FULL PAPER

High yield preparation of (100)_c-oriented (K,Na)NbO₃ thick films by hydrothermal method using amorphous niobium source

Yoshiharu ITO¹, Akinori TATEYAMA¹, Yoshiko NAKAMURA¹, Takao SHIMIZU¹,
 Minoru KUROSAWA², Hiroshi UCHIDA³, Takahisa SHIRAISHI⁴, Takanori KIGUCHI⁴,
 Toyohiko J. KONNO⁴, Mutsuo ISHIKAWA⁵, Nobuhiro KUMADA⁶ and Hiroshi FUNAKUBO^{1,†}

¹Department of Materials Science and Engineering, Tokyo Institute of Technology,
 J2-43, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

²Department of Electrical and Electronic Engineering, Tokyo Institute of Technology,
 G2-32, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

³Department of Materials and Life Sciences, Sophia University, 7-1 Kioto-cho, Tokyo 102-8554, Japan

⁴Institute for Materials Research, Tohoku University, Building 2, 6th Floor, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

⁵Department of Clinical Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama 225-8503, Japan

⁶Center for Crystal Science and Technology, Department of Science for Advanced Materials, Yamanashi University,
 7-32 Miyamae-cho, Kofu 400-8511, Japan

(K,Na)NbO₃ thick films were prepared at 240 °C on (100)_cSrRuO₃/(100)SrTiO₃ substrates by hydrothermal method. Film thickness increased using an amorphous niobium source instead of conventionally used crystalline one and have the maximum thickness at 0.5 mmol of input mass of niobium source within the range of 0.02–7.5 mmol in case of the 20 h deposition. The yield of (K,Na)NbO₃ films from 0.5 mmol amorphous niobium source becomes 20 times higher than that from conventionally used a 2 mmol crystalline niobium source. In addition, crystal structure, surface morphology, dielectric constant, and ferroelectric and piezoelectric properties of these films were almost independent of the kinds of niobium sources and their input mass within the limitation of the present results.

©2020 The Ceramic Society of Japan. All rights reserved.

Key-words : Hydrothermal synthesis, Lead-free (K,Na)NbO₃ films, High yield, Ferroelectric and piezoelectric properties

[Received February 2, 2020; Accepted May 4, 2020]

1. Introduction

Piezoelectric devices have been widely used for various applications, for example, ultrasonic sensor, vibration power generation, energy harvester and so on.^{1)–6)} The most widely used piezoelectric materials are Pb(Zr,Ti)O₃-based ones which are solid solutions of lead titanate and lead zirconate. However, lead is a toxic element, so that lead-free piezoelectric materials have been attracted such as (K,Na)NbO₃-, (Bi,Na)TiO₃-, (Bi,K)TiO₃- and BaTiO₃-based materials.^{7)–12)} Among them, (K,Na)NbO₃-based materials have been expected as one of the first alternative candidates of lead-free piezoelectric materials in the form of not only the sintered body but also thin films. This is because (K,Na)NbO₃-based materials show good piezoelectric properties and relatively high Curie temperature

compared with other lead-free piezoelectric materials. However, (K,Na)NbO₃-based materials include elements with high vapor pressure such as potassium and sodium. Therefore, the difficulty to prepare (K,Na)NbO₃-based materials has been pointed out due to the easy loss of potassium and sodium that results in the degradation of the properties in the case of the sintered body. This difficulty is also pointed out in the film form prepared by a sputtering method, sol-gel method and chemical vapor deposition to require high temperature.^{13)–15)}

Hydrothermal method can deposit (K,Na)NbO₃-based materials at a relatively low temperature below 250 °C.^{16)–20)} Dense films with stoichiometric composition were obtained without the volatilization of potassium and sodium elements. In fact, 5 μm-thick epitaxial (K,Na)-NbO₃ films were grown at 240 °C on single crystal substrates.²¹⁾ In addition, about 50 μm-thick epitaxial (K,Na)-NbO₃ films were deposited by the repeated hydrothermal method.²²⁾ Using this hydrothermally synthesized (K,Na)-NbO₃ films deposited on Ni-based metal foil substrates, we demonstrated the flexible piezoelectric devices act as

[†] Corresponding author: H. Funakubo; E-mail: funakubo.h.aa@m.titech.ac.jp

[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.128.P8-1>

an energy harvester. Their power density was relatively high value in an ambient frequency among lead-free piezoelectric films.²³⁾ To increase power generation i.e. act as energy harvesters, the thicker films are required because the generated power is proportional to the film thickness.²⁴⁾ Therefore the deposition of thicker films at one process is a critical issue to get thicker films. Thicker film growth at one process was achieved by the selection of an amorphous niobium source instead of conventionally used crystalline one.²¹⁾ This is due to the suppression of a powder formation that was generated together with the films. This realizes longer deposition time using an amorphous source.

In the present study, we investigated the increase of the film thickness by the repeat of the process using an amorphous niobium source. In addition, the effect of the input mass of amorphous niobium source on the deposition amount was investigated to increase the yield of the films together with the ferroelectric and piezoelectric properties of the obtained films.

2. Experimental methods

($K_{0.88}Na_{0.12}$)NbO₃ films were deposited at 240 °C on (100)_cSrRuO₃/(100)SrTiO₃ substrates by the hydrothermal method. The 50 nm-thick epitaxial SrRuO₃ layers were grown by the radio frequency magnetron sputtering method as the bottom electrodes. The mixed solution of KOH and NaOH (Kanto Chemical co., Inc.) with 6 mol/L and $[KOH]/([KOH] + [NaOH]) = 0.9$, and amorphous niobium sources²⁵⁾ with about 0.02–7.5 mmol were used as starting materials. The amorphous niobium source was prepared from molten salt and showed the halo X-ray diffraction pattern characterized by short-range order. Also, when the amorphous niobium was heated up to 700 °C, it was crystallized to Nb₂O₅ and the weight loss was 24.2%. It must be noted that yield was calculated with consideration of this weight loss. A commercially available crystalline niobium source, Nb₂O₅ (Kanto Chemical co., Inc.) was also used as a reference. 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.²⁶⁾ The substrate faced to the bottom of the bottle. This autoclave was heated in an oven maintained at 240 °C for 3–24 h. The deposition time was counted when the autoclave was put on the heated oven. The obtained films were ultrasonically cleaned with distilled water, ethanol, acetone and methanol. These films were dried at 150 °C for 1 h in air under atmospheric pressure.

The film thickness and chemical composition of the obtained films were determined by X-ray fluorescence spectroscopy (PANalytical Axios Advance PW4400) calibrated using standard samples. The crystal structure of these films was characterized by an X-ray diffractometer (XRD, Philips X'Pert MRD system) with Cu K α_1 radiation. The cross-sectional and surface morphology was observed by scanning electron microscope (SEM, Hitachi S-4800).

Pt top electrodes with 100- μ m in diameter were deposited by an electron beam evaporation to make capacitor structures of Pt/($K_{0.88}Na_{0.12}$)NbO₃/SrRuO₃. Dielectric, ferroelectric and piezoelectric properties were measured at room temperature using an impedance analyzer (HP4194A) and ferroelectric tester (Toyo Technica FCE fast) and atomic force microscopy (SII SPA400) calibrated using standard samples, respectively.

3. Results and discussion

3.1 Film thickness as a function of deposition cycle

Figure 1(a) shows the deposition cycle dependence of the film thickness for the films prepared from crystalline and amorphous niobium sources with 2.0 mmol. Film thickness monotonously increased with increasing the number of deposition cycles, and the cycle number to obtain about 50 μ m thick films was about one-third cycles using amorphous niobium source instead of crystalline one. In addition, the film thickness reached 130 μ m by 7 cycle-repeated hydrothermal processes using amorphous niobium source as shown in Fig. 1(a). Figure 1(b) shows the cross-sectional SEM images of the films prepared by 7

Fig. 1. (a) Dependence of film thickness on the number of deposition cycles for (K,Na)NbO₃ films deposited from amorphous (triangles) and crystalline (circles) niobium sources and the cross-sectional SEM images of the obtained films by 7 and 9 times cycles from (b) amorphous and (c) crystalline niobium sources,²²⁾ respectively.

and 9 cycles from amorphous and crystalline niobium sources, respectively. Dense films were observed without obvious micro-cracks and pores in the film for the films using the amorphous source as shown in Fig. 1(b). The surface shape of the grains and the roughness of the thick films look no big differences with the films by 9 cycles repeated using the crystalline source as shown in Fig. 1(c) as already reported.²⁷⁾ Further studies are under investigation to clarify the detailed morphologies of these films using transmittance electron microscopy. Low thermal strain due to the low process temperature is considered to realize crack-free thick films beyond 100 μm in thickness. This also shows that thicker films were obtained by the repeat of the deposition cycle using an amorphous niobium source. In fact, Shiraishi et al., reported that 130- μm thick KNbO₃ film was obtained by the repeat of the deposition cycle.²⁷⁾

3.2 Effect of input mass of niobium source on film thickness

Figure 2(a) shows the film thickness as a function of input mass of the starting amorphous niobium source for (K_{0.88}Na_{0.12})NbO₃ films deposited on (100)_cSrRuO₃//(100)SrTiO₃ substrates for 20 h. It must be noted that the conventional standard input mass of the niobium source was set to be 2.0 mmol.²⁸⁾ Film thickness increased with increasing input mass of the starting amorphous niobium

and reached the maximum value at 0.5 mmol, but the contrary decreased above this value. Figure 2(a) also shows the photographs of collected residual powder after the hydrothermal process. The amount of residual powder monotonously increased with increasing input mass of niobium sources. This means that the amount of residual powder increases with the increase of the input mass of niobium source, but the film thickness does not simply follow. Figure 2(b) shows the calculated yield of the niobium element from the source to the films as a function of the input mass of niobium source. The yield was calculated by the molar of the Nb in obtained films, $n(\text{film})$, against the input one in source materials, $n(\text{source})$. The $n(\text{source})$ was obtained taking account of the weight loss by the high temperature heating, while $n(\text{film})$ was calculated from the film thickness and the density of the films (4.5 g/cm³) reported in Ref. 22). Here, density of the films was ascertained to be the identical one from the weight change of the substrates before and after the film deposition as well as film thickness. This yield is calculated for the thickness of the films on the substrates with 15 $\times$ 15 mm² areas and corresponds to how much niobium source transform to the film, not a powder because these two are competitive reaction. As shown in Fig. 2(b), this yield of the film monotonously decreased with increasing input mass of niobium source. Continuous decrease of the yield with input mass of niobium source can be explained as follows; when the input mass of niobium source increases, the concentration of niobium ion in the solution is possible to increase that enhance the homogeneous nucleation in the solution to generate powders. Once the powder is generated, the powder surface becomes a nucleation site of the (K_{0.88}Na_{0.12})NbO₃ as the surface of the substrate. The increase of the concentration of niobium ion in the solution enhances the homogeneous nucleation in the solution that results in powder generation. Almost all niobium sources become powder and the yield of these films decreased. As a result, the yield of the film formation decreased even if the amount of niobium source increased. This explains the decrease of the film thickness with increasing input mass of the niobium source above 0.5 mmol.

Figure 3(a) shows the film thickness as a function of the deposition times prepared by 0.2 and 2 mmol of the input mass of the niobium source. The deposition was hardly observed for both cases up to about 2 h because it needs about 2 h to reach the vessel temperature of 240 °C.²⁸⁾ After about 2 h, film thickness almost linearly increased with the deposition time but was saturated at a certain time for both cases. The times when the deposition amount saturated of about 15 h using and 2.0 mmol of niobium sources is almost twice as long as that for 0.2 mmol sources, although the amount of source is ten times larger. This fact might reveal that the exhaust of source is dominant to determine the film thickness when the smaller Nb source was employed, while the (K,Na)NbO₃ powder formation and growth is a major factor to prevent the deposition of films by using larger niobium source. Figure 4 shows XRD θ -2 θ profiles of the residual powders obtained for 6 and 20 h

Fig. 2. (a) Film thickness as a function of input mass of the starting amorphous and crystalline niobium sources and (b) calculated yield of the niobium element to the films from the source as a function of input mass of two niobium sources for the substrates with 15 $\times$ 15 mm² area size. Inserts in (a) are photographs of collected residual powder after the process.

obtained from the 0.2 mmol of input mass of amorphous niobium sources. A mixture of $K_4Na_4Nb_6O_{19} \cdot 9H_2O$ and $(K,Na)NbO_3$, and single phase of $(K,Na)NbO_3$ powders were identified from the XRD patterns for 6 and 20 h,

Fig. 3. Film thickness as a function of the deposition time for the films deposited from the 0.2 and 2 mmol of input mass in amorphous niobium source.

Fig. 4. XRD θ - 2θ profiles of the residual powders when the input mass of amorphous niobium sources is 0.2 mmol for 6 and 20 h.

respectively as shown in Fig. 4. It was already ascertained from the previous study that when the residual powder includes $K_4Na_4Nb_6O_{19} \cdot 9H_2O$, it is possible to become a source for film deposition and the films continuously grow.²¹⁾ On the other hand, the remained powder becomes a single phase of $(K,Na)NbO_3$ powders, film deposition was stopped. Results shown in Figs. 3 and 4 well agreed with our previous results.²¹⁾ When the input mass of the niobium source was less than 0.52 mmol to deposit these films, the saturation time of these films is considered to below 16 h and increase with the input mass of the niobium source. This is a reason why the film thickness increased with the input mass of the niobium source in Fig. 2(a) measured at 20 h deposition.

It must be emphasized that about 20% yield at 0.5 mmol in which the maximum film thickness of 20 μm was obtained [see Fig. 2(a)] is 5 times higher than a conventionally used condition of 2.0 mmol. Moreover, this value is about 15 times higher than the yield when the 2.0 mmol of crystalline niobium source is used as amorphous niobium source. The amount of yield and film thickness for the 2.0 mmol of crystalline niobium source was 1.4% and 5.6 μm shown as red circles in Figs. 2(a) and 2(b). It must be noted that the absolute value of this yield is expected to increase when the substrate with larger surface areas or multiple numbers of substrates were set on the autoclave because the same film thickness was ascertained to achieve on the substrates with $15 \times 15 \text{ mm}^2$ and half size of $7.5 \times 15 \text{ mm}^2$.

3.3 Crystal structure, surface morphology, and electric properties

Figure 5(a) shows XRD θ - 2θ profiles of films deposited for 20 h from various input mass of amorphous niobium sources. $\{100\}_c$ -oriented films were ascertained to be deposited, irrespective of the input mass. These films are ascertained to be epitaxially grown films by the XRD pole figure measurement. Figure 5(b) shows the enlarged XRD profiles from $2\theta = 68$ – 74° . Two split peaks identified as

Fig. 5. (a, b) XRD θ - 2θ profiles of $(K_{0.88}Na_{0.12})NbO_3$ films prepared for 20 h under various input mass of amorphous niobium source and (c, d) SEM surface images of the films prepared from (c) 2.0 mmol and (d) 0.36 mmol of amorphous niobium source.

Fig. 6. (a, b, c) Frequency dependences of ϵ_r and $\tan \delta$ and (d, e, f) polarization–electric field (P – E) curves measured at 10 kHz and (g, h, i) strain–electric field (S – E) curves measured at 5.2 kHz for as-deposited films prepared under (a, d, g) 0.36 mmol, (b, e, h) 0.52 mmol and (c, f, i) 2.0 mmol of amorphous niobium source.

diffraction peaks of orthorhombic 330 and $\bar{3}30$, and 0–30 were observed, showing the existence of multi domain structure in the films as we already reported.²⁸⁾ It must be noted that the intensity ratio of these two peaks was almost the same, suggesting a similar volume fraction of these domains, irrespective of the input mass of the amorphous niobium source. Figures 5(c) and 5(d) show the surface SEM images of films obtained from 2.0 and 0.36 mmol of the amorphous niobium source. Almost the same surface morphology consisting of the square-shape grains was observed. This means that the surface morphologies did not strongly depend on the input mass of the amorphous niobium sources within the limit of the present study.

Figures 6(a)–6(c) show the frequency dependence of relative dielectric constant, ϵ_r , and the dielectric loss, $\tan \delta$, for as-deposited films prepared for 20 h from 0.36, 0.52 and 2.0 mmol of amorphous niobium source, respectively. Similar ϵ_r and $\tan \delta$ were obtained for these films. Figures 6(d)–6(f) show polarization–electric field (P – E) hysteresis loops measured at 10 kHz for the same films shown in Figs. 6(a)–6(c), respectively. Remanent polarization was almost the same as approximately $30 \mu\text{C}/\text{cm}^2$ independent of the input mass of amorphous niobium sources. It must be noted that these films show the shift along the electric field axis, so-called “imprint”, that is a typical characteristic of hydrothermally deposited films as already reported including us.^{26),29)} Figures 6(g)–6(i) show the strain–electric field (S – E) curves measured at 5.2 Hz

for the same films shown in Figs. 6(a) and 6(d), Figs. 6(b) and 6(e) and Figs. 6(c) and 6(f), respectively. The curve originating from the ferroelectricity was observed for both films. The effective values of the piezoelectric coefficient, d_{33} , of these films were approximately 35 pm/V. These results show that ferroelectric and piezoelectric properties are almost independent of the input amount of the niobium sources.

4. Conclusions

(K_{0.88}Na_{0.12})NbO₃ films were prepared by the hydrothermal method on (100)_cSrRuO₃/(100)SrTiO₃ substrates. The film thickness showed maximum value against the input mass of amorphous niobium source at 0.5 mmol. 20 times higher yield of the niobium source was achieved using 0.52 mmol amorphous sources instead of conventionally used 2.0 mmol crystalline source. This shows that a high yield of (K_{0.88}Na_{0.12})NbO₃ film deposition was achieved using an amorphous niobium source by adjusting optimum input mass. The obvious change of surface morphology, crystal structure and ferroelectric and piezoelectric properties by the input mass of amorphous source was not detected within the limit of the present study.

Acknowledgments This research was partially supported by the Japan Science and Technology Agency and Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) Grant Number JPMJTS1616.

References

- 1) S. G. Kim, S. Priya and I. Kanno, *MRS Bull.*, **37**, 1039–1050 (2012).
- 2) R. Ahmed, F. Mir and S. Banerjee, *Smart Mater. Struct.*, **26**, 085031 (2017).
- 3) Q. Zhou, S. Lau, D. Wu and K. K. Shung, *Prog. Mater. Sci.*, **56**, 139–174 (2011).
- 4) A. Abdullah, M. Shahini and A. Pak, *J. Electroceram.*, **22**, 369 (2009).
- 5) Y. Tsujiura, E. Suwa, H. Hida, K. Suenaga, K. Shibata and I. Kanno, *Jpn. J. Appl. Phys.*, **52**, 09KD13 (2013).
- 6) Y. Xuan, A. Wang and N. Zhang, *IOP Conf. Ser.: Mater. Sci. Eng.*, **470**, 012043 (2019).
- 7) Q. Zhang, B. Zhang, H. Li and P. Shang, *Rare Metals*, **29**, 220–225 (2010).
- 8) D. Gao, K. W. Kwok, D. Lin and H. L. W. Chan, *J. Mater. Sci.*, **44**, 2466–2470 (2009).
- 9) M. Hagiwara and S. Fujihara, *Jpn. J. Appl. Phys.*, **54**, 10ND10 (2015).
- 10) Y. Hiruma, H. Nagata and T. Takenaka, *J. Appl. Phys.*, **105**, 084112 (2009).
- 11) Y. S. Sung, J. M. Kim, J. H. Cho, T. K. Song, M. H. Kim and T. G. Park, *Appl. Phys. Lett.*, **96**, 202901 (2010).
- 12) L. Wu, J. L. Zhang, C. L. Wang and J. C. Li, *J. Appl. Phys.*, **103**, 084116 (2008).
- 13) F. Söderlind, P. O. Käll and U. Helmersson, *J. Cryst. Growth*, **281**, 468–474 (2005).
- 14) K. Shibata, F. Oka, A. Nomoto, T. Mishima and I. Kanno, *Jpn. J. Appl. Phys.*, **47**, 8909–8913 (2008).
- 15) A. Onoe, A. Yoshida and K. Chikuma, *Appl. Phys. Lett.*, **69**, 167–169 (1996).
- 16) T. Shiraishi, N. Kaneko, H. Einishi, T. Shimizu, M. Kurosawa and H. Uchida, *Jpn. J. Appl. Phys.*, **52**, 09KA11 (2013).
- 17) T. Shiraishi, Y. Muto, Y. Ito, A. Tateyama, H. Uchida, T. Kiguchi, M. K. Kurosawa, H. Funakubo and T. J. Konno, *J. Ceram. Soc. Jpn.*, **127**, 388–393 (2019).
- 18) Y. Muto, T. Shiraishi, Y. Ito, A. Tateyama, H. Uchida, T. Kiguchi, H. Funakubo and T. J. Konno, *Jpn. J. Appl. Phys.*, **58**, SLLB12 (2019).
- 19) C. Sun, X. Xing, J. Chen, J. Deng, L. Li, R. Yu, L. Qiao and G. Liu, *Eur. J. Inorg. Chem.*, **13**, 1884–1888 (2007).
- 20) M. Zhang, M. Guo and Y. Zhou, *Int. J. Appl. Ceram. Tec.*, **8**, 591–596 (2011).
- 21) A. Tateyama, Y. Ito, Y. Nakamura, T. Shimizu, Y. Orino, M. Kurosawa, H. Uchida, T. Shiraishi, T. Kiguchi, T. J. Konno, N. Kumada and H. Funakubo, *J. Cryst. Growth*, **511**, 1–7 (2019).
- 22) T. Shiraishi, Y. Ito, M. Ishikawa, H. Uchida, T. Kiguchi, M. K. Kurosawa, H. Funakubo and T. J. Konno, *J. Ceram. Soc. Jpn.*, **126**, 281–285 (2018).
- 23) T. Shiraishi, N. Kaneko, M. Kurosawa, H. Uchida, Y. Suzuki, T. Kobayashi and H. Funakubo, *Jpn. J. Appl. Phys.*, **54**, 10ND06 (2015).
- 24) T. Yoshimura, H. Miyabuchi, S. Murakami, A. Ashida and N. Fujimura, *IOP Conf. Ser.: Mater. Sci. Eng.*, **18**, 092026 (2011).
- 25) N. Kumada, Q. Dong, Y. Yonesaki, T. Takei and N. Kinomura, *J. Ceram. Soc. Jpn.*, **119**, 483–485 (2011).
- 26) T. Morita and Y. Cho, *Appl. Phys. Lett.*, **88**, 112908 (2006).
- 27) T. Shiraishi, H. Einishi, M. Ishikawa, T. Hasegawa, M. Kurosawa and H. Funakubo, *Mater. Res. Soc. Symp. Proc.*, **1494**, 291–296 (2013).
- 28) Y. Ito, A. Tateyama, Y. Nakamura, T. Shimizu, M. Kurosawa, H. Uchida, T. Shiraishi, T. Kiguchi, T. J. Konno, M. Ishikawa and H. Funakubo, *Jpn. J. Appl. Phys.*, **58**, SLLB14 (2019).
- 29) Y. Ito, A. Tateyama, Y. Nakamura, T. Shimizu, M. Kurosawa, H. Uchida, T. Shiraishi, T. Kiguchi, T. J. Konno, M. Ishikawa and H. Funakubo, *J. Ceram. Soc. Jpn.*, **127**, 478–484 (2019).