Preparation of epitaxial LiNbO₃ films on sapphire by dipping-pyrolysis process

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Epitaxially grown $LiNbO_3$ thin films were prepared on α-Al_2O_3 (sapphire) substrates by dipping-pyrolysis process using Li-2-ethylhexanoate and Nb-naphthenate as starting materials. Amorphous films pyrolyzed at 400°C were crystallized by heat treatments at 600°C and higher, and [110]-oriented epitaxial $LiNbO_3$ films were obtained on sapphire (110). On the other hand, [100]-oriented $LiNbO_3$ films, containing a small amount of [012]-oriented grains, were obtained on sapphire (012) by similar heat treatments. Orientation of $LiNbO_3$ films on sapphire (012) substrates is discussed on the basis of crystal structures and lattice misfit relationship between them.

1. INTRODUCTION

Lithium niobate ($LiNbO_3$) is a typical ferroelectric material and shows high piezoelectric, electro-optic and acoustic properties. And $LiNbO_3$ films are expected for many applications in the fields of active optical wave-guides, optical modulators and switches, and surface acoustic wave (SAW) devices. Due to strong anisotropy of the properties of $LiNbO_3$, epitaxial films are required for these applications. Various preparation methods have been reported for epitaxial growth of $LiNbO_3$ thin films, including physical dry processes such as pulsed laser deposition (PLD) [1,2] and chemical solution processes such as sol-gel process [3-6].

A chemical solution process has advantages that it requires no high vacuum apparatus and is easily applicable to substrates with any shape and size. Recently, epitaxial $LiNbO_3$ films have been prepared by sol-gel process using metal alkoxides as starting materials. Compared with metal alkoxides, metal organic acid salts have the following advantages: lower cost and more stability against moisture. However, there have been few reports on the preparation of epitaxial $LiNbO_3$ films by dipping-pyrolysis (DP) process or metalorganic deposition

(MOD) using metal organic acid salts as starting materials [6]. In this paper, we prepared $LiNbO_3$ films by DP process using Li-2-ethylhexanoate and Nb-naphthenate, and investigated the in-plane alignment of the final films. In particular, orientation of $LiNbO_3$ films on α-Al_2O_3 (sapphire) (012) substrates is discussed on the basis of crystal structures and lattice misfit relationship between them.

2. EXPERIMENTAL

Details of the fabrication procedure of $LiNbO_3$ films are described elsewhere [6]. Briefly, the starting solution was prepared by mixing of Li-2-ethylhexanoate and Nb-naphthenate, in which the molar ratio of Li/Nb was set as 1.0. This solution was spin-coated on sapphire (012) (R-plane) or (110) (A-plane) substrates. The coated films were pyrolyzed at 400°C for 10 min in air. The spin coating and pyrolysis were repeated to adjust the thickness of the precursor films until the final films having a thickness of about 0.5 μm were obtained. The precursor films were subsequently heat-treated at 600°C or at 800°C for 1 h in air. Alignment of the product films were investigated using x-ray

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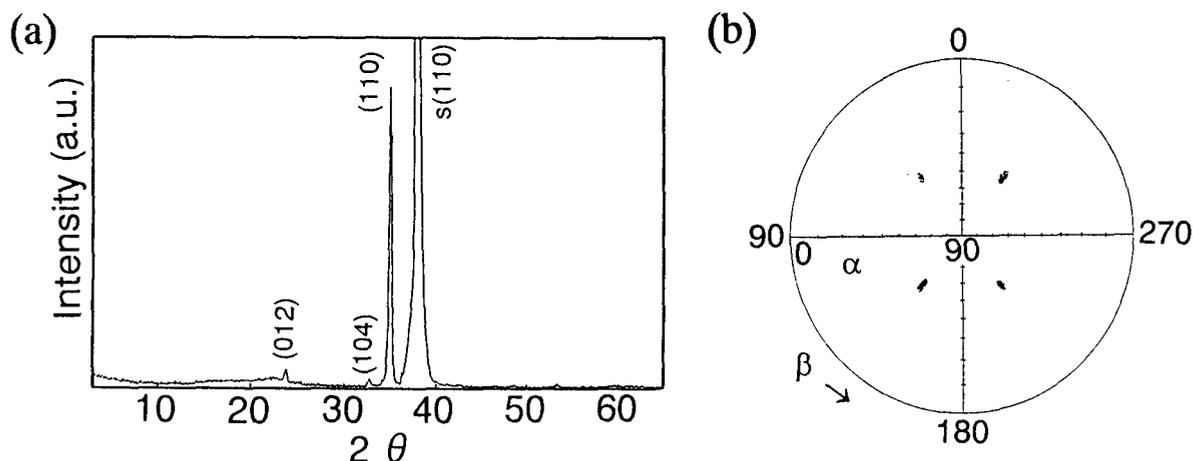* On leave from Dept. Chemical Engineering, Yosu Fisheries Univ., Yosu 550-749, Korea

Figure 1   An XRD θ-2θ scan (a) and (012)-pole figure (b) of a LiNbO$_3$ film on sapphire (110) heat-treated at 600°C. Spots in the pole figure correspond to [110]-orientation.

diffraction (XRD) θ-2θ scans and pole-figure analysis.

3. RESULTS AND DISCUSSION

An XRD θ-2θ scan of a LiNbO$_3$ film on sapphire (110) heat-treated at 600°C is shown in Fig. 1(a). Amorphous films pyrolyzed at 400°C were crystallized by heat treatment at 600°C to give highly oriented films, of which the [110]-axis was perpendicular to the substrate surface. Figure 1(b) shows the pole figure of LiNbO$_3$ (012) reflection for the film shown in Fig. 1(a). Four sharp spots were clearly observed, all of which correspond to the [110]-orientation. The results of the pole figure analysis indicate that the LiNbO$_3$ film has an epitaxial relationship with the substrate.

As described above, epitaxial LiNbO$_3$ films were prepared by the heat treatment as low as at 600°C, using metal organic acid salts as starting materials. If we consider the lattice misfit value between LiNbO$_3$ and sapphire (~8%), this temperature, i.e., ~600°C, seems unusually low for preparation of epitaxial oxide thin films by DP process. For example, epitaxially grown superconducting YBa$_2$Cu$_3$O$_{7-y}$ were obtained on SrTiO$_3$ (misfit: ~1%) by annealing at 700°C and higher [7,8], and on MgO (misfit: ~8%) at around 900°C [9]. In

addition, heat treatments at 700°C and higher were required for epitaxial BaTiO$_3$ films on SrTiO$_3$ (misfit: ~3%) [10]. One possible reason for such a low heat-treatment temperature for epitaxial growth of LiNbO$_3$ is considered to be the lower decomposition temperature of intermediate Li$_2$CO$_3$ than that of BaCO$_3$. On the other hand, highly oriented LiNbO$_3$ films have been grown by heat treatment at around 400°C by sol-gel process using metal alkoxide solution [3,4], probably by avoiding the formation of intermediate Li$_2$CO$_3$. Thus, further investigation is required to lower the annealing temperature, and to elucidate the crystallization behavior of LiNbO$_3$.

Next, an XRD θ-2θ scan of a LiNbO$_3$ film on sapphire (012) heat-treated at 600°C is shown in Fig. 2(a). Amorphous films pyrolyzed at 400° C were similarly crystallized by heat treatment at 600°C. In this case, however, a strong peak of LiNbO$_3$ (300) reflection was observed besides intense (012) reflection as shown in Fig. 2(a); the intensity ratio I(300)/I(012) was approximately 0.82. Considering that the ratio I(300)/I(012) for the LiNbO$_3$ powder is 0.10 [11], we can conclude that this film consists mainly of [100]-oriented grains with a small amount of [012]-oriented grains.

Figure 2(b) shows the pole figure of LiNbO$_3$ (012) reflection for the film shown in Fig. 2(a). Six
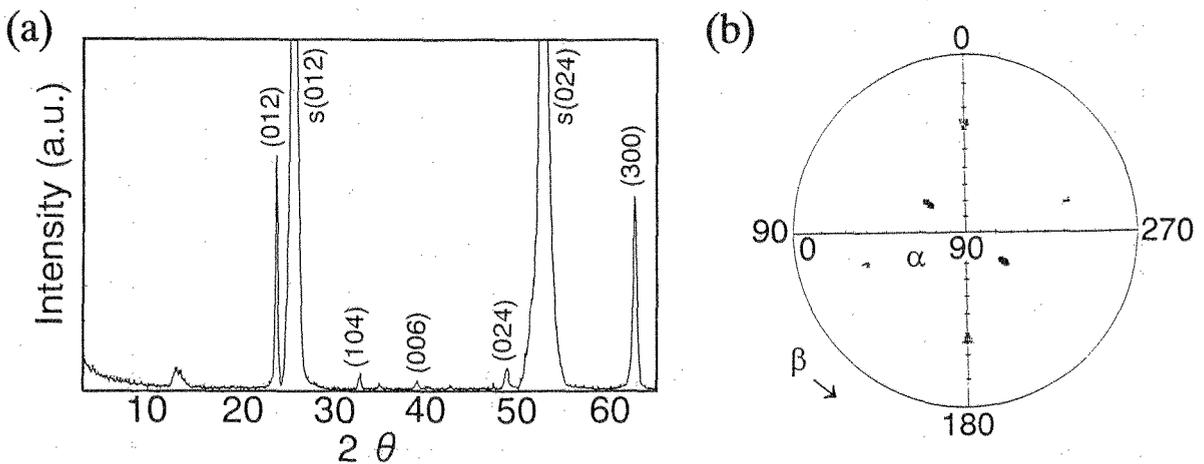
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(a)

(b)

Figure 2 An XRD θ-2θ scan (a) and (012)-pole figure (b) of a LiNbO₃ film on sapphire (012) heat-treated at 600°C. Spots in the pole figure correspond to [100]-orientation.

sharp spots were clearly observed; all of which correspond to [100]-orientation. So, [100]-oriented LiNbO₃ grains were epitaxially grown on sapphire (012).

It is worth mentioning that, on sapphire (012) substrates, epitaxial films, not with [012]-orientation but with predominant [100]-orientation, have been obtained. LiNbO₃ and sapphire have similar crystal structures in which the oxygen ions are arranged as a hexagonal closest packing. Figure 3 shows schematic drawing of oxygen ion arrangement in the LiNbO₃ (100) and sapphire (012) planes, in which the gray spheres represent oxygen ions, and a dashed-lined parallelogram stands for a projection of the trigonal unit cell of each crystal. As shown in Fig. 3, surface oxygen of both structures are arranged so as to form pseudo-square configuration depicted in solid lines, thereby epitaxial growth is considered to occur by sharing these pseudo-squares. The lattice misfit values between the pseudo-squares of LiNbO₃ (100) and sapphire (012) planes are 0.4% and -2.9% along the directions indicated by the arrows in the figure. It is interesting to note that these misfit values are smaller than those between the pseudo-squares of LiNbO₃ (012) and sapphire (012) planes (7.1% and 8.2%) [2]. Thus, on sapphire (012), the [100]-oriented LiNbO₃ is more favorable to grow than the [012]-oriented LiNbO₃ from the viewpoint of
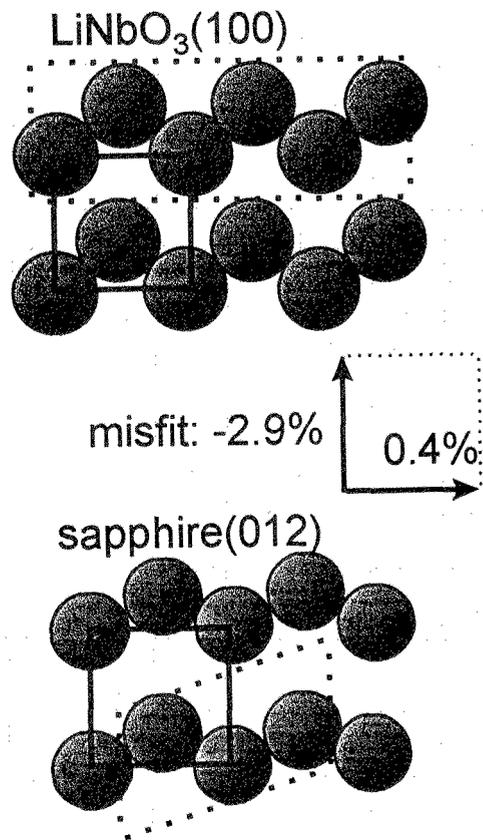

Figure 3 Schematic drawing of oxygen ion arrangement in the LiNbO₃ (100) and sapphire (012) planes.
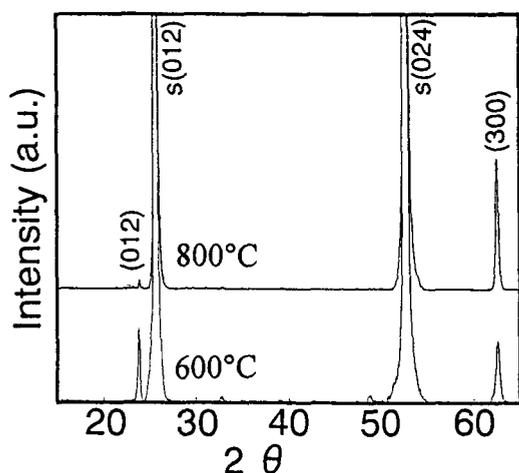
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Figure 4 XRD θ-2θ scans for LiNbO$_3$ films on sapphire (012) heat-treated at 600°C and 800°C.

4. SUMMARY

LiNbO$_3$ thin films were prepared on sapphire substrates by dipping-pyrolysis process using Li-2-ethylhexanoate and Nb-naphthenate as starting materials. Amorphous films pyrolyzed at 400°C were crystallized by heat treatments as low as at 600°C to obtain epitaxial LiNbO$_3$ films; [110]-orientation was preferred on sapphire (110), whereas [100]-orientation was predominantly formed on sapphire (012). The peak intensity ratio of XRD θ-2θ scans corresponding to the [100]- and [012]-orientations for LiNbO$_3$ thin films on sapphire (012) strongly depends on the heat-treatment temperature.

minimizing the misfit of oxygen ion arrangement between the two materials. Actually, [100]-oriented LiNbO$_3$ is reported to exhibit smaller fluctuation of alignment than [012]-oriented grains in the LiNbO$_3$ films prepared by PLD [2].

In the case of LiNbO$_3$ films on sapphire (012) prepared by PLD, the Li/Nb ratio was found to play an important role in determining the preferred orientation of the films [2]. To examine the effect of Li/Nb ratio on the orientation behavior of LiNbO$_3$ films by DP process, LiNbO$_3$ films were prepared on sapphire (012) by varying the molar ratio of Li/Nb. However, after the heat treatment at 600°C, no significant difference was recognized in the alignment of LiNbO$_3$ films by DP process, starting with the Li/Nb ratios ranging from 0.5 to 2.0, in contrast to the films prepared by PLD. The detailed results will be published elsewhere [6].

Up to now, the preferred orientation of LiNbO$_3$ films by DP process on sapphire (012) , i.e., [100]- or [012]-orientation, seems to be closely related to the heat-treatment temperatures rather than to the Li/Nb ratios. Figure 4 shows XRD θ-2θ scans of the LiNbO$_3$ films on sapphire (012) heat-treated at 600°C and 800°C. By annealing at higher temperatures, the LiNbO$_3$ (300) peak became more intense and predominantly [100]-oriented films were obtained at 800 °C.

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