Lithium niobate thin film growth by LPE method and its application

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1. Introduction

Lithium niobate ($LiNbO_3$: LN) is one of the most promising materials for optical waveguide applications such as optical modulators, switches, second-harmonic generation (SHG) devices. Although optical waveguide devices have been developed using diffusion processes, serious drawbacks have been revealed such as optical damage and DC-drift for Ti-indiffused waveguides or reduction of the electro-optic effect for proton-exchanged waveguides. These problems are intrinsically due to the degradation of crystallinity or crystalline damage induced by those diffusion processes.

The liquid-phase epitaxial (LPE) technique is expected to be applicable to the improvement of crystalline quality and/or the fabrication of high-quality thin-film optical waveguides with a step index profile without the need for any diffusion processes.

First, we tried to grow LN thin films of high crystalline quality, and found a new LPE technique that uses a solid-liquid coexisting melt has yielded LN single-crystal films of higher crystalline quality than conventional optical-grade LN bulk crystals[1,2,3].

And next, a multilayered optical waveguide, consisting of the LN waveguiding epitaxial layer and $LiNb_{1-x}Ta_xO_3$ (LNT) solid-solution cladding layer on LN substrate is fabricated. Because, they are attractive for optical applications because refractive indices or electro-optic properties can be varied from those of x = 0 ($LiNbO_3$) to those of x = 1 ($LiTaO_3$)[4,5].

2.Experimental

LiNbO3 epitaxial films were grown on LiNbO3 substrates using a horizontal dipping technique, and optical grade Z-plate LiNbO3 (Crystal Technology, Inc.) 1mm in thickness was used as substrates. A fluxed melt of 20mol% LiNbO3- 80mol% LiVO3 was used for LPE growth. The melt was held at about 1200°C for 12 hours, and was then cooled to about 980°C at a rate of 60°C/h, where it was held for over 3 hours.

Conventional LPE procedure is a growth method that the melt was cooled to the growth temperature (925-955°C) at a rate of 60°C/h and held for 30min at this temperature, after which the substrate was introduced. Then the melt was supercooled state and the grown film was not so good.

The new LPE growth method from a solid-liquid coexisting melt was employed . The melt was cooled below 925°C and held at least 12 hours at this temperature. Although this led to the crucible wall being covered with solid LiNbO3 generated by nucleation, the melt surface was in a completely uniform liquid phase. At this time, the liquid phase was in a saturated state at this temperature, corresponding to a solid-liquid equilibrium (no film growth occurred after 30min's dipping). The melt was then cooled ΔT (1-

5°C) to achieve a supercooled state, and held for 30min at this temperature (750-920°C), at which time the substrate was dipped in the melt.

LNT epitaxial films were grown on Z-plate LN substrates by the same LPE method using a flux system, which the starting composition of the melt was 16mol% LiNbO3 -4mol% LiTaO3 -80mol% LiVO3, and the growth temperature ranged from 850 to 1050 °C. Some films were grown from melts containing MgO. The tantalum composition of the film was determined by the quantitative analysis of Nb and Ta by EPMA.

The crystallinity of each film and the lattice mismatch between the film and the substrate were characterized by XRC analysis using a double crystal method. The c-axis was analyzed using a (0 0 12) diffraction spot. A (4 2 2) reflection from a GaAs single crystal was used to monochromate the incident Cu Kα X-rays. Crystallinity of the film was evaluated based on the full width at half maximum (FWHM) of the peak.

2. Result and Discussion

2-1. LN thin film growth condition and composition control

Figure 1 show the change of X-ray rocking curves and the dependence of the FWHM on film thickness, respectively when the film was grown at 915℃ using the solid-liquid coexisting technique. The growth rate was 1-2μm/min and the film thickness was controlled by changing the dipping time. The change of FWHM is similar to that of the conventional method, However, in this case, the crystallinity of the epitaxial films evidently exceeds that of the original substrate crystal. (For example, the FWHM of the film of 24-μm thickness and the original substrate are 5.6sec and 6.8 sec, respectively.)

This can be explained by differences in nucleation energies. When film growth is performed by a conventional method from a uniform liquid phase melt, the substrate is the first solid phase which contacts the liquid phase (except for the crucible wall). Nucleation (film growth) occurs abruptly only at the substrate surface, because it is the lowest nucleation energy point in the system (figure 2(a)).

On the other hand, when the film is grown from a solid-liquid coexisting melt, the liquid phase is already in contact with a solid phase which is the same material as the substrate. In this case, the substrate is not the first such solid phase in the melt, and film growth can start smoothly under the same conditions as the coexisting solid phase (figure 2(b)). Furthermore, with this technique, the reproducibility of film properties such as film thickness can be better than with the conventional technique because the degree of supercooling is not affected by changes in the melt composition.

The composition of the film can be controlled from about 50.5 Li_2O mol% to congruent composition (48.6 Li_2O mol%) by changing the growth temperature from 800°C to 900°C. The phase-matching wavelength of SHG becomes shorter with increasing Li_2O mol% of the film. Other electro-optical and nonlinear optical properties related to the Li/Nb ratio must be controlled with high crystalline quality.

2-2. Growth of LiNbO3 / LiNb1-xTaxO3 multilayered films

Figure 3 shows scanning electron microscopy of the cross section of as-grown LN/LNT epitaxial layers on an LN substrate. LNT film was grown at 980°C using the solid-liquid coexisting technique, next LN film was grown at 900°C. Multilayered structure with sharp interfaces was successfully grown.

Film thicknesses of the LNT layer and the LN layer are 20 μm and 10 μm respectively. The composition distributions in each layer are quite uniform, and a perfect step profile at the interfaces has been obtained by EPMA analysis. The substituted tantalum ratio of the LNT layer was estimated to be x = 0.30.

Figure 4(a) shows the XRC of the LNT film on LN substrate. The crystallinity of the film appears good from the small full width at half maximum (FWHM) of the peak (11 sec), though a slight tailing is observed in the higher angle region. The substituted tantalum ratio of the film is estimated to be about x = 0.34 from the separation of the peaks ($\Delta\theta$ = 370 sec). In addition, the film was single-poled as a result of the etching experiment, which was expected because the Curie temperature of the substrate is adequately higher than the growth temperature.

Figure 4(b) shows the XRC of LN/LNT layers on LN substrate, which have been fabricated by additional growth of LN film on LNT film represented in Fig. 4(a). The LN epitaxial film shows good epitaxy with a sharp peak (FWHM = 9 sec) despite degradation of the crystallinity of the underlying LNT layer. The composition of the LN layer was approximately stoichiometric based on estimations of the difference of diffraction angles between the substrate (congruent) and the film.

The tantalum composition linearly increases with increasing growth temperature, and can be precisely controlled. LNT film with x=0.20 is obtained at around 900°C, and one with x=0.40 is obtained at around 1000°C. This controllability is due to the partition ratio of Nb and Ta depending on the temperature in the liquid and solid phases in the solid-liquid coexisting melt.

Figure 5(a) shows the experimental setup for the optical measurement, and Fig. 5(b) shows the near-field pattern from the end surface of the LN layer. A light beam was successfully propagated with good confinement in the LN epitaxial layer. From these results, the multilayered structure fabricated by the LPE method was shown to have a potential for high-performance optical waveguide devices.

3. Conclusion

The multilayered structure fabricated by the LPE method was shown to be promising for application to high-performance optical waveguide devices. The fabrication of large-size uniform films is a key technology from the viewpoint of practical device applications. A 3-inch wafer-size epitaxial film with a perfect mirror-smooth surface morphology that is available in conventional device fabrication processes is successfully grown.

References

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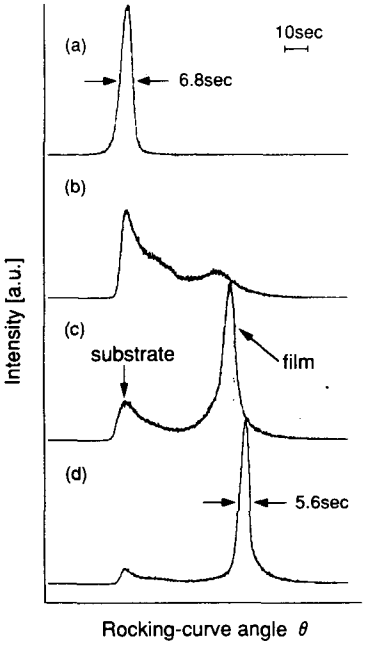

Fig. 1. X-ray rocking curves of films grown from a solid-liquid coexisting melt. Film thicknesses are (a) 0μm(substrate), (b) 3μm, (c) 10μm and (d) 24μm.

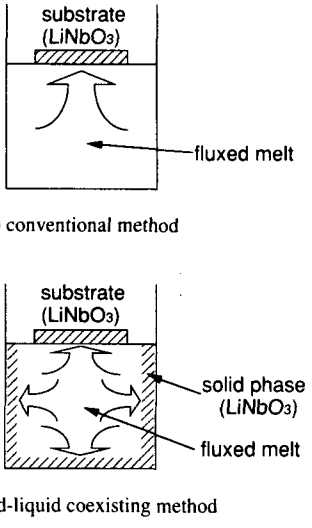

Fig. 2. Nucleation schemes : (a) conventional method, (b) solid-liquid coexisting method.

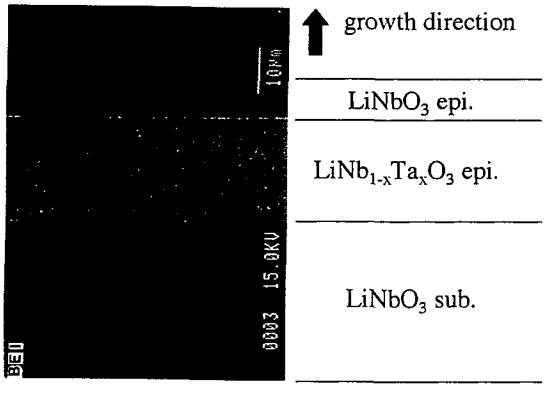

Fig. 3. Scanning electron micrograph showing the cross section of LiNbO and $LiNb_{1-x}Ta_xO_3$ multilayered films grown on $LiNbO_3$ substrate.

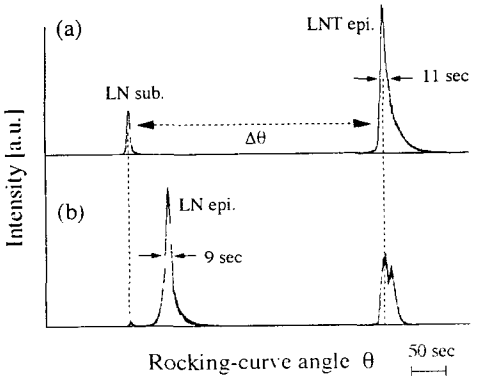

Fig. 4. X-ray rocking curves: (a) LNT film on LN substrate and (b) LN/LNT multilayered films.

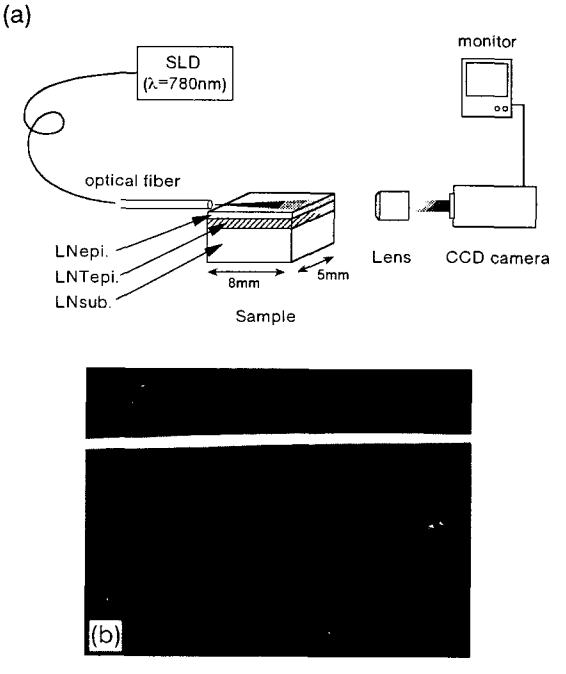

Fig. 5. Optical waveguiding observation: (a) experimental setup and (b) near-field pattern from the end surface of LN layer