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Growth of Er : $LiNbO_3$ single crystal thin film with high crystal quality by LPE method

Tong-Ik Shin, Hyun Lee, Joong-Won Shur, Byungyou Hong* and Dae-Ho Yoon

School of Metallurgical and Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea
**School of Electrical and Computer Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

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Abstract High quality of Er_2O_3 doped $LiNbO_3$ single crystal thin films were grown by the liquid phase epitaxial (LPE) method using Er_2O_3 doped at concentrations of 1, 3, and 5 mol% respectively. After the growth of single crystal thin film, the crystallinity and the lattice mismatch along the c-axis between the film and the substrate was examined as a function of the variations of Er_2O_3 dopant concentration using a X-ray double crystal technique. There was no lattice mismatch along the c-axis for the undoped film and those doped with 1 and 3 mol% of Er_2O_3. For 5 mol% of Er_2O_3 doped film, the lattice mismatch was 7.86×10^{-4} nm along the c-axis.

1. Introduction

Recently, $LiNbO_3$ crystal has been widely studied for applications in optical devices due to its excellent electro-optical, acousto-optical and nonlinear-optical properties [1]. Rare-earth ion doped $LiNbO_3$ could be used for integrated optical amplifiers and laser materials. In particular, the recent advances in the $LiNbO_3$ waveguide fabrication and the improvement in the doping technique with Er ions has made possible the development of the new integrated devices based on optical pumped Er doped $LiNbO_3$ lasers such as acousto-optically turnable lasers [2], DBR(Distributed Bragg Reflection) lasers [3] and mode locked lasers [4] by exploiting the excellent electro-optic and acousto-optic properties of $LiNbO_3$ crystal [5]. Indeed the first mode-locked waveguide laser and amplifiers based on Er doped $LiNbO_3$ have already been fabricated [6].

Although several doping (Er) techniques have been examined, there are still a number of problems to be solved related to device fabrication and processing costs. Er doped $LiNbO_3$ thin films for use as optical waveguides have been prepared by the vertical Liquid Phase Epitaxial (LPE) method. $LiNbO_3$ of congruent composition grown by Czochralski (CZ) method has been the most popular material for optical use and many attempts have been made to improve the quality of these bulk crystals [7-9]. Achieving improved crystal perfection and optical quality (such as resistance to optical damage [10]) has become more important with the successful development of device fabrication processes. LPE techniques are the most promising for improving the quality of grown crystal, because film growth can be achieved at temperatures (~950°C) much lower than those (~1253°C) of the CZ method. At lower temperatures, a number of defects developed in the crystal is low because films of in incongruent (approximately stoichiometric) composition can be grown. The LPE method is particularly favorable for dopant addition [11-14].

In this work, $LiNbO_3$ thin films were grown at Er_2O_3 dopant concentration of 1, 3, and 5 mol%. The crystallinity of the films, which has an effect on optical properties, was observed as a function of the amount of dopant added.

2. Experimental procedure

$LiNbO_3$ epitaxial films were grown on z-cut $LiNbO_3$ substrate ($20\times5\times0.5$ mm^3) using the LPE method. For liquid phase epitaxy, the choice of a suitable flux is very importat. Baudrant et als solvent study [13, 15] has shown that a Li_2O-V_2O_5 mixture is the most convenient flux for $LiNbO_3$ compared to other solvents such as $LiBO_2$, KBO_2, $LiMoO_4$ and K_2WO_4 because $LiVO_3$ is deliquescent and is easily removed from the as grown specimen by water washing. The composition of fluxed melts was 20 mol% $LiNbO_3$-80 mol% $LiVO_3$. Er_2O_3 was added at concentrations of 1, 3, and 5 mol% respectively. Exact control of temperature is important and the LPE furnace was designed specially.

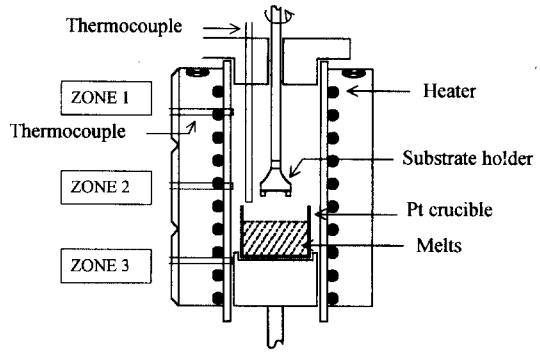

Fig. 1. A schematic diagram of the LPE furnace.

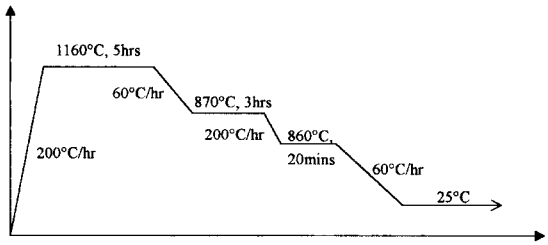

Fig. 2. A growth procedure for Er : $LiNbO_3$ thin film by LPE method.

A schematic diagram of the LPE furnace apparatus which was of the vertical type with 3 zone heating to minimize the temperature gradient is shown in Fig. 1. In the furnace, the noted points indicate the location of thermocouples. The temperature of melt was controlled by the thermocouple attached vertically just above the melt surface.

Figure 2 shows a growth procedure. The melt was held at about 1160°C for 5 hours. During this time, it was stirred for 3 hours to achieve homogeneity state, cooled to about 870°C at a rate of 60°C/h, and then held at this temperature for over 3 hours. In this state, spontaneous nucleation did not occur in the melt and the melt remained in a homogeneous supercooled state. Next, the melt was cooled to a growth temperature (860°C) at a rate of 200°C/h and held for 20 mins before the substrate was dipped into the melt for the film growth. Under these conditions, nucleation occurred in the melt and on the crucible wall, and the uniform supercooled state was destroyed.

The lattice constant was evaluated using X-ray diffraction methods. The crystallinity and the lattice mismatch along the c-axis between the film and the substrate with the variation of Er_2O_3 dopant was examined using the X-ray double crystal technique. The c-axis was defined by a (0012) diffraction spot. The incident $CuK_{\alpha 1}$ X-ray was reflected from a GaAs single crystal oriented to (004) which plays a role of monochrometer. Crystallinity of the film was evaluated as the full width at half maximum (FWHM) of the peak. The lattice mismatch along the c-axis was evaluated from the difference between the substrate and the film diffraction angle:

$$\Delta a_c/a_c = -\Delta\theta/\tan\theta_B \quad (1)$$

where Δa_c is the lattice mismatch between the film and the substrate. a_c is the lattice constant of substrate. θ_B is the Bragg angle for the (0012) reflection and $\Delta\theta$ is the difference between the diffraction peaks.

3. Results and discussion

3.1. Crystallinity of Er : $LiNbO_3$ thin film

It is well known that crystallinity of thin film depends on film thickness. Kawaguchi *et al.* [1] reported that when the thickness of thin film is about 20~30 μm, the crystallinity and surface morphology is excellent. The thickness of thin film grown was kept at about 20~25 μm and the growth rate was about 1~1.2 μm/min for this work.

Figure 3 shows the lattice mismatch between the substrate and the thin film by X-ray rocking curves (XRC). From the Fig. 3, it can be seen that the undoped, 1 and 3 mol% Er_2O_3 doped $LiNbO_3$ thin films show no difference in the Bragg angle (lattice mismatch) between the substrate and the thin film ($\Delta\theta_B$). The 5 mol% Er_2O_3 doped $LiNbO_3$ thin film showed some deviation. When $\Delta\theta_B$ was a 101.25 arcsec by Eq. (1), the lattice mismatch was 7.86×10^{-4} nm. This result suggests that if Er_2O_3 is added in amounts greater than 5 mol%, then the crystallinity will decrese and the lattice mismatch will increase.

Figure 4 shows the dependence of FWHM on the amount of Er_2O_3 dopant by the XRC and indicates the crystal quality of $LiNbO_3$ single crystal thin film dependent on the amount of Er_2O_3 dopant. When the epitaxial thin film was undoped, and doped with 1 and 3 mol% Er_2O_3, the crystallinity was better than the substrate. For example, the FWHM of the undoped, 1, and 3 mol% Er_2O_3-doped film was 27.3, 29.2, and 30.2 arcsec respectively. And the FWHM of the substrate was 31.2 arcsec. However, crystallinity of 5 mol% Er_2O_3 doped $LiNbO_3$ thin film was worse than the substrate.

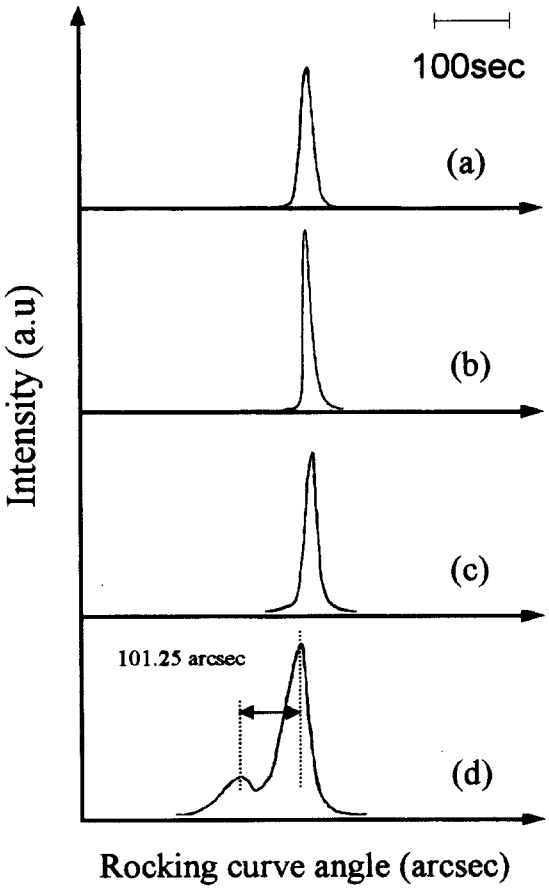

Fig. 3. X-ray rocking curves of film with amount of Er_2O_3 dopant; (a) Substrate, (b) Undoped, (c) 3 mol% Er_2O_3, (d) 5 mol% Er_2O_3.

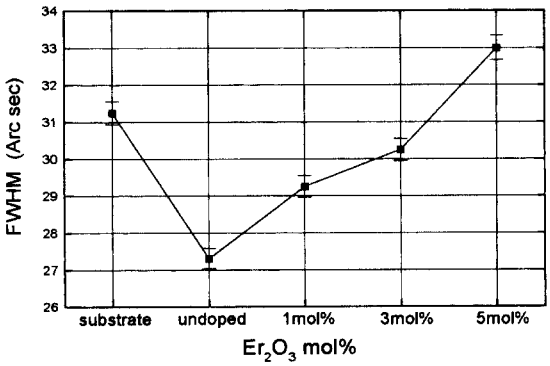

Fig. 4. Crystallinity of $LiNbO_3$ single crystal thin film with amount of Er_2O_3 dopant by X-ray double crystal method.

3.2. *Lattice constant of Er : $LiNbO_3$ thin film*

Figure 5 shows the change of lattice constant of the c-axis with amount of Er_2O_3 dopant. The lattice constants of undoped, 1, 3, and 5 mol% Er_2O_3 doped $LiNbO_3$ thin films were 1.38638, 1.38632, 1.38629, and 1.38570 nm respectively. It is seen that the lattice constant of c-axis decreases with increased amount of Er_2O_3 dopant. The lattice constants of undoped, 1, and 3 mol% Er_2O_3 doped $LiNbO_3$ thin films were a little smaller than substrate. In the case of 5 mol% Er_2O_3 doped $LiNbO_3$ thin film, lattice constant was considerably smaller than substrate.

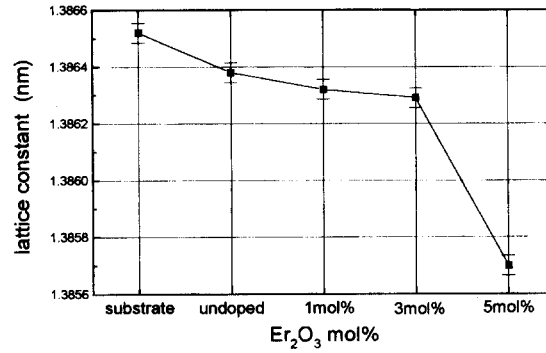

Fig. 5. Lattice constant of the c-axis with amount of Er_2O_3 dopant.

Most impurities lie at the Li octahedron along the c-axis [16-19]. The transition metals substitute for Li at the regular position very approximately, whereas Er ions shift their position by a few Å toward the nearest oxygen plane [17-19]. Therefore, as amount of Er_2O_3 dopant was increased, the lattice constant of c-axis was decreased. The results are in good agreement with those from XRC analysis, and indicate that the observed changes in separation of diffraction peak between the substrate and the grown film are caused due to changes of the lattice constant of the thin film.

4. Summary

Er_2O_3 doped $LiNbO_3$ single crystal thin films with high crystallinity were grown by the LPE method. For the undoped, 1, and 3 mol% of Er_2O_3 doped films, the crystalline quality of grown films was better than that of $LiNbO_3$ substrate. However, for 5 mol% of Er_2O_3 doped film, crystalline quality was decreased. There were no lattice mismatchs along the c-axis for the undoped and films doped with 1, and 3 mol% of Er_2O_3. For 5 mol% of Er_2O_3 doped film, there was a lattice mismatch of 7.86×10^{-4} nm along the c-axis. Further-

more, lattice constants of the c-axis with the increased amounts of Er_2O_3 dopant were decreased.

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