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Processing of highly oriented $LiNbO_3$ thin films through a metal-organic precursor solution

S. Hirano[a,*], T. Yogo[a], W. Sakamoto[a], Y. Takeichi[a], S. Ono[b]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan*
[b]*Nagoya Municipal Industrial Research Institute, Rokuban, Atsuta, Nagoya 456-0058, Japan*

Abstract

A novel processing method for highly oriented pattered $LiNbO_3$ films is developed using a chemically modified precursor molecule with UV sensitive chemical bonds. Patterned $LiNbO_3$ films can be also synthesized via water-based precursor solution by applying a photolithographic technique. Patterned $LiNbO_3$ films crystallized on sapphire substrates with a highly preferred orientation along the *c* axis, by heat treatment at temperatures around 500 °C. $LiNbO_3$ films prepared from aqueous precursor solutions were characterized in terms of the hydroxyl content of their surface layers, determined from their crystallization and optical properties.

Keywords: Films; $LiNbO_3$; Niobates; Optical properties; Sol-gel processes

1. Introduction

$LiNbO_3$ single crystal is an excellent material for electro-optic and nonlinear-optic devices such as optical waveguides, surface acoustic wave devices and holographic memory. Improvement of the processing method of high quality stoichiometric $LiNbO_3$ films is under intensive study in the miniaturizing and integrating of optical waveguide devices. Several methods for preparing $LiNbO_3$ films have been reported, including RF magnetron sputtering,[1] pulsed laser deposition,[2–4] chemical vapor deposition,[5] liquid phase epitaxy,[6,7] and the sol-gel method.[8–26]

By controlling the metal-organic reaction, precursor films can be crystallized epitaxially on sapphire substrates. The key control factor was to synthesize the designed alkoxide as an intermediate molecule in which metal–oxygen–metal bonds are formed, such as –O–Li–O–Nb–O– bonds. The present authors have already reported the preparation of stoichiometric $LiNbO_3$ powders, epitaxial films and fibers using the sol-gel processing with metal alkoxide ethanol solution.[8–20] In this synthesis, we learned that the precipitate gels obtained after complete hydrolyzation of precursor solutions were water-soluble. This makes it possible to apply hydroxide aqueous solutions for coating instead of alkoxide ethanol solutions.[16–19] In addition, patterned thin films can be synthesized in two differing ways: by ultraviolet patterning and by a combination of photolithography and aqueous solution deposition. Patterning of thin films provides a novel route to process the patterned dielectrics and waveguides. This paper describes our recent work on the processing and characterization of $LiNbO_3$ films prepared by metal-organic precursor solution.

2. Processing and ultraviolet patterning of $LiNbO_3$ epitaxial films

2.1. Ultraviolet patterning

A new process was developed by which patterned $LiNbO_3$ films can be synthesized from a chemically modified precursor containing UV sensitive 1-phenyl-1,3-butanedione (PBD) using ultraviolet irradiation. PBD was selected as a ligand on an alkoxide precursor for sensitive absorption of UV light. The modified precursor was chosen to be $LiNb(OEt)_{6-n}(PBD)_n$, with a specific UV absorption at 330 nm. The precursor films

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* Corresponding author. Tel.: +81-52-789-3343; fax: +81-52-789-3182.

E-mail address: hirano@apchem.nagoya-u.ac.jp (S. Hirano).

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were prepared by dip coating on glass and sapphire (001) substrates; these were then irradiated with UV light through a mask (Fig. 1). The resulting sharp pattern of the $LiNbO_3$ film arises from the difference in solubility between irradiated and unirradiated regions in the ethanol solvent. The exposed films were rinsed with ethanol and dried under nitrogen. The patterned films were then heat-treated at 400–550 °C for 2 h in a flow of oxygen. This UV patterning of alkoxy-derived $LiNbO_3$ films offers the possibility of a feasible and low temperature process for fabricating $LiNbO_3$ waveguides.

2.2. UV irradiation of precursor films

Fig. 2 shows changes in the UV spectra of the $LiNbO_3$ precursor films on glass substrates with irradiation time. Since UV light below 300 nm is absorbed by $LiNb(OEt)_6$, UV light from the deep-UV lamp was filtered through UV-28 to cut out the short wavelengths and UV light at 330 nm was selected for patterning of the precursor films.

The 330 nm peak intensity decreases with increasing exposure time to UV, and almost wholly disappears after 10 min. When UV-36 (0% transmittance at 340 nm) is used, the peak did not reduce after exposure to UV light under the same conditions. This decrease of the 330 nm peak suggests changes in molecules in the precursor films. IR results indicate that this change is due to oligomerization between the double bonds in the enol form of PBD, leading to the formation of –O–Li–O–Nb– bonds. This oligomerization drastically reduces the solubility in ethanol of precursor molecules in the irradiated area.

2.3. Patterning and crystallization of $LiNbO_3$ films

After UV irradiation, patterned precursor films fabricated on glass and sapphire substrates were soaked in ethanol. The unirradiated region of the film was dissolved in ethanol to yield a pattern corresponding to the mask. Fig. 3 shows photographs of the patterned $LiNbO_3$ films after heat treatment at 550 °C. The irradiated area has a smooth surface and consists of small grains. The patterned edge is sharp, and the patterned sidewall is smooth.[13] The UV-irradiated $LiNbO_3$ films crystallized on sapphire (001) substrates with a highly preferred orientation along the c-axis.

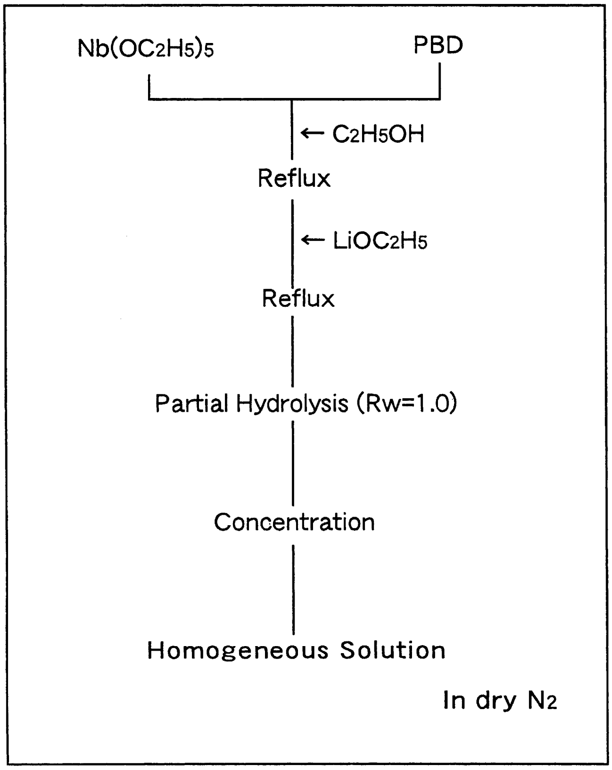

Fig. 1. Processing sequence for UV-patterned $LiNbO_3$ films.

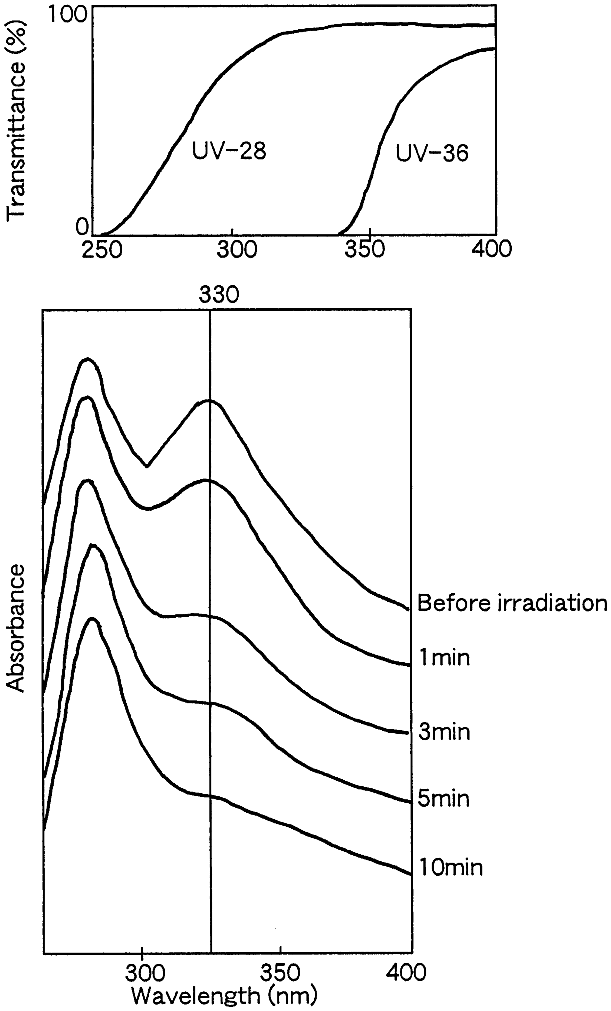

Fig. 2. Changes in UV spectra of precursor films on glass substrates with duration of UV irradiation.

3. Characterization of $LiNbO_3$ films derived from aqueous precursor solution

3.1. Preparation of $LiNbO_3$ films from aqueous precursor solution

Lithium ethoxides (99.9%) and niobium ethoxides (99.9%) were dissolved in absolute ethanol in a molar ratio of 1:1 to form a double alkoxide ethanol solution, and refluxed for 20 h under a dry nitrogen atmosphere. The double alkoxide was completely hydrolyzed with 7.5 equivalent mole of deionized water, followed by refluxing for a further 20 h. After evaporation of the ethanol solvent, precipitated gel was dissolved in excess deionized water and concentrated to about 0.5 mol/l by heating carefully below 80 °C. Acetic acid (0.1 mol/l) was used as neutralizer in the preparation of the neutralized precursor solutions. The precursor solution was filtered through a 0.2-μm membrane filter and was dropped onto sapphire substrates placed in petri dishes. The solution was drained by tilting the petri dish to form a gel film over the substrate. The coated gel films were retained overnight in a desiccator and were then subjected to heat treatment in a flow of oxygen.[16–19] $LiNbO_3$ films were prepared on sapphire (001) substrates with a highly preferred orientation along the *c* axis by heat-treating at temperatures above 325 °C (Fig. 4).

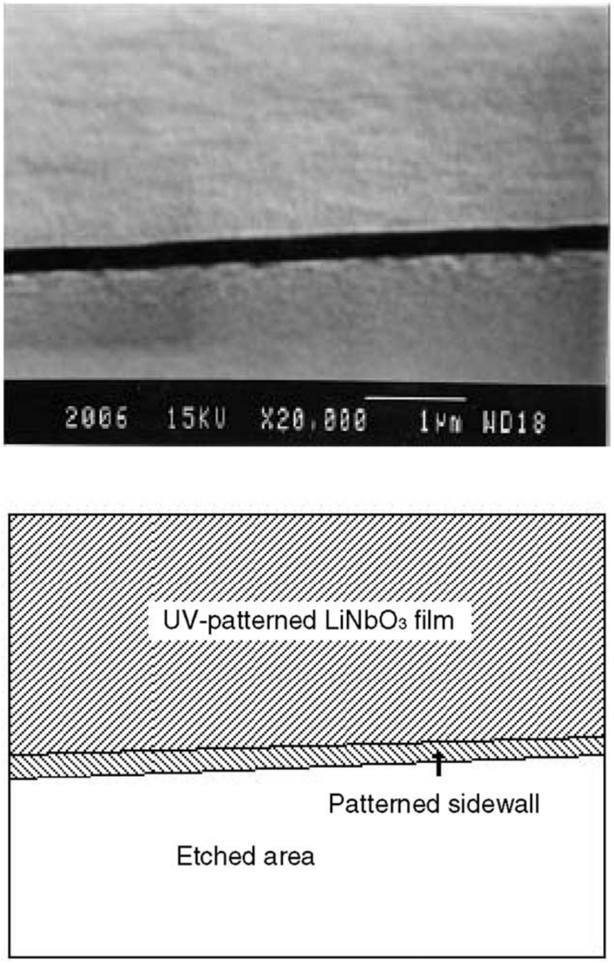

Fig. 3. SEM photograph of patterned film on glass substrate after heat treatment at 550 °C.

3.2. Surface analysis of $LiNbO_3$ films

A small proportion of hydroxyl groups and carbonate groups remained in the films heat-treated at 200 °C. However, it is not easy to estimate hydroxyl residues remaining in heat-treated films on sapphire substrates by means of X-ray photoelectron spectroscopy (XPS) analysis, because it is difficult to distinguish O_{1s} spectra of –OH from that of –O– in oxide films. In this case, the F-labeling technique is capable of evaluating small amounts of hydroxyl residues in surface layers of heat-treated films. These hydroxyl residues are analyzed by labeling them with trifluoroacetates to distinguish OH from –O–. Fig. 5 shows the reaction scheme for labeling hydroxyl residues (–OH) with trifluoroacetate residues (–O–CO–CF_3). The films were exposed to the labeling agent in a closed reaction vessel overnight at room temperature.

$LiNbO_{m/2}(OH)_{6-m}$ and Li_2CO_3 are the main species given by crystallization. $LiNbO_{m/2}(OH)_{6-m}$ is a polymerized intermediate. Li_2CO_3 is formed because Li–Nb hydroxide solution is basic and absorbs CO_2 from the

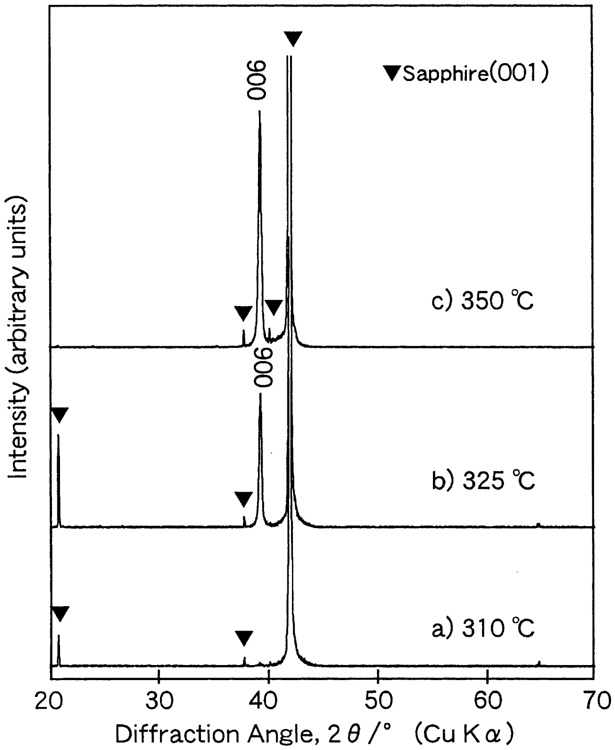

Fig. 4. XRD profiles of $LiNbO_3$ films heat-treated on sapphire (001) substrates, (a) 310 °C, (b) 325 °C, (c) 350 °C.

atmosphere during handling. XPS results indicate that half of the OH residues should be polymerized in the surface layers of the films heat-treated at 200 °C, and 98% at 350 and 500 °C. Table 1 indicates ratios between $LiNbO_{m/2}(OH)_{6-m}$ and Li_2CO_3 at 200, 350 and 500 °C. Seventy-four percent of the Li_2CO_3 remained in the surface layers of films at 200 °C, but the content was reduced to 3% in the surface layers of the films at 500 °C. A speculative model for the chemical reactions in the surface layers is given in Fig. 6. Li ions loosely bind carbonate ions in the top layers of the films at 200 °C, and Nb hydroxides are hidden under those complexes. Li ions react with Nb hydroxides to form $LiNbO_3$, releasing free CO_2 through crystallization.

3.3. Optical property of $LiNbO_3$ films

The refractive indices (at 632.8 nm) of $LiNbO_3$ films prepared on the sapphire (001) substrates were 2.007 (350 °C), 2.094 (500 °C) and 2.156 (600 °C) according to ellipsometry measurements. The refractive indices of the films tend to increase with increasing heat-treatment temperature. This is due to the increase in the film density at higher temperatures. The propagation modes in the films were measured by the prism coupling method using a He–Ne (632.8 nm) laser beam, and the propagation losses were measured in the TE_0 mode and TM_0 mode by the scattering detection method with a fiber probe detecting system. Optical losses were 6 dB/cm for the TE_0 mode of $LiNbO_3$ films (~500 nm) that were crystallized at 500 °C on sapphire (001) substrates prepared from neutralized precursor solution. The $LiNbO_3$ films therefore underwent O_2 annealing at 500 °C for 2 h to reduce the optical losses. The optical losses at 632.8 nm decreased remarkably, down to 2 dB/cm, in the TE_0 mode, and 4 dB/cm in the TM_0 mode of the $LiNbO_3$ films (~670 nm).

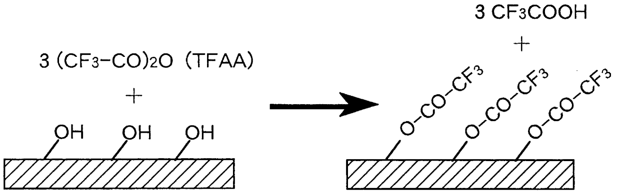

Fig. 5. Reaction scheme for labeling hydroxyl residues with trifluoroacetate residues.

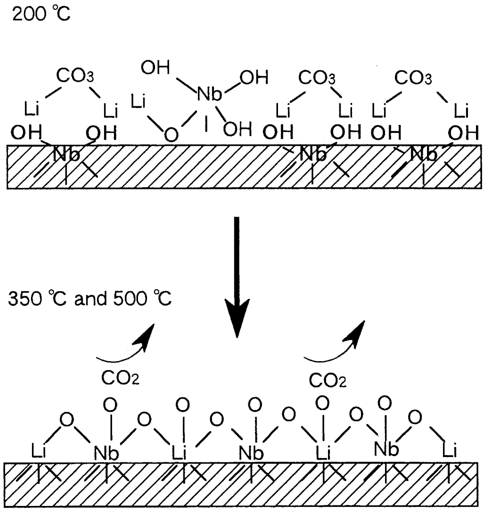

Fig. 6. Speculative model of chemical reactions in surface layers.

Optical losses in thin films used in slab waveguide applications are required to be less than 5 dB/cm. There have been several reports of the optical losses in thin films.[22,24,26,27] Xie et al. reported that optical losses in epitaxial $LiTaO_3$ films on sapphire substrates grown by MOCVD are 5.9 dB/cm in unannealed films, and 2 dB/cm in O_2 annealed films.[27] Optical losses in the TE_0 mode of sol-gel derived $LiNbO_3$ film on sapphire are reported to be 3 dB/cm (22) or 6 dB/cm (24). Optical losses of 2 dB/cm in the TE_0 mode, and 4 dB/cm in the TM_0 mode, are acceptable for the optical quality in the optical waveguide, and the values are among the better reported optical losses in sol-gel derived films.

3.4. Patterning of $LiNbO_3$ films derived from aqueous precursor solution

The patterning procedure is shown in Fig. 7. The sapphire substrate was first coated with aluminium by

Table 1
Composition distributions on surface layers of heat-treated films

Temperature (°C)	Composition
200	Li_2CO_3 (74%), $LiNbO_{1.6}(OH)_{2.8}$ (26%),
350	Li_2CO_3 (6%), $LiNbO_{2.95}(OH)_{0.1}$ (94%),
500	Li_2CO_3 (3%), $LiNbO_{2.95}(OH)_{0.1}$ (97%),

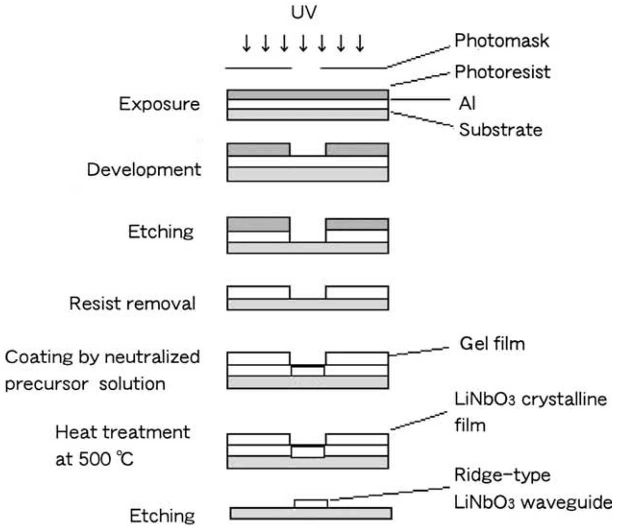

Fig. 7. Patterning procedure for $LiNbO_3$ films.

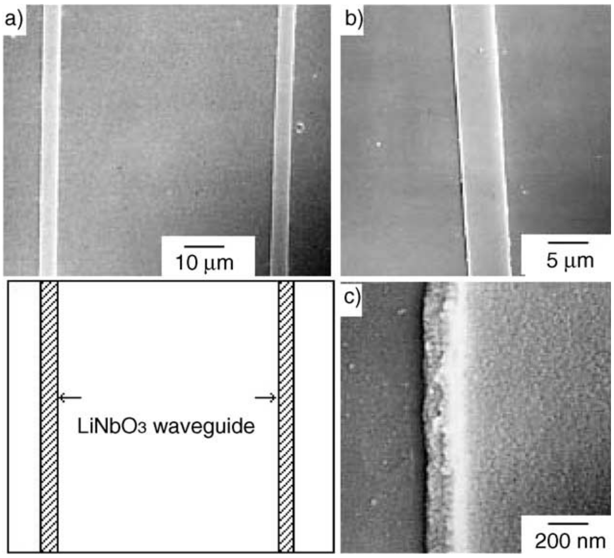

Fig. 8. SEM photographs of patterned $LiNbO_3$ films prepared at 500 °C on sapphire (001) substrate, (a) fabrication pattern, (b) greater magnification of the waveguide, (c) edge region of the waveguide.

physical vapor deposition (PVD). The photoresist was coated onto the aluminum film by spin coating. A finely patterned photomask was then placed on the substrate and exposed to the UV. After development, etching was executed in an etching solution of phosphoric acid, acetic acid, nitric acid and water (15:3:1:1) at 28 °C. After removal of the remaining photoresist, the patterned sapphire substrate was coated with a precursor solution. The precursor films were kept in the desiccator overnight and were then subjected to heat treatment at 500 °C in a flow of oxygen in order to be crystallized. The patterned aluminum mask was etched by the etching solution at 65 °C. By this process, a ridge-type $LiNbO_3$ waveguide was created.

Fig. 8 shows SEM photographs of surface and ridge regions of patterned $LiNbO_3$ thin films that were heat-treated at 500 °C on sapphire (001) substrate by double coating. Two lines, 5 µm wide and 208 nm thick, were fabricated corresponding precisely to the photomask pattern. The surface appears smooth and homogeneous, with no cracks or pores. The edge region also shows as clear-cut.

4. Conclusions

A chemically modified $LiNbO_3$ precursor with a chelate ligand was designed in order to prepare micro-patterned $LiNbO_3$ epitaxial films using ultraviolet irradiation. $LiNbO_3$ films prepared from aqueous precursor solutions were characterized in terms of the hydroxyl contents on their surface layers, through their crystallization and optical properties. About 98% of the hydroxyl residues on surface layers of crystalline films were polymerized after heat-treatment at 350 or 500 °C, and 50% of hydroxyl residues remained on surface layers of amorphous films heat-treated at 200 °C. Optical losses at 632.8 nm were 2 dB/cm in the TE_0 mode, and 4 dB/cm in the TM_0 mode of $LiNbO_3$ films (~670 nm) prepared on sapphire (001) substrates after O_2 annealing at 500 °C. Micro-patterning of $LiNbO_3$ thin film was successfully carried out by applying the photolithographic technique with the aqueous precursor solution.

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