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Multi-layered $LiNbO_3$ films prepared by a polymeric precursor method

V. Bouquet[a,*], E.R. Leite[a], E. Longo[a], J.A. Varela[b], M. Guilloux Viry[c], A. Perrin[c]

[a]Department de Química, LIEC, UFSCar, PO Box 676, 13565-905 São Carlos-SP, Brazil
[b]Instituto de Química, UNESP, PO Box 355, 14801-970 Araraquara-SP, Brazil
[c]LCSIM, Univ. de Rennes 1, Av. du Général Leclerc, 35042 Rennes cedex, France

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Abstract

The polymeric precursor method was used to prepare multi-layered $LiNbO_3$ films. The overall process consists of preparing a coating solution from the Pechini process and the deposited film is subsequently heat-treated. Two-layered films were prepared by this process, onto (0001) sapphire substrates. Two different routes were investigated for the heat-treatment. The "amorphous route" consisted of performing, after each deposition, a pre-treatment at low temperature to eliminate the organic material. In this case, the crystallization heat-treatment was performed only after the two layers had been deposited. On the other hand, a process "layer-after-layer crystallization" was used. Both routes led to (000l) $LiNbO_3$ oriented films. However, only the film prepared by the "layer-after-layer crystallization" presented an epitaxial growth and a crack-free morphology. Moreover, the "layer-after-layer crystallization" process led to a film exhibiting the best optical properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Films; Microstructure-final; Niobates; Optical properties

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1. Introduction

In addition to its excellent ferroelectric and piezoelectric properties[1], lithium niobate ($LiNbO_3$: LN) has large electro-optic and nonlinear optical coefficients.[2] These characteristics make LN an attractive material for optoelectronic and acousto-optical applications such as waveguides, modulators, second harmonic generators and transducers.[3] Compared to bulk devices, thin films are of much interest because they allow the miniaturization of the devices and a monolithic integration with microelectronic or optoelectronic components. However, the film must present well-defined features such as an epitaxial growth and a minimal thickness estimated at 200–300 nm.[4]

In previous works, we have reported the preparation of LN thin films by the polymeric precursor method.[5,6] The overall process consists of preparing a coating solution by the Pechini process, based on metallic citrate polymerisation.[7] The precursor film is deposited by dip or spin coating and then heat treated to eliminate the organic material and synthesize the desired phase. The thickness of a LN film prepared by this process, from a coating solution of 10 cP, is typically 40 nm. A higher viscosity can be used for the coating solution in order to increase the film thickness but it can lead to the formation of cracks during the heat-treatment of the precursor film. Another route is the deposition of several layers. The aim of this present study is to determine the best heat-treatment process that must be used for multi-layered films prepared by the polymeric precursor method.

2. Experimental

The preparation of the coating solution is based on the Pechini process and has been reported in detail previously.[5] Lithium and niobium citrate solutions were prepared separately and then mixed together. The subsequent addition of ethylene glycol and the heating of the mixture led to a polymeric precursor solution, the viscosity of which was then adjusted by adding a controlled amount of H_2O.

Two-layered films were deposited by dip coating, from a solution of 10 cP viscosity, on (0001) sapphire substrates and then heat-treated under flowing oxygen.

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* Corresponding author. Tel.: +55-16-260-8214; fax: +55-16-260-82140.

E-mail address: p-bouquet@iris.ufscar.br (V. Bouquet).

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One heat-treatment process, called hereafter "layer-after-layer crystallization", consisted of performing, after each deposition, a pre-treatment at 300°C for 4h (to eliminate the organic material), followed by the crystallization treatment at 550°C for 1 h. The other heat-treatment process, called hereafter "amorphous route", consisted of performing, after each deposition, only the pre-treatment at 300°C for 4 h. The crystallization treatment at 550°C was performed only after the two layers had been deposited.

The structural characteristics of the films were investigated by X-ray diffraction (XRD) on a standard powder diffractometer (Siemens D5000) using CuK_α radiation. To study the in-plane orientation of the films, electron channeling patterns (ECP) were carried out with a JEOL JSM-6400 scanning electron microscope. The film surface morphology was observed with a field emission scanning electron microscope (FE-SEM) operating at 7 kV and by atomic force microscopy (AFM). The roughness values R_{RMS}, calculated by geometric average, were determined for observed area size of 1×1 μm. The optical transmittance measurements were carried out in the wavelength range of 200–800 nm using a Cary 5G spectrophotometer and the refractive index was determined with an ellipsometer (Jobin Yvon) using a He–Ne laser beam ($\lambda = 632.8$ nm).

3. Results and discussion

3.1. Structural characterizations

Fig. 1a shows the XRD patterns obtained for the films. The only peak characteristic of LN that can be observed is the (0006) reflection, indicating high c-axis orientation for both films. However, another peak is detected just beside the (0006) LN reflection for the film heat-treated by the "amorphous route". This additional peak cannot be indexed as a LN reflection or as a substrate peak and, thus, may be due to another phase. A similar peak was already observed for LN thin films grown on sapphire substrate by pulsed laser deposition and was ascribed, in that case, to the (−602) $LiNb_3O_8$ reflection.[8,9] The authors succeeded in eliminating this Li-depleted phase, which is undesirable because it is not ferroelectric, using Li-enriched targets[9] or increasing the oxygen flow during deposition.[8] In this present study, the "amorphous route" process may lead to the formation of the $LiNb_3O_8$ phase at the film-substrate interface, as a result of a possible difficulty for the oxygen flow to reach this region or/and due to a lithium loss occurring during the heat-treatment.

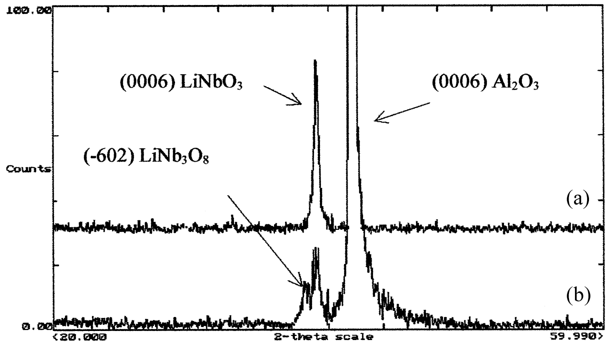

Fig. 1. XRD patterns for the films heat-treated by the process (a) layer-after-layer crystallization and (b) amorphous route.

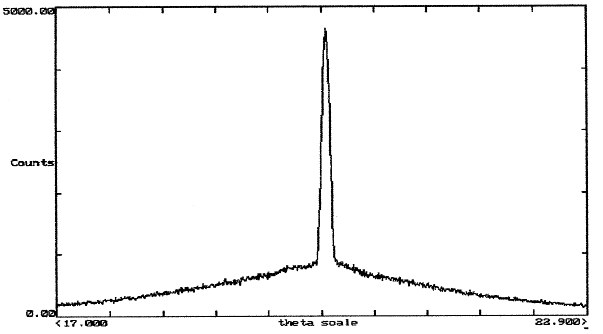

Fig. 2. Rocking curve obtained around the (0006) $LiNbO_3$ peak.

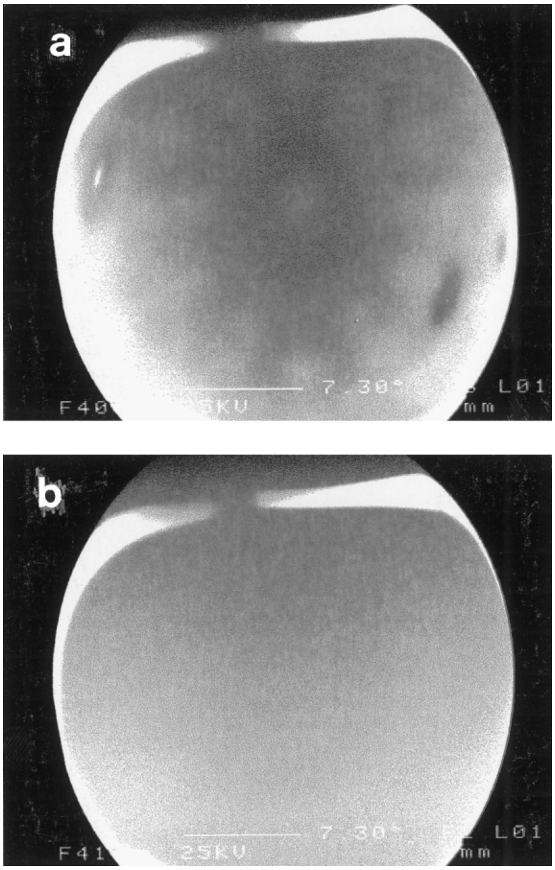

Fig. 3. Electron channelling patterns obtained for the films heat-treated by the process (a) layer-after-layer crystallization and (b) amorphous route.

The (0006) LN rocking curves obtained for both films presented similar profiles, illustrated in Fig. 2. A very narrow peak, with FWHM as low as 0.09°, can be observed, revealing the high degree of orientation. This value is in agreement with FWHM reported in literature.[10,11] Note that the rocking curves of the films present a broad tail, already observed by some authors for the same film/substrate couple[10] and also for other systems such as CeO_2/sapphire.[12] In the case of CeO_2 grown on sapphire by pulsed laser deposition, Castel et al.[12] suggested that the top surface had a very good crystallographic structure whereas the interface with the substrate was distorted. Nashimoto et al.[10] also proposed a “two-layer” structure in the case of LN thin films prepared by sol–gel, but considering the highly oriented layer near the film-substrate interface. In our case, it is difficult to conclude the nature of the structure without performing other experiments.

The electron channeling patterns (ECP) obtained for both films are illustrated in Fig. 3. As reported by Perrin et al.,[13] ECP is a very easy and fast method to characterize the in-plane orientation of crystalline films and consequently to determine the nature of the growth (epitaxial or textured). Well-defined stripes are observed for the film heat-treated by the process “layer-after-layer crystallization”, which reveals an epitaxial growth for this sample. On the other hand, no feature is visible for the film treated by the “amorphous route” which means that this sample is only textured (the film is disordered in its plane). Note that phi-scans performed on both films confirmed these results.

3.2. Surface morphology

The heat-treatment process also influenced the microstructure of the films, as shown in Figs. 4 and 5. The SEM micrographs (50,000×) show the presence of some small circular pores in both samples with an average ~12 nm diameter. Some cracks can be observed only for the film treated by the “amorphous route”, probably due to the fact that the crystallization treatment was performed only after the 2-layers had been deposited, which can lead to high strain in this sample. Both films present a smooth surface ($R_{RMS} < 2$ nm) but the sample heat-treated by the process “layer-after-layer crystallization” presents a surface more regular (Fig. 5).

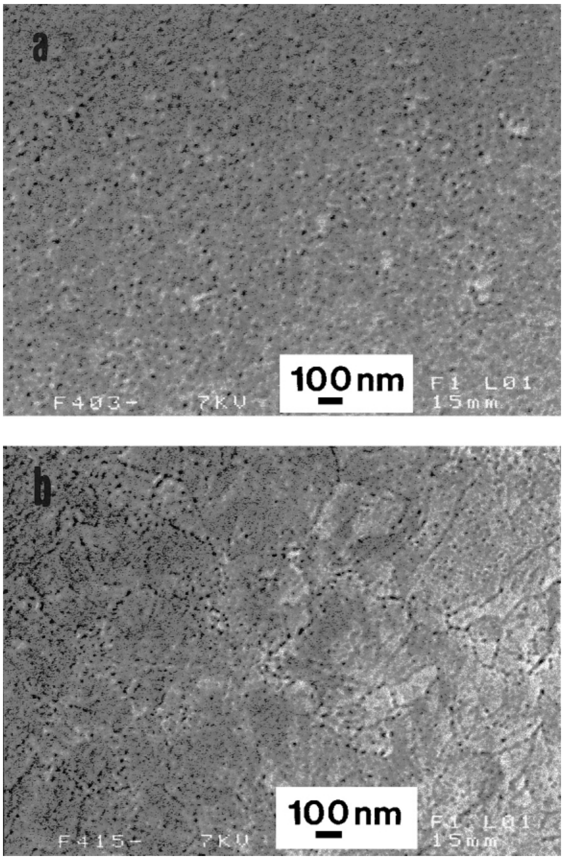

Fig. 4. FE-SEM micrographs of the films heat-treated by the process (a) layer-after-layer crystallization and (b) amorphous route.

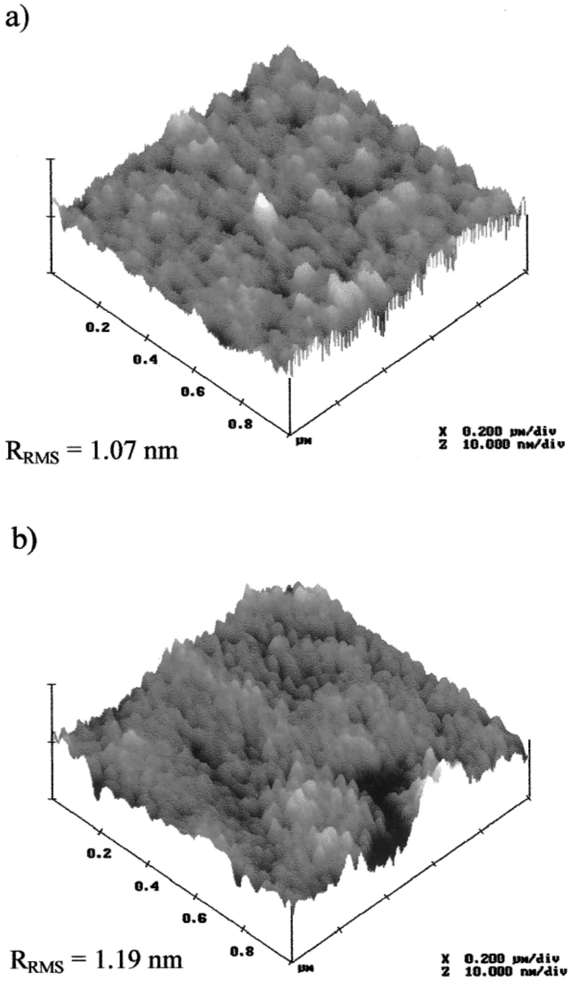

Fig. 5. AFM images of the films heat-treated by the process (a) layer-after-layer crystallization and (b) amorphous route.

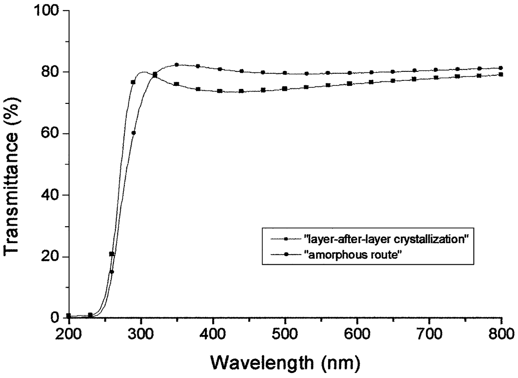

Fig. 6. UV-vis transmission spectra obtained for both films.

3.3. Optical properties

Fig. 6 shows the transmission spectra in the ultraviolet-visible region obtained for both films. From $\lambda = 250$ nm, the transmittance begins to increase and is superior to 70% at $\lambda = 350$ nm. Hur et al.[14] observed a drastic rise of the transmittance at a longer wavelength, about 300 nm, with LN films prepared by sol–gel. In the spectral region of 400–800 nm, the samples exhibit a high transmission, which confirms that the films are relatively homogeneous.

The films presented a refractive index of 2.24 and 2.21 for the "layer-after-layer crystallization" and for the "amorphous route" processes, respectively. These values are in agreement with those reported in literature for $LiNbO_3$.[8,10] Note that the refractive index is mainly influenced by the crystallinity and density of the film,[15] which explains the lower value obtained for the sample heat-treated by the "amorphous route".

4. Conclusion

Multi-layered $LiNbO_3$ thin films can be prepared by the polymeric precursor method but the process "layer-after-layer crystallization" must be used for the heat-treatment, instead of the "amorphous route". It avoids the formation of the $LiNb_3O_8$ phase (not ferroelectric), guarantees the epitaxial growth of the film and leads to a microstructure more homogeneous, crack-free and denser. Finally, the two-layered film prepared by this process "layer-after-layer crystallization" presented optical properties (transmittance spectrum and refractive index) close to those of a single $LiNbO_3$ crystal.

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