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Single-Crystalline $KNbO_3$Thin Film Grown by Liquid Phase Epitaxy

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Abstract. The effects of melt composition on the transmittance of single-crystalline $KNbO_3$ films grown on $SrTiO_3$ substrates by liquid phase epitaxy (LPE) technique were investigated. The growth morphology and transmittance of the $KNbO_3$ films strongly depended on the extra K_2CO_3 self-flux content in K_2CO_3 (K_2O)-Nb_2O_5 system. With increasing K_2CO_3 content close to the eutectic composition (≈66 mol%) in the phase diagram, the transmittance of $KNbO_3$ film/$SrTiO_3$ substrate increased up to 70% in the visible wavelength range. Atomic force microscopy (AFM) clearly showed that the parallel flat steps formed toward the dipping direction and their interval decreased with increasing the K_2CO_3 content.

Keywords: liquid phase epitaxy (LPE), $KNbO_3$, $SrTiO_3$, single-crystalline film, transmittance

Introduction

Potassium niobate ($KNbO_3$) crystals have attracted much attention from the application fields of electro-optical and electro-mechanical transducer devices because of their excellent nonlinear optical properties, high photorefractive coefficient and large piezoelectricity [1–3]. $KNbO_3$ is an incongruently melting oxide (Fig. 1) and crystals are generally synthesized from a K_2O-rich (flux), non-stoichiometric high-temperature solution by the top-seeded solution growth (TSSG) method. Liquid phase epitaxy (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. Planner 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 azimuth relation with substrates.

Khachaturyan et al. [4] and Bohac et al. [5] investigated the possibility of $KNbO_3$ film growth on Al_2O_3, $KTaO_3$ and $SrTiO_3$ substrates from the high-temperature melt of K_2O-V_2O_5-Nb_2O_5 system by the LPE technique. However, their $KNbO_3$ films consisted of many faceted crystals with small size in dimension and contained multi-domains and inclusions, which resulted in milky-colored films.

In the preceding paper, we have reported for the first time that transparent single-crystalline $KNbO_3$ film could be obtained by the LPE technique using simple K_2O-Nb_2O_5 system with excess K_2O flux [6]. This film was epitaxially grown on $SrTiO_3$ substrate with (001) orientation and demonstrated large second harmonic generation (SHG). However, the relationship between the process conditions and film morphology is still unclear. The present paper deals primarily with the effect of melt composition on the film quality and transmittance to obtain a better understanding of the $KNbO_3$ film growth in K_2O-Nb_2O_5 system by the LPE technique.

Experimental

K_2O-enriched (self-flux) K_2O-Nb_2O_5 system (Fig. 1) [7] was utilized in this LPE experiment. For comparison, three kinds of the mixture molar ratios of $K_2O(K_2CO_3)/Nb_2O_5 = 52.5/47.5$, $60.0/40.0$ and $65.0/35.0$ were selected as high-temperature solutions.

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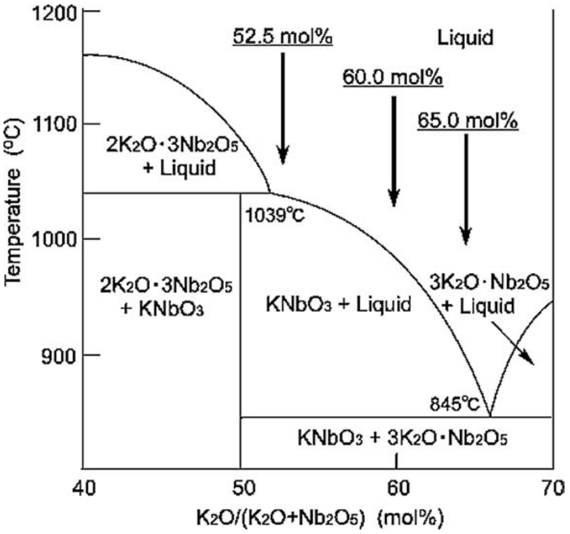

Fig. 1. Limited part of the K_2O-Nb_2O_5 phase diagram.

Excess K_2O works as a high temperature flux (self-flux) to reduce the temperature of liquidus, as indicated in Fig. 1.

The starting material was a powder mixture of K_2CO_3 (99.99%) and Nb_2O_5 (99.9%). The mixtures were placed in a 100 ml platinum crucible, and 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. Heating and cooling cycles for source supplementation and its calcination were repeated several times to prepare a chemically stable K_2O-Nb_2O_5 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 to the film growth temperature. The film growth temperatures were 1051, 969 and 900°C for the melts of $K_2O(K_2CO_3)/Nb_2O_5$ = 52.5/47.5, 60.0/40.0 and 65.0/35.0, respectively. At the film growth temperature, a substrate was dipped vertically into the melt to form films on the surface. The substrates used in this study were mirror-polished $SrTiO_3$ (001) single crystals. The $SrTiO_3$ 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.

X-ray diffraction (XRD) measurement with CuK*a* radiation was carried out to examine the crystallinity of the film. The surface morphology of the grown film was observed using an atomic force microscope (AFM, Seiko Instruments SPI-4000). The transmittance data of the grown film was collected by an UV/Visible/NIR spectrometer (JASCO V-570).

Results and Discussion

Figure 2 shows the XRD patterns of three films grown from the different solutions (hereafter abbreviated to film (52.5/47.5), film (60/40) and film (65/35)). Single–phase $KNbO_3$ film growth with (001) orientation on the (001) $SrTiO_3$ substrate was observed for all the cases. In the previous study [6], the precession X-ray photography revealed that the $KNbO_3$ film formed a single crystal with a monoclinic structure in which $a = 4.00$ Å, $b = 4.02$ Å (in-plane, $\alpha = \beta = 90°$), and $c = 3.96$ Å (along the surface normal, $\gamma = 90.65°$) within the measurement accuracy. Its unit cell formed a rotation angle of 2.5–6.0° in the plane of $SrTiO_3$ substrate.

The top external view of the $KNbO_3$ film / $SrTiO_3$ substrate is presented in Fig. 3. The film (52.5/47.5) is cloudy white and showed around 30% of transmittance in the visible wavelength range (Fig. 4). With increasing the molar content of K_2CO_3 flux, the

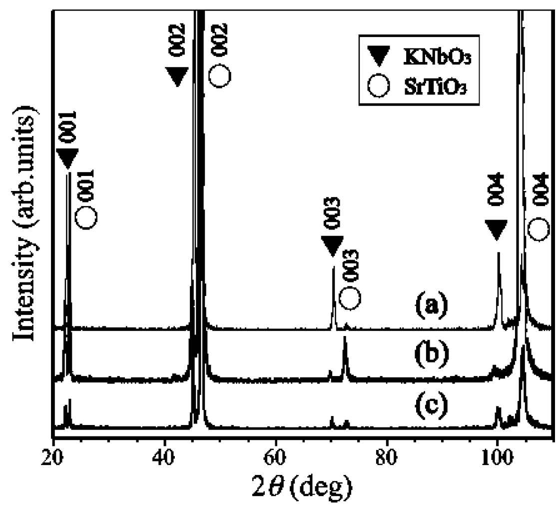

Fig. 2. XRD patterns of the $KNbO_3$ films (a) 52.5/47.5, (b) 60/40 and (c) 65/35 grown on $SrTiO_3$ substrates.

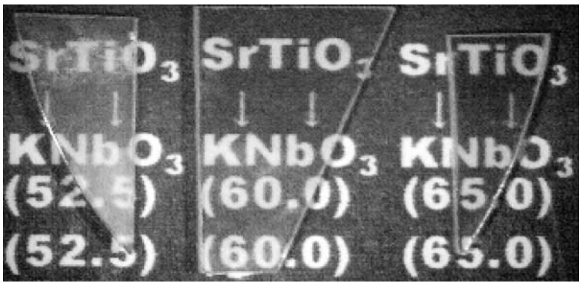

Fig. 3. Top external view of $KNbO_3$ films 52.5/47.5 (left), 60/40 (center) and 65/35 (right) grown on $SrTiO_3$ substrates.

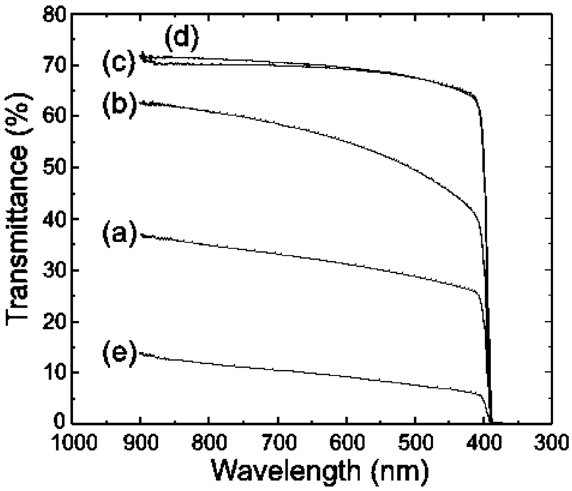

Fig. 4. Transmittance curves measured for the $KNbO_3$ films (a) 52.5/47.5, (b) 60/40 and (c) 65/35 on $SrTiO_3$ substrates. For comparison, the curves of (d) $SrTiO_3$ substrate and (e) the film (52.5/47.5) grown from a short stirred solution only for 30 min instead of 5 h are also presented.

grown film becomes more optically transparent; approximately 55% and 70% of transmittance were measured for the films (60/40) and (65/35), respectively. The film (65/35) demonstrates a nearly identical transmittance curve to that measured for a pure $SrTiO_3$ substrate, which may imply a possibility that the $KNbO_3$ film owns much more transmittance than the $SiTiO_3$ substrate.

It is well known that a colorless and transparent bulk single crystal can be grown when the K_2O is more than 51 mol% but less than 54 mol% in the K_2O-Nb_2O_5 system, and reported that the K_2O content of around 52 mol% is the most suitable for the stable growth of $KNbO_3$ single crystals, because of the lower surface energy of the melt and lower activation energy of the viscous flow [8–10]. Actually, the K_2O/Nb_2O_5 molar ratio of approximately 52.5/47.5 is mostly utilized as the starting composition of the molten solution to grow $KNbO_3$ single crystals by the TSSG method. The film (52.5/47.5) demonstrated the best crystallinity of all the films prepared, but showed inferior transmittance to the other films with higher content of K_2CO_3 flux. In the preceding paper [6], we reported a possibility that high-temperature melt reacted with $SrTiO_3$ substrate at the film dipping temperature of 1051°C. Scanning electron microscopy showed that a large number of pits, which was formed by substrate erosion, with a diameter of 10 μm distributed over the film surface. These defects lowered transmittance in the film (52.5/47.5).

The magnified AFM image shows that the film (52.5/47.5) also contains small-size defects within the terraced crystal surface, as shown in Fig. 5(b). For comparison, Fig. 5(a) represents the image of the film (52.5/47.5) grown from a short stirred melt only for 30 min instead of 5 h. This clearly shows that the film formed rough surfaces as well as defects, which resulted in strong light scattering with a low transmittance of 15% or less (Fig. 4). It is apparent that the longer stirring process of high-temperature solution prior to the film dipping process is of importance to form parallel flat steps of $KNbO_3$ crystals.

Both of the films (60/40) and (65/35) did not show noticeable defects on the surface, since lower film-dipping temperature (solid-liquid line) could avoid erosion reaction between the melt and the $SrTiO_3$ substrate. Typical AFM images for both films (60/40) and (65/35) are presented in Fig. 5(c) and (d), respectively. Noteworthy is that the interval of the flat steps toward the dipping direction decreases with increasing the flux content of K_2CO_3 in the order (52.5/47.5) $>$ (60/40) $>$ (65/35), which enhanced the transmittance because of smaller light scattering. The interval of the flat steps seems to be determined by the reduction of film growth rates with an increase of K_2CO_3 flux. Actually, the growth rate of the film (52.5/47.5) showed 5 times or more higher than that of the film (65/35), although the former film contained inevitable defects due to the reaction between the melt and $SrTiO_3$ substrate. Even in the case for the latter film, however, longer dipping period or a modified dipping process, e.g., horizontal dipping process, can work effectively for preparing thicker film.

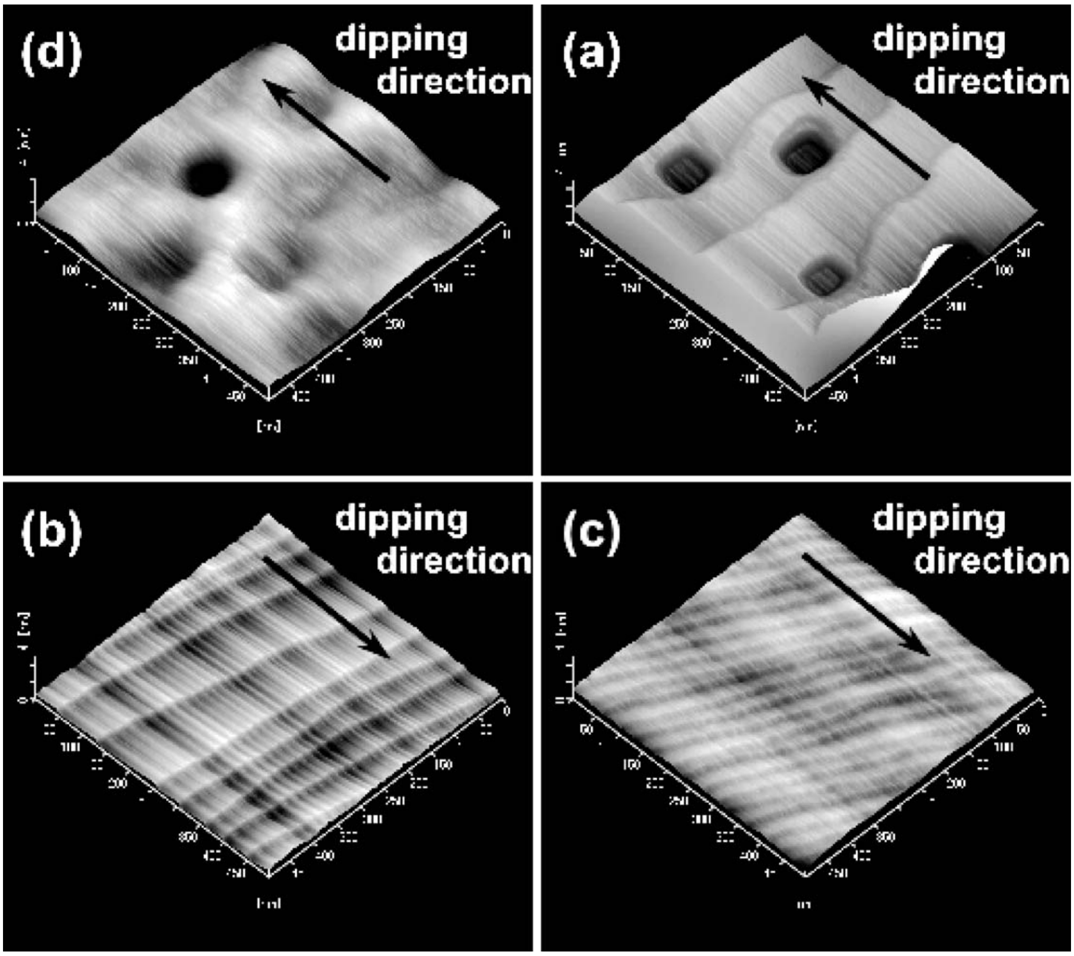

Fig. 5. AFM images of the surface of films (b) 52.5/47.5, (c) 60/40 and (d) 65/35. For comparison, the image of (a) the film (52.5/47.5) grown from a short stirred solution only for 30 min instead of 5 h are also presented.

Conclusion

A transparent single-crystalline $KNbO_3$ film was successfully grown on $SrTiO_3$ substrate from high-temperature melts of K_2O-enriched (self-flux) K_2O-Nb_2O_5 system using the LPE technique. Higher K_2O flux content close to the eutectic composition ($\approx$66 mol%) was desirable for the increase of the transmittance of the film. The single-crystalline $KNbO_3$ film (65/35)/$SrTiO_3$ substrate reached a high transmittance of 70% in the visible wavelength range.

Acknowledgments

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References

1. J.-C. Baumert, P. Günter, and H. Melchior, *Opt. Commin.*, **48**, 215 (1983).
2. M. Zgonik, R. Schlesesser, I. Biaggio, and P. Günter, *Ferroelectrics*, **158**, 217 (1994).
3. K. Yamanouchi, H. Odagawa, T. Kojima, and T. Matsumura, *Electron Lett.*, **33**, 193 (1997).
4. O.A. Khachaturyan and R.S. Madoyan, *Crystal Research and Technology*, **19**, 461 (1984).

5. P. Bohac, P. Buchmann, and H. Melchior, *Jpn. J. Appl. Phys. Suppl.*, **24**(2), 613 (1985).
6. K. Kakimoto, S. Ito, I. Masuda, and H. Ohsato, *Jpn. J. Appl. Phys.*, **41**, 6908 (2002).
7. A. Reisman and F. Hoolzberg, *J. Am. Ceram. Soc.*, **77**, 2115 (1955).
8. W. Xing, H. Looser, H. Wüest, and H. Arend, *J. Cryst. Growth.*, **78**, 431 (1986).
9. X. Hong, K. Lu, Y. Zhao, and X. Wu, *J. Cryst. Growth.*, **147**, 104 (1995).
10. X. Hong and 6y. Chen, *J. Cryst. Growth.*, **165**, 81 (1996).