Development of transparent single-crystalline KNbO₃ thin film by LPE technique

Ken-ichi Kakimoto*, Tomohiko Hibino, Izumi Masuda, Hitoshi Ohsato

Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Received 13 April 2004; revised 16 June 2004; accepted 22 June 2004
Available online 10 December 2004

Abstract

Single-crystalline KNbO₃ thin film has been successfully formed on SrTiO₃ substrate from high-temperature K₂CO₃–Nb₂O₅ solution by the liquid phase epitaxy (LPE) technique. The growth morphology was strongly influenced by the melt composition and film growth temperature. The starting material for the film preparation was a powder mixture of K₂CO₃ and Nb₂O₅. The oxides were mixed in non-stoichiometric proportion with excess K₂CO₃ as flux. Under the optimized film growth conditions using melt compositions including K₂CO₃/Nb₂O₅ 52.5/47.5, 60.0/40.0 and 65.0/35.0, transparent single-crystalline KNbO₃ thin films could be obtained. The synthesized KNbO₃ thin film was subjected to precession X-ray photography in order to evaluate the crystallographic relationship with SrTiO₃ substrate, and the result was compared with a simulated diffraction pattern. The precession X-ray photography clearly indicated that the [010]KNbO₃ is not placed on the same diffraction line as [010]SrTiO₃ but is slightly shifted with a difference in angle of approximately 3°, while the [100] and [001] agree in direction for KNbO₃ and SrTiO₃. The observed lattice parameter c of KNbO₃ film was calculated to be 4.043 Å which was slightly (1.7%) larger than 3.974 Å reported for KNbO₃ bulk crystal. In-plane rotation and elongation toward substrate normal for KNbO₃ lattice on SrTiO₃ substrate were discussed from the viewpoint of release of elastic energy accumulated by lattice mismatch on the substrate.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: KNbO₃; SrTiO₃; Lead-free; Liquid phase epitaxy (LPE); Single-crystalline film

1. Introduction

Lead (Pb) and its oxide-based compounds, which have been widely used as excellent resources for ferroelectric materials, are considered as one of the hazardous substances that should be restricted. This is due to the facts that the toxicity of lead oxide itself and its high reactivity with acid rain in waste electrical and electronic equipments to produce toxic chemicals soluble to the source of water. Nevertheless, development of alternative lead-free candidates that are environmental friendly have been got behind. Over the past few years, increasing attention has been paid to several classes of bismuth layer-structured ferroelectric (BLSF) film for the application field of ferroelectric random access memory (FeRAM). However, none of presently available BLSF film can match excellent piezoelectric performance of lead-oxide-based film, because of their poor electromechanical coupling factor and low piezoelectric constants.

On the other hand, potassium niobate (KNbO₃) is receiving considerable interest as a candidate of lead-free piezoelectrics, since the single crystal shows a large electromechanical coupling coefficient ($k^2=0.53$) of the surface acoustic wave (SAW) on the Y-cut plane [1], compared to $k^2$ of only 0.05 for lithium niobate (LiNbO₃) crystal. It has also reported that X-cut KNbO₃ single crystals rotated by 49.5° along the Y-axis demonstrated the electromechanical coupling coefficient ($k_t$) as high as 0.69 for the thickness mode [2]. This value of $k_t$ is the highest among all known piezoelectrics including even lead-oxide-based crystals. In line with these findings, we launched out into the research and development of high-performance single-crystalline KNbO₃ thin films.

A thin-film synthesis has been extensively carried out recently by aiming application to integrated functional
devices. In the fields of ferroelectrics and piezoelectrics, its compatibility with the advancing semiconductor technology is regarded as the most important priority. Moreover, transparent thin-film synthesis is an important item when it is applied to integrated optoelectronic devices. In a previous paper [3], we reported for the first time in our knowledge that KNbO₃ thin film grown from high-temperature melt demonstrated large second harmonic generation (SHG) at a specific incident light angle, and its transparency was improved by using higher K₂O self-flux content in the melt composition. This paper primary deals with the engineering of the transparent thin-film growth and evaluation of epitaxial relationship between the film and substrate by using precession X-ray photography.

2. Experimental procedure

KNbO₃ is an incongruently melting oxide (Fig. 1) and crystals are generally synthesized from a K₂O-rich (flux), non-stoichiometric high-temperature solution by the top-seeded solution growth (TSSG) method. In our study, liquid phase epitaxy (LPE) technique was utilized for KNbO₃ thin-film growth. The LPE technique operates in a manner similar to the TSSG method and is much closer to the chemical equilibrium, compared to other thin-film growth techniques. Plain substrates, instead of a seed crystal in the TSSG technique, are utilized for the film growth in the LPE technique. As a result, the LPE method is believed to permit the synthesis of single-crystalline epitaxial films with a specific azimuthal relation with substrates.

The starting material for the film preparation was a powdered mixture of K₂CO₃ (99.99%) and Nb₂O₅ (99.9%). Three different mixture molar ratios of K₂O(K₂CO₃)/Nb₂O₅ = 52.5/47.5, 60.0/40.0 and 65.0/35.0 were selected for this experiment. Excess K₂O works as a high-temperature flux (self-flux) to reduce the liquidus temperature, as indicated in Fig. 1. The mixtures were placed in a platinum crucible, then heated up to 1100°C above the liquidus by using a three-zone spiral resistor vertical furnace which was designed for minimization of the temperature fluctuations, as schematically shown in Fig. 2. Heating and cooling cycles for source supplementation and its calcinations were repeated several times to prepare a chemically stable K₂O–Nb₂O₅ melt with large volume. Finally, the melt was stirred at the required temperature for 5 h and left for 1 h to make it homogeneous, followed by step-cooling consisting of several different rates leading to the film growth temperature.

The film growth temperature varied in the range of 889–1058°C. At the film growth temperature, a rotating substrate was dipped vertically into the melt to form films on the surface. The substrates used in this study were mirror-polished SrTiO₃ (001) single crystals. The SrTiO₃ substrates were cleaned in tetrahydrofuran (THF), acetone and ethanol, followed by rinsing in de-ionized water. After the dipping process, the film/substrate was removed from the melt and moved into an upper area in the furnace, followed by cooling to room temperature at 1.5°C/min. External view of the prepared film/substrate was observed by an optical microscope. The relationship of in-plane orientation between epitifilms and substrates was investigated.

![Fig. 1. Limited part of the K₂O–Nb₂O₅ phase diagram.](image1)

![Fig. 2. Schematic diagram of three-zone spiral resistor vertical furnace designed for LPE technique.](image2)
by X-ray photography using a precession camera system (Rigaku) with Mo Kα radiation.

3. Results and discussion

Table 1 summarizes the relationship between the film growth temperature and the growth morphology formed on SrTiO₃ substrate for the cases where the K₂CO₃ contents are 52.5, 60.0 and 65.0 mol%. The film growth temperature was monitored using a thermocouple in contact with the melt surface. No film growth was observed at the film growth temperature lower than 1051 °C for K₂CO₃ content of 52.5 mol%. Instead of film growth, small crystallites of 1–2 and 3–5 mm in size were precipitated on the surface of SrTiO₃ substrate when the substrate was dipped into the melt at 1047 and 1042 °C. At 1034 and 1031 °C, the melt surface was already covered by a large number of crystallites before the substrate could be dipped into the melt. These results show that the nucleation of KNbO₃ is actively generated at 1047 °C or lower temperatures during this cooling process. Fukuda and co-workers [4] also reported the freezing point of the melt with K₂CO₃ content of 52.5 mol% was 1045 °C in the experiment of single crystal growth.

In general, the K₂CO₃(K₂O)/Nb₂O₅ molar ratio of 52.5/47.5 is mostly utilized as the starting composition of the molten solution to grow KNbO₃ single crystals [5], since it is known that a colorless and transparent crystal can be grown when the K₂O is more than 51 mol% but less than 54 mol%. Hong et al. [6,7] reported another reason that the K₂O content of around 52 mol% is the most suitable for the stable growth of KNbO₃ single crystals within the composition range of 51–54 mol% because of the lower surface energy of the melt and lower activation energy of the viscous flow. In the present film synthesis, however, it was not possible to obtain colorless and smooth KNbO₃ films on SrTiO₃ substrate, even when the K₂CO₃ content was selected to 52.5 mol%. This was due to the substrate erosion caused by chemical reaction with high-temperature melt. The film contained a large number of erosion pits with a diameter of 10 μm. Actually, differential thermal analysis (DTA) detected that small continuous endothermic signals appeared at temperature over 900 °C when SrTiO₃ coexists with the melt.

On the other hand, the films grown from the melts with K₂CO₃ content of 60.0 and 65.0 mol% did not include noticeable defects in the film structure, since lower film-dipping (solid–liquid line) temperature could avoid erosion reaction between the melt and the SrTiO₃ substrate. However, experimental conditions for uniform film growth on SrTiO₃ substrate were more severe than expected. Slight differences of film growth temperature and cooling rate formed a variety of crystal morphology on the surface of SrTiO₃ substrate. To ascertain the effects of the temperature gradient on the morphology of precipitates, a specific steep temperature program was designed in the vertical dipping technique by controlling three-zone heater carefully. Fig. 3 presents a model example of top external view of precipitates grown from the melt with K₂CO₃ contents of 60.0 mol% in the above model experiment. The left-hand tip of SrTiO₃ substrate located inside the melt near the bottom of platinum crucible, and formed pale blue cubic crystallites in size less than 1 mm on the surface. According to the study by Fukuda and co-workers [4], the increase of K₂CO₃ content over 55 mol% produces blue-colored KNbO₃ crystal. This observation matches well with the present result. On the other hand, a center region of the substrate was covered with rough and cloudy white precipitates. These precipitates were neither of cubic crystal nor film form. Only the right-hand tip, namely final immersed region within the melt, showed relatively transparency, but contains a large number of visible defects within the structure. This model experiment certainly demonstrated

| Melt composition of K₂CO₃ (mol%) | Film growth temperature (°C) | Morphology          |
|---------------------------------|-------------------------------|---------------------|
| 52.5                            | 1031                          | Melt crystallization |
|                                 | 1034                          | Melt crystallization |
|                                 | 1042                          | Bulk growth         |
|                                 | 1047                          | Bulk growth         |
|                                 | 1051                          | Film growth         |
|                                 | 1058                          | Film growth         |
| 60.0                            | 967                           | Film growth         |
|                                 | 970                           | Film growth         |
|                                 | 990                           | Bulk growth         |
|                                 | 1005                          | Bulk growth         |
| 65.0                            | 889                           | Melt crystallization |
|                                 | 895                           | Melt crystallization |
|                                 | 912                           | Bulk growth         |
|                                 | 915                           | Bulk growth         |
|                                 | 918                           | Film growth         |
|                                 | 930                           | Film growth         |

Fig. 3. Top external view of various kinds of KNbO₃ precipitates on SrTiO₃ substrate by a model experiment using the melt with K₂CO₃ contents of 60.0 mol%.
difficulties in the control of dipping temperature program to obtain an uniform material onto substrate by the vertical LPE technique.

In contrast, Fig. 4 shows an example of uniform thin-film growth from the same melt composition (60.0 mol% K$_2$CO$_3$) by the vertical LPE technique under precisely controlled growth conditions. Half left-hand side of SrTiO$_3$ substrate is covered with KNbO$_3$ thin film with approximately 100 nm in thickness. This film demonstrated around 55% of average transmittance in the visible wavelength range, and consisted of terrace-like smooth growth surface with step interval of 100 nm and vertical roughness per one step of 0.6 nm or less [8]. In general, thin films requested for the application to high-performance functional devices on silicon-based platforms should be transparent, stoichiometric, single phase, epitaxial, dense and smooth. It is possible that the present KNbO$_3$ thin film satisfies all above requests in the fields of piezoelectrics and optoelectronics.

Fig. 5(a) and (b) present the precession X-ray photographs of the KNbO$_3$ film grown on SrTiO$_3$ substrate from the melt with K$_2$CO$_3$ content of 60.0 mol%, where X-rays irradiated the film/substrate surface from the (a) horizontal and (b) vertical directions. In these photographs, the reciprocal lattice points originating from both (001) KNbO$_3$ film and (001) SrTiO$_3$ substrate are superimposed. The symbols {$a^*$, $b^*$, $c^*$} represent the reciprocal lattice axes of both KNbO$_3$ and SrTiO$_3$. It can be observed that each reciprocal lattice point in these X-ray photographs stands in the diffraction lines and forms a pair of two by two, indicating epitaxial relationship between KNbO$_3$ and SrTiO$_3$. Within two reciprocal lattice points in which they become a pair, the inside one toward the center is the reciprocal lattice point of KNbO$_3$ having a larger lattice parameter, and the outside one is that of SrTiO$_3$. It is noteworthy that the $b^{*}_{\text{KNbO}_3}$ is not placed on the same diffraction line as $b^{*}_{\text{SrTiO}_3}$ but is slightly shifted with a difference in angle of approximately 3°, while the $a^*$- and $c^*$-axes agree in direction for KNbO$_3$ and SrTiO$_3$.

This observation indicates that in-plane $a^*$- and $b^*$- reciprocal axes (also each real axes) did not form an angle of 90°.

Fig. 6(a) and (b) give illustrations of simulated diffraction patterns of cubic SrTiO$_3$ ($Pm3m$, $a=3.905\ \text{Å}$) and orthorhombic KNbO$_3$ ($Cm2m$, $a=5.695$, $b=5.721$, $c=3.974\ \text{Å}$) in $hk0$ plane, respectively. While SrTiO$_3$ has no systematically absent reflections in the diffraction patterns, diffraction spots under the condition represented by $h+k=2n+1$ ($n$: natural number) disappear from the $hk0$ plane of KNbO$_3$. The orthorhombic coordinate system has a crystallographically equivalent relationship to the monoclinic coordinate system, when lattice conversion from [100] and [010] to [110] and $\frac{1}{2}1/2\ 1/2$ times the length of lattice parameters for the orthorhombic coordinate system. For KNbO$_3$, $a=b=4.036\ \text{Å}$, $c=3.974\ \text{Å}$ and $\gamma=90.3^\circ$ are obtained. As a result, the converted lattice parameters of KNbO$_3$ in the monoclinic coordinate system close to those of cubic SrTiO$_3$. Under this crystallographic condition, KNbO$_3$ thin film is expected to grow epitaxially on SrTiO$_3$ substrate. In other words, it can be compared that KNbO$_3$ epifilm formed a monoclinic structure on the cubic SrTiO$_3$ substrate.
It is noteworthy that the observed lattice parameter \( c \) of KNbO\(_3\) film was 4.043 Å within the measurement accuracy, and slightly (1.7%) larger than 3.974 Å reported for KNbO\(_3\) bulk crystal. This indicates that \( c \) axis of the KNbO\(_3\) thin film was lengthened under in-plane stress due to the existence of the SrTiO\(_3\) substrate. Namely, it is considered that an elastic energy accumulated by the mismatch of in-plane lattice constants between KNbO\(_3\) thin film and SrTiO\(_3\) substrate was released by the \( c \)-axis elongation of the film toward substrate normal and in-plane rotation on the substrate. As seen in the precession X-ray photographs (Fig. 6(b)), \( b^*_{\text{KNbO}_3} \) is not placed on the same diffraction line as \( b^*_{\text{SrTiO}_3} \). Its deviation angle is approximately 3° and ten times larger than 0.3° deviation (\( \gamma = 90.3° \)) in the calculated primitive cell in the monoclinic coordinated system for KNbO\(_3\). This seems to result from the effect of compensation for the lattice misfit generated between KNbO\(_3\) and SrTiO\(_3\).

4. Conclusion

The regulation on environmental preservation has been strengthened in the global scale. European union (EU) has already determined on restriction, from 2006, of the use of certain hazardous substances (RoHS) in electrical and electronic equipment. Although RoHS is planning to exclude the high-functional electroceramics from the initial subject, use of toxic lead (Pb) and its compounds, which are indispensable to current high-performance ferroelectric and piezoelectric materials, should be lowered as low as possible or completely stopped for environmental preservation. In this paper, we reported the engineering of the transparent KNbO\(_3\) thin-film growth by using the LPE technique. KNbO\(_3\) has been receiving considerable interest as a candidate of lead-free piezoelectric material, and thin-film synthesis is also considered as one of the most important priority for compatibility with the advancing semiconductor technology. We succeeded in the synthesis of uniform single-crystalline KNbO\(_3\) thin film on SrTiO\(_3\) that is often used as a buffer-layer material on Si substrate. Moreover, crystallographic relationship between the grown film and SrTiO\(_3\) substrate was investigated by using precession X-ray photography. This technique clearly demonstrated that the synthesized KNbO\(_3\) thin film formed epitaxially on SrTiO\(_3\) substrate and had different lattice parameters from those of standard crystal due to in-plane stress induced by lattice misfit between film and substrate.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research for Encouragement of Young Scientists (B) (No. 15760499) form the Japan Society for the Promotion of Science (JSPS), by a grant from the Tatamatsu Foundation (2003), and by a grant from the NITECH 21st Century COE Program ‘World Ceramics Center for Environmental Harmony’.

References

[1] K. Yamanouchi, H. Odagawa, T. Kojima, T. Matsumura, Theoretical and experimental study of super-high electromechanical coupling surface acoustic wave propagation in KNbO\(_3\) single crystal, Electron. Lett. 33 (1997) 193–194.
[2] K. Nakamura, Y. Kawamura, Electromechanical coupling factor of KNbO\(_3\) single crystal, Proc. IEEE Ultrasonics Symp. 1999; 1013–1018.
[3] K. Kakimoto, I. Masuda, H. Ohsato, Growth morphology and crystal orientation of KNbO\(_3\) film on SrTiO\(_3\) by liquid phase epitaxy, Jpn. J. Appl. Phys. 41 (2002) 6908–6911.
[4] T. Fukuda, Y. Uematsu, Preparation of KNbO\(_3\) single crystal for optical applications, Jpn. J. Appl. Phys. 11 (1972) 163–169.
[5] W. Xing, H. Looser, H. Wiest, H. Arend, Progress in KNbO\(_3\) crystal growth, J. Cryst. Growth 78 (1986) 431–437.
[6] W. Hong, K. Lu, Y. Zhao, X. Wu, Density and surface tension properties of molten potassium niobate system, J. Cryst. Growth 147 (1995) 104–110.
[7] W. Hong, Y. Chen, Variation of the viscosity of molten potassium niobate with annealing time, J. Cryst. Growth 165 (1996) 81–89.
[8] K. Kakimoto, I. Masuda, T. Hibino, H. Ohsato, Single-crystalline KNbO\(_3\) thin film grown by liquid phase epitaxy, J. Electroceram. 13 (2004) 579–583.
[9] B. Jaffe, W.R. Cook Jr., H. Jaffe, Piezoelectric Ceramics, Non-metallic Solids, No. 3, 1971, p. 54.