FULL PAPER

Preparation of {001}_c-oriented epitaxial (K, Na)NbO₃ thick films by repeated hydrothermal deposition techniqueTakahisa SHIRAISHI^{1,†}, Yoshiharu ITO², Mutsuo ISHIKAWA³, Hiroshi UCHIDA⁴, Takanori KIGUCHI¹, Minoru K. KUROSAWA⁵, Hiroshi FUNAKUBO² and Toyohiko J. KONNO¹¹Institute for Materials Research, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai 980–8577, Japan²Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226–8502, Japan³Department of Clinical Engineering, Faculty of Biomedical Engineering, Tooin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama 225–8503, Japan⁴Department of Materials and Life Sciences, Sophia University, Chiyoda-ku, Tokyo 102–8554, Japan⁵Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, Yokohama 226–8502, Japan

{001}_c-oriented (K_{0.86}Na_{0.14})NbO₃ thick films were prepared at 240°C on (100)_cSrRuO₃/(100)SrTiO₃ substrates by repeated hydrothermal deposition technique. The film thickness was found to increase linearly with the number of deposition cycles, and 60 μm-thick film was obtained after nine repetitions of the deposition. The K/(K+Na) ratio of the deposited thick films, measured by X-ray fluorescence spectroscopy, showed constant values regardless of the number of deposition cycles. Cross-sectional scanning electron microscopy images revealed uniformity of the obtained dense films with no obvious micro cracks and pores. Structural characterization based on X-ray diffraction, XRD 2θ-ω patterns and X-ray pole figure measurement, showed that the epitaxial relationship between the films and substrates with a {001}_c orientation was maintained throughout the deposition cycles. In addition, cross-sectional Raman spectra showed that 60 μm-thick (K_{0.86}Na_{0.14})NbO₃ film had an orthorhombic structure. The dielectric constant, ε_r, and tan δ showed frequency dependence. The average remanent polarization measured at 100 Hz was 8 μC/cm².

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1. Introduction

Piezoelectric films have been of great technological importance in the fields of sensors, actuators, and energy harvesting devices.^{1)–3)} Especially, KNbO₃-based films have been widely investigated as candidates for the application in various devices because of their excellent piezoelectric and electromechanical properties, high Curie temperature, and the environmental friendliness.^{4),5)} In order to improve the performance of these devices, it is necessary to design and control the physical properties of KNbO₃-based films, such as the film composition,⁴⁾ crystal orientation,⁶⁾ microstructure including the domain structure,^{7),8)} and the remaining strain.⁹⁾

Film thickness is also an important factor for enhancing piezoelectric properties.^{10)–12)} It is especially well known that submillimeter-thick (~100 μm) films are required to achieve a high input/output signal range.^{13)–15)} So far,

KNbO₃-based thick films have been prepared by various deposition methods, such as the sputtering, sol–gel, pulsed laser deposition, and aerosol deposition methods.^{16)–19)} There are many reports on the preparation of ~10 μm-thick films, but it is difficult to achieve submillimeter thicknesses due to the low deposition rates.

The hydrothermal method is a simple wet process using alkaline source solutions.²⁰⁾ One of the important characteristics of this method is the ability of the film thickness to be increased easily by repetition of the process itself. We reported, for example, that 130 μm-thick KNbO₃ film with epitaxial growth was prepared by repeated the hydrothermal deposition.²¹⁾ This finding indicated that the hydrothermal method may be suitable for the preparation of the submillimeter-thick KNbO₃-based films.

In the present study, we sought to extend this technique to a wider composition. Namely, we prepared a solid solution of KNbO₃–NaNbO₃, which is known to show superior piezoelectric properties to those of KNbO₃, with thicknesses of over 10 μm by repeated hydrothermal deposition technique. We also report the effect of repeated deposition on the composition, microstructure, and crystal structure.

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2. Experimental

(K, Na)NbO₃ thick films were deposited at 240°C on (100)_cSrRuO₃/(100)SrTiO₃ substrates by repeated hydrothermal deposition technique. 50 nm-thick epitaxial SrRuO₃ layers were deposited as bottom electrodes by the radio-frequency magnetron sputtering method. The raw materials used for the hydrothermal deposition were Nb₂O₅ powders (0.25 g) and a mixed solution of KOH and NaOH (7.0 mol/dm³ and 20 cm³ in total). The mixed ratio of alkaline solutions [KOH]/([KOH]+[NaOH]) was 0.9 because of the maximum deposition rate was ascertained to be obtained in the [KOH]/([KOH]+[NaOH]) ratio.²²⁾ These source materials and substrates were sealed in an autoclave, which was set in a thermostat bath maintained at 240°C for 6 h. After the obtained films were removed from the autoclave, they were washed ultrasonically in distilled water, ethanol, acetone, and methanol, and then dried at 150°C for 1 h in air. In this study, the hydrothermal process from deposition to drying was defined as one cycle, which was repeated for nine cycles to obtain the final films.

The K/(K+Na) ratio of the deposited thick films was determined using X-ray fluorescence spectroscopy (PANalytical PW2404). The film thickness was measured using a surface profile meter (Veeco DEKTAK 3ST). The cross-sectional morphology of the deposited films was observed by scanning electron microscopy (SEM, HITACH S-4800). The crystal structure was investigated by X-ray diffractometry (XRD, Philips X'Pert MRD system). A pseudocubic index denoted as $\{hkl\}_c$ was used to indicate the diffraction peaks. Cross-sectional Raman spectra were measured across the thickness of the deposited films using the 514.5 nm line from an Ar⁺ laser. The spot size of laser was about 1 μm.

Pt top electrodes of 100 μm in diameter were deposited by electron beam evaporation to fabricate the capacitor structure of Pt/(K, Na)NbO₃/SrRuO₃. The dielectric and ferroelectric properties were measured using an impedance analyzer (Agilent 4194A) and ferroelectric tester (Toyo Technica, FCE fast).

3. Results and discussion

Figure 1(a) shows the film thickness and the deposition amount as functions of the number of deposition cycles. Both the film thickness and deposition amount increased linearly with the number of deposition cycles. 60 μm-thick film was obtained after nine deposition cycles, and the deposition was estimated to be about 6.5 μm per one cycle. Therefore, we confirmed that it was easy to prepare thick films by repeating hydrothermal deposition. **Figure 1(b)** shows the changes in the K/(K+Na) ratio of the deposited film for the number of deposition cycles. The measured K/(K+Na) ratio of 0.86 did not vary throughout the deposition cycles, indicating that it is possible to control the K/(K+Na) ratio with the hydrothermal method. It should be noted that the density of the films estimated from the deposition amount and the film thickness shown

Fig. 1. Dependence of (a) film thickness (circle) and deposition amount (triangle) and (b) the K/(K+Na) ratio of deposited thick films on the number of deposition cycles.

Fig. 2. Cross-sectional SEM image for 60 μm-thick (K_{0.86}Na_{0.14})NbO₃ film deposited on (100)_cSrRuO₃/(100)SrTiO₃ substrate.

in Fig. 1(a) is about 4.5 g/cm³, a value almost identical to that of (K_{0.86}Na_{0.14})NbO₃.^{23),24)}

Figure 2 shows a cross-sectional SEM image of the 60 μm-thick (K_{0.86}Na_{0.14})NbO₃ film. As seen, there were no obvious micro cracks or pores in the film, and the prepared film was dense, as already expected based on Fig. 1. It should be noted out that no obvious interfaces were observed between the (K_{0.86}Na_{0.14})NbO₃ layers deposited in each cycle.

Figure 3(a) shows the XRD 2θ - ω patterns for films obtained after selected deposition cycles. All the patterns show only two sets of peaks originating from the $\{001\}_c$

Fig. 3. (a) XRD 2θ - ω patterns for films after various numbers of repeated deposition cycles; (b) X-ray pole-figure-plot measured at 2θ at an inclination angle of about 45° for films deposited after nine cycles; and (c) the film thickness dependencies of out-of-plane lattice spacings estimated from the 002_c and 020_c diffraction peaks in Fig. 3(a).

planes. Figure 3(b) shows the X-ray pole-figure-plot measured at 2θ corresponding to the peak originating from the $\{110\}_c$ plane for the films deposited after nine cycles. Four-fold spots at an inclination angle of about 45° were observed, indicating that the $60\text{-}\mu\text{m}$ -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film was epitaxially grown with a $\{001\}_c$ out-of-plane orientation. This also means that the epitaxial relationship between the film and substrate was maintained for all the films after various numbers of repeated deposition cycles. Figure 3(c) shows the film thickness dependencies of the out of-plane lattice spacings estimated from the 002_c and 020_c diffraction peaks in Fig. 3(a). For all the film thicknesses, the lattice spacings of 002_c and 020_c were almost the same at 0.404 nm and 0.397 nm , respectively, and these values are in reasonable agreement with those reported for $(\text{K}, \text{Na})\text{NbO}_3$ bulk at room temperature.²⁵⁾ This observation suggests that the domain structures of hydrothermally-deposited $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ thick films originated from the 002_c and 020_c diffraction peaks.

Fig. 4. (a) Cross-sectional Raman spectra measured at the position shown in Fig. 4(b) for $60\text{-}\mu\text{m}$ -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film. (c) Film thickness dependence of Raman shifts estimated from ν_1 , ν_2 , and ν_5 in Fig. 4(a).

Figure 4(a) shows the cross-sectional Raman spectra measured at the positions shown in Fig. 4(b) for $60\text{-}\mu\text{m}$ -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film. These spectra were measured at about $6\text{-}\mu\text{m}$ intervals to avoid overlapping of the measurement positions. (The spectrum measured at position X was different from the spectra measured at other positions, because position X corresponded to the SrTiO_3 substrate.) Raman spectra derived from $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ (position I–IX) showed a similar spectrum regardless of the measurement position. It is considered that the crystal structure of $60\text{-}\mu\text{m}$ -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film is orthorhombic, because the pattern of Raman spectra correspond to that reported for orthorhombic $(\text{K}, \text{Na})\text{NbO}_3$ material.^{26)–28)} According to a theoretical analysis, orthorhombic $(\text{K}, \text{Na})\text{NbO}_3$ material has Raman active optical modes of $4A_1 + 4B_1 + 3B_2 + A_2$.^{26),29),30)} In this case, Raman shifts at around 275 , 539 , and 602 cm^{-1} were assigned to the vibration modes of ν_5 , ν_2 , and ν_1 , respectively. Figure 4(c) shows the film thickness dependence of the Raman shifts estimated from ν_1 , ν_2 , and ν_5 shown in Fig. 4(a). As is apparent, no remarkable change was observed for the three Raman shifts, suggesting that uniform film with the same

Fig. 5. (a) Frequency dependencies of the relative dielectric constant, ϵ_r , and $\tan \delta$ and (b) P - E hysteresis loops for 60 μm -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film.

crystal structure in the film thickness direction was prepared by the repeated hydrothermal deposition technique.

Figure 5(a) shows the frequency dependencies of the relative dielectric constant, ϵ_r , and $\tan \delta$ for the 60 μm -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film. ϵ_r decreased from 310 to 243 with increases in measurement frequency and showed 261 at 100 kHz. This value was larger than the value (of $\epsilon_r = 130$) for the hydrothermally-deposited $(\text{K}_{0.88}\text{Na}_{0.12})\text{NbO}_3$ film with a thickness of 6 μm . There are some reports that ϵ_r increases with increases in the film thickness.²²⁾ It is therefore considered that the hydrothermally-deposited (K, Na)NbO₃ films also showed the same tendency. In addition, a low dielectric loss of below 0.13 was observed in this frequency region. Figure 5(b) shows polarization–electric (P - E) hysteresis loops measured at 100 Hz for 60 μm -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film. Typical hysteresis loops due to ferroelectricity were observed, and the average remanent polarization was about 8 $\mu\text{C}/\text{cm}^2$. This value was smaller than the value ($= 17 \mu\text{C}/\text{cm}^2$) for the hydrothermally-deposited $(\text{K}_{0.88}\text{Na}_{0.12})\text{NbO}_3$ film with a thickness of 6 μm .²²⁾ In addition, the P - E hysteresis loops were imprinted to the negative electric field region. In our previous report, it was observed that P - E hysteresis loops of 6 μm -thick $(\text{K}_{0.88}\text{Na}_{0.12})\text{NbO}_3$ film were imprinted to the negative electric field region. The degree of the P - E hysteresis loop shift to the negative electric field region was almost the same with the present study. This means

that the cause of the imprinting behavior was not the film itself but the film-SrRuO₃ interface. As one possibility, Schottky barriers at the interface between electrode and film is considered.³¹⁾ Since the P - E hysteresis loops shown in Fig. 5(b) were measured using the capacitor structure of Pt/ $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ //SrRuO₃, this asymmetric interface may have contributed to the imprinting behavior. The other is the contribution of impurities existing at interface.³²⁾ We have previously demonstrated that hydrothermally-synthesized (K, Na)NbO₃ films include impurities, such as H₂O and OH⁻, arising from alkaline solutions.³³⁾ The present imprinting behavior can be explained if such impurities are present at the film-SrRuO₃ interface formed by repeated deposition.

4. Conclusions

60 μm -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film was prepared at 240°C on (100)_cSrRuO₃/(100)SrTiO₃ substrates by repeated hydrothermal deposition technique. The film thickness increased linearly with increases in the number of deposition cycles, and the deposition was estimated to be about 6.5 μm per one cycle. The K/(K+Na) ratio of the deposited thick films were constant throughout the deposition cycles. Cross-sectional SEM images indicated that no micro cracks or pores were present in the 60 μm -thick $(\text{K}_{0.86}\text{Na}_{0.14})\text{NbO}_3$ film. Thick films possessing orthorhombic symmetry and were epitaxially grown on (100)_cSrRuO₃/(100)SrTiO₃ substrates. The dielectric constant, ϵ_r , decreased from 310 to 243 with increases in measurement frequency. The average remanent polarization measured at 100 Hz was 8 $\mu\text{C}/\text{cm}^2$. It was hence demonstrated that the repeated hydrothermal deposition technique is an effective way of preparing submicron-thick piezoelectric films.

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