Effect of preannealing on the morphology of LiTaO₃ thin films prepared from the polymeric precursor method

A.H.M. González*, A.Z. Simões, M.A. Zaghete, J.A. Varela

Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos, Instituto de Química-UNESP/Araraquara, Rua Prof. Francisco Degni s/n, Quitandinha, Araraquara, PO Box 355, São Paulo, CEP 14801-970, Brazil

Received 11 February 2003; accepted 16 April 2003

Abstract

Lithium tantalate (LiTaO₃) thin films with 50:50 stoichiometry were deposited on silicon (100) substrates with two layers by the spin coating method using a polymeric organic solution. In order to study the influence of preannealing on the crystallinity, microstructure, grain size and roughness of the final film, two annealing procedures, “slow preannealing” and “fast preannealing,” were used. X-ray diffraction (XRD) results showed that LiTaO₃ thin films are polycrystalline. It was observed by scanning electron microscopy (SEM) that the thin film, which had been thermally treated using slow preannealing, was characterized by a dense and homogeneous surface. The atomic force microscopy (AFM) studies showed that the roughness is strongly influenced by preannealing temperature.

© 2003 Elsevier Inc. All rights reserved.

Keywords: LiTaO₃; Thin films; Polymeric precursor

1. Introduction

Lithium tantalate (LiTaO₃) is currently one of the most widely used electrooptic materials because of its characteristic ferroelectric, piezoelectric and pyroelectric properties [1]. LiTaO₃ has gained interest in similar fields due to its large NLO coefficients and photorefractive damage resistance [2]. Applications of LiTaO₃ include laser devices [3], pyroelectric infrared detectors [4], channel waveguides [5], periodically poled structures [6] and electrooptic devices [7]. Recently, the rapid development of integrated optics has stimulated the preparation of optical thin films, especially the optical waveguiding thin films that demand a consistency of lattice constant, crystal structure and a high difference of refractive index between the film and the substrate [8].

For miniaturizing and integrating the devices, different processing methods have been developed to prepare LiTaO₃ thin films. Techniques explored include chemical vapor deposition (CVD) [9], liquid phase epitaxy (LPE) [10], chemical beam epitaxy (MBE) [11], sol–gel [12], r.f. sputtering [13] and pulsed laser deposition (PLD) [8]. However, there have been no reports of LiTaO₃ film prepared by the polymeric precursor method.
The polymeric precursor method, also known as the Pechini method, is attractive because it allows high stoichiometric control as well as the possibility of working with aqueous solution. Moreover, it is a low-temperature process and a cost-effective method.

The aims of the present study were to prepare LiTaO₃ thin films from the polymeric precursor method and to study the effect of preannealing on the crystallization and microstructure of films deposited on Si (100).

2. Experimental details

Lithium and tantalum precursor solutions were initially prepared by Pechini’s method. This method involves dissolving the precursor salt in citric acid and ethylene glycol solution at 90 °C under continuous stirring. Lithium carbonate, Li₂CO₃ (Montedison) and tantalum ethoxide (Ta(OC₂H₅), Alfa Aesar) were the raw materials. A final solution with the atomic ratio of Li/Ta = 1 was obtained by mixing individual cations solutions, and the viscosity was adjusted at 20 cP by adding a controlled amount of water.

Silicon (100) substrates were cleaned with Extran solution (Merck) prior to use. LiTaO₃ films consisting of two layers were deposited on the substrates by the spin coating method at a rotation speed of 5000 rpm. Then, the thin films were thermally treated using two routes of annealing procedures: “slow preannealing” and “fast preannealing.” “Slow preannealing” consisted in two-step heat treatment: heating at a rate of 2 °C/min to 300 °C for a 1 h low temperature anneal and then heating at a rate of 5 °C/min to 600 °C for a 3 h anneal to promote crystallization.

Fig. 1. XRD patterns of two-layered LiTaO₃ thin films deposited on silicon (100) and thermally treated at 600 °C for 3 h using (a) slow preannealing and (b) fast preannealing.

Fig. 2. SEM micrographs of cross-section samples for the determination of film thickness for the two-layered LiTaO₃ thin films deposited on silicon (100) and thermally treated at 600 °C for 3 h using (a) slow preannealing and (b) fast preannealing.

Table 1

<table>
<thead>
<tr>
<th>Preannealing route</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>71</td>
<td>3.7</td>
<td>46</td>
</tr>
<tr>
<td>Fast</td>
<td>74</td>
<td>6.4</td>
<td>48</td>
</tr>
</tbody>
</table>
On the other hand, the LiTaO$_3$ thin film thermally treated using fast preannealing was heated directly at 300 °C in a hot plate to eliminate water, excess of ethylene glycol and polyesterification. Then, a fast heating rate of 20 °C/min up to 600 °C followed by a 3 h anneal was used to promote the crystallization.

The crystallization process of thin films was analyzed by X-ray diffraction (XRD) using X-ray diffractometer (Rigaku). The film surface morphol-

![AFM images](https://example.com/afm_images.png)

Fig. 3. AFM images of two-layered LiTaO$_3$ films deposited on silicon (100) and thermally treated at 600 °C for 3 h using slow preannealing: (a) two-dimensional image and (b) three-dimensional image.
ogy was examined using an atomic force microscope (AFM, Digital Instruments Nanoscope IIIA), whereas a scanning electron microscope (SEM, Zeiss 940 A) was used to determine the thickness of films.

3. Results and discussion

Fig. 1 shows XRD patterns of LiTaO$_3$ thin films heat treated at 600 °C for 3 h. No preferential orientation was observed indicating that the films

Fig. 4. AFM images of two-layered LiTaO$_3$ films deposited on silicon (100) and thermally treated at 600 °C for 3 h using fast preannealing: (a) two-dimensional image and (b) three-dimensional image.
are randomly oriented and polycrystalline. This result is not surprising because the silicon crystal structure and lattice parameters are significantly different when compared with the LiTaO₃, making epitaxial growth difficult. It can be seen that the preannealing route used during the thermal treatment has influence on the development of LiTaO₃ crystalline phase. For the film treated (Fig. 1b), the diffraction peaks are clearly evident. The decomposition of organic material is faster for the fast preannealing treatment, and this appears to enhance the crystallization of LiTaO₃ phase. Also, no secondary phases were observed in any of XRD patterns.

To determine the thickness of LiTaO₃ thin films, high magnification SEM observation (50,000 ×) was performed. Fig. 2 shows the transverse section of films thermally treated using different preannealing treatments. The thickness data of the films prepared by polymeric precursor method and deposited by spin coating are presented in Table 1. This table summarizes the thickness, roughness and grain size data of LiTaO₃ thin films prepared by polymeric precursor method and heat treated at 600 °C for 3 h using different routes of annealing.

Average grain size and surface roughness of the LiTaO₃ thin films were estimated using a contact mode AFM. The surface morphology and roughness analysis of LiTaO₃ thin film annealed at 600 °C for 3 h with slow heating rate and prepared by spin coating technique is illustrated in Fig. 3.

Fig. 4 shows the AFM micrographs of the surface LiTaO₃ film annealed at 600 °C for 3 h with the fast heating rate. The regions evaluated contained no cracks and also appeared to be relatively dense. As can be seen, the films have a granular structure of spherical grains with homogeneous grain size in the order of 46 nm for LiTaO₃ with slow heat treatment and 48 nm for fast heat treatment.

The roughness data, \( R_{MS} \), were obtained for an area of 1 × 1 μm. The thin film heat treated using fast rate of organic decomposition (Fig. 4b) exhibited a topography with greater roughness. It is speculated that the fast heating rate may promote grain growth and possible deterioration of the film surface. The change of the film surface topography with increased heating rate may be related to surface tension effects between film and substrate. It was observed that the preannealing route did not appear to affect the thickness and grain size. It is possible that deposition of only two layers may not be sufficient to verify this effect.

It should be pointed out that it is important to control the film roughness, particularly for optical applications. A highly densified film is expected to have a high refractive index close to the single crystal value.

4. Conclusions

Polycrystalline LiTaO₃ thin films deposited on silicon (100) substrates can be prepared from polymeric precursor method. It is very important to control the preannealing route to guarantee the formation of good-quality thin films. Thus, it appears that the “slow preannealing” process should be used for the heat treatment. Although the decomposition of organic material is faster when the fast preannealing treatment is used, this promotes an improvement in the crystallization of the film. This route, however, leads to the degradation of film surface and promotes somewhat greater roughness. In this way, the slow preannealing rate appears as an efficient way to obtain thin films with microstructure more homogeneous, crack free and denser.

Acknowledgements

The authors gratefully acknowledge the financial support of the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) proj. 01/06515-5.

References


