Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 299–303
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Microstructure of $LaNiO_3$ thin films obtained by the spin-on technique from citrate precursors

M. Počuča [a,*], G. Branković [a], Z. Branković [a], D. Vasiljević-Radović [b], D. Poleti [c]

[a] *Center for Multidisciplinary Studies, University of Belgrade, Kneza Višeslava 1a, 11000 Belgrade, Serbia*
[b] *IHTM, Institute of Microelectronic Technologies and Single Crystals, Njegoševa 12, 11000 Belgrade, Serbia*
[c] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*

Received 20 February 2006; received in revised form 28 July 2006; accepted 3 October 2006
Available online 13 December 2006

Abstract

The morphology of perovskite $LaNiO_3$ (LNO) thin films is a very important feature considering the fact that they could be used as an electrode material in ferroelectric devices. In this work, LNO films were prepared from citrate precursors. The films were deposited on Si (100) and Pt covered Si substrates [Pt (111)/Ti/SiO_2/Si] using the spin-on technique. The phase composition of the films was confirmed by X-ray powder diffraction analysis, while the microstructures were investigated by atomic force microscopy. The influence of the metal ion:citric acid:ethylene glycol ratio on the morphology of the films was investigated. After optimization of these parameters, very homogenous, uniform and crack-free LNO films were obtained.

Keywords: A. Sol–gel processes; B. Microstructure-final; E. Electrodes

---

1. Introduction

The quality and aging of memory devices strongly depends on the nature and quality of the conducting bottom electrode. Apart from many good properties, Pt electrodes, which are commonly used in these devices, exhibit some disadvantages: weak adhesion with the ferroelectric layer, oxygen diffusion from the ferroelectric into the Pt layer, fatigue effect and high price. In order to overcome these problems, investigations are concentrated on the preparation of new materials to substitute Pt-based electrodes in ferroelectric devices. Some simple, such as RuO_2 and IrO_2, and complex, such as La, Sr and Ni based oxides, have been suggested as possible solutions for this purpose [1]. Among these oxides, $LaNiO_3$ has proved itself to be a good alternative [2]. It exhibits high conductivity over a wide temperature range, and its perovskite structure with lattice parameters close to those of typical ferroelectrics (such as PZT), enables its good adhesion to the ferroelectric layer [3]. Various physical and chemical methods for preparing LNO have been described. Epitaxial LNO thin films were successfully obtained by physical methods, e.g., RF magnetron sputtering [4], PLD [5] and MPE [6]. On the other hand, chemical methods, such as sol–gel [7], MOD [8] and chemical solution decomposition [2,3] are simpler and enable easier control over the stoichiometry of the final product.

In this work, LNO was synthesized from citrate precursor solutions by a modified Pechini method [9]. The procedure is based on the preparation of complex compounds between citric acid and La^{3+} and Ni^{2+} ions. Ethylene glycol is added to a mixture of metal citrates, where it forms polyester chains with the citric acid. These complex molecules further build an organic network (matrix) with metal ions homogeneously distributed inside. LNO is obtained after combustion of the organic material and annealing at higher temperatures. There are numerous literature data reporting the influence of viscosity [10], concentration [2,11], annealing temperature [12] or pH of the precursor solution [13] on the microstructure and other features of LNO and other complex metal oxide thin films. The atmosphere during thermal treatment plays an important role in controlling the stoichiometry, as well as electrical and transport properties of LNO [14,15]. The experimental results have shown that the preparation of good quality LNO films requires

---

[*] Corresponding author. Tel.: +381 11 2085032; fax: +381 11 3055289.
E-mail address: milicaka@ibiss.bg.ac.yu (M. Počuča).

0272-8842/$34.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.10.003

further investigation and optimization of certain parameters. It is extremely important to study the chemistry of the precursor solutions, since this is a crucial factor for the stoichiometry, homogeneity and microstructure of the obtained films.

The aim of this work is to determine in what way the microstructure of the film depends on the metal ion:citric acid:ethylene glycol molar ratio.

2. Experimental

Four precursor solutions with metal ions, citric acid and ethylene glycol in the following molar ratios: 1:4:16, 1:4:20, 1:4:60 and 1:5:25 were prepared. The starting ratio (1:4:16) was the most commonly used one [9,13,16]. The calculated amount of citric acid was added to an aqueous suspension of lanthanum oxide (La_2O_3) and the mixture was refluxed for two hours at 120 °C. The amorphous lanthanum citrate was dissolved in ammonia by adjusting the pH of the solution to 7 [17]. Nickel citrate was synthesized by heating an aqueous solution of nickel acetate [$Ni(CH_3COO)_2 \cdot 4H_2O$] with the calculated amount of citric acid. The LNO precursor solution was prepared by mixing two citrate solutions (in 1:1 molar ratio of La:Ni), and adding the appropriate amount of ethylene glycol. Finally, by addition or evaporation of water, the viscosity of all solutions was adjusted to 30 cP using a Haake Rotovisco RV 20viscometer.

The solutions were deposited onto Pt covered Si [Pt (111)/Ti/SiO_2/Si] and Si (100) substrates using the spin-on technique at 3000 rpm for 30 and 20 s, respectively. After every layer, the films were thermally treated in an air atmosphere in the following manner: dried at 100 °C, slowly heated up to 300 °C at a heating rate of 1 °C/min and further heated up to 700 °C at a heating rate of 20 °C/min, at which temperature they were annealed for 30 min. These thermal conditions are based on our earlier investigations. After optimization of the metal ion:citric acid:ethylene glycol molar ratio, the influence of thermal treatment in flowing oxygen atmosphere was investigated. Films were prepared in an oxygen atmosphere under the same heating conditions as the films prepared in air.

The microstructure of the thin films was analyzed by AFM (AutoProbe CP Research, TM microscopes). The characteristic parameters: R_a (average roughness), RMS (Root Mean Square), D_1 (longest diameter of the grain) and D_2 (diameter normal to D_1) were determined from the obtained micrographs. X-ray diffraction (XRD) analysis was performed on a Siemens D500 instrument using Ni filtered Cu Kα radiation.

3. Results and discussion

Citric acid has three carboxyl groups and potentially, when not coordinated, it could make three ester bonds with ethylene glycol. On the other hand, when polymeric lanthanum citrate is formed, two of the three COO^- groups are involved in coordination [18]. In order to obtain a well-defined polyester network, which should provide the preparation of smooth and uniform films, it is necessary to establish the appropriate amounts of citric acid and ethylene glycol and to optimize their ratio. It was recommended previously that the amount of citric acid should be four times the amount of metal ions [13,14], although some researchers suggested that this ratio could be smaller [19]. For this reason, the initial ratio employed in this work was 1:4:16.

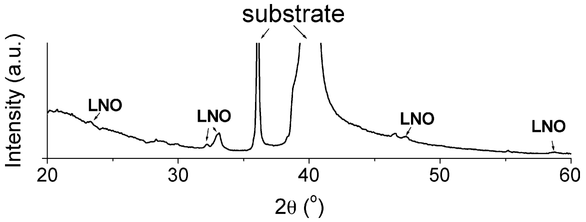

Fig. 1. XRD pattern of LNO film deposited on Pt substrate from 1:4:16 solution.

The XRD pattern of the LNO thin film obtained from a 1:4:16 solution and deposited on a Pt substrate is shown on Fig. 1. Almost identical patterns were obtained using the other precursor solutions, and they all confirmed the presence of well-crystallized LNO films.

The structure of a three-layer LNO thin film obtained from a 1:4:16 precursor solution on a Pt substrate is shown in Fig. 2. The surface contains large cracks and it is difficult to distinguish particular grains. The films deposited on a Si substrate had a similar structure. If it is assumed that the amount of citric acid in the solution was sufficiently high, then the observed cracks were probably caused by low amount of ethylene glycol in the precursor solution. A possible explanation is a poorly formed organic network, the combustion of which causes large thermal stress and produces cracks on the film surface.

LNO thin films obtained from 1:4:20 precursor solutions exhibited a completely different surface (Fig. 3a and b). The addition of a larger quantity of ethylene glycol in the precursor solution greatly improved the microstructure of the films. Oval grains appeared on the surface and the cracks were much smaller than in the case when 1:4:16 solution was used.

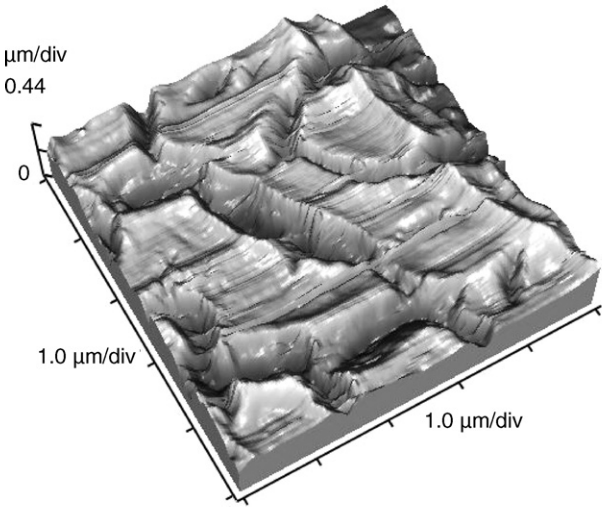

Fig. 2. AFM micrograph of three-layered LNO thin film deposited on Pt substrate from 1:4:16 solution.

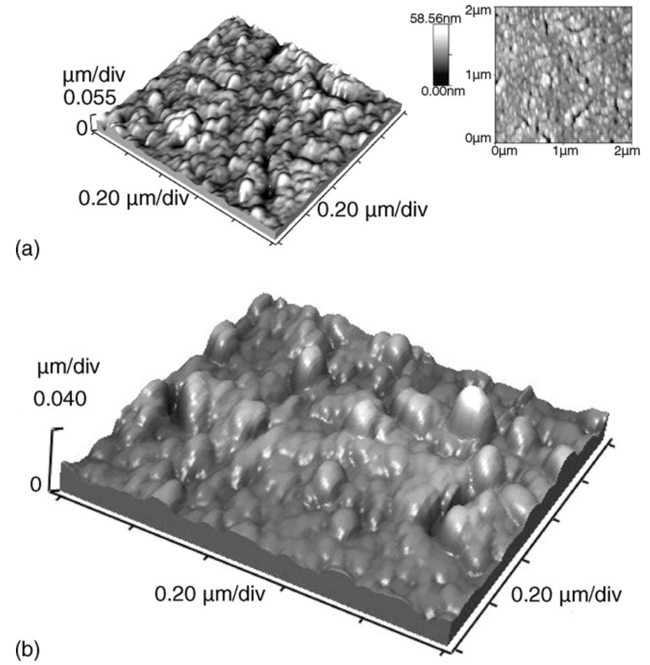

Fig. 3. AFM micrographs of LNO thin films obtained from 1:4:20 solution and deposited on (a) Pt substrate (one layer) and (b) Si substrate (two layers).

Thin films deposited on Pt substrates had smaller grains than those on Si substrates (Table 1) suggesting a greater number of crystallization centers on the Pt substrates [20], probably because of the catalytic effect of platinum on the formation of LNO films. The grain size and roughness increased with increasing the number of layers deposited on Pt substrates.

Deposition of a 1:4:60 solution, with the highest quantity of ethylene glycol, on Si substrates resulted in highly textured LNO thin films with smooth, crack-free surfaces and oval-shaped grains. The size of the grains decreased with increasing the number of deposited layers (Fig. 4b, Table 2). The roughness of these films was lower in comparison to films obtained from 1:4:16 and 1:4:20 precursor solutions, and slightly increased with the number of layers.

LNO films deposited on Pt substrates from the same precursor solution had a very fine microstructure (Fig. 4a). They were very smooth without cracks or pores. Contrary to the results for Si substrates (Fig. 4b), the roughness of these films decreased with increasing number of layers (Table 2). This is very important because lower roughness enables better contact between the conducting thin films and other materials.

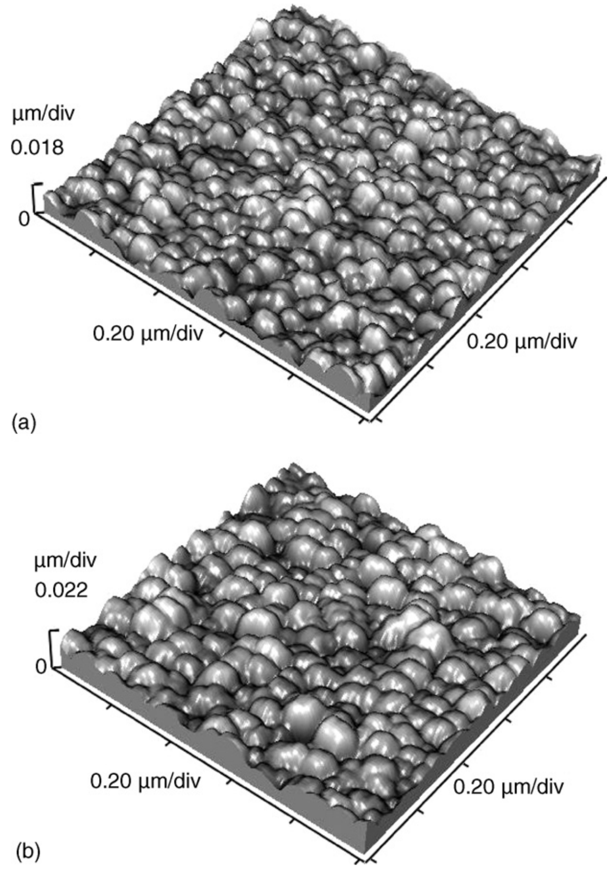

Fig. 4. AFM micrographs of two-layered LNO thin films deposited from 1:4:60 solution on (a) Pt and (b) Si substrate.

Obviously, the addition of a larger amount of ethylene glycol greatly improves the microstructure of LNO thin films. Simoes et al. showed that decreasing the of viscosity of the precursor solution from 40 to 20 cP led to better surfaces of some thin films prepared using a similar method and similar precursors [10]. Considering the fact that in this work the viscosity of all the precursor solutions was adjusted to 30 cP, and that the films obtained from the solution with the highest concentration of ethylene glycol had the best microstructure, it seems that the crucial parameters are not, individually, the viscosity or metal ion:citric acid ratio, but the overall metal ion:citric acid:ethylene glycol ratio. Therefore, ethylene glycol is the key factor which controls the structure of the organic matrix in which the metal ions are distributed and consequently, it influences the structure of the thin film itself. A larger amount of ethylene glycol enables a better connection between the polyester chains

Table 1
Grain size and roughness of LNO films obtained from 1:4:20 solution

Substrate/number of layers	Grain size (nm)		Roughness (nm)	
	D_1	D_2	R_a	RMS
Pt/1	91	48	5.0	6.5
Pt/2	96	62	6.2	8.1
Si/1	205	86	3.2	4.1
Si/2	130	62	3.6	4.5

Table 2
Grain size and roughness of LNO films obtained from 1:4:60 solution

Substrate/number of layers	Grain size (nm)		Roughness (nm)	
	D_1	D_2	R_a	RMS
Pt/1	122	99	4.3	5.4
Pt/2	68	49	2.6	3.2
Pt/4	99	60	2.4	3.0
Si/1	98	69	2.0	2.6
Si/2	82	59	2.7	3.3
Si/4	80	46	3.0	3.8

Table 3
Grain size and roughness of LNO films obtained from 1:5:25 solution

Substrate/number of layers	Grain size (nm)		Roughness (nm)	
	D_1	D_2	R_a	RMS
Pt/1	130	85	2.4	3.3
Pt/2	161	133	1.3	1.6
Pt/4	124	65	1.5	1.9
Si/1	144	91	2.0	2.5
Si/2	172	86	1.5	2.1
Si/4	190	62	3.2	4.1

and decreases the stress during the thermal treatment of the films, which as a result prevents the formation of cracks [11,12].

In order to investigate the influence of the amount of citric acid on the quality of the obtained films, a 1:5:25 solution was also prepared. The thin films obtained from this solution had a smooth surface and were crack-free. On the other hand, there was no uniform grain size distribution and no relation between the grain size and the number of deposited layers was observed (Table 3). The grains in these films were larger and not quite oval, while the roughness was smaller than that of the other investigated films. Some grains elongated with the number of deposited layers, while others grew abnormally grow in the *Z*-direction (Fig. 5).

Furthermore, a 1:4:60 solution was deposited on Si substrates and thermally treated under an oxygen atmosphere. It was expected that thermal treatment in flowing oxygen would additionally improve the microstructure and, consequently, the electrical properties of the films [14,15]. Indeed, LNO films prepared in oxygen showed significantly different microstructures (Fig. 6). The grains of these films were aligned along one direction. They were not oval and were much bigger (around 290 nm) than those of corresponding LNO films treated in air. This could be the result of a faster diffusion of oxygen which led to the faster grain growth and easier oxidation of Ni^{2+} to Ni^{3+}, but also to the formation of some cracks on the surface of the films. However, the roughness was higher (R_a = 5.2 nm and RMS = 6.5 nm) than that of films treated in air, which makes them less suitable for electrode application. In order to improve properties of thin films obtained in oxygen atmosphere it will be necessary to perform additional optimization of the thermal treatment conditions.

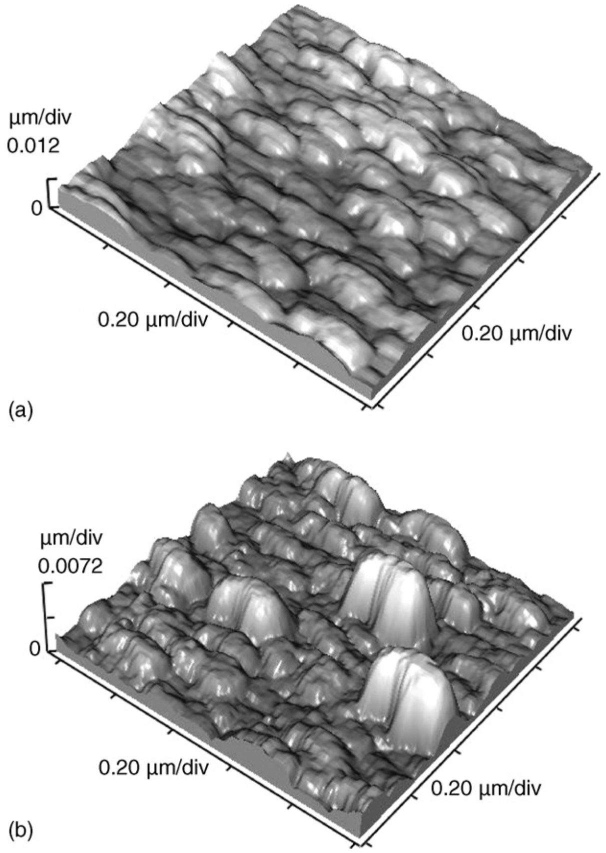

Fig. 5. AFM micrographs of two-layered LNO thin films obtained from 1:5:25 solution and deposited on (a) Pt and (b) Si substrate.

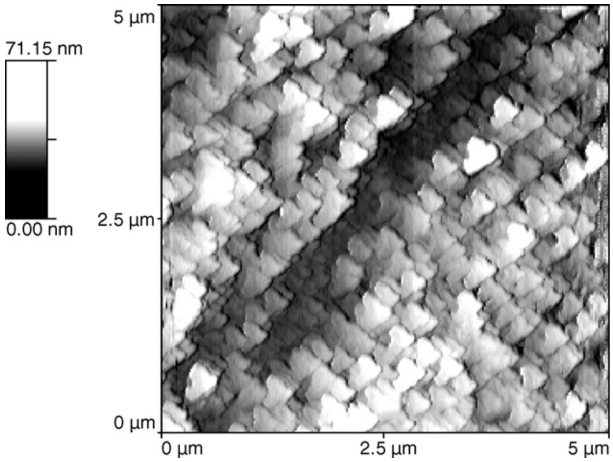

Fig. 6. AFM micrograph of LNO thin film (one layer) obtained from 1:4:60 solution, deposited on Si substrate and thermally treated in oxygen atmosphere.

4. Conclusions

In this work, crystalline LNO thin films were obtained by the polymeric precursor method on both Pt and Si substrates. It was shown that the microstructure of the obtained films is greatly dependent on the molar ratio of the chemicals (metal ions:citric acid:ethylene glycol) in the precursor solution. By adjusting this ratio to 1:4:60, uniform, crack-free thin films were obtained with an average grain size of around 80 nm and RMS of around 3 nm. Films thermally treated in an oxygen atmosphere have a different microstructure with larger grains and, consequently, greater roughness than those treated in an air atmosphere. This work also proved that the amount of employed ethylene glycol plays a very important role in forming LNO thin films with a good microstructure; when it is added in a very high excess, the surface of the film is without cracks or pores and much smoother.

Acknowledgment

This work was financially supported by the Ministry of Science and Environmental Protection of Republic of Serbia.

References

[1] C.R. Cho, D.A. Payne, Solution deposition and heteroepitaxial crystallization of $LaNiO_3$ electrodes for integrated ferroelectric devices, Appl. Phys. Lett. 71 (20) (1997) 3013–3015.

[2] H. Miyazaki, T. Goto, Y. Miwa, T. Ohno, H. Suzuki, T. Ota, M. Takahashi, Preparation and evaluation of $LaNiO_3$ thin film electrode with chemical solution deposition, J. Eur. Ceram. Soc. 24 (6) (2004) 1005–1008.

[3] D. Bao, X. Yao, N. Wakiya, K. Shinozaki, N. Mizutani, Preparation of conductive $LaNiO_3$ film electrodes by a simple chemical solution deposition technique for integrated ferroelectric thin film devices, J. Phys. D: Appl. Phys. 36 (10) (2003) 1217–1221.

[4] N. Wakiya, T. Azuma, K. Shinozaki, N. Mizutani, Low-temperature epitaxial growth of conductive $LaNiO_3$ thin films by RF magnetron sputtering, Thin Solid Films 410 (1/2) (2002) 114–120.

[5] F. Sanchez, C. Ferrater, C. Guerrero, M.V. Garcia-Cuenca, M. Varela, High-quality epitaxial $LaNiO_3$ thin films on $SrTiO_3$ (100) and $LaAlO_3$ (100), Appl. Phys. A 71 (1) (2000) 59–64.

[6] H. Huang, X. Yao, M. Wang, X. Wu, $BaTiO_3$ on $LaNiO_3$ and Si thin films prepared by mist plasma evaporation, J. Cryst. Growth 263 (1–4) (2004) 406–411.

[7] S. Miyake, S. Fujihara, T. Kimura, Characteristics of oriented $LaNiO_3$ thin films fabricated by the sol–gel method, J. Eur. Ceram. Soc. 21 (10–11) (2001) 1525–1528.

[8] Y. Zhang, Q.F. Zhou, H.L.W. Chan, C.L. Choy, Conducting lanthanum nickel oxide as electrodes for lead zirconate titanate films, Thin Solid Films 375 (1–2) (2000) 87–90.

[9] M.P. Pechini, U.S. Patent 3,330,697, 11 July 1967.

[10] A.Z. Simoes, A.H.M. Gonzales, M.A. Zaghete, M. Cilense, J.A. Varela, B.D. Stojanovic, Influence of viscosity and ionic concentration on morphology of PLZT thin films, Appl. Surf. Sci. 172 (1/2) (2001) 68–74.

[11] Y. Zhang, Y. Zhu, R. Tan, W. Yao, L. Cao, Influence of PEG additive and precursor concentration on the preparation of $LaCoO_3$ film with perovskite structure, Thin Solid Films 388 (1/2) (2001) 160–164.

[12] Y. Zhu, H. Wang, P. Liu, W. Yao, L. Cao, Preparation and conducting performance of $LaNiO_3$ thin film on Si substrate, Thin Solid Films 471 (1/2) (2005) 48–52.

[13] A.Z. Simoes, A. Ries, F. Moura, C.S. Riccardi, E. Longo, J.A. Varela, Influence of the solution pH on the morphological, structural and electrical properties of $Bi_{3.50}La_{0.50}Ti_3O_{12}$ thin films obtained by the polymeric precursor method, Mater. Lett. 59 (22) (2005) 2759–2764.

[14] A. Li, C. Ge, P. Lu, N. Ming, Preparation of perovskite conductive $LaNiO_3$ films by metalorganic decomposition, Appl. Phys. Lett. 68 (10) (1996) 1347–1349.

[15] A. Li, D. Wu, Z. Liu, C. Ge, X. Liu, G. Chen, N. Ming, TEM and AFM study of perovskite conductive $LaNiO_3$ films prepared by metalorganic decomposition, Thin Solid Films 336 (1998) 386–390.

[16] A.Z. Simoes, M.A. Ramirez, C.S. Riccardi, A. Ries, E. Longo, J.A. Varela, Influence of temperature on the dielectric and ferroelectric properties of bismuth titanate thin films obtained by the polymeric precursor method, Mater. Chem. Phys. 92 (2/3) (2005) 373–378.

[17] A. Hardy, D. Mondelaers, M.K. Van Bael, J. Mullens, L.C. Van Poucke, G. Vanhoyland, J. D'Haen, Synthesis of $(Bi,La)_4Ti_3O_{12}$ by a new aqueous solution–gel route, J. Eur. Ceram. Soc. 24 (6) (2004) 905–909.

[18] R. Baggio, M. Perec, Isolation and characterization of a polymeric lanthanum citrate, Inorg. Chem 43 (22) (2004) 6965–6968.

[19] Y.L. Chai, D.T. Ray, G.J. Chen, Y.H. Chang, Synthesis of $La_{0.8}Sr_{0.2}Co_{0.5}Ni_{0.5}O_{3-\delta}$ thin films for high sensitivity CO sensing material using the Pechini process, J. Alloys Comp. 333 (1/2) (2002) 147–153.

[20] R. Pasqual, M. Sayer, A. Lo, S. Herbert, L.C. Rolim, N. Townley, Simulatiom of the crystallization of thin films by rapid thermal processing, J. Appl. Phys. 79 (1) (1996) 493–499.