Journal of the European Ceramic Society 24 (2004) 1607–1613
www.elsevier.com/locate/jeurceramsoc

Influence of oxygen atmosphere on crystallization and properties of $LiNbO_3$ thin films

A.Z. Simões[a,*], M.A. Zaghete[a], B.D. Stojanovic[a,b], A.H. Gonzalez[a], C.S. Riccardi[a], M. Cantoni[c], J.A. Varela[a]

[a]*Chemistry Institute, Department of Chemistry–Physics, UNESP C.P. 355, CEP 14801-970 Araraquara-SP, Brazil*
[b]*Center for Multidisciplinary Studies University of Belgrade, Yugoslavia*
[c]*Swiss Federal Institute of Technology, CH- 1015 Lausanne, Switzerland*

Abstract

Thin films of lithium niobate were deposited on the $Pt/Ti/SiO_2$ (111) substrates by spin coating from the polymeric precursor method (Pechini process). Annealing in static air and oxygen atmosphere was performed at 500 °C for 3 h. The films obtained were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The dielectric constant and dissipation factor were measured in frequency region from 10 Hz to 10 MHz. Electrical characterization of the films pointed to ferroelectricity via hysteresis loop. The influence of oxygen atmosphere on crystallization, morphology and properties of $LiNbO_3$ thin films is discussed.

Keywords: Ferroelectric Properties; Films; Niobates; X-ray methods

1. Introduction

Lithium niobate ($LiNbO_3$) is an important ferroelectric material because of its excellent piezoelectrical, electrooptical, pyroelectrical and photo-refractive properties.[1] In the recent past, thin films of lithium niobate have received considerable attention for potential electrical, optical and acoustic applications. The majority of these efforts were directed towards obtaining good quality films for integrated optics applications. Conventionally, polycrystalline ferroelectric thin films were grown on Pt-coated Si substrates. It was observed that the interaction which occurred on film/Pt interfaces degraded the film performance substantially.[2] Various deposition techniques such as epitaxial growth by melting, chemical vapor deposition, liquid phase epitaxy, sputtering and sol–gel have been attempted.[3–6] By conventional processing $LiNbO_3$ was prepared by calcination of mixture of Li_2O and Nb_2O_5 powders.[7] This process requires high sintering temperature and causes the Li_2O loss. In recent years sol–gel processing and co-precipitation method have become popular for producing ceramic materials with improved compositional homogeneity and with lower sintering temperature.[8,9] Although the sol–gel process utilizes expensive precursors and depends on a critical drying process, the co-precipitation process is limited by cation solutions with similar solubility constants. On the other hand, Pechini's process which employs complexing of cations in an organic media, makes use of low cost precursors and results in a homogeneous ion distribution at molecular level.[10] Due to the formation of a polyester resin during the synthesis, no segregation of cations was observed during the thermal decomposition of organic material. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with the high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments).

It has been reported that the crystallization process is affected by variables such as composition (Li/Nb ratio), substrate, annealing temperature, atmosphere, drying condition.[11] It was noticed that the oxygen atmosphere has a prominent influence on crystallization process of $LiNbO_3$. The effect of oxygen atmosphere on the crystallization of the $LiNbO_3$ phase is to prevent the volatility of Li_2O, control the stoichiometry and improve the electric properties of the film.[12] The random oriented

---

* Corresponding author. Tel.: +55-201-6600; fax: +55-16-222-7932.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00453-9

$LiNbO_3$ thin films have potential for many applications including: optical waveguides, frequency doublers and holographic storage system. The main reason is that in random or epitaxial films the grain boundaries are more homogeneous resulting in films with low roughness and low stress induced by the lattice mismatch and improving the yielding of this material for optical applications. On the other hand, polycrystalline lithium niobate films also has important technological applications for sensors, piezoelectric and pyroelectric devices due to its dielectric properties.

The main objective of this work is to verify the effect of oxygen atmosphere on crystallization, morphology and properties of $LiNbO_3$ thin films deposited by a spin-coating process using a polymeric solution.[13]

2. Experimental procedure

Lithium carbonate (Li_2CO_3—Montedison) and niobium oxide (Nb_2O_5—Aldrich) were used as purchased without further purification. The precursor solutions of lithium and niobium were prepared by adding the raw materials into ethylene glycol and citric acid with heating and stirring at 90 °C. The viscosity of the solution was adjusted at 20 cPs by the addition of water and measured using a Brookfield viscosimeter. To obtain homogeneous and crack-free films of $LiNbO_3$, the precursor were deposited by spin-coating on the (111) Si/Ti/Pt substrates at a spinning speed of 3000 rpm. The heating rate was 1 °C/min up to 300 and 5 °C/min from 300 to 500 °C. Films with eight layers were prepared through annealing of each layer at 500 °C in static air and oxygen atmosphere. Phase analysis of the films was performed at room temperature by X-ray diffraction using a Bragg-Brentano diffractometer (Siemens D-500) and CuK_α radiation. Microstructural characterization of the films was carried out using transmission electron microscopy (TEM) with a Philips CM-20 unit. The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) observing the transversal section of films. The results of thickness obtained by SEM represent an average value of three measurements. In order to study the electrical properties of $LiNbO_3$ film, circular gold electrodes of $2.83.10^{-3}$ cm^2 area were sputtered on the surface of the annealed film using a shadow mask. The relative dielectric constant ϵ_r, dissipation factor tan δ and resistance were measured versus frequency using an impedance analyser (model 4194 A, Hewlett Packard). The ferroelectric behaviour of the films was investigated by determining the remanent polarization and coercitive field in a computer controlled standardized ferroelectric test system (Radiant technology 66A).

For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

It is well known that the films' properties are significantly affected by the crystallographic orientation of thin film which is controlled by the orientation of the underlying layer, film thickness and atmosphere flow. It is important to control the thickness of the layer due to strong influences on the grain size, dielectric and ferroelectric properties. It was observed that for thinner films interfacial "dead layers" could appear at the interface of films and substrate. These layers possess poor dielectric properties influencing the performance of the device.[14] These dead layers are originated from oxygen interdiffusion, chemical reaction, or structural defects at the interfaces and could be suppressed with higher thickness of films ranging from 200 to 300 nm. This critical thickness could be obtained by multi layer depositions. To obtain films with desired thickness ranging from 200 to 300 nm it was necessary to deposit eight layers on the substrate.

The X-ray diffraction data obtained of $LiNbO_3$ thin films deposited with eight layers on platinum coated silicon (111) substrates and annealed at 500 °C for 3 h in static air and oxygen atmosphere are shown in Fig. 1. The peaks located at $2\theta = 23.8°$, 32.8°, 34.9° and 46.4° corresponds to polycrystalline $LiNbO_3$ phase for films annealed in static air and oxygen atmosphere (Fig. 1). The characteristic peak for platinum coated silicon (111) substrates was observed in the range $38° < 2\theta < 41°$. In investigated cases, no preferential orientation was observed for $LiNbO_3$ films deposited on platinum coated silicon substrates. It was also observed that an increase of peak intensities for films annealed in oxygen atmosphere pointed to better crystallinity. The obtained results suggest that the oxygen atmosphere

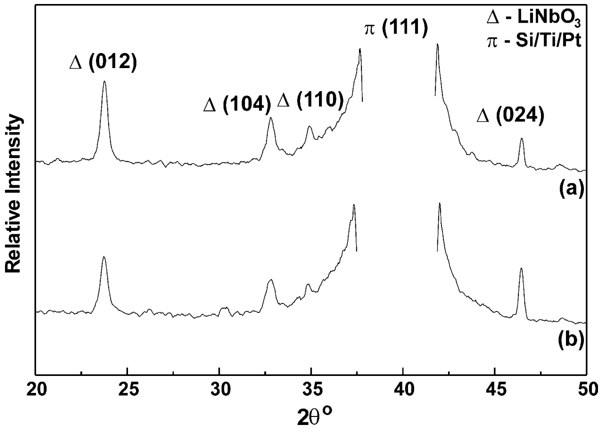
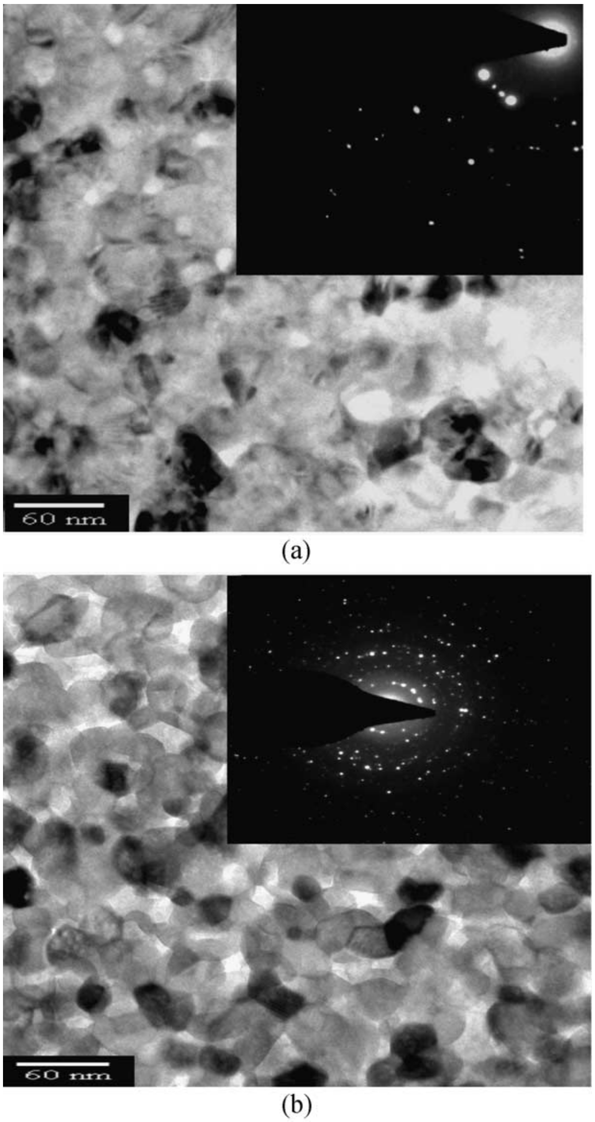


Fig. 1. XRD pattern of $LiNbO_3$ thin film annealed at 500 °C for 3 h at: (a) Static air and (b) Oxygen atmosphere.
]]>

flow during annealing influenced on the amount of $LiNbO_3$ crystalline phase.

A plan-view TEM image of the films shows the microstructure and the selected area diffraction (SAD) patterns. The polycrystallinity of the grains in the plane of the films was noticed. The grains were regularly shaped and the estimated size obtained from dark field images was about 70 nm for film annealed in static air and 50 nm for film annealed in oxygen atmosphere (Fig. 2a and b, respectively). Tiny pores less than 10 nm in size are present within the grains and along the grain boundaries. The role of oxygen atmosphere is to eliminate the vacancies present in the system that act as point defects and therefore decrease the surface heterogeneity in the films.



(a)

(b)

Fig. 2. Plan view TEM micrograph of $LiNbO_3$ film annealed at 500 °C for 3 h at: (a) Static air and (b) Oxygen atmosphere.

It is well known that the dielectric constant and dissipation factor depends on several factors such as annealing temperature, type of electrodes, defects, domain walls and phase composition. The data of electric characterizations presents the average measurement values of three samples. The dielectric constant and dissipation factor of the films are presented in the Fig. 3. According to literature data pure $LiNbO_3$ could be presented by the following model:

$$Li^{+}_{(1\text{-}x)}Nb^{+5}_{(1+x)\square(x\text{-}\varepsilon)}O_3^{-2} \tag{1}$$

Where $\square$ represents a cation vacancy and $x=5\epsilon$ which is necessary for electrical neutrality in this formulation. The Nb^{+5} vacancy concentration is negligible compared with the concentration of Li^{+1} vacancies due to the much larger imbalance involved with highly charged ion. The oxygen vacancies (positive charges) may be originated during the process of heat treatment of the films due to the organometallic decomposition of the polymeric precursor. The negative charges could be associated with the presence of negatively charged oxygen trapped at the grain boundary and/or at the film's electrode/interface.[15] The negative charge of the oxygen may be caused by charge transference between the metal vacancy and the oxygen, as is shown in:

$$V''_m + 1/2O_2^x \rightarrow V_m^x + 1/2O''_2. \tag{2}$$

When the films are annealed in static air, the phenomenon of the space charge polarization appeared and a large dielectric relaxation is observed. For films annealed in oxygen atmosphere the concentration of lithium decreases, slightly affecting the decrease of lithium and oxygen vacancies influencing the change of dielectric properties.[16]

However, it is noticed (Fig. 3) that there is a tendency for the dielectric constant to decrease and the dissipation factor to increase with an increase of frequency. Several possible reasons exist for such dispersion, including the influence of a barrier layer between the film and the electrode surface, or leaky grain boundaries. These phenomena have also been reported for dielectric thin films prepared by other techniques.[16] It is noticed that the dispersion is more evident for films annealed in static air than in oxygen atmosphere. It is possible that this dispersion is caused by space charge polarization or Maxwell-Wagner type interfacial polarization. The space charge polarization is inherently related to the nonuniform charge accumulation and is more evident in static air atmosphere. The obtained results suggested that the films annealed in static air possess a dielectric constant higher than films annealed in oxygen atmosphere due to differences in the charge compensation mechanism. Bearing in mind that films annealed in oxygen atmosphere possess lower grain size compared with films annealed in static atmosphere, a frequency dependence of dielectric constant and losses are more expressed because each individual grain can act as a single domain favouring the pinning of the

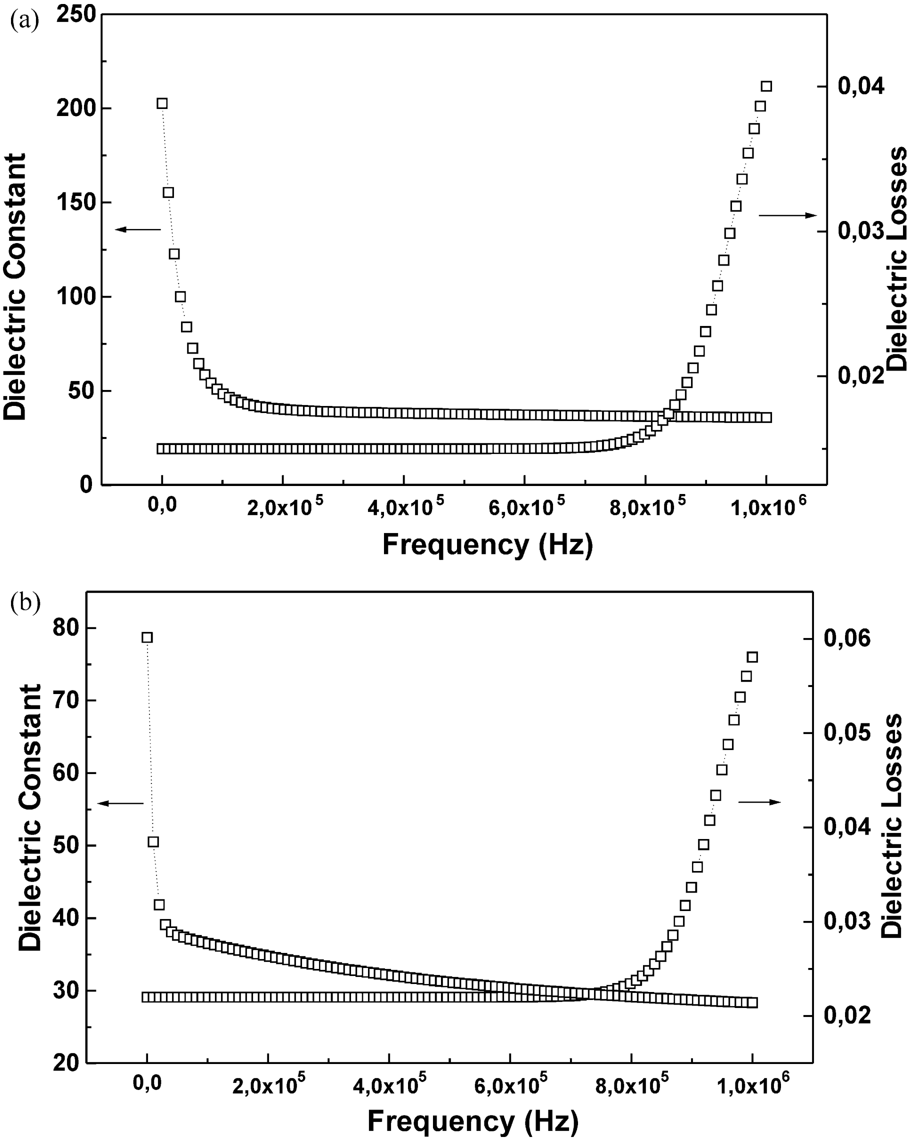


Fig. 3. Dielectric constant and dissipation factor as a function of frequency for $LiNbO_3$ film annealed at 500 °C for 3 h at: (a) Static air and (b) Oxygen atmosphere.

domain wall by defects segregated in the wall region.[17] The increase of losses with the frequency might be caused by the finite conductivity arising from some space charge layer and can also be attributed to the parasitic series resistance in the circuitry. As a consequence of these results one can say that the atmosphere of annealing deeply influences on the dielectric properties of lithium niobate thin films.

Ferroelectricity in the $LiNbO_3$ thin films was performed in a standardized ferroelectric tester and the results were presented in Fig. 4. The hysteresis loop for films annealed in oxygen atmosphere pointed that the polarization process could be easier accomplished in comparing with films annealed in static air. More regularly shaped hysteresis loop is observed after annealing in oxygen atmosphere. The trapped charge (O_2'') located in the grain boundary and in electrode film interface can promote a local stoichiometry deviation. The O_2'' associated with other defects (V_0'' or even defect dipole complexes such as oxygen vacancies associated with lithium vacancies ($V'Li-V_0''$) located near the grain boundary or and electrode/film interface can influence on the shape of the hysteresis loops.

Ferroelectricity in the films was observed with remanent polarization of 10 $\mu C/cm^2$ and coercive field of 60 KV/cm for films annealed in air atmosphere and 20 $\mu C/cm^2$ and 30 KV/cm for films annealed in oxygen atmosphere. The spontaneous polarization value in bulk single crystal of lithium niobate is 70 $\mu C/cm^2$ which is much higher than the corresponding value in the present thin films.[18] This could be due to fact that the loop presented in Fig. 4 was obtained from smaller signal and could not be saturated. It was not possible to apply a maximum voltage without distorting the loop due to

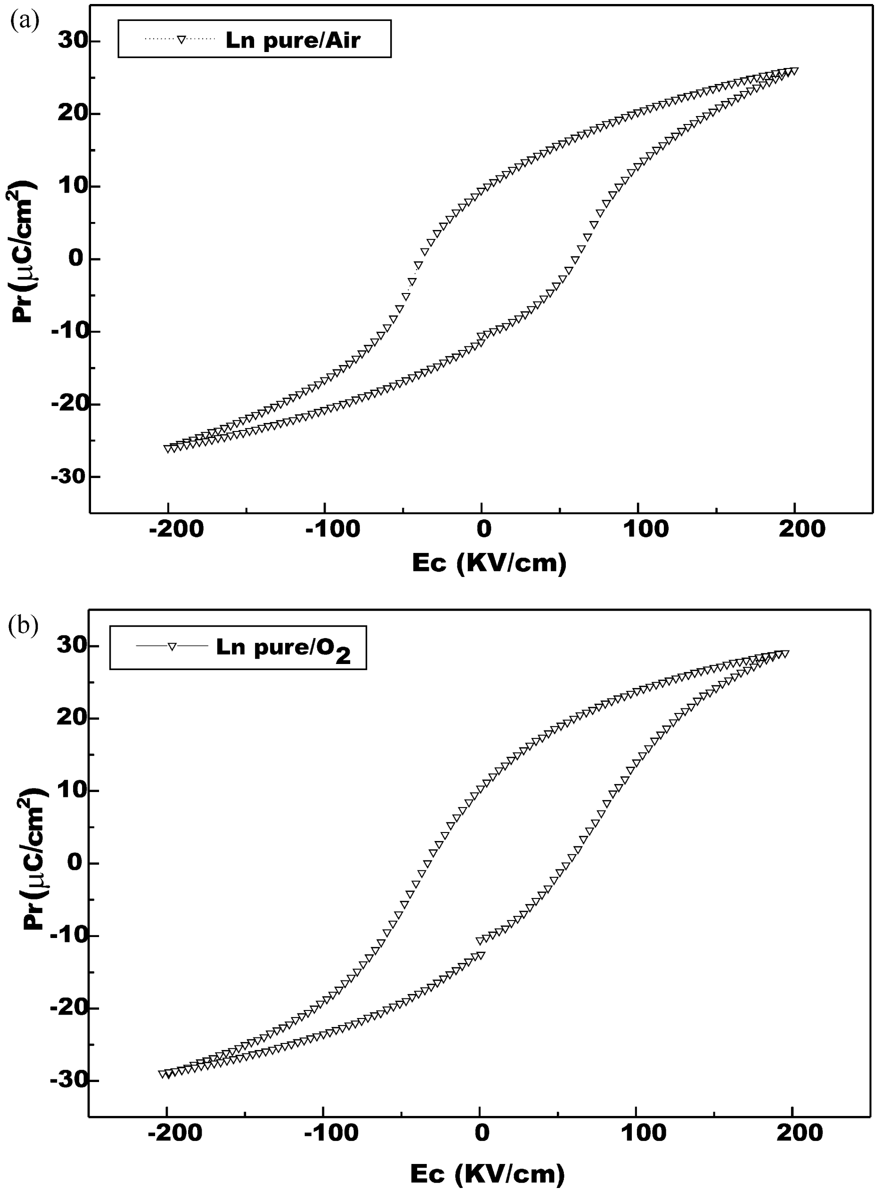


Fig. 4. Hysteresis loop for $LiNbO_3$ thin films annealed at 500 °C for 3 h at: (a) Static air and (b) Oxygen atmosphere.

the charge accumulation along the film-substrate interface. These problems are associated with lithium and oxygen vacancies, which contributed to the low value of remanent polarization, especially in films annealed in air atmosphere. The lack of reversal polarization was provoked by the high Curie temperature of lithium niobate and the small grain size, as was observed by TEM.

The fatigue endurance of $LiNbO_3$ thin films as a function of switching cycles was examined by applying 8.6 μs wide bipolar pulses with a 10 mV amplitude (Fig. 5). Generally, the fatigue mechanisms in the ferrolectric thin films include: (1) formation of a surface layer (2) pinning of domain walls by defects segregated in the wall region, (3) clamping of polarization reversal by volume defects, (4) supression of nucleation of oppositely oriented domains at the surface and (5) damage of electrode/film interface.[17]

Fatigue resistance was observed up to 10^8 cycles for films annealed in static atmosphere. For films annealed in oxygen atmosphere different behaviour is observed from 10^4 to 10^7 cycles and could be caused by supression of nucleation of oppositely oriented domains at the surface. Up to 10^4 cycles the fatigue is independent of frequency and amplitude of electrical field; the fatigue in this region is noncumulative. In the region from 10^4 to 10^7 cycles an increase of switching polarization occurs which leads to a local increase of conductivity of the films in the regions around the block nucleation sites. In this region fatigue is dependent on the amplitude of the field and on the total duration of fatigue pulses. It could be supposed that in the region from 10^7 to 10^8 cycles the

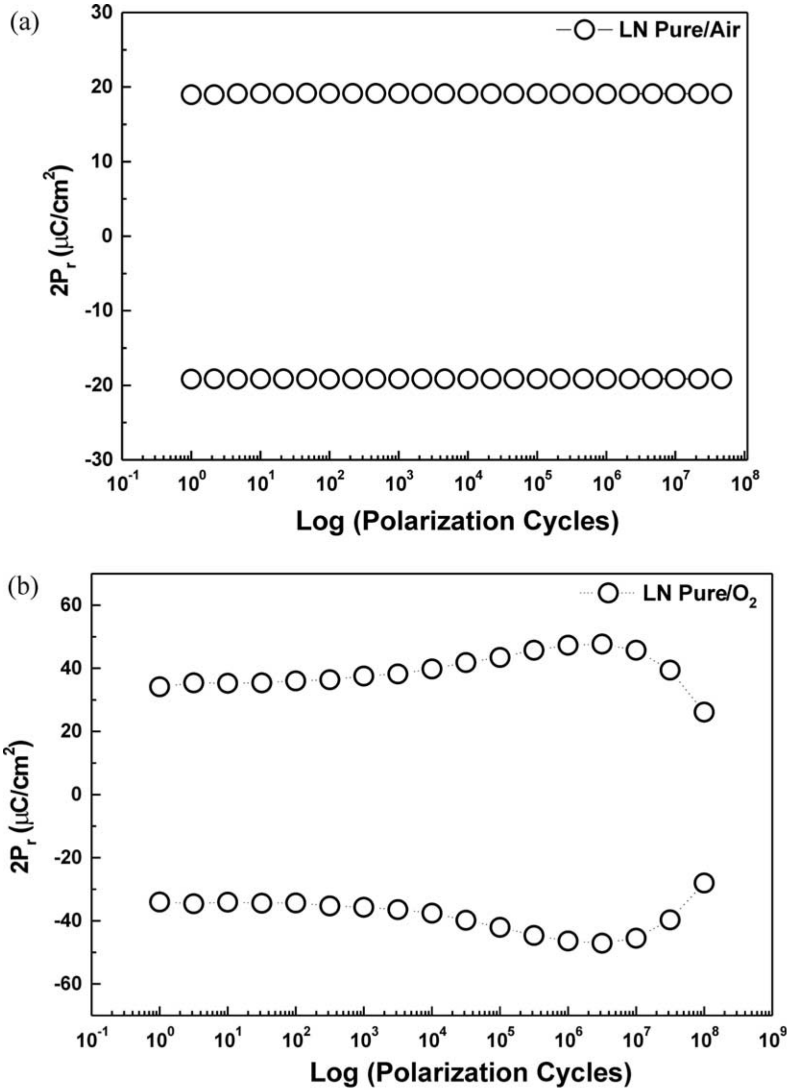


Fig. 5. Fatigue as a function of polarization cycles for $LiNbO_3$ thin films annealed at 500 °C for 3 hours at: (a) Static air and (b) Oxygen atmosphere.

increase of local current eventually destroys locally, the film/electrode interface leading to a decrease of switching cycles.[17]

4. Conclusions

Dense lithium niobate films on (111) platinum coated silicon substrate were obtained through Pechini solution by spin coating technique. Films annealed in static air possess a dielectric constant higher than films annealed in oxygen atmosphere due to differences in the charge compensation mechanism. A more regularly shaped hysteresis loop is observed after annealing in oxygen atmosphere. The obtained results suggest that the annealing in air atmosphere can increase the trapped charge and the relaxation phenomenon. The fatigue resistance was observed for films annealed in static atmosphere. Films annealed in oxygen atmosphere showed the dependence of fatigue with the number of switching cycles.

Acknowledgements

The authors acknowledge the Brazilian agencies CNPq, CAPES and FAPESP for financial support of this work.

References

1. Weis, R. S. and Gaylord, T. K., Lithium Niobate: summary of physical properties and crystal structure. *Appl. Phys.*, 1985, **A37**, 191–203.
2. Cheng, C., Xu, Y. and Mackenzie, J. D., Photoelectric properties of undoped and Fe doped lithium niobate films made by sol–gel method. *Mat. Res. Soc. Symp.*, 1992, **43**, 5551–5561.

3. Kaigawa, K., Kawaguchi, T., Imaeda, M., Sakai, H. and Fukuda, T., Crystal structure of LPE grown $LiNbTaO_3$ epitaxial films. *J. Cryst. Growth*, 1998, **191**, 119–124.
4. Wernberg, A. A., Gysling, H. J., Filo, A. J. and Blanton, T. N., Epitaxial Growth of $LiNbO_3$ thin films from a single source organometallic precursor using CVD. *Appl. Phys. Lett.*, 1993, **62**, 946–948.
5. Tan, S. and Schlesinger, T. E., The role of Si_3N_4 layers in determining the texture of sputter deposited $LiNbO_3$ thin films. *Appl. Phys. Lett.*, 1996, **68**, 2651–2653.
6. Hu, W. S., Liu, Z. G. and Feng, D., Low electric field induced (001) oriented growth of $LiNbO_3$ films by pulsed laser ablation. *Solid State Commun.*, 1996, **97**, 481–485.
7. Birnie, D. P., Model for the ferroelectric transition in non-stoichiometry lithium niobate and lithium tantalite. *J. Am. Ceram. Soc.*, 1991, **74**, 988–993.
8. Hirano, S. and Kato, K., Synthesis of $LiNbO_3$ by hydrolysis of metal alkoxides. *Adv. Ceram. Mater.*, 1987, **2**, 142–145.
9. Hirano, S., Yogo, T., Kikuta, K., Isobe, Y. and Ono, S., Study of crystallization of $LiNbO_3$ films from metal alkoxides. *J. Mater. Sci.*, 1992, **28**, 4188–4192.
10. Pechini, M. P., Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. *US Patent*, 1967, **3**, 330–697.
11. Marsh, A. M., Harkness, S. D., Qian, F. and Singh, R. K., Pulsed laser deposition of high quality $LiNbO_3$ thin films from sapphire substrates. *Appl. Phys. Lett.*, 1993, **62**, 952–954.
12. Park, S. K., Baek, M. S., Bae, S. C., Kwun, S. Y., Tim, K. T. and Kim, K. W., Properties of $LiNbO_3$ thin film prepared from ceramic Li-Nb-K-O target. *Solid. Stat. Commun.*, 1999, **111**, 347–352.
13. Simões, A. Z., Gonzalez, A. H., Zaghete, M. A., Stojanovic, B. D., Cavalheiro, A. A., Moeckli, P., Setter, N. and Varela, J. A., Influence of oxygen flow on the crystallization and morphology of $LiNBO_3$ thin films. *Ferroelectrics*, 2003, accepted for publication.
14. Raymond, M. V. and Smyth, D. M., Defects and charge transport in perovskite ferroelectrics. *J. Phys. Chem. Solids.*, 1996, **57**, 1507–1511.
15. Pontes, F. M., Leite, E. R., Longo, E., Araujo, E. B. and Varela, J. A., Effect of the postannelaing atmosphere on the dielectric properties of (Ba, Sr) TiO_3 capacitor: Evidencial of an interfacial space charge layer. *Appl. Phys. Lett.*, 2000, **76**, 1–3.
16. Nassau, K. and Lines, M. E., Stacking-Fault model for stoichiometry deviation in $LiNbO_3$ and $LiTaO_3$ and the effect on the Curie temperature. *J. Appl. Phys.*, 1979, **41**, 533–537.
17. Damjanovic, D., Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films. *Rep. Prog. Phys.*, 1998, **61**, 1267–1324.
18. Ro, J. H., Jeon, OC.-Y., Kim, T. H., Ro, J. H. and Lha, M., Non-stoichiometry defect effect on coercitive field in $LiNbO_3$ crystals. *Ferroelectrics*, 2003, accepted for publication.