Characterization of LiNb$_{1-x}$Ta$_x$O$_3$ epitaxial films prepared by thermal plasma deposition

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Abstract

In this work, we prepared epitaxial lithium niobate-tantalate (LiNb$_{1-x}$Ta$_x$O$_3$) films on sapphire substrates by thermal plasma spray chemical vapor deposition (CVD). Mixtures of metalorganic solutions containing lithium-niobium and lithium-tantalum alkoxide precursors were used as liquid source materials. LiNb$_{0.5}$Ta$_{0.5}$O$_3$ films could achieve a (006) rocking curve full-width at half-maximum value of 0.15° which is comparable with those of LiNbO$_3$ and LiTaO$_3$ films grown by other conventional deposition techniques. Under optimized conditions, the interface between the films and the substrate showed only a small number of misfit dislocations, and twins and grains with different orientations could not be observed by transmission electron microscopy (TEM). The refractive indices were somewhat lower than those for bulk materials.

1. Introduction

Recently, the thermal plasma vapor deposition method has been applied by our group to the high growth rate and large-area deposition of high-quality films [1-4]. In case of YBa$_2$Cu$_3$O$_{7-x}$,
film deposition, nanometer-scale clusters were reported to play important roles in the high 
growth rate and good crystalline quality of the deposited films [1,2].

In this work, we report on the preparation and characterization of lithium niobate-tantalate
(LiNb$_{1-x}$Ta$_x$O$_3$, LNT) films on z-cut sapphire substrates by thermal plasma spray chemical 
vapor deposition (TPS CVD). LNT, being a solid solution of lithium niobate (LiNbO$_3$, LN) 
and lithium tantalate (LiTaO$_3$, LT), is a ferroelectric material with potentially good properties.
It is very attractive due to the possibility of varying the Ta content, $x$=Ta/(Nb+Ta), and consequently the physical properties, from those of LN to those of LT [5,6].

In previous works, we succeeded in preparing LiNb$_{1-x}$Ta$_x$O$_3$ films with $x$=0.3-0.7 by TPS 
CVD [3,4]. The c-axis orientation and the crystalline quality of LNT films were mainly 
discussed on the basis of the results of X-ray diffraction (XRD) analysis. However, structural 
and physical properties of the films, such as the surface morphology and optical properties, 
were not reported. In this work, the structural and optical properties of LNT films are 
discussed.

2. Experimental Procedure

The TPS CVD experimental setup consists of a radio-
frequency (RF) power supply, a plasma torch, a vacuum 
reaction chamber, a vacuum pump, a cooling water 
system, a liquid source feeder, and a substrate heater.
Figure 1 shows a photograph of the chamber used; the 
chamber’s door is opened, and the substrate holder and 
inductively coil heater are clearly seen in the center. The 
outline of TPS CVD was described elsewhere [3,4]. In 
brief, mixtures of metalorganic solutions containing 
lithium-niobium and lithium-tantalum alkoxide 
precursors were used as liquid source materials. A z-cut 
single-crystal sapphire was used as the substrate. The 
initial liquid mixture was fed into O$_2$/Ar thermal plasma as 
a mist through an injection probe. The mist of the sprayed

Fig. 1. The photograph of the 
chamber for TPSCVD.
mixture was evaporated and decomposed by an RF thermal plasma, quenched at the boundary between the plasma and the substrate, and then complex oxide film was deposited onto the substrate.

The crystallinity and film orientation were investigated using XRD analysis. The surface morphology was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The film thickness was measured by cross-sectional SEM. The microstructure between the film and the substrate was observed by transmission electron microscopy (TEM). Refractive indices were measured using spectroscopic ellipsometry.

3. Results and Discussion

Figure 2 shows the variation of (006) rocking curve full-width at half-maximum (FWHM) values as a function of liquid feeding rate (R). For this dependency, a series of LiNb0.5Ta0.5O3 films with similar thicknesses of 170-190nm was grown using different liquid feeding rates (R). The substrate temperature was maintained at 660±10°C and the liquid feeding rate was varied from 0.5 to 10ml/min. It is clearly seen that as R increases, the rocking curve FWHM decreases, reaching the minimum at R=6-8ml/min. At R>8ml/min, the film improvement appears to be limited by gas-phase nucleation and large particle embedment into the growing film under very high ad-species concentration. Thus, the FWHM values could reach 0.15° at R=6-8ml/min. This result is comparable with those for LN and LT films deposited by other vapor phase deposition techniques, such as metalorganic CVD, sputtering or pulsed laser deposition. Table 1 compares some of the data available in the literature [7-12] for several vapor phase deposition methods.

As reported in our previous work [4], the Ta/Nb ratios in the LNT films were very close to those used in the initial source solutions. This implies that the TPS CVD method enables us to

![Fig. 2. The effect of liquid feeding rate on (006) rocking curve FWHM value for LNT films.](image)
accurately control the chemical composition of the LNT films produced. Although the growth rates were relatively fast under optimized conditions, all of the films had very high c-axis orientation, implying good epitaxy. The c-axis-textured LNT films are expected to be useful for optical applications and acoustic applications [13]. At the feeding rate of R=10.0ml/min, however, a fraction of (110)- and (104)-oriented grains tended to appear, giving rise to randomly oriented LNT films. The growth rate at R=6-8ml/min was estimated to be up to approximately 6nm/s, which was significantly faster than those of other vapor phase methods.

LiNb$_{0.5}$Ta$_{0.5}$O$_3$ film with a (006) rocking curve FWHM value of 0.15° was prepared under optimal conditions, i.e., a substrate temperature of 660±10°C and R of 7ml/min. A cross-sectional TEM image of the film is shown in Figure 3 with a selected area diffraction (SAD) pattern of the film included. It revealed that the LNT film was grown epitaxially on the sapphire substrate.

Twinned grains could not be found in this film. The interface between the films and the substrate shows only a small number of misfit dislocations, which results from the lattice mismatch of approximately 8% and the large difference in thermal expansion coefficients [14]. At the same time, the films prepared at R=1ml/min and R= 10ml/min (non-optimal conditions) had twinned grains and a sufficient amount of the amorphous phase, resulting in much poorer crystallinity of the films. These TEM results are in good agreement with the XRD results shown in Fig. 2.

<table>
<thead>
<tr>
<th>Method</th>
<th>Film</th>
<th>FWHM [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCD $^{[7][8]}$</td>
<td>LN</td>
<td>0.15</td>
</tr>
<tr>
<td>Sputtering $^{[9][10]}$</td>
<td>LT</td>
<td>0.5</td>
</tr>
<tr>
<td>PLD $^{[11][12]}$</td>
<td>LN</td>
<td>0.15</td>
</tr>
<tr>
<td>TPS CVD</td>
<td>LNT</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 1. The comparison of the films by some other vapor deposition methods.

Fig. 3. TEM image of LiNb$_{0.5}$Ta$_{0.5}$O$_3$ film on sapphire substrate. SAD pattern is inserted. Feeding rate (R) [ml/min]

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Fig. 4. Variation of surface roughness as a function of liquid feeding rate.
ness of the surface was also determined by AFM. The films had somewhat irregular morphologies. As is well known, for the waveguide application, LNT films are required to have a smooth surface with rms roughness on the order of 2-3nm [15]. Figure 4 shows the variation of the surface roughness for LiNb_{0.5}Ta_{0.5}O_{3} films deposited at the same temperature and with similar thicknesses as a function of the liquid feeding rate. The roughness increased gradually when the liquid feeding rate rose. The causes of this behavior are not yet clear. Therefore, further experimental studies on the mechanisms of grain nucleation and growth are necessary in order to decrease surface roughness.

The refractive indices of LNT films with various x=Ta/(Ta+Nb) values were evaluated by spectroscopic ellipsometry techniques. LiNb_{0.5}Ta_{0.5}O_{3} films had refractive indices of 2.15-2.18 at a wavelength 632.8 nm. The data were calculated by Δ and Ψ in the ellipsometry measurement under the assumption that the films had a film adsorption coefficient of zero and taking the surface roughness into account. The assumed absorption coefficient factor affects the refractive index. Figure 5 exhibits the refractive indices of the LNT films with x=0.5, 0.6 and 0.7, which were prepared at R=2ml/min. These films had 170 nm thickness and (006) rocking curve FWHM values of approximately 0.30-0.35°. The refractive indices of the films decrease as the Ta content of the films increases, which agrees well with the date in the literature (at λ=632.8nm, LN and LT bulk materials have refractive indices of 2.287 and 2.188, respectively [14]). Although the refractive indices of LNT films were expected to be between those of LN and LT, the refractive indices in Fig. 5 are relatively low.

4. Conclusions

Epitaxial LiNb_{1-x}Ta_{x}O_{3} films with x=0.3-0.7 were prepared using thermal plasma spray CVD. Highly (001)-oriented LiNb_{1-x}Ta_{x}O_{3} films were fabricated on sapphire (001) substrates with deposition rates up to approximately 6nm/s, which was about 100 times as fast as those of most.

Fig. 5. Refractive indices of LNT films with x=0.5, 0.6, and 0.7.
conventional vapor phase deposition methods. LiNb$_{0.5}$Ta$_{0.5}$O$_3$ films achieved a (006) rocking curve full-width at half-maximum value of 0.15, which is comparable with those of LiNbO$_3$ and LiTaO$_3$ films grown by other conventional deposition techniques. The refractive indices measured by spectroscopic ellipsometry were equal to 2.14-2.16 at $\lambda=632.8$nm, which is somewhat lower compared with those of bulk materials. Further experimental studies on the mechanisms of grain nucleation and growth are necessary in order to reduce the surface roughness.

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References


