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Structural and Surface Morphology Characterizations of Oriented $LiNbO_3$ Thin Films Grown by Polymeric Precursor Method

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Abstract

Polymeric precursor solution was used to deposit $LiNbO_3$ thin films by dip coating on sapphire substrates. The effects of processing variables, such as heat treatment conditions and number of deposited layers, on crystallinity and morphology of the final films were investigated. X-ray diffraction patterns show the oriented growth of the films. The rocking curves, obtained around the (006) $LiNbO_3$ peak, revealed that the shape peak and the FWHM value were influenced by the processing variables. According to these parameters, some films presented very homogeneous dense and smooth surfaces, as shown by the SEM and AFM studies. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Research in the field of thin films is very intense due to the many advantages they offer, in particular, miniaturization, which is very attractive in microelectronic devices. Generally, crystalline thin films are required for the applications, and it is also very important to know the nature of the film growth. The film surface morphology (such as homogeneity, smoothness) is a very important parameter too, in particular in optical devices.

The aim of this work was to study the effects of processing variables (heat treatment conditions, layer number) on $LiNbO_3$ thin films grown on sapphire substrate by polymeric precursor method.[1] This ferroelectric material presents various physical properties which makes it very interesting for many applications such as waveguides, modulators and optical switches.[2,3]

2 Experimental

The films were deposited by dip coating from a polymeric precursor solution whose preparation is based on the Pechini process.[4] This one consists to chelate cations with citric acid in aqueous solution, and ethylene glycol is used to form an organic ester. The heating of the final mixture leads to polymerization and results in an homogeneous resin. To obtain the coating solution, the viscosity of the resin is adjusted by addition of a controlled amount of water. The preparation of the $LiNbO_3$ coating solution is reported in detail elsewhere.[1]

In the present study, different types of heat treatment, under oxygen flow, were performed in the precursor films, deposited on (0001) sapphire substrates, and are summarized in Table 1. Several heating rates for treatments at 550°C during one hour were considered, with or without pre-treatment at 300°C during 4 h. In all cases, the cooling rate used was $1°C\,min^{-1}$. Note that the role of a pre-treatment is to eliminate the organic material before synthesizing the crystalline phase at higher temperature. The heating and cooling rates used for the pre-treatment were $1°C\,min^{-1}$. In the case of multilayer films (Table 1, films 6 and 7), the heat treatment was performed after each deposition.

Structural characterizations were realized by X-ray diffraction, using 'θ–2θ' configuration and rocking curves around the (006) $LiNbO_3$ peak.

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The full width at half-maximum (FWHM) values were determined by curve adjustment using a Gaussian approximation. The surface morphology was studied by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The roughness values R_{RMS}, mathematically calculated by geometric average (RMS = 'Root Mean Square'), were determinated for observed area size of $1 \times 1\ \mu m$.

3 Results and Discussion

3.1 Effects of temperature

Figure 1 illustrates the 'θ–2θ patterns obtained for films 1 and 2. The very intense peak observed at $2\theta = 41{\cdot}68°$ corresponds to (006) sapphire. The other peaks of relatively low intensity at $2\theta = 20{\cdot}5°$, $37{\cdot}5°$ and $39{\cdot}9°$ are also ascribed to the substrate. Finally, the peak observed at $2\theta = 38{\cdot}9°$ corresponds to the (006) $LiNbO_3$. No other $LiNbO_3$ characteristic peak appeared in the patterns, which means that the films are oriented, with the same substrate orientation. Note that the $LiNbO_3$ peak intensity increased with the temperature.

Table 1. Heat treatment conditions

Film	*Pre-treatment*	*Heat treatment*	*Heating rate*	*Layer number*
1	—	550°C/1 h	1°C min^{-1}	1
2	—	650°C/1 h	1°C min^{-1}	1
3	—	550°C/1 h	5°C min^{-1}	1
4	300°C/4 h	550°C/1 h	5°C min^{-1}	1
5	300°C/4 h	550°C/1 h	30°C min^{-1}	2
6	—	550°C/1 h	1°C min^{-1}	2
7	—	550°C/1 h	1°C min^{-1}	4

According to the temperature, the experimental rocking curves presented different shapes as shown in Fig. 2(a) and (b). The rocking curve of film 1 seems to be composed of two peaks, a very fine one and a broader one. However, the curve adjustment took in consideration only the broad peak and led to a FWHM value of 1·73°. Note that this value is in agreement with FWHM reported in literature.[5]

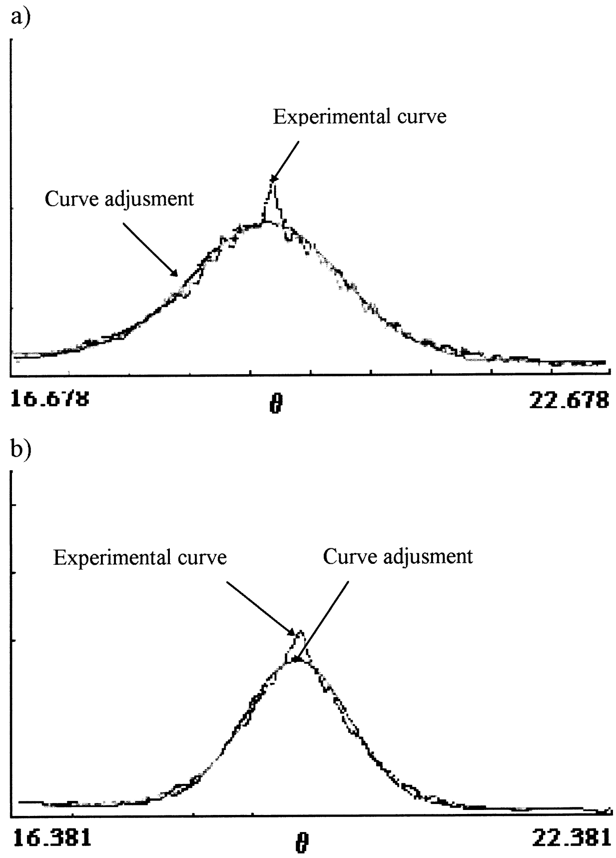


Fig. 2. Rocking curves for films crystallized using heating rate of 1°C min^{-1}: (a) film 1 heat treated at 550°C/1 h and (b) film 2 heat treated at 650°C/1 h.

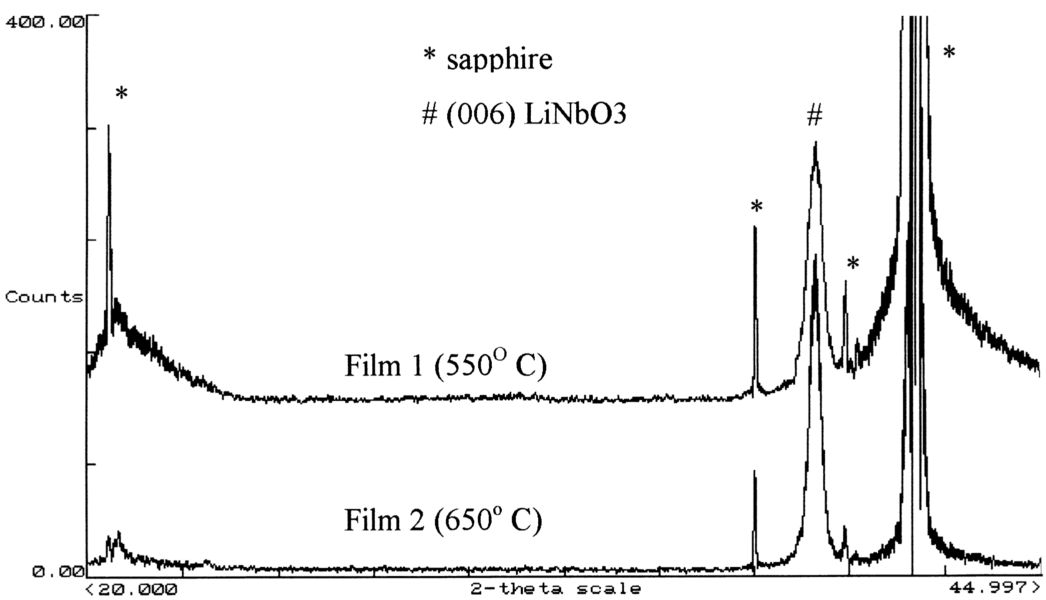
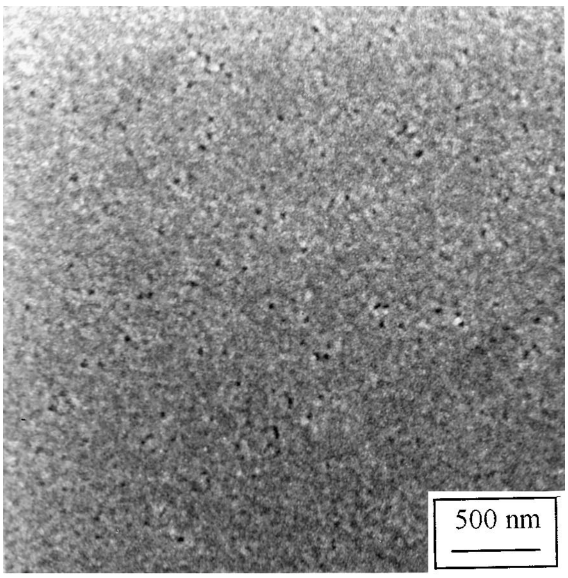


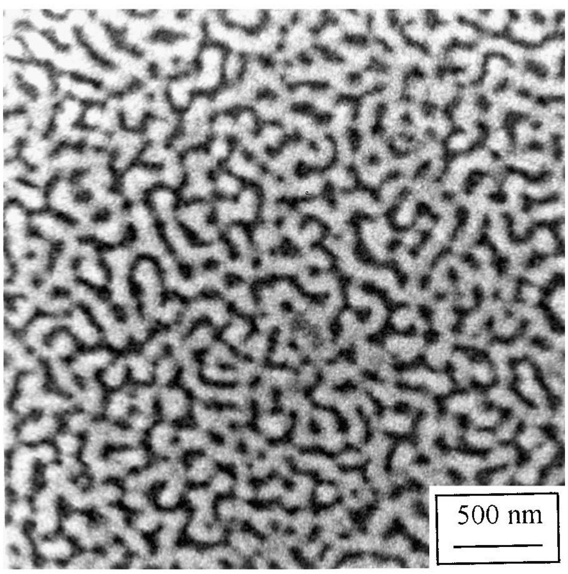
Fig. 1. XRD patterns 'θ–2θ' of films treated at different temperatures.

The presence of the fine peak, which FWHM can be estimated to 0.2°, is probably due to a region presenting a better orientation and may be localized at the interface substrate-film. For treatment at higher temperature (film 2), it can be observed only one peak which FWHM is 1.24°, a value inferior to the one obtained for the broad peak in the previous case.

Figure 3(a) and (b) illustrate SEM micrographs of both the samples. As can be observed, film 1 presents a surface without cracks, very homogeneous and relatively dense (not many pores are observed). On the other hand, the sample 2 presents a heterogeneous microstructure and the film is not continuous any more. The higher temperature (650°C) caused grain growth which deteriorated the film, surface. Moreover, AFM images [Fig. 4(a) and (b)] revealed that the film treated at 650°C is rougher.



(a)



(b)

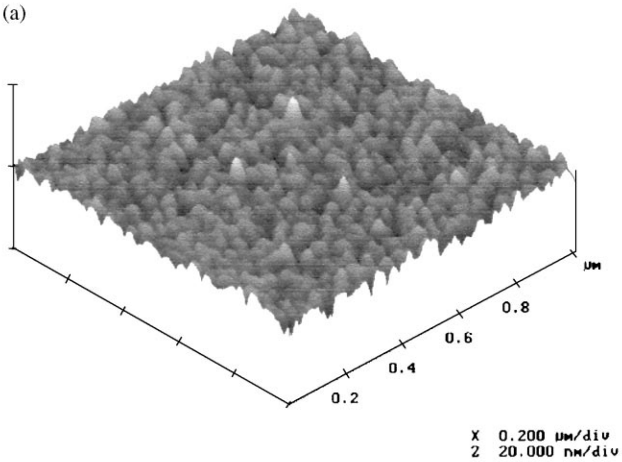
Fig. 3. SEM micrographs of (a) film 1 heat treated at 550°C/1 h and (b) film 2 heat treated at 650°C/1 h.

All results (R_{RMS} and FWHM values) obtained for both films are summarized in Table 2. These results also showed that an increase of the temperature improved the film crystallinity but in exchange, led to an increase of the roughness, due to grain growth.

3.2 Effects of heating rate

As shown in Fig. 5, the only peak characteristic of $LiNbO_3$ observed in the θ–2θ patterns for films

(a)



(b)

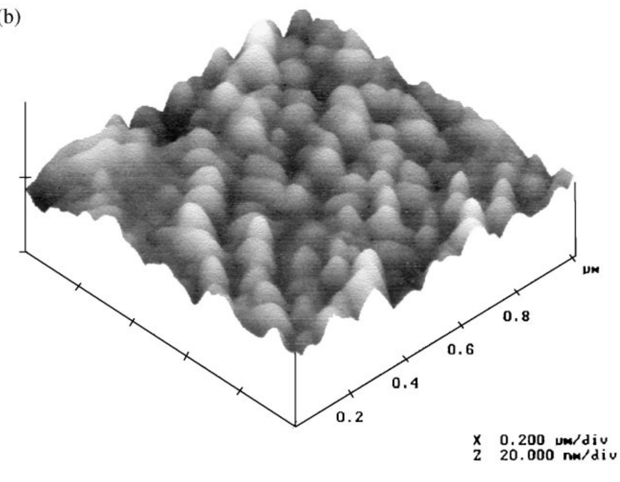


Fig. 4. AFM images of (a) film 1 heat at 550°C/1 h and (b) film 2 heat treated at 650°C/1 h.

Table 2. FWHM and R_{RMS} values obtained for the different films

Film	*FWHM*	*Roughness* R_{RMS} *(nm)*
1	1·73°	1·38
2	1·24°	1·93
3	0·09° 2·17	0·90
4	2·11°	0·63
5	0·14° 2·09°	1·02
6	2·09°	0·92
7	1·86°	0·65

3, 4 and 5, is (006). Consequently, these samples are oriented. Note that the peak intensity decreased when the heating rate increased.

The rocking curve of film 4 presented the same shape as the one obtained for film 1. In the case of the samples 3 and 5, two peaks were also observed but the fine peak appeared more defined and more intense for these films and consequently it has been taken in consideration by the curve adjustment. The different FWHM values obtained are summarized in Table 2.

The SEM micrographs revealed crack-free and very homogeneous surfaces as shown in Fig. 6 (film 3). Note that this film appeared denser than film 1. Moreover, the R_{RMS} values obtained are very low (Table 2), in particular for sample 4.

All these results showed that, for the same type of heat treatment, the heating rate influenced, in particular, the rocking curve shape. Increasing the heating rate, the fine peak appeared more defined, which means that the region of highly oriented growth increased. With a fast heating rate, the different crystallites took immediately the substrate orientation without having time to orientate in another direction. On the other hand, for heat treatments with the same heating rate, the film roughness decreased when a pre-treatment is realized.

3.3 Effects of layer number

The two and four layer films are oriented as show Fig. 7. Note that the (006) $LiNbO_3$ peak intensity is proportional to the number of layers.

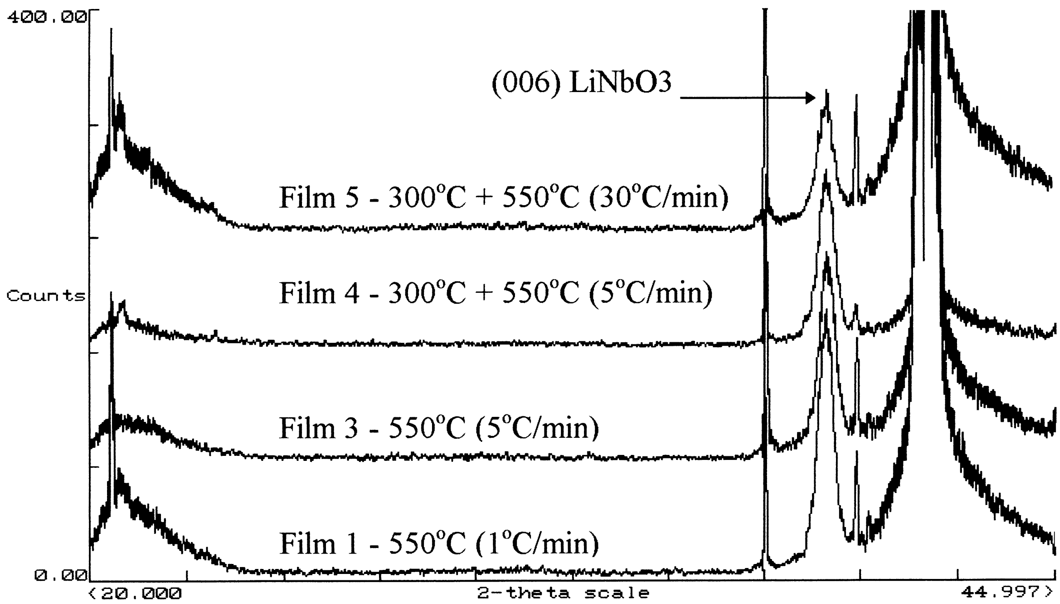


Fig. 5. XRD pattern 'θ–2θ' of films treated with different types of heat treatment and heating 650°C/1 h.

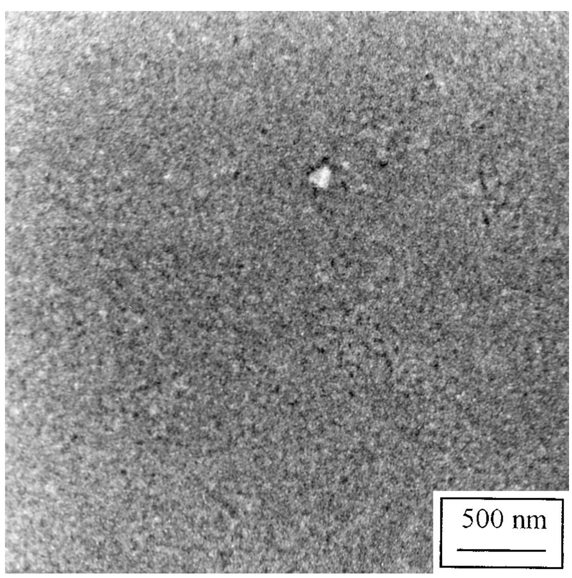


Fig. 6. SEM micrograph of the film crystallized using heating rate of 5°C min^{-1} and heat treated at 550°C/1 h (film 3).

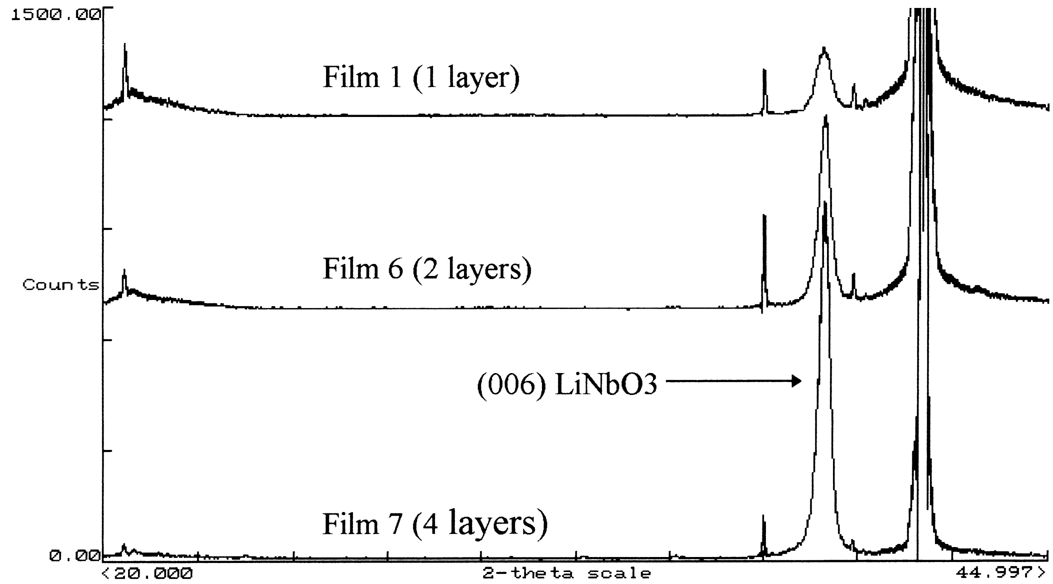


Fig. 7. XRD patterns 'θ–2θ' of films constituted of one, two, and four layers.

The rocking curves presented only one peak with FWHM values which are larger than the value obtained for the one layer film treated in the same conditions (film 1, Table 2). The two and four layer film surfaces appeared homogeneous and dense and a smooth texture was observed by AFM (Table 2). Note that R_{RMS} values obtained are smaller than the one observed for film 1.

The increase of FWHM values observed with increasing the number of layers may be explained the following way: added layers probably leads to increased stresses during the heat treatment, due to the larger thickness of the film, and makes the crystallites orientation more difficult. However, each layer added can 'fill' the possible holes present in the previous layers, leading to a final smooth surface.

4 Conclusion

This work showed that oriented $LiNbO_3$ thin films can be obtained by polymeric precursor method. The orientation quality, determinated by FWHM values, and the morphology surface were influenced by the heat treatment conditions and number of layers. To obtain highly oriented growth and very smooth, dense and homogeneous films, the use of a fast heating rate and a pre–heating treatment seems to be necessary. Moreover, multilayer films, which are not only oriented but also present a very smooth texture, were obtained.

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