₀.₈₈Na₀.₁₂)NbO₃ films at 240 and 150°C on flexible metal and organic substrates, respectively.⁶⁻⁸ In particular, 10-μm-thick (K₀.₈₈Na₀.₁₂)NbO₃ films prepared on 50-μm thick metal foils generate electric power from vibration using flexible characteristics of the (K₀.₈₈Na₀.₁₂)NbO₃ films; i.e., act as energy harvesters. To increase a generated power, thicker films are required because the generated power is proportional to the film thickness.
As the film thicknesses become larger, the films are prone to peel off from the substrates. To avoid peeling off, inserting appropriate adhesion layer is one of the practical solutions. The previous study on growth of \((K_{0.88}Na_{0.12})_3NbO_3\) films on SrTiO\(_3\) substrates with various orientations prepared by hydrothermal method have showed that the films on (100)SrTiO\(_3\) substrates had a significantly large growth rate as compared with the films on (110)SrTiO\(_3\) and (111)SrTiO\(_3\) substrates.\(^{18,19}\) The result gives us to expect that the (100) orientation increases with the thickness in the \((K_{0.88}Na_{0.12})_3NbO_3\) films by hydrothermal method. Assuming the preferred (100) orientation, we expect that the buffer layer with (100) preferred orientation, for example, LaNiO\(_3\) might improve adhesion.

In the present study, we try to increase the thickness of \((K_{0.88}Na_{0.12})_3NbO_3\) films on Ni-based alloy substrates by repeating the hydrothermal cycles. We employed the SrRuO\(_3\) single layer and SrRuO\(_3\)/LaNiO\(_3\) multi-layer; the latter one has (100) preferred orientation. Crystal structure and ferroelectric and piezoelectric properties of the films were investigated as a function of film thickness.

### 2. Experimental procedure

\((K_{0.88}Na_{0.12})_3NbO_3\) films were prepared at 240°C by hydrothermal method. We selected \((K_{0.88}Na_{0.12})_3NbO_3\) composition because the thickest film was obtained from the mixed solution of KOH and NaOH.\(^{13}\) In addition, this composition was suitable for the energy harvest applications due to its relatively large piezoelectric response and low dielectric constant among the hydrothermally deposited films.\(^{16}\) In addition, there is no phase separation for \((K_{0.88}Na_{0.12})_3NbO_3\) films that are different from the two-phase coexistence films between \((K_{0.75}Na_{0.25})_3NbO_3\) and \((K_{0.36}Na_{0.64})_3NbO_3.\(^{17}\)

The metal substrate used in this work was Ni-based alloy with a 300-μm thick (Inconel 600, hereafter denoted as “Inconel”) because Inconel has high thermal stability and resistance to chemical solutions. Two types of the buffer layers, SrRuO\(_3\) (SrRuO\(_3\)/Inconel) and SrRuO\(_3\)/LaNiO\(_3\) stack (SrRuO\(_3\)/LaNiO\(_3\)/Inconel), were deposited on Inconel substrates. The 50-nm-thick conductive SrRuO\(_3\) and LaNiO\(_3\) layers were deposited on Inconel substrates by radio frequency magnetron sputtering method because it was confirmed that the conductive buffer layers with perovskite structure effectively promote \((K_{0.88}Na_{0.12})_3NbO_3\) film deposition on Inconel.\(^{9}\) The LaNiO\(_3\) layer is ascertained to have (100), self-orientation characteristics, and the overgrown SrRuO\(_3\) is also expected to show the same (100), orIENTATION orientation following the orientation of LaNiO\(_3\) layer.\(^{18}\) In addition, (100),SrRuO\(_3\)//(100)SrTiO\(_3\) substrate was also used to grow epitaxial \((K_{0.88}Na_{0.12})_3NbO_3\) films as a reference. In this study, we describe the crystal orientations as follows. SrTiO\(_3\) has a cubic symmetry, so we simply used \((hkl)\). On the other hand, the pseudo-cubic unit cells denoted by \((hhl)\) were employed for SrRuO\(_3\) and LaNiO\(_3\) despite their orthorhombic and rhombohedral symmetries, respectively because of the small anisotropy. \((K_{0.88}Na_{0.12})_3NbO_3\) also has an orthorhombic symmetry, but the anisotropy is significantly larger than SrRuO\(_3\) and LaNiO\(_3\), probably due to the ferroelectric nature. This relatively large anisotropy leads to the distinguishable multiple-peaks. Since it is difficult to regard the unit cell showing apparent peaks splitting in X-ray diffraction (XRD) as a simple cubic cell, “\((hhl)\)” were used in the case where we treat the planes belonging \((hhl)\) together, for example, \((100)_c\) for \((100)_c\), \((010)_c\), and \((001)_c\). Indeed, we have confirmed multi-domain nature in \((K_{0.88}Na_{0.12})_3NbO_3\) films.

A mixed solution of KOH and NaOH (Kanto Chemical co., Inc.) with 7 mol/dm\(^3\) and \([KOH]/([KOH]+[NaOH]) = 0.9,\) and Nb\(_2\)O\(_5\) powder (Kanto Chemical co., Inc.) with 0.25 g were used as starting materials. These starting materials and substrates were put into a Teflon bottle and sealed in an autoclave. The substrates were suspended by Teflon fixture that is almost the same as reported one by Morita.\(^{19}\) The substrate faced onto the bottom of the bottle. This autoclave was heated in an oven maintained at 240°C for 6 h. The counting of deposition time was started when the autoclave was placed in the oven. The obtained films were ultrasonically cleaned with distilled water, ethanol, acetone and methanol. Finally, these films were dried at 150°C for 1 h in air under atmospheric pressure. In this study, the hydrothermal process from deposition to drying was defined as one cycle and repeated this cycle to obtain thicker films.

The thickness and chemical composition of the obtained films were determined by X-ray fluorescence spectroscopy (XRF, Panalytical Axsios Advance PW4400). The composition of the films was estimated by the fundamental parameter method calibrated with standard methods. The film thickness of \((K_{0.88}Na_{0.12})_3NbO_3\) films was also estimated from their intensity of Nb(K\alpha). The linear relationship between an intensity of Nb(K\alpha) and thickness was confirmed by cross-sectional scanning electron microscopy (SEM, JEOL JEM-6610LA). The crystal structure and preferred orientation of these films were characterized by XRD (Bruker D8 DISCOVER) with Cu K\alpha radiation. XRD 2θ-θ scans were repeated for each sample inclination angle normal to the scattering plane (ψ angle) under the sample rotation condition. The detail of 2θ-ψ area mapping measurement method was already described.\(^{20}\) The surface morphologies of the deposited films were observed by SEM.

Pt top electrodes with 100 μm in diameter were deposited by an electron beam evaporation to fabricate capacitor structure of Pt/(K\(_{0.88}Na_{0.12})_3NbO_3$/SrRuO\(_3\). Ferroelectric and piezoelectric properties were measured at room temperature using a ferroelectric tester (Toyo Technica FCE fast) and atomic force microscopy (AFM; SII SPA400) calibrated using standard samples, respectively.

### 3. Results and discussion

#### 3.1 Film thickness and composition

Figure 1(a) shows the deposition cycles dependence of the film thickness for films deposited on SrRuO\(_3$/LaNiO\(_3$/Inconel and SrRuO\(_3$/Inconel substrates together with those on SrRuO\(_3$/SrTiO\(_3\) substrates. Film thickness increased...
with increasing the deposition cycles irrespective of the kinds of substrates. In addition, 27 µm-thick film was obtained on SrRuO$_3$/LaNiO$_3$/Inconel substrates after the fourth cycle of the deposition. On the contrary, the film on SrRuO$_3$/Inconel substrate cannot reach such thickness, because of the peeling off from the substrate. Figure 1(b) shows K/(K+Na) ratio as a function of the deposition cycles. The measured K/(K+Na) ratio was 0.88, which did not depend on the number of deposition cycles and the kind of substrates. It was confirmed on our previous work that the composition is a similar value to K/(K+Na) of 0.86, for which we had demonstrated high temperature XRD. According to this study, the multiple peaks at room temperature merged into a single peak by phase transition to cubic phase above 500°C, indicating the single phase without phase separation. On the other hand, a film with K/(K+Na) of 0.24 showed two peaks even at high temperature, indicating phase coexistence.

3.2 Crystal structure

(K$_{0.88}$Na$_{0.12}$)NbO$_3$ have the orthorhombic perovskite structure in powder form. The orthorhombic crystal structure has already confirmed by the high-temperature XRD for the (K$_{0.86}$Na$_{0.14}$)NbO$_3$ film deposited by hydrothermal technique, where the successive phase transitions with temperature were observed. In addition, the Raman scattering spectroscopy showed orthorhombic phase even for thick films prepared by the numbers of deposition cycles. Thus, the present (K$_{0.88}$Na$_{0.12}$)NbO$_3$ is expected to have the orthorhombic structure.

Figure 2(a) shows the XRD $\theta$-2$\theta$ patterns for (K$_{0.88}$Na$_{0.12}$)NbO$_3$ films deposited on SrRuO$_3$/LaNiO$_3$/Inconel substrates with different cycle number together with that of the substrates. The film on the SrRuO$_3$/LaNiO$_3$/Inconel substrate already orientated to [100]$_c$ after the first cycle, that is ascertained from the strongest $\{001\}_c$ peaks together with weak $\{110\}_c$ one. The relative intensity of $\{110\}_c$ peak with respect to those of $\{001\}_c$ ones becomes weaker with increasing cycling numbers as shown in Fig. 2(a). This suggests the increase of $\{001\}_c$ orientation with increasing film thickness.

Figure 2(b) shows the XRD $\theta$-2$\theta$ patterns for (K$_{0.88}$Na$_{0.12}$)NbO$_3$ films deposited on SrRuO$_3$/Inconel substrates with different cycle numbers together with that of the substrates. The film on SrRuO$_3$/Inconel substrate deposited on the first cycle already shows weak $\{001\}_c$ orientation preference. In addition, the peak intensity of $\{110\}_c$ also becomes relatively weak compared with that of $\{001\}_c$ ones with increasing cycling numbers as shown in Fig. 2(b).

To analyze the effect of LaNiO$_3$ buffer layers on the crystal structure more in detail, 2θ-ψ area mappings were performed for these films. Figures 3(a) and 3(b) show 2θ-ψ area mappings of SrRuO$_3$/LaNiO$_3$/Inconel and SrRuO$_3$/Inconel substrates. Line-shape intensity is ob-
served at around $2\theta = 45^\circ$ for both substrates that originate from polycrystalline Inconel. Concentrated spots were observed at around $2\theta = 23$ and $46^\circ$ and $\psi = 0^\circ$, and $2\theta = 33^\circ$ and $\psi = 45^\circ$ for SrRuO$_3$/LaNiO$_3$/Inconel substrate as shown in Fig. 3(a). These can be assigned to be the $\{h00\}_c$ and $\{110\}_c$ of SrRuO$_3$ and LaNiO$_3$ layers when these layers oriented to $\{100\}_c$ along surface normal directions. On the other hand, the line-shape intensity was observed at around $2\theta = 33^\circ$ for SrRuO$_3$/Inconel substrate as shown in Fig. 3(b), suggesting that there is no preferred orientation for SrRuO$_3$ layers.

Figures 3(c)–3(f) and 3(h) show the change of $2\theta$–$\psi$ area mappings for (K$_{0.88}$Na$_{0.12}$)NbO$_3$ films deposited on SrRuO$_3$/LaNiO$_3$/Inconel and SrRuO$_3$/Inconel substrates by various deposition cycles, respectively. The spots of $\{100\}_c$ at $2\theta = 22^\circ$ and $\psi = 0^\circ$, $\{200\}_c$ at $2\theta = 45^\circ$ and $\psi = 0^\circ$, $\{110\}_c$ at $2\theta = 31^\circ$ and $\psi = 45^\circ$ indicate the $\{100\}_c$ preferred orientations. In addition, these spots become more concentrated as the cycle number increase; it is confirmed again that $\{100\}_c$ orientation becomes evident with increasing thickness.

$\{100\}_c$ orientation characteristics and their enhancement with film thickness independent of the kinds of substrates can be explained the faster deposition rate of $\{100\}_c$ orientations as already reported for films on SrRuO$_3$/SrTiO$_3$ substrates with (100), (110) and (111) cut. Although a significant increase in the $\{100\}_c$ orientation without a LaNiO$_3$ layer, the film thickness could not increase due to peeling off. Thus, LaNiO$_3$ layer improves the adhesion between films and substrates and helps us to increase the thickness of the films.

Figure 4 shows integral $\psi$ scans between $2\theta = 30^\circ$ and $34^\circ$ corresponding to the $\{110\}_c$ peak of (K$_{0.88}$Na$_{0.12}$)NbO$_3$ for films deposited on both substrates. Concentrated peak was located around $\psi = 45^\circ$ for all films, suggesting the $\{100\}_c$ preferred orientations of all films. This scan is basically the same as rocking curve of the $\{100\}_c$ peak. Figure 5 plots full width at half maximums (FWHM) of the $\psi$ scan for peaks as functions of deposition cycle numbers, where the peaks are located at around $2\theta = 31^\circ$ and $\psi = 45^\circ$. 
\( \psi = 45^\circ \), and \( 2\theta = 22^\circ \) and \( \psi = 0^\circ \) corresponding to the \((K_{0.88}Na_{0.12})NbO_3\) \{110\}c and \((K_{0.88}Na_{0.12})NbO_3\) \{100\}c reflections, respectively. The FWHM values decreased with increasing deposition cycle number, corresponding to increase film thickness (see Fig. 1), for both films, indicating the improvement of the mosaicity of films. This originates from the self \{100\}c-orientation characteristic of hydrothermally deposited \((K_{0.88}Na_{0.12})NbO_3\) films, based on the faster deposition rate of \{100\}c orientation.14),15) Although, the FWHM of the film on the SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrate after the second deposition cycle was still larger than those on the SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrate. This is because the well \{100\}c-orientation of SrRuO\(_3\) was provided by the self-orientation characteristic of the LaNiO\(_3\) layer, as well as the \((K_{0.88}Na_{0.12})NbO_3\) films at the first deposition, as shown in Figs. 3(a) and 4(a).

In the following, we focus on the well \{100\}c-oriented thickest \((K_{0.88}Na_{0.12})NbO_3\) films on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrates by four deposition cycles and it is compared with the epitaxial films.

### 3.3 Microstructure

Figure 6(a) shows the surface morphology of 27 \( \mu m \)-thick \((K_{0.88}Na_{0.12})NbO_3\) film deposited on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrate after the fourth deposition cycle, while Fig. 6(b) shows the (100)-oriented epitaxial film on the (100)SrRuO\(_3\)/(100)SrTiO\(_3\) substrate with almost the same thickness. The film on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrate consists of square shape grains with the grain size of the sub to several micrometers. This morphology is very similar to that of the epitaxial film grown on (100)SrRuO\(_3\)/(100)SrTiO\(_3\) substrate as shown in Fig. 6(b). A noticeable difference between these two films is the in-plane alignment of square grains; grains are randomly-oriented and aligned for films on SrRuO\(_3\)/LaNiO\(_3\)/Inconel and (100)SrRuO\(_3\)/(100)SrTiO\(_3\) substrates, respectively.

### 3.4 Ferroelectric and piezoelectric properties

Figures 7(a) and 7(b) respectively show room temperature polarization-electric-field \((P-E)\) hysteresis loops measured at 5 kHz for the same films shown in Fig. 6. Both films exhibited hysteresis loops originating to their ferroelectricity. Their remnant polarization \((P_r)\) and coercive fields \((E_c)\) were 12 \( \mu C/cm^2 \) and 70 kV/cm, and 15 \( \mu C/cm^2 \) and 70 kV/cm, respectively for the films prepared on SrRuO\(_3\)/LaNiO\(_3\)/Inconel and (100)SrRuO\(_3\)/(100)SrTiO\(_3\) substrates. It must be noted that both films show the shift toward the negative electric-field, so-called “imprint character”, that is a typical characteristic of hydrothermally-deposited films as already reported in Refs. 6 and 22. Figures 7(c) and 7(d) show the strain \((S)\)-electric-field \((E)\) curve measured at 5.2 Hz. Both films...
exhibited \(S-E\) butterfly curves originating to their ferroelectricity. It must be noted that both \(S-E\) curves also show the imprint character as well as \(P-E\) curves. The effective piezoelectric coefficient, \(d_{33}\), values of the films deposited on \(100\)\(_2\)SrRuO\(_3\)/(100)SrTiO\(_3\) and SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrates estimated from \(S-E\) curves were almost the same value of about 35–40 pm/V, indicating that films on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrates with preferred [100] orientation show similar ferroelectric and piezoelectric properties to those of epitaxial films grown on (100)\(_2\)SrRuO\(_3\)/(100)SrTiO\(_3\) substrates. These results show that repeated hydrothermal deposition technique is one of the effective ways to prepare thick (K,Na)NbO\(_3\) films on metal substrates.

Figures 8(a) and 8(b) respective show remnant polarization \(\left(P_r\right)_r\) and coercive electric field \(\left(E_c\right)_c\), and the effective piezoelectric constant \(d_{33}\) as functions of deposition cycles for (K\(_{0.88}\)Na\(_{0.12}\))NbO\(_3\) films deposited on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrates. \(P_r\), \(E_c\), and \(d_{33}\) values of (K\(_{0.88}\)Na\(_{0.12}\))NbO\(_3\) films were almost constant with increasing the number of deposition cycles, i.e., increasing film thickness, although the film orientations changed with increasing thickness. Indeed, the small variation in \(P_r\), \(E_c\), and \(d_{33}\) values of (K\(_{0.88}\)Na\(_{0.12}\))NbO\(_3\) films among the [100]\(_c\), [110]\(_c\), and [111]\(_c\)-orientations were confirmed, probably due to the multi-domain structure in these films, which provides the almost averaged electrical properties.\(^{14,15}\)

4. Conclusions

(K\(_{0.88}\)Na\(_{0.12}\))NbO\(_3\) thick films were deposited at 240°C on metal substrates by repeated hydrothermal deposition. Film thickness increased with the increasing deposition cycles. A 27μm-thick film was obtained after four depositions on SrRuO\(_3\)/LaNiO\(_3\)/Inconel substrate without peeling off. The degree of [100]\(_c\) orientation of films on metal substrates with SrRuO\(_3\)/LaNiO\(_3\) buffer layer without peeling off the degree of [100]\(_c\) orientation of films on metal substrates with SrRuO\(_3\)/LaNiO\(_3\) buffer layer was higher than those of the films with only SrRuO\(_3\) buffer layer at the first deposition. In addition, this degree of orientation increased with increasing deposition cycles. Average coercive field and remnant polarization measured at 5 kHz were 70 kV/cm and 12 μC/cm\(^2\), respectively for 27μm-thick [100]\(_c\)-oriented films deposited on metal substrates, while effective \(d_{33}\) value was almost 35–40 pm/V. In addition, these properties were almost constant against the film thickness despite the change of film orientation. These results show that repeated hydrothermal deposition technique is one of the effective ways to prepare thick (K,Na)NbO\(_3\) films on metal substrates.

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