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Synthesis, microstructural and optical characterization of $LiNbO_3$ thin films deposited by aerosol assisted chemical vapor deposition

Síntesis, caracterización micro-estructural y óptica de películas delgadas de $LiNbO_3$ depositadas mediante depósito químico de vapor asistido por aerosol

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ABSTRACT

This work reports the synthesis, micro-structural characterization and optical properties of lithium niobate ($LiNbO_3$) thin films deposited by aerosol assisted chemical vapor deposition (AACVD) on silicon substrates. The films deposited were polycrystalline, uniform, dense, non-light scattering and firmly adhered to the substrate. This was deduced from high resolution electron microscopy studies and spectral reflectance measurements. The films were not epitaxial; however, they are considered smooth enough to be employed in optical waveguide applications, since their roughness is very low compared to the wavelength of the utilizable radiation.

RESUMEN

En este trabajo se reporta la síntesis, la caracterización micro-estructural y las propiedades ópticas de películas delgadas de niobato de litio ($LiNbO_3$) depositadas sobre sustratos de silicio mediante el método de depósito químico de vapor asistido por aerosol (AACVD). Las películas depositadas fueron poli-cristalinas, uniformes, densas, no dispersoras de luz y firmemente adheridas al sustrato. Esto se dedujo de la realización de estudios de microscopía electrónica de alta resolución y de mediciones de espectros de reflectancia óptica. Las películas no fueron epitaxiales, sin embargo, se considera que son suficientemente lisas para ser empleadas en aplicaciones de guías de onda ópticas, dado que la rugosidad es muy baja comparada con la longitud de onda de la radiación con posibilidades de uso.

INTRODUCTION

Lithium niobate ($LiNbO_3$) is an extraordinary piezoelectric material which exhibits very strong electro-optic behavior and high photoconductive effects connected to high optical non-linearity. Some of these properties of $LiNbO_3$ have been used in a large variety of optical devices including electro-optic modulators, frequency doublers, multiplexors and guided wave optics, among other applications of great interest (Arizmendi, 2004; Bornand, Huet, Bardeau, Chateigner & Papet, 2002; Suarez & Lifante, 2009; Wooten *et al.*, 2000). The structural, electrical and optical properties of $LiNbO_3$ have been studied intensively since they were available in large single crystals synthesized by the Czochralski technique in the mid 1960´s (Nassau, Levinstein & Loiacono, 1966). $LiNbO_3$ typically presents a large concentration of intrinsic defects and can also be doped with a lot of different impurities. After controlling both the intrinsic defects and type of doping, it is possible to obtain a wide range of response variation (Arizmendi, 2004). Consequently, $LiNbO_3$ has been the object of extensive research in order to know, understand, change and tailor its electrical and optical properties which could

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Palabras clave:
Películas delgadas de niobato de litio; depósito químico de vapor asistido por aerosol; material piezoeléctrico.

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be required in a specific application. In fact, $LiNbO_3$ could be one of the silicon substitutes in the areas of optoelectronics and photonics in the following years (Arizmendi, 2004). Nevertheless, thin films of this ferroelectric oxide have attracted a great deal of interest recently, mainly because it is not an expensive starting material for useful devices with potential use in the telecommunications area. On the other hand the confinement of electromagnetic waves expected in thin films is greater than in single crystals, which could yield for example electro-optic modulators with a lower drive voltage and higher band width (Arizmendi, 2004). Moreover, the growth procedure of bulk $LiNbO_3$ single crystals is more complex than the one required to synthesize thin films of the same material. Growth of bulk single crystals by methods such as Czochralski, for example, requires high temperatures (over 1300 K), while the synthesis of films by any usual method requires temperatures around 600 K – 800 K. This provides an advantage to films over bulk samples. Therefore, development of new growing methods that permit to control the stoichiometry and provide a low temperature processing to obtain $LiNbO_3$ thin films are required (Kao, Chen, Yang, Chen, Hsieh & Yu, 2008).

Literature reports several deposition techniques of $LiNbO_3$ thin films employed as sol-gel (Kao *et al.*, 2008; Nashimoto, Cima, McIntyre & Rhine, 1995; Takahashi *et al.*, 2004; Terabe, Iyi, Kitamura & Kimura, 1995; Terabe, Kurashima, Gruverman, Matsui, Iyi & Kitamura, 1997), metalorganic chemical vapor deposition (MOCVD) (Akiyama, Shitanaka, Murakami, Shin, Yoshida & Imaishi, 2007; Lee & Feigelson, 1998), pulsed laser deposition (PLD) (Kilburger, Millon, Di Bin, Boulle, Guinebretière & Di Bin, 2010; Wang, Ye, Li & Zhao, 2007), radio-frequency magnetron sputtering (RFMS) (Bornand & Papet, 2003; Yilmaz, 2003), and ultrasonic spray pyrolysis (USP) process (Bornand *et al.*, 2002; Bornand & Papet, 2003). The structural and morphological characterization of samples prepared, and requirements to obtain thin films of $LiNbO_3$ have been shown in those reports. In fact, the use of hybrid techniques to obtain good samples of films of this material have been reported (Bornand *et al.*, 2002; Bornand & Papet, 2003). However, there are no reports about the synthesis of high optical quality $LiNbO_3$ thin films by using exclusively the aerosol assisted chemical vapor deposition (AACVD) method (Yilmaz, 2003).

The aim of this work is to report the synthesis of high optical quality thin films of $LiNbO_3$ obtained by AACVD, and its morphological, micro-structural and optical characterization.

Experimental details

This work reports the synthesis, micro-structural and optical characterization of $LiNbO_3$ thin films deposited by the AACVD method onto (0 0 1) oriented silicon substrates (1.5 cm^2 × 1.5 cm^2). We have considered silicon substrates because nowadays a lot of optoelectronic devices are developed directly on silicon wafers. In consequence, it is relevant to determine the structural and optical properties of $LiNbO_3$ thin films deposited onto silicon plates.

First, we optimized the deposition conditions to obtain $LiNbO_3$ layers with a thickness of about 135 nm, and with a very low surface roughness (~10 nm). A deposition spraying setup described in figure 1 which is based on a pyrolytic system described elsewhere (Paraguay, Estrada, Acosta, Andrade & Miki-Yoshida, 1999) has also been used. The deposition system uses an ultrasonic nebulizer (a) working at 2.4 MHz to generate the aerosol that was conveyed by a carrier gas and directed towards the substrate by a fixed nozzle (c). The substrate is directly in contact with a metallic plate heated at the selected temperature. The carrier gas flow, the distance from the nozzle to the substrate and the time of deposition were also varied in order to determine the optimum deposition conditions. The starting solutions were dilutions of niobium ethoxide and lithium acetylacetonate in methanol employing concentrations of 0.02 mol dm^{-3} and 0.01 mol dm^{-3}, respectively. The films were prepared at different temperatures between 623 K and 773 K. After deposition, a heat treatment was performed in order to stabilize the microstructure and enhance the crystallinity of the samples. The films were annealed during five hours at 900 K using linear ramps (1 K min^{-1}) for both the heating and cooling stage to avoid any damage by thermal shock. Table 1 summarizes the principal synthesis conditions of the analyzed samples.

The surface morphology and films thickness were studied by field emission scanning electron microscope (SEM) using a JEOL JSM-7401F operated at 2 kV. The uniformity, compactness and continuity of thin films layer were determined by observing the surface morphology both before and after thermal treatment on the samples. The thickness of annealed samples was measured by observing the cross section of the films. Bright field images in scanning transmission electron microscopy (STEM) were used to analyze the microstructure of films. The crystalline phases present in the films were determined by grazing incidende x-ray diffraction (GIXRD) patterns in a PANalytical X-Pert system using Cu Kα radiation (λ = 0.15418 nm) at 40 keV

and 35 mA. The grazing incidence angle was fixed at 0.5° and scanning angle 2θ was varied from 20° to 85° at 0.1° min^{-1} step. AFM images were obtained using a multimode Nanoscope IVa SPM device (Veeco) recorded in tapping mode using commercial n-type standard silicon cantilever with a spring constant of 20 N/m. Surface root mean square (RMS) roughness was estimated from measurements of several atomic force microscopy (AFM) images on the films.

On the other hand, the optical properties in the range between 250 nm and 1100 nm corresponding to the energy range from 1 eV to 5 eV were determined from specular reflectance (at an incidence angle less than 7° from the normal to the surface) spectra employing a UV-Vis-NIR double beam Perkin Elmer lambda 35 spectrophotometer. From these measurements, the absorption coefficient as a function of photon energy of films deposited on silicon substrates was obtained.

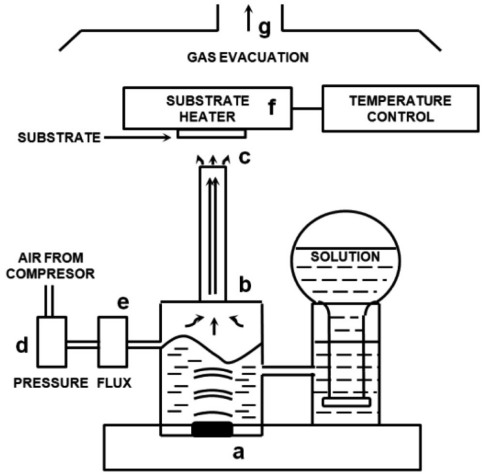

Figure 1. Simplified scheme of the deposition system used for the growth of $LiNbO_3$ thin films in the present work. From bottom to top: *a*) ultrasonic nebulizer; *b*) spraying chamber; *c*) fixed nozzle; *d*) pressure regulator; *e*) flow meter; *f*) overhead hot-plate; *g*) gas evacuation.
Source: Authors own elaboration.

Table 1.
Principal parameters of films analyzed.

Sample name	Deposition rate (nm/hr)	Thickness (nm)	Roughness RMS (nm)	Grain size (nm)
LNTFS-1	117	117 ± 5	11.3 ± 0.8	131
LNTFS-2	67	135 ± 5	16.8 ± 0.8	125
LNTFS-3	110	110 ± 5	13.9 ± 0.8	403

Source: Authors own elaboration.

RESULTS AND DISCUSSION

Structural properties

A large number of films were prepared by the AACVD method onto silicon (0 0 1) substrates 1.5 cm^2 × 1.5 cm^2 in order to determine the optimal deposition conditions. The best samples were obtained at 653 K using a deposition time of about 1 h. After deposition, the films were annealed during 5 h at 900 K, determined as the optimum annealing temperature because at this temperature the crystallinity of samples was remarkably increased. In general the films were polycrystalline, uniform and non-light scattering. Some micrographs of representative samples deposited on silicon substrates are shown below.

Figure 2(a) shows a secondary electron SEM micrograph of the surface morphology, and figure 2(b) shows a backscattered electron SEM micrograph of the cross section of sample LNTFS-1 deposited on silicon (0 0 1) substrate after a heat treatment at 900 K. The film was smooth, dense and firmly adhered to the substrate. The average grain size of this sample was equal to 131 nm which was determined from a statistical study of several SEM micrographs of the surface of the film. As it can be seen from figure 2(b) the thickness of this film was around 117 nm.

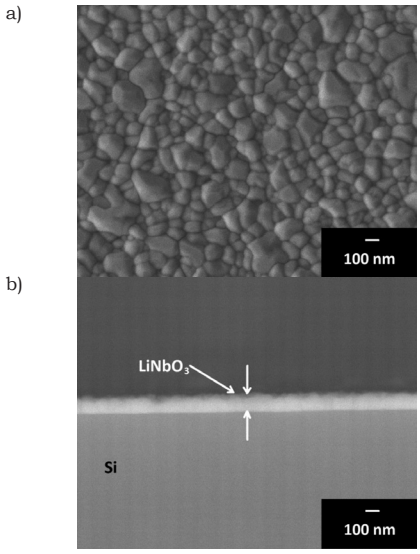

Figure 2. *a*) Secondary electron SEM micrograph of surface; and *b*) backscattered electron SEM micrograph of cross section of $LiNbO_3$ (LNTFS-1) based thin film deposited at 653 K onto a silicon substrate with a deposition time of 1 h, after heat treatment at 900 K during 5 h.
Source: Authors own elaboration.

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The polycrystalline nature of sample LNTFS-1 was determined from its GIXRD patterns showed in figure 3(a). The crystalline structure of the film corresponded to $LiNbO_3$ hexagonal phase (Joint Committee on Powder Diffraction Standards, Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, 2006. card 01-070-8451). The roughness of film LNTFS-1 was measured by AFM in tapping mode. The RMS value of roughness of film LNTFS-1 was 11.3 nm ± 0.8 nm which was determined from several AFM micrographs such as the one showed in figure 3(b) plotted with WSXM software (Horcas, Fernández, Gómez-Rodríguez, Colchero, Gómez-Herrero & Baro, 2007). In spite of the film was not epitaxial, due to the synthesis method, we consider that it is smooth enough to be employed in optical waveguide applications, since its roughness is very low compared to the wavelength of the radiation. GIXRD results were confirmed by high resolution transmission electron microscopy studies. Figure 4(a) shows a bright field high resolution TEM image near the interface between Si substrate and $LiNbO_3$ film. In the central region of this figure a sharp interface of amorphous native silicon oxide is shown. The lattice fringes measurement in figure 4(a) was consistent with the interplanar distance of the (0 1 2) plane of lithium niobate hexagonal phase. Additionally, the analyses of the selected area electron diffraction patterns also confirm the existence of the hexagonal phase as shown in figure 4(b).

Optical properties

In order to determine the optical properties of the thin films deposited on silicon substrates, the reflectance spectra of optimized films were obtained. These measurements were carried out at near normal incidence and room temperature.

Figure 5 (a) shows the variation of measured optical reflectance as a function of photon energy in the range from 1 eV to 4.13 eV (300 nm to 1100 nm) of sample LNTFS-1 deposited on silicon substrate. From this measurement, the refractive index n of sample LNTFS-1 as a function of wavelength λ of radiation was determined using TFcalc 3.5.14 software, assuming known data of the refractive index and the extinction coefficient of the substrate:

$$n(\lambda) = \left(3.1547 + \frac{1.1040 \times 10^{-1}\, \lambda^{2}}{\lambda^{2} - 8.633 \times 10^{-2}} \right)^{1/2}. \qquad (1)$$

Figure 5 (b) shows the magnitude of the ordinary refractive index, given by equation (1), of sample LNTFS-1 deposited onto silicon substrate plotted as a function of photon energy. It was observed that the magnitude of the refractive index (~1.995) of the sample LNTFS-1 was slightly lower than the value reported in the literature for thin films and bulk samples of $LiNbO_3$ at 633 nm wavelength corresponding to a photon energy of 1.96 eV (Kirkby & Florea, 2002; Takahashi *et al.*, 2004; Wang *et al.*, 2007). As shown in figure 5 (b), the refractive index of sample LNTFS-1 has the expected behavior showing a continuous increase as the photon energy increases. The slightly lower value of the refractive index can be attributed to the marginally lower density of the film compared to that of dense bulk samples.

Next, the extinction coefficient k was calculated using its well-known relation with the refractive index n, and the reflectance R at normal incidence, given by:

$$k = \left(\frac{R\,(n+1)^2 - (n-1)^2}{1-R} \right)^{1/2}. \qquad (2)$$

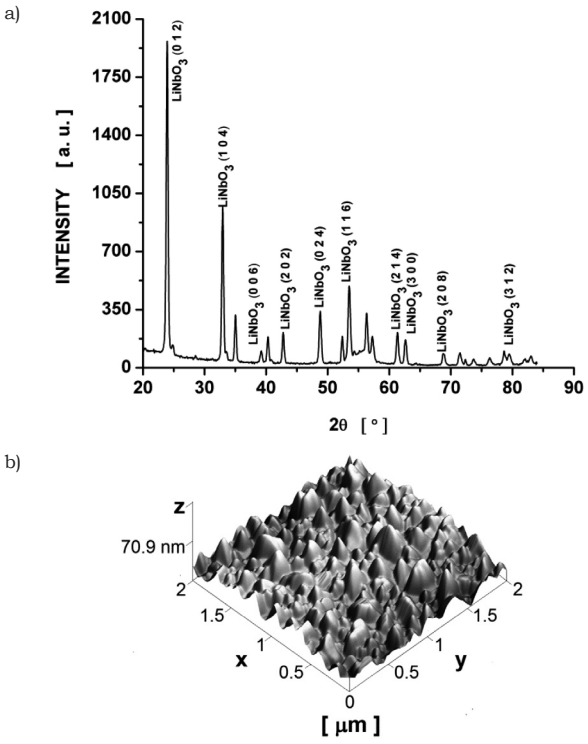

Figure 3. *a*) GIXRD pattern; and *b*) atomic force micrograph of $LiNbO_3$ (LNTFS-1) based film deposited at 653 K onto a silicon substrate (0 0 1) with a deposition time of 1 h, after heat treatment at 900 K during 5 h. Scale x → 0.5 μm per graduation; y → 0.5 μm per graduation; z → 73.1 nm per graduation.
Source: Authors own elaboration.

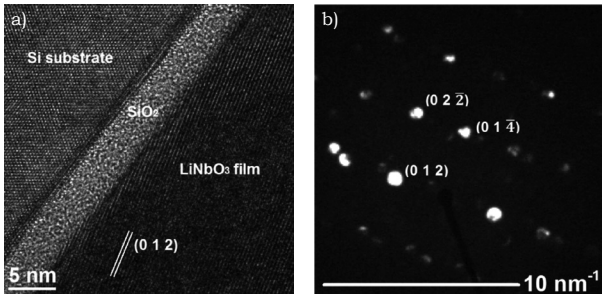

Figure 4. *a*) Bright field high resolution image of the interface between Si substrate and LNTFS-1 film; *b*) selected area electron diffraction pattern showing the hexagonal phase of $LiNbO_3$ film LNTFS-1.
Source: Authors own elaboration.

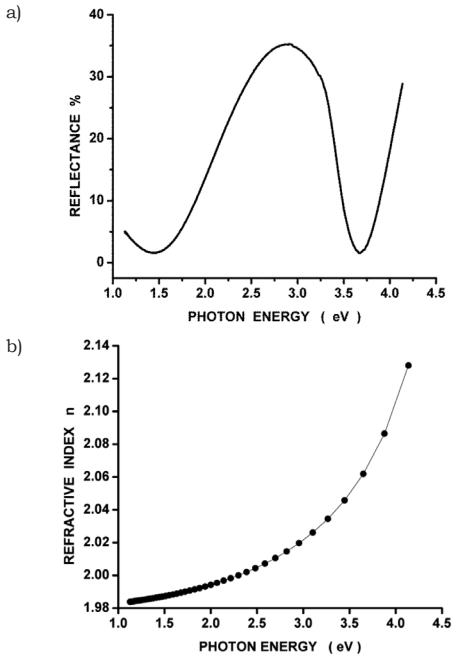

Figure 5. *a*) Reflectance as a function of photon energy of $LiNbO_3$ (LNTFS-1) thin film deposited at 653 K on a silicon substrate (0 0 1) with a deposition time of 1 h, after heat treatment at 900 K during 5 h; *b*) ordinary refractive index •-•-• as a function of photon energy of $LiNbO_3$ (LNTFS-1) thin film.
Source: Authors own elaboration.

Finally, the absorption coefficient was calculated from the extinction coefficient obtained from the equation (2). Figure 6 shows the absorption coefficient as a function of photon energy in the range from 1 eV to 4.13 eV (300 nm to 1100 nm) of sample LNTFS-1 deposited on silicon substrate.

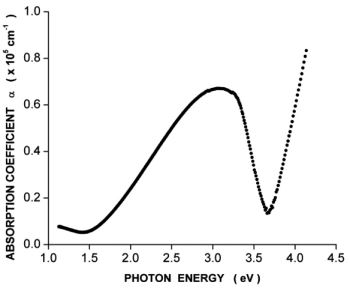

Figure 6. Absorption coefficient α as a function of photon energy of thin film LNTFS-1
Source: Authors own elaboration.

CONCLUSIONS

High uniformity, non-light scattering and highly transparent polycrystalline $LiNbO_3$ based thin films were deposited by the AACVD method onto silicon substrates. The optimum substrate temperature to obtain high quality films with high uniformity and a typical thickness around a few hundred nanometers was 653 K. The deposition rates attained with our deposition setup were around 100 nm•h. The crystallinity of the deposited films increased remarkably after the five hours heat treatment at a temperature of 900 K. The $LiNbO_3$ films were smooth, dense and firmly adhered to the substrate. Nevertheless, in spite of the non-epitaxial method used to synthesize the films we think that they are smooth enough to be employed in optical waveguide applications, since roughness is very low (~10 nm) compared to the wavelength of the radiation.

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REFERENCES

Akiyama, Y., Shitanaka, K., Murakami, H., Shin, Y., Yoshida, M. & Imaishi, N. (2007). Epitaxial growth of lithium niobate film using metalorganic chemical vapor deposition. *Thin Solid Films, 515*, 4975-4979.

Arizmendi, L. (2004). Photonic applications of lithium niobate crystals. *Physical Status Solidi* (a), *201*, 253-283.

ISSN 0188-6266

Bornand, V., Huet, I., Bardeau, J. F., Chateigner, D. & Papet, P. (2002). An alternative route for the synthesis of oriented $LiNbO_3$ thin films. *Integrated Ferroelectrics, 43*, 51-64.

Bornand, V. & Papet, P. (2003). Growth technologies and studies of ferroelectric thin films. Application to LiTaO3 and $LiNbO_3$ materials. *Ferroelectrics, 288,* 187-197.

Horcas, I., Fernández, R., Gómez-Rodríguez, J. M., Colchero, J., Gómez-Herrero, J. & Baro, A. M. (2007). *Review of Scientific Instruments*, *78,* 013705.

International Center for Diffraction Data (2006). *Joint Committee on Powder Diffraction Standards - Powder Diffraction File card 01-070- 8451*, Swarthmore, PA.

Kao, M. C., Chen, H. Z., Yang, S. L., Chen, Y. C., Hsieh, P. T. & Yu, C. C. (2008). Pyroelectric Ta-modified $LiNbO_3$ thin films and devices for thermal infrared detection. *Thin Solid Films, 516*(16), 5518-5522.

Kilburger, S., Millon, E., Di Bin, P., Boulle, A., Guinebretière, R. & Di Bin, C. (2010). Properties of $LiNbO_3$ based heterostructures grown by pulsed-laser deposition for optical waveguiding application. *Thin Solid Films, 518*(16), 4654-4657.

Kirkby, C. J. G. & Florea, C. (2002). Dispersion properties of Lithium Niobate and tables. In K. K. Wong (Ed.), *Properties of lithium niobate* (pp. 119-128). London: INSPEC/IEEE.

Lee, S. Y. & Feigelson, R. S. (1998). Reduced optical losses in MOCVD grown lithium niobate thin films on sapphire by controlling nucleation density. *Journal of Crystal Growth, 186*(4), 594-606.

Nashimoto, K., Cima, M. J., McIntyre, P. C. & Rhine, W. E. (1995). Microstructure development of sol-gel derived epitaxial $LiNbO_3$ thin films. *Journal of Materials Research, 10*(10), 2564-2572.

Nassau, K., Levinstein, H. J. & Loiacono, G. M. (1966). Ferroelectric lithium niobate. 2. Preparation of single domain crystals. *Journal of Physics and Chemistry of Solids, 27*(6-7), 989–996.

Paraguay, F., Estrada, D. W., Acosta, L. D. R., Andrade, E. & Miki-Yoshida, M. (1999). Growth, structure and optical characterization of high quality ZnO thin films obtained by spray pyrolysis. *Thin Solid Films, 350*(1-2), 192-202.

Suarez, I. & Lifante, G. (2009). Detailed study of the two steps for fabricating $LiNbO_3$:Zn optical waveguides. *Applied Physics Express, 2*(2), 022202-1 022202-3.

Takahashi, M., Yamauchi, K., Yagi, T., Nishiwaki, A., Wakita, K., Ohnishi, N., Hotta, K. & Sahashi, I. (2004). Preparation and characterization of high-quality stoichiometric $LiNbO_3$ thick films prepared by the sol–gel method. *Thin Solid Films, 458*(1-2), 108-113.

Terabe, K., Iyi, N., Kitamura, K. & Kimura, S. (1995). Effect of substrates on the crystallinity and morphology of sol-gel-derived epitaxial $LiNbO_3$ films. *Journal of Materials Research, 10*(7), 1779-1783.

Terabe, K., Kurashima, K., Gruverman, A., Matsui, Y., Iyi, N. & Kitamura, K. (1997). Transmission electron microscopy study on epitaxial growth behaviors of sol-gel-derived $LiNbO_3$ films. *Journal of Crystal Growth, 179*(3-4), 577-584.

Wang, X., Ye, Z., Li, G. & Zhao, B. (2007). Influence of substrate temperature on the growth and optical waveguide properties of oriented $LiNbO_3$ thin films. *Journal of Crystal Growth, 306*(1), 62-67.

Wooten, E. L., Kissa, K. M., Yi-Yan, A., Murphy, E. J., Lafaw, D. A., Hallemeier, P. F., Maack, D., Attanasio, D. V., Fritz, D. J., McBrien, G. J. & Bossi, D. E. (2000). A review of lithium niobate modulators for fiber-optic communications systems. *IEEE Journal of Selected Topics in Quantum Electronics, 6*(1), 69-82.

Yilmaz, S. (2003). Optical properties of $LiNbO_3$ thin films. *Ferroelectrics, 193*(1), 169-176.