Processing of highly oriented lithium tantalate films by chemical solution deposition

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The synthesis of lithium tantalate films by a chemical solution deposition method was studied. A precursor solution was prepared by dissolving lithium ethoxide and tantalum pentaethoxide in ethanol. The addition of formic acid to this precursor solution was very effective in the preparation of homogeneous and transparent precursor films on substrates by spin coating. Lithium tantalate films crystallized on sapphire (001) substrates with a highly preferred orientation along the *c* axis with heat-treating at temperatures above 450 °C. The refractive index of the film prepared at 550 °C was 2.049, which is close to the value for single crystals of lithium tantalate (2.176).

I. INTRODUCTION

Lithium tantalate ($LiTaO_3$) single crystals are widely used in electro-optic, piezoelectric, and pyroelectric devices, including optical waveguides, surface acoustic wave devices, and pyrosensor devices. Processing methods for high-quality $LiTaO_3$ films are under intensive study to allow the miniaturization and integration of optical waveguide devices. Methods for preparing $LiTaO_3$ films include pulsed laser deposition,[1] chemical vapor deposition,[2,3] solid-phase epitaxy,[4,5] radio frequency (rf) magnetron sputtering,[6] and the sol-gel method.[7–15] Table I summarizes reports of highly oriented $LiTaO_3$ films prepared on sapphire (001) substrates. The sol-gel method is superior in providing good-quality films at low temperatures. Synthesis of highly oriented $LiTaO_3$ films on sapphire (001) substrates at 700 °C has been reported using a lithium tantalum double ethoxide precursor solution.[12] However, the preparation of $LiTaO_3$ films with highly preferred orientation and a smooth surface at lower temperatures around 500 °C has not yet been reported.

We have previously reported the processing of lithium niobate from lithium and niobium double alkoxide with acetic acid.[16–19] Carboxylic acids such as acetic acid and formic acid act not only as catalysts but also as ligands, allowing ready control of hydrolysis. It is important to regulate the rate of hydrolysis, since the hydrolysis rate of tantalum ethoxide is faster than that of niobium ethoxide, making it difficult to prepare a stable precursor solution.[20]

This paper describes the modification of an ethanol precursor solution by adding formic acid to prepare highly oriented $LiTaO_3$ films on sapphire (001) substrates and evaluates the refractive indices of these films.

II. EXPERIMENTAL

A. Preparation of $LiTaO_3$ gel powders and films

Gel powders were prepared by drying the precursor solution at room temperature. Figure 1 shows the preparation procedure for $LiTaO_3$ films. Lithium ethoxide (99.9%), tantalum pentaethoxide (99.999%) (Kojundo Chemical Lab. Co., Ltd., Saitama, Japan), and acetic acid (99.7%) or formic acid (99%) were dissolved in a molar ratio of 1:1:10 or 2, respectively, into absolute ethanol, and the solutions (0.2 mol/l) were stirred at room temperature. Homogeneous transparent precursor films were formed on sapphire (001) (Kyocera, Kyoto, Japan) and Corning (7059) glass substrates by spin coating (1st, 600 rpm for 6 s; 2nd, 2700 rpm for 30 s). The substrates were cleaned ultrasonically in ethanol before coating. The gel powders and the precursor films were retained overnight in a desiccator and subjected to heat treatment at 350–550 °C (heating rate, 2 °C/min) for 2 h or at 1000 °C (heating rate, 10 °C/min) for 10 min in a flow of oxygen.

B. Characterization of $LiTaO_3$ powder and films

Gel powders were characterized using differential thermal analysis, thermogravimetry (TG-DTA, heating rate, 5 °C/min) (TG/DTA 2000, MAC Science Co., Ltd., Tokyo, Japan), and infrared spectroscopy (IR) (FT/IR-410, JASCO, Tokyo, Japan). Crystallization of the powders and films was examined by x-ray diffraction (XRD, Cu K_α, 40 kV, 150 mA) (Rint 2000, Rigaku, Tokyo, Japan). Morphology of the films was observed by scanning electron microscopy (SEM) (JSM-6300F, JEOL, Tokyo, Japan). The composition of the film surface was analyzed by x-ray photoelectron spectroscopy (XPS, monochromatic Al K_α, 15 kV, 10 mA) (AXIS-HSi,

TABLE I. Preparation of highly oriented $LiTaO_3$ films on sapphire (001) substrates.

Processing method	Precursor	Crystallization temp. (°C)	Optimum process temp. (°C)	Ref.
PLD (pulsed laser deposition)	$LiOH \cdot H_2O$ and Ta_2O_5 1.1:1 Mixed powder target	525	650–700	1
MOCVD (metalorganic chemical vapor deposition)	Lithium tantalum hexa-*t*-butoxide	~550	700–750	2, 3
SPE (solid phase epitaxy)	Lithium dipivaloylmethanate and tantalum(V) ethoxide or $LiTa(OEt)_6$	542	700	4, 5
rf magnetron sputtering	$LiTaO_3$ powder target Li:Ta = 49.4:50.6	400 (polycrystalline)	600–650	6
Chemical solution deposition	$LiTa(OEt)_{6-x}(OFo)_x$	450	550	This paper
(sol-gel)	$LiTa(OEt)_6$	500	700	7, 12

Shimadzu/KRATOS, Kyoto, Japan). The peak positions of the binding energy are calibrated with C 1*s* as 284 eV.[21] Refractive indices of films were measured with an ellipsometer using a He–Ne (632.8 nm) laser beam (Model DV-36S, Mizojirikogaku-kogyosyo, Tokyo, Japan).

III. RESULTS AND DISCUSSION

A. Preparation of transparent precursor films

Figure 2 shows the effect of carboxylic acids in the precursor solution on the transparency of films deposited on Corning (7059) glass substrates by spin coating. A

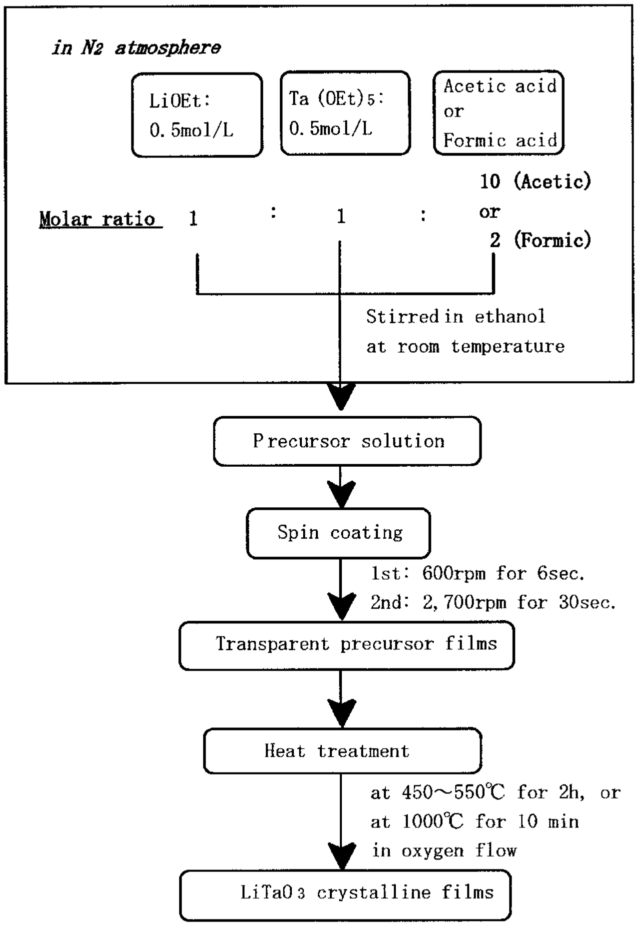

FIG. 1. Preparation procedure for $LiTaO_3$ films.

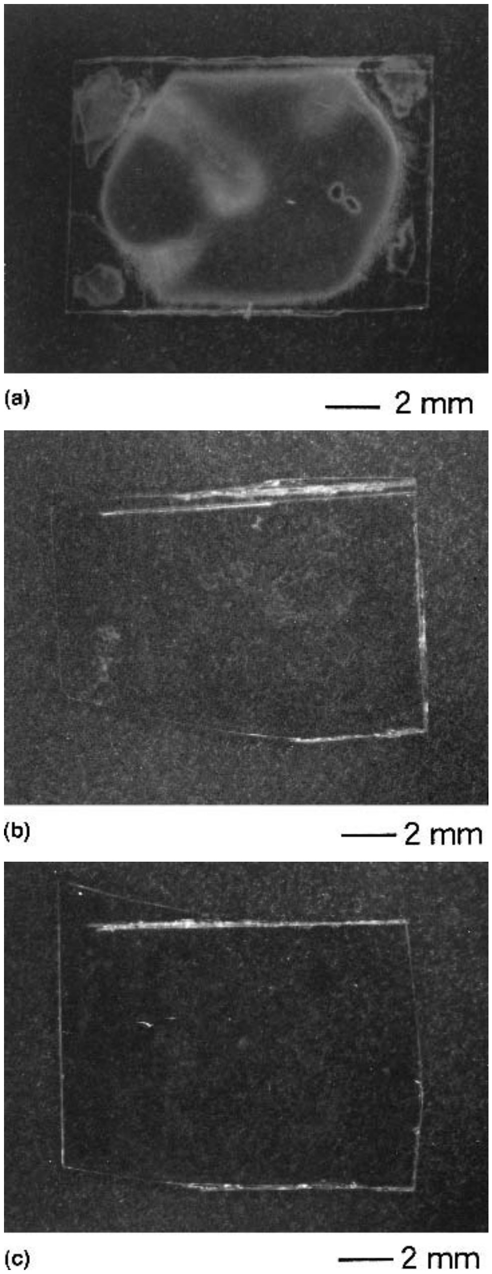

FIG. 2. Effect of adding carboxylic acids to the precursor solution upon the transparency of deposited films: (a) no acid; (b) with acetic acid; (c) with formic acid.

precursor film, prepared from a precursor solution with no acid, was clouded [Fig. 2(a)]. It is found that the optical transparency of the precursor films is improved, according to the amount of carboxylic acid in the precursor solution. Acetic acid or formic acid was added to the precursor solution in varying molar ratios. Precursor solution with a 10 molar ratio of acetic acid or a 2 molar ratio of formic acid proves to be optimum for controlling hydrolysis, giving transparent precursor films [Figs. 2(b) and 2(c)]. Formic acid ($pK_a = 3.75$) is a stronger acid than acetic acid ($pK_a = 4.75$), so that the molar ratio used of formic acid is lower. It is clear that acidity is a significant factor in the formation of transparent films. Also, formate ions react with ethoxy groups of tantalum pentaethoxide to control the hydrolysis as follows:

$$\mathrm{Ta(OC_2H_5)_5} + x\mathrm{HCOOH} \rightarrow \mathrm{Ta(OC_2H_5)_{5-x}(OOCH)_x} + x\mathrm{C_2H_5OH} \quad .$$

However, the precursor solution is not stable and has to be prepared shortly before coating. It should be used within one day.

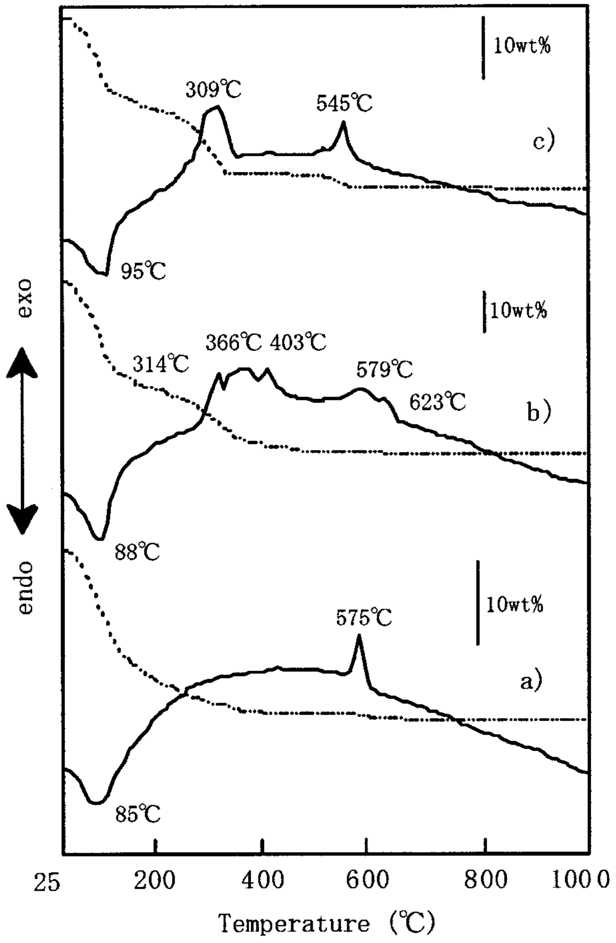

FIG. 3. Thermal analyses of gel powders prepared from precursor solution: (a) no acid; (b) with acetic acid; (c) with formic acid (TG, dotted line; DTA, solid line).

B. Characterization of $LiTaO_3$ powders

Figure 3 shows TG-DTA data for gel powders prepared from the precursor solution with no acid, with acetic acid, and with formic acid. The broad endothermic peaks around 85–95 °C with weight loss in TG are due to dehydration [Figs. 3(a)–3(c)]. The exothermic peak patterns are different for the three samples. An exothermic peak at 575 °C is observed in the gel powder with no acid [Fig. 3(a)]. In the gel powder with acetic acid, exothermic peaks are observed at 314, 366, 403, 579, and 623 °C [Fig. 3(b)]. Two exothermic peaks are apparent in the gel powder with formic acid, around 309 and 545 °C [Fig. 3(c)]. All these exothermic peaks are associated with weight loss in TG. The 545 °C peak in the gel powder with formic acid is at a lower temperature than the corresponding 575 °C peak in the gel powder with no acid and the 623 °C peak in the gel powder with acetic acid. These results indicate that formate ligands can be eliminated from the films by heating at lower temperatures. Formic acid is superior to acetic acid in the modification of the precursor solution.

Figure 4 shows changes in the IR spectra of powders prepared from the precursor solution with formic acid

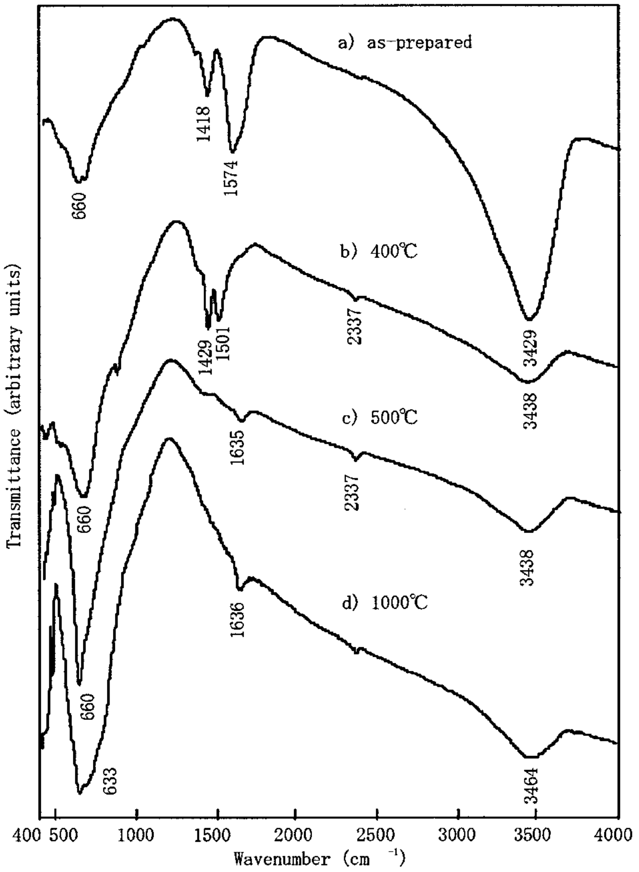

FIG. 4. Changes in IR spectra of gel powders with heat treatment at various temperatures.

and heat-treated at various temperatures. The spectrum of the gel powder as prepared indicates a COO^- group in formate ligands with vibrations at 1418 and 1574 cm^{-1} [Fig. 4(a)].[11] These absorption bands remain in the IR spectrum of the powders heat-treated at 450 °C (data not shown) but reduce with heat treatment at higher temperatures. In the spectra of the powders heat-treated at 400 and 500 °C [Figs. 4(b) and 4(c)], the 2337-cm^{-1} band corresponds to carbon dioxide ($O{=}C{=}O$).[22] The $O{=}C{=}O$ absorption bands appear in the IR spectra because the carboxylic groups present in the powder burn to CO_2 and H_2O during heating and some of the CO_2 and H_2O molecules are adsorbed on the powders. The 1635–1636-cm^{-1} [Figs. 4(c) and 4(d)] and 3429–3464-cm^{-1} [Figs. 4(a)–4(d)] absorption bands could be from the water molecules in both KBr and in the powders.[22]

Figure 5 shows the XRD profiles of the powders. The powder is amorphous when heat-treated at 400 °C [Fig. 5(a)]. It begins to crystallize at 450 °C [Fig. 5(b)] and is well crystallized at 500 °C [Fig. 5(c)]. The XRD and IR results suggest that the exothermic peak at

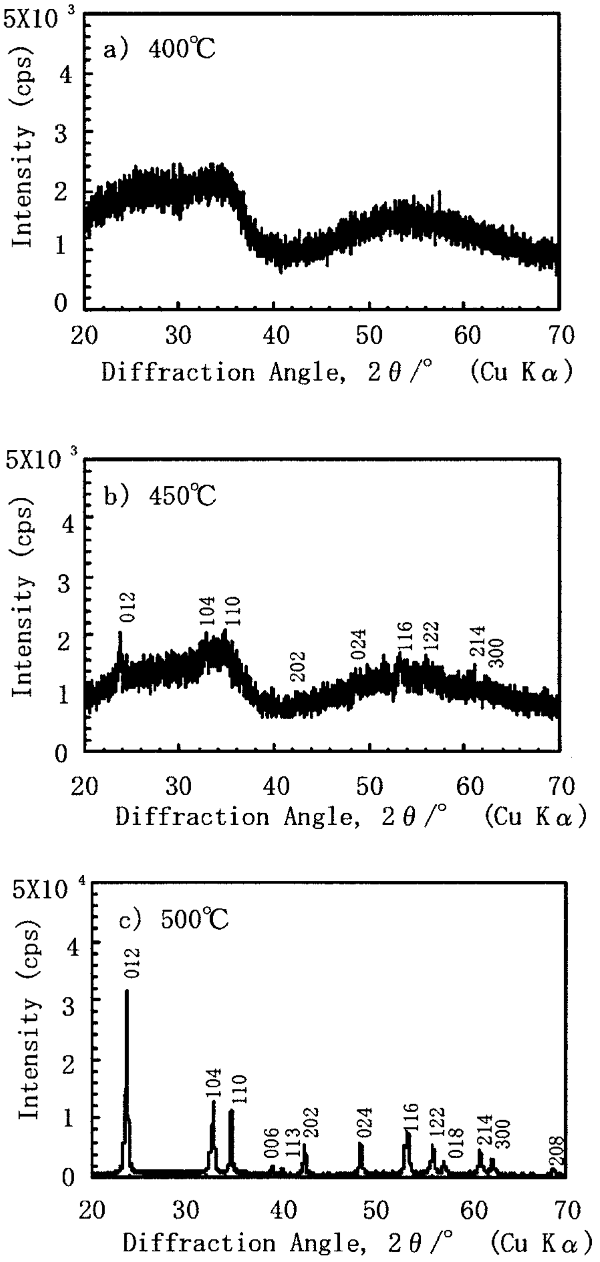

FIG. 5. XRD profiles of $LiTaO_3$ powders prepared at (a) 400 °C, (b) 450 °C, and (c) 500 °C using a precursor solution with formic acid.

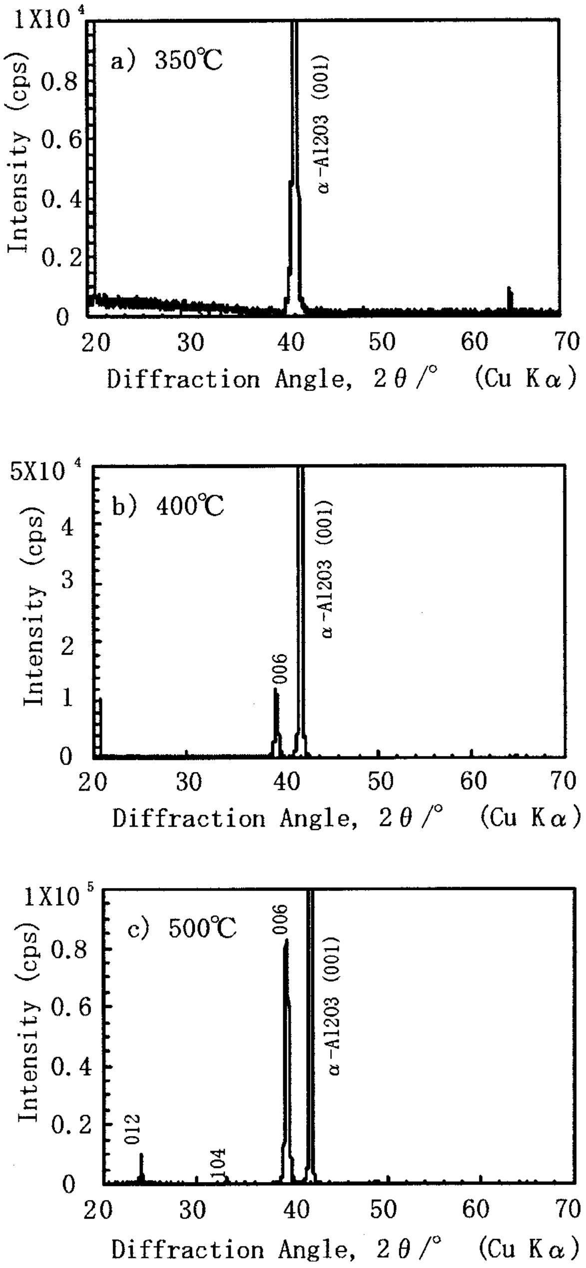

FIG. 6. XRD profiles of $LiTaO_3$ films prepared on sapphire (001) substrates at (a) 350 °C, (b) 400 °C, and (c) 500 °C using a precursor solution with no acid.

545 °C with weight loss in TG-DTA [Fig. 3(c)] results from decarbonation and crystallization of $LiTaO_3$. The temperature discrepancy between 500 and 545 °C is due to the difference in the heating rate between the XRD sample (2 °C/min) and the TG-DTA sample (5 °C/min).

C. Characterization of $LiTaO_3$ films

To study the crystallization of $LiTaO_3$ films, precursor films were deposited on sapphire (001) substrates using the precursor solution with no acid and were heat-treated at various temperatures. Gel film heat-treated at 350 °C was amorphous [Fig. 6(a)] but began to crystallize at 400 °C [Fig. 6(b)]. $LiTaO_3$ films crystallized with the *c* axis preferentially perpendicular to the surface, though some other diffraction peaks are observed in the profile at 500 °C [Fig. 6(c)].

Figure 7 shows XRD profiles of $LiTaO_3$ films prepared on sapphire (001) substrates using precursor solution with formic acid. The crystallization temperature increases to 450 °C with formic acid. Crystallinity is reduced for precursor solution with acetic acid (Fig. 8).

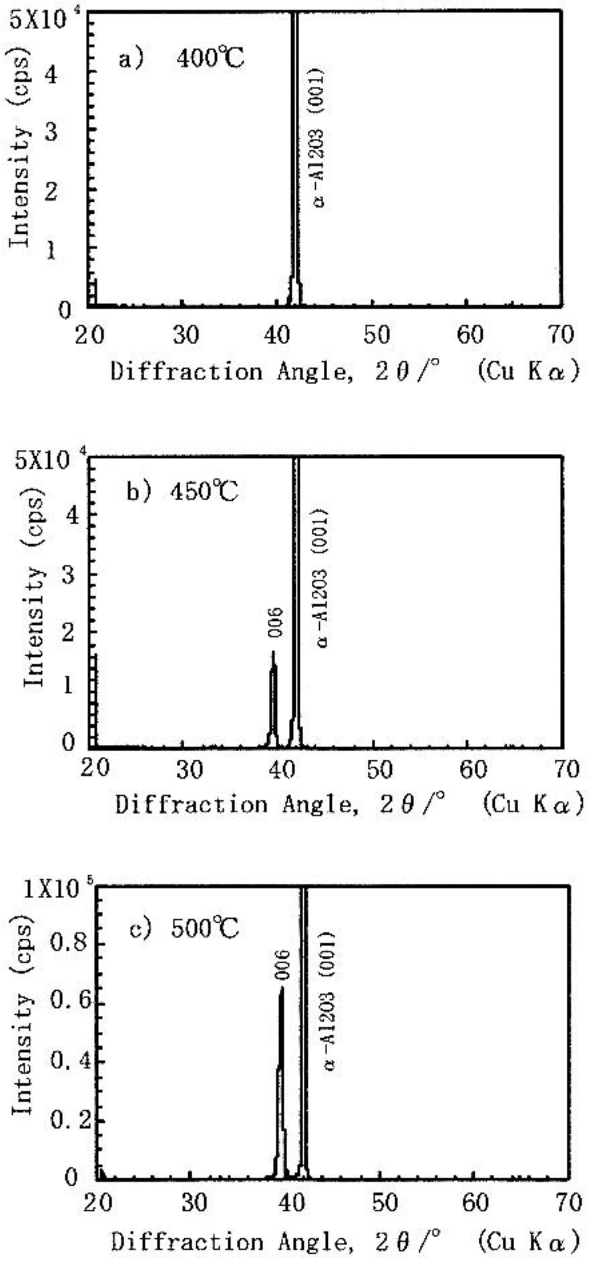

FIG. 7. XRD profiles of $LiTaO_3$ films prepared on sapphire (001) substrates at (a) 400 °C, (b) 450 °C, and (c) 500 °C using a precursor solution with formic acid.

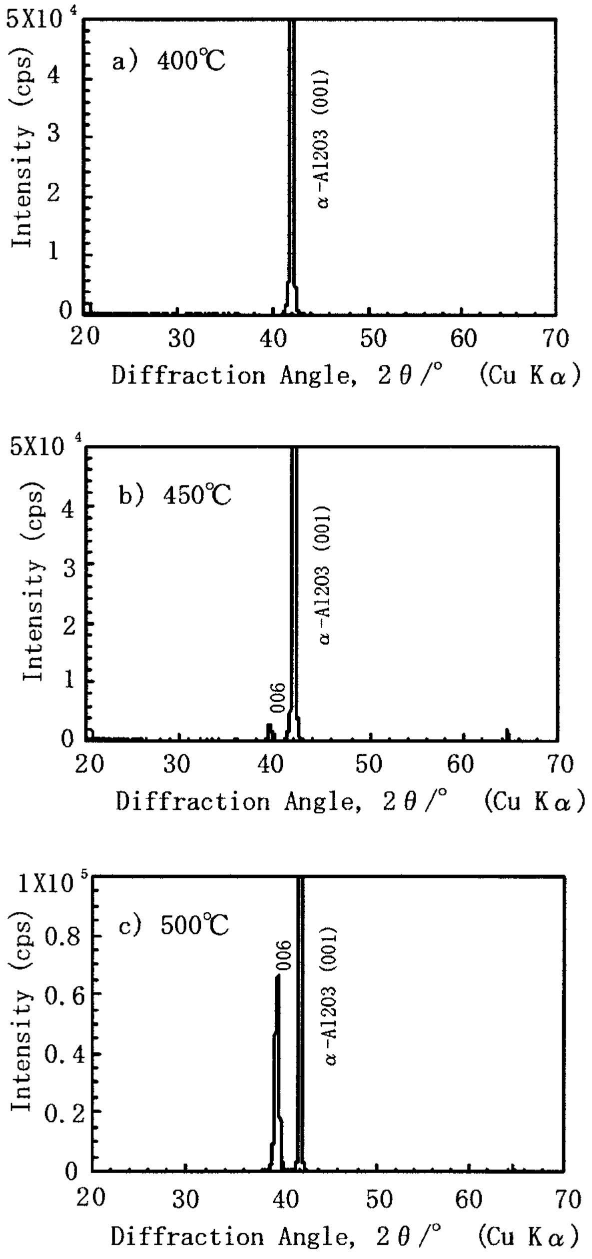

FIG. 8. XRD profiles of $LiTaO_3$ films prepared on sapphire (001) substrates at (a) 400 °C, (b) 450 °C, and (c) 500 °C using a precursor solution with acetic acid.

However, in both profiles, the $LiTaO_3$ films crystallized at 500 °C with a highly preferred orientation along the *c* axis.

The crystallographic orientation of $LiTaO_3$ films is possibly influenced by the arrangement of the oxygen atoms in the crystal structure of the sapphire (α–Al_2O_3) substrates. $LiTaO_3$ (*a,* 5.1530 Å; *c,* 13.755 Å) and α–Al_2O_3 (*a,* 4.758 Å; *c,* 12.991 Å) have the same rhombohedral crystal structure and lattice mismatch of 8.3% in the *a* axis and 5.9% in the *c* axis. In initiation of the crystallization process, some $LiTaO_3$ crystalline nuclei occur on sapphire substrates influenced by the oxygen arrangement in α–Al_2O_3. Crystal growth begins from the crystalline nuclei and proceeds to other particles. Precursor films prepared by the solution deposition method consist of dense nano-order particles at the early stage of high-temperature heat treatment. These precursor nanoparticles are transformed into $LiTaO_3$ nanoparticles due to the further heat treatment. The crystallographic orientation of each particle is therefore effected

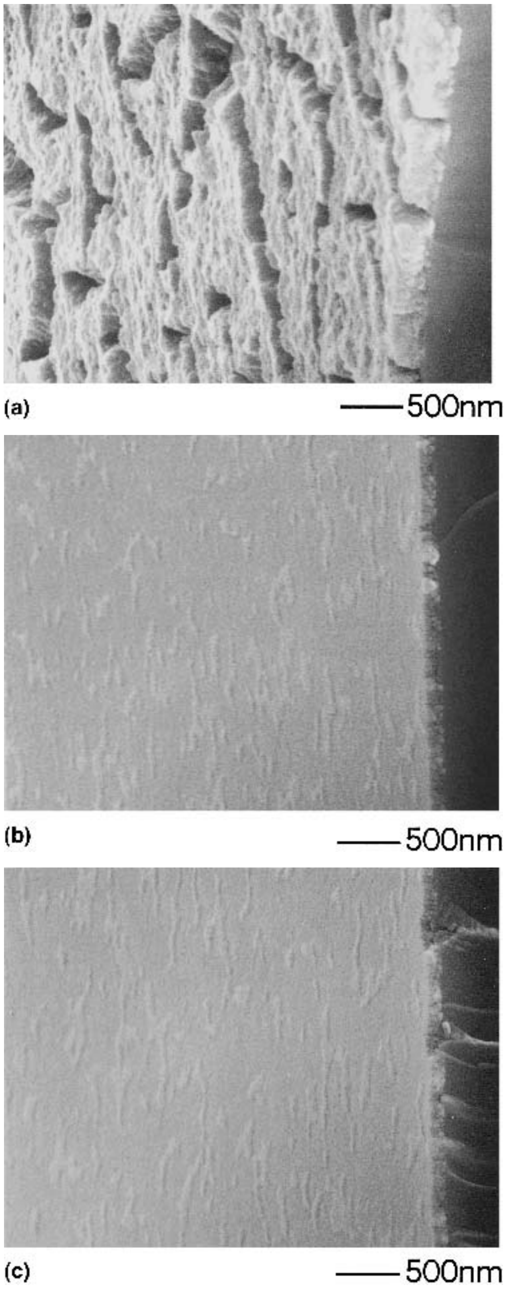

FIG. 9. SEM photographs of the surfaces of $LiTaO_3$ films prepared on sapphire (001) substrates at 500 °C using a precursor solution: (a) no acid; (b) with acetic acid; (c) with formic acid.

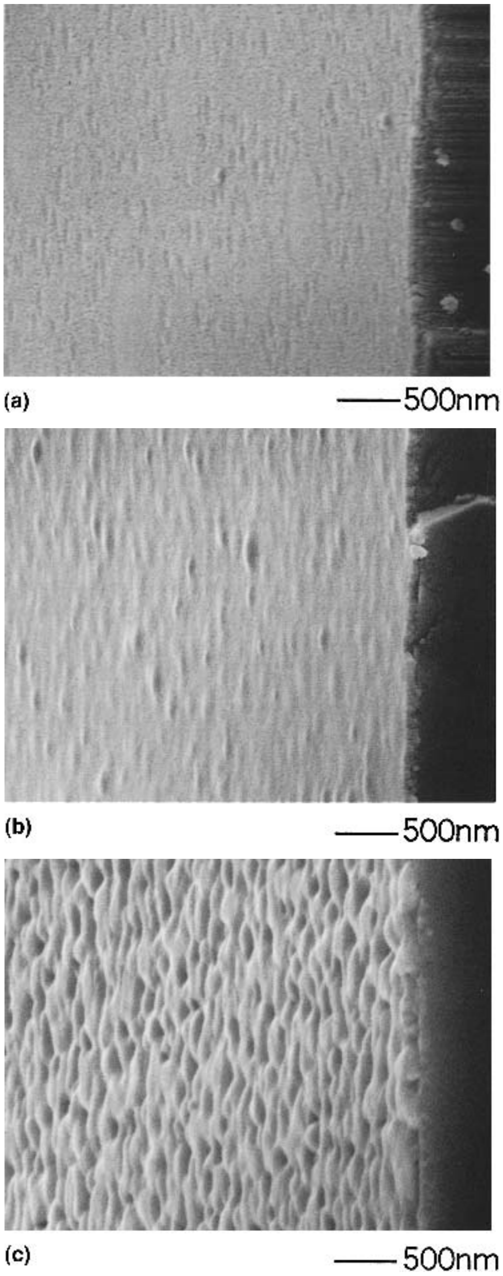

FIG. 10. SEM photographs of $LiTaO_3$ films heat-treated at (a) 450 °C, (b) 550 °C, and (c) 1000 °C using a precursor solution with formic acid.

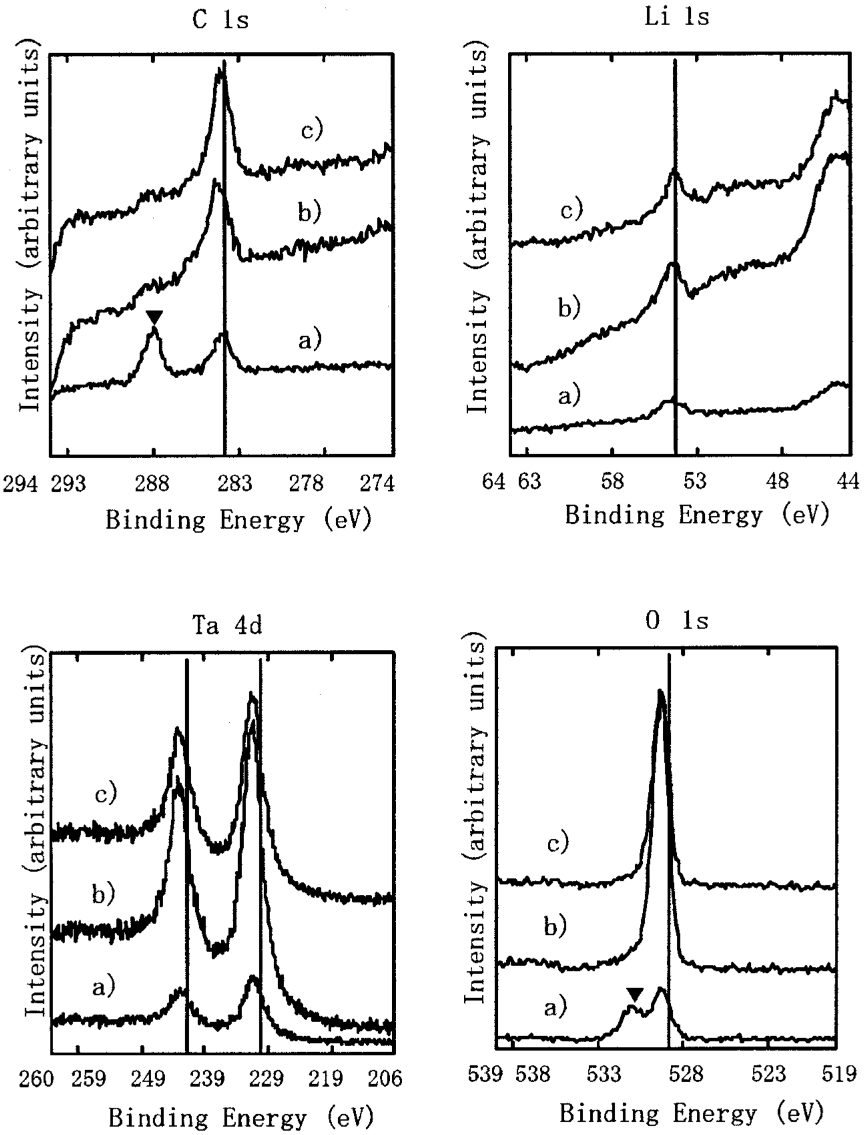

FIG. 11. XPS spectra of $LiTaO_3$ films prepared on sapphire (001) substrates at (a) 350 °C, (b) 550 °C, and (c) 1000 °C using a precursor solution with formic acid.

TABLE II. Composition analysis by XPS.[a]

		Composition (at.%)					
			C				
Sample	Preparation temp. (°C)	O	C–C	O = C–O	Ta	Li	Li/Ta
LT350	350	55	7.3	8.7	10	18	1.8
LT550	550	62	7.1	0	16	15	0.94
LT1000	1000	57	10	0	16	16	1.0

[a] $LiTaO_3$ films prepared on sapphire (001) substrates.

TABLE III. Refractive indices of $LiTaO_3$ films prepared on sapphire (001) substrates using precursor solution containing 2 molar ratio formic acid.[a]

Sample	Preparation temp. (°C)	Refractive index	Absorption coeff.
LT400	400	1.928	0.09
LT450	450	1.950	0.09
LT500	500	1.989	0.10
LT550	550	2.049	0.10
LT1000	1000	2.097	0

[a] $LiTaO_3$ films prepared on sapphire (001) substrates.

sequentially, resulting in a highly preferred orientation of the film according to the crystallographic orientation of the substrates.

Figure 9 shows SEM photographs of the surfaces of $LiTaO_3$ films prepared on sapphire (001) substrates at 500 °C using the precursor solution with no acid, with acetic acid, and with formic acid. The surface of the film prepared with no acid is extremely rough, with granular islands [Fig. 9(a)]. However, the films prepared with acetic acid and formic acid have very smooth surfaces [Figs. 9(b) and 9(c)].

Figure 10 shows SEM photographs of the surfaces of $LiTaO_3$ films prepared on sapphire (001) substrates at 450, 550, and 1000 °C, using the precursor solution with formic acid. The 450 °C film is free from cracks and pores and has a smooth surface [Fig. 10(a)]. Grain growth has taken place in the film heat-treated at 550 °C [Fig. 10(b)]. On the surface of the $LiTaO_3$ film heat-treated at 1000 °C, grains of size about 250 nm are clearly observed [Fig. 10(c)]. The thickness of the 550 and the 1000 °C films according to SEM is about 100 nm.

Figure 11 shows XPS spectra of $LiTaO_3$ films prepared on sapphire (001) substrates heat-treated at 350, 500, and 1000 °C using the precursor solution with formic acid. Differences are seen in C 1*s* and O 1*s* peaks of the XPS spectra of the film heat-treated at 350 °C, but there is no significant difference in the other Li 1*s* (55 eV) and Ta 4*d* (230, 242 eV) spectra. In C 1*s* spectra of the film heat-treated at 350 °C, the main peak is located at 284 eV, with a further peak at 288 eV. The 288 eV peak was still present in the spectra of film heat-treated at 450 °C but was absent at 500 °C (data not shown). This C 1*s* (288 eV) peak is attributed to C in the O=C–O group, which derives from the carboxylic groups in the precursor molecules.[21] Similarly, in the O 1*s* spectrum of the film heat-treated at 350 °C, a broad peak at 531 eV adjacent to the main peak (530 eV) is attributed to O in the O=C–O group.[21] Table II summarizes the results of composition analysis by XPS performed on the surface of the films. Films prepared at 350 °C had an excess of lithium and retained an O=C–O group at their surface. The films approached the stoichiometric composition on further heat treatment, since the composition must be stoichiometric when crystallization in the film is complete. The carbon content in the 550 °C film (7.1%) is low compared with that in the 1000 °C film (10%). Chemical analysis verifies that a crystallized film free from carboxylic residues can be prepared by heat treatment at 550 °C.

Table III shows refractive indices of $LiTaO_3$ films prepared on sapphire substrates using the precursor solution with formic acid. The refractive index of the film increases with heat-treatment temperature. The films prepared at 550 and 1000 °C have refractive indices 2.049 and 2.097, respectively, close to the value for Z-cut lithium tantalate single crystal (n_0: 2.176).[6] Nashimoto[12] reports that the refractive index of $LiTaO_3$ films prepared on sapphire (001) substrates by annealing at 700 °C is 1.982. Our 550 °C film has a higher refractive index, indicating that heat treatment of precursor films at 550 °C is adequate to process high-quality $LiTaO_3$ films. Refractive indices of $LiTaO_3$ films prepared using the precursor solution with acetic acid were also examined. However, reliable data were not obtained for the films prepared around 500 °C. The TG-DTA data [Fig. 3(b)] suggest that carbon is retained in the film prepared at 500–550 °C using the precursor solution with acetic acid; this may inhibit the ellipsometric measurements.

IV. CONCLUSIONS

Modification of a lithium and tantalum double alkoxide with formic acid is highly effective in preparing transparent films by spin coating. Highly oriented crystalline $LiTaO_3$ films were successfully prepared on sapphire substrates by heat treatment at temperatures above 450 °C. These crystalline films had a smooth surface with no cracks or pores. Heat treatment of precursor films at 550 °C is recommended to prepare high-quality $LiTaO_3$ films.

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