Morphological and Structural Evolution of Chemically Deposited Epitaxially LaNiO$_3$ Thin Films

Mircea Nasui 1,*, Ramona Bianca Sonher 1,2, Ecaterina Ware 2, Andrada Daniel 1, Traian Petrisor, Jr. 1, Mihai Sebastian Gabor 1, Lelia Ciontea 1 and Traian Petrisor 1

Abstract: We report the preparation and characterization of epitaxial LaNiO$_3$ (LNO) thin films by chemical solution deposition method using lanthanum and nickel acetylacetonates as starting reagents dissolved in propionic acid. In order to obtain further information regarding the decomposition behavior of the film, the precursor solution was dried to obtain the precursor powder, which was investigated by thermal analyses and X-ray diffraction measurements (XRD). The LNO perovskite thin films were deposited by spin coating on SrTiO$_3$(100) single crystal substrates. A detailed study with different crystallization temperatures (600–900 °C) at two different heating ramps (5 and 10 °C/min) was performed. Oriented LaNiO$_3$ thin films with good out-of-plane textures were obtained with optimal surface morphologies.

Keywords: LNO thin films; chemical deposition; epitaxial growth

1. Introduction

Functional perovskite oxides such as LaNiO$_3$ (LNO) are one of several conductive oxides having crystal structures suitable for use in epitaxial heterostructures. Colossal magnetoresistance materials, metal-insulator transition temperatures, high-temperature superconductors, and ferroelectrics, can be noted as technological potential applications [1–3]. It is known that LNO has a rhombohedral distorted perovskite-type structure. LNO has also attracted attention in recent years as a conducting layer [4] for applications as bottom electrodes involving the growth of high-quality ferroelectric thin films and active oxidation catalysts [5]. Moreover, nickelates present interest due to the bandwidth-controlled metal-insulator transition [6]. LNO shows a metallic conduction down to 0.4 K [7]. Because LNO has a structure similar to that of perovskite ferroelectrics, textured and epitaxially grown LNO film has been studied intensively as electrodes [8]. The lattice parameters of its pseudocubic or rhombohedral unit cells are $a = 3.84$ Å and $a = 5.46$ Å with $\beta = 60.8^\circ$, respectively. LaNiO$_3$ was n-been fabricated with different solution-based and vacuum-based methods. Studies concerning the preparation of La$_{n+1}$Ni$_n$O$_{3n+1}$ epitaxial films are rather scarce, particularly for La$_2$NiO$_{4+\delta}$, and have evidenced the difficulty to prepare pure phases, intergrowth defects being common in these compounds, particularly for $n > 1$ [9]. Satyalakshmi et al. grew epitaxial LaNiO$_3$ thin films on LaAlO$_3$, (LAO) and YSZ by pulsed laser deposition method using an oxygen partial pressure of 350 mTorr and a substrate temperature of 700 °C. The as-deposited LaNiO$_3$ films are metallic down to 10 K [10]. Other authors grew epitaxial LaNiO$_3$ thin films on (001) SrTiO$_3$ substrates by laser molecular-beam epitaxy [11], ozone-assisted molecular-beam epitaxy [12], and nebulized spray pyrolysis [13]. The resistivity of the thin film measured in this case was 0.28 mΩ·cm
at 278 K. The chemical solution deposition (CSD) process is a wet-chemical process that has been used to design a wide variety of amorphous and crystalline oxide thin films. Compared to vapor and plasma processes, the thermodynamic driving force for the formation and crystallization of a solid phase from liquid-based solutions is much smaller [14]. It is generally agreed that the chemical solution deposition (CSD) technique represents a successful tool for thin film processing. The CSD method is very promising since it fulfills requirements for the fabrication of functional oxide thin films, even at the industrial level (versatility, low vacuum, inexpensiveness, high deposition rate, easy control of the stochiometry, etc.). Moreover, due to the fact that the solubility of metal-organic compounds in polar solvents can be tuned by modifying the organic part of the molecule and because the organic moiety pyrolyzes in oxidizing ambient atmosphere without residue, CSD presents important advantages [15,16]. A.D. Li et al. [17] reported the synthesis and characterization of LNO films from metal-organic precursors starting from lanthanum 2-ethylhexanoate and nickel 2-ethylhexanoate deposited on different substrates. These LNO films exhibit a resistivity in the range $10^{-5}$–$10^{-6}$ $\Omega$·cm. More recently, R.A.C. Amoresi et al. [18] obtained LaNiO$_3$ films based on polymeric precursor solution. Through this synthesis route, the resistivity of the films was about $10^{-4}$ $\Omega$·cm. S. Kuprenaite et al. [19] studied the growth of LaNiO$_3$ thin films using three different metal organic chemical vapor deposition methods on different substrates (0112) R-sapphire, (100) Si, and (0112) LaAlO$_3$. In all three cases, “cube on cube” growth was dominant. For chemical solution-deposited LNO thin films, a novel flashlight sintering method was reported by J. Park et al. [20]. This synthesis route reduces the sintering time of perovskite LNO thin films with resistivity values of $9.923 \times 10^{-4}$ $\Omega$·cm.

The conductivity of LNO material depends on the ratio of Ni atoms that are in the Ni$^{3+}$ state. LaNiO$_3$ has trivalent Ni$^{3+}$, which is metallic. However, in most of the cases, LNO thin films contained a combination of Ni$^{3+}$ and Ni$^{2+}$ ions. Ni$^{3+}$ is not the stable oxidation state of nickel, leading to the formation of oxygen vacancies in these structures impacting the conductivity of the layers. At lower Ni$^{3+}$/Ni$^{2+}$ ratio, the LaNiO$_{2.64}$ film exhibits semi-conductive behavior, while at a higher ratio, the LaNiO$_{2.84}$ film presents electronic conductivity [21–23].

This paper presents the results on the preparation and characterization of epitaxial lanthanum nickelate LaNiO$_3$ perovskite thin films deposited by the chemical solution deposition method. The novelty of the present work lies in the use of acetylacetonate type precursors and propionic acid as solvent to obtain epitaxial LNO thin films with good conducting properties. The precursor solution was concentrated by the removal of solvent under vacuum. The precursor powder was investigated by TG-DTA thermal analyses and X-Ray diffraction measurements. LaNiO$_3$ thin films were deposited by spin-coating on SrTiO$_3$(100) single crystalline substrates using two different heating ramps 5 and 10 $^\circ$C/min and different annealing temperatures between 600–900 $^\circ$C. The as-obtained films were characterized by structural, morphological, and electrical points of view.

2. Experimental

Coating solutions for the deposition of LNO thin films were prepared using the metal organic precursors lanthanum (La(CH$_3$COCHCOCH$_3$)$_3$, Alfa Aesar, 99.9%, CAS: 64424-12-0, Ward Hill, MA, USA) and nickel acetylacetonate (Ni(CH$_3$COCHCOCH$_3$)$_2$, Alfa Aesar, 99.9%, CAS: 3264-82-2, Ward Hill, MA, USA) as starting materials and propionic acid (Alfa Aesar, CAS: 769-09-4, Ward Hill, MA, USA) as a solvent. The two reagents were separately dissolved in propionic acid and stirred at room temperatures for 1 h. The as-obtained two clear solutions were mixed together in the stoichiometric ratio La:Ni = 1:1 and concentrated by distillation under vacuum (45 mbar, bath temperature 76 $^\circ$C) for the removal of solvents in excess. The final total metal ions concentration was 0.8 M. The as-prepared LNO coating solution was spun on (100) STO substrates at a spinning rate of 3000 rpm for 60 s. The dried films were heat treated in a conventional furnace at two different heating rates of 5 and 10 $^\circ$C/min in static air in the temperature range 600–900 $^\circ$C for one hour and cooled down
to room temperature at the same rate. Figure 1 illustrates the schematic representation of the experimental procedure. LNO thin films were then structurally characterized by XRD in a θ-2θ scan mode (steps of 0.02°), which was recorded on a Bruker D8 Discover diffractometer (Bruker, Karlsruhe, Germany) using Cu Kα1 radiation equipped with a Goebel mirror (Bruker AXS, Karlsruhe, Germany) for the incident radiation. A Veeco D3100 atomic force microscope (Veeco Metrology Inc., Plainview, NY, USA) was employed to obtain a bi-dimensional image of the sample surface. These images enabled us to attain an accurate analysis of the sample surface and to quantify some of parameters such as roughness and grain size. The Atomic Force Microscopy (AFM) images were analyzed using WSxM software [24]. The temperature dependence of the electrical resistance of these films was measured by using the standard direct current four-probe method.

![Diagram](attachment:image.png)

Figure 1. The schematic representation of the experimental procedure of LNO thin films.

3. Results and Discussion

The precursor thermal decomposition behavior may considerably influence the film composition and final properties. Such as, the lanthanum nickelate precursor solution was dried on hot plate at 80 °C for 2 h to obtain the precursor powder and investigated using TG-DTA analysis. Thermal analyses, illustrated in Figure 2a, were performed in static air from room temperature up to 1000 °C, at a rate of 10 °C/min. Based on TG-DTA data, it was observed that the decomposition temperature of the LNO precursor starts at 50 °C and ends up above 750 °C. TG-DTA analysis showed that the decomposition of the LaNiO3 precursor powder takes place in three steps. In the first step, two endothermic peaks appearing at temperatures of 115 and 300 °C are associated with water evaporation and with the melting of the propionate precursor complex, respectively. The partial mass loss of 9% corresponds to the water evaporation. In the second step, from 300 to 600 °C, DTA analysis finds one broad exothermic peak corresponding to the thermal decomposition and the burn off of the organic part with partial mass loss of 51%. In this stage, the corresponding intermediate decomposition phases are La2O(CO3)2 and NiO (JCPDS 22-1189), as confirmed by XRD pattern of the quenched sample from a temperature of 600 °C (Figure 3). Taking into consideration the thermal decomposition of individual precursors, the lanthanum [25], and nickel propionate-based precursors [26], it can be observed that the decomposition of the LNO precursor powder follows a similar pattern. Moreover, a reaction mechanism of the LNO decomposition can be proposed:
the decomposition of the LNO precursor powder follows a similar pattern. Moreover, a main species, respectively.

decomposition of Ni and La precursors that forms NiO and an intermediate La species, respectively.

proximity to a temperature of 300 and 340 °C, respectively, and can be related to the thermal decomposition of Ni and La precursors that forms NiO and an intermediate La species, respectively.

In the third stage, ranging from 600–900 °C, the phases present at a temperature of 300 and 340 °C, respectively, and can be related to the thermal decomposition of Ni and La precursors that forms NiO and an intermediate La species, respectively.

Considering these studies, one can presume that the decomposition of the precursor mainly takes place according to the following subsequent and superposed reactions:

\[
\begin{align*}
[\text{La}_2\text{(C}_3\text{H}_5\text{O}_2)_6\cdot(\text{H}_2\text{O})_3] 3.5\text{H}_2\text{O} + 2\text{Ni(C}_3\text{H}_7\text{O}_2)(\text{C}_3\text{H}_5\text{O}_2) + 4.25\text{O}_2 & \rightarrow \text{La}_2\text{O(C}_3\text{O}_3)_2 + \text{NiO} + \text{volatile product} (300–600 °C) \\
\text{La}_2\text{O(C}_3\text{O}_3)_2 + 2\text{NiO} & \rightarrow 2\text{LaNiO}_3 (600–700 °C) \\
2\text{LaNiO}_3 & \rightarrow \text{La}_2\text{NiO}_4 + \text{NiO} + 0.5\text{O}_2 (<900 °C).
\end{align*}
\]

By comparing the results of the thermal decomposition of the separate precursor with those of LNO precursor (Figure 2b), the third and fourth mass losses started in close proximity to a temperature of 300 and 340 °C, respectively, and can be related to the thermal decomposition of Ni and La precursors that forms NiO and an intermediate La species, respectively.

In the third stage, ranging from 600–900 °C, the phases present at a temperature of 600 °C are NiO and La$_2$O(CO$_3$)$_2$, respectively, as indicated by XRD pattern performed on the precursor powder (Figure 3). In this temperature range, the decomposition of the oxycarbonate phase takes place and a further reaction with NiO to form the LaNiO$_3$ phase. The crystallization of LNO as single phase with the pseudo-cubic perovskite structure was evidenced in the XRD pattern of the precursor powder annealed at 800 °C (Figure 3).
3.1. Thin Films Deposition and Characterization

Taking into account the thermal decomposition behavior of the LNO precursor powder, the LNO thin films were deposited on (100)STO substrate and crystallized in the temperature range 600–900 °C with two different heating ramps of 5 and 10 °C/min.

3.1.1. Heating Ramp: 5 °C/min

Figure 4 presents the θ-2θ scans of X-ray diffraction of the LaNiO$_3$ films obtained using a thermal treatment with 5 °C/min heating ramp. The θ-2θ patterns performed on the films annealed between 600–800 °C present only the (h00) reflections, indicating that these films are epitaxially grown with the epitaxial relationship ([1]LNO//[1]STO). These LNO films present a good crystallinity and no other peaks were observed, except for the diffraction peaks of (100)STO substrate. These observations indicate a good temperature stability of thin films. The indexing of the reflections was based on the pseudocubic perovskite lattice cell of LNO with a lattice parameter of $a_{\text{LNO}} = 3.84$ Å. It is to be noted that even if the DTA-TG analysis is performed on powder, the decomposition is not finished at 600 °C; the film heat treated at this temperature is crystallized. This is explained by the difference behavior of the decomposition processes when the analyzed species are decomposed in the form of films with respect to the powders due to low film/substrate mass ratio [27].

As reported by P. Odier et al. [28], an annealing temperature higher or equal to 800 °C leads to a phase instability. This phase instability can be observed also at 900 °C where two supplementary peaks appear, attributed to the La$_2$NiO$_4$ (JCPDS 34-1028) phase. Thus, at a higher temperature, LaNiO$_3$ decomposes in La$_2$NiO$_4$ and NiO, as explained by the following equation [29]:

$$2\text{LaNiO}_3 \rightarrow \text{La}_2\text{NiO}_4 + \text{NiO} + 0.5\text{O}_2$$  \hspace{1cm} (1)

The morphology of the LNO thin films heat treated at different temperatures and using a heating ramp of 5 °C/min was investigated using AFM, presented in Figure 5. The obtained images of the LNO thin films annealed in the temperature range 600–900 °C indicate a homogeneous distribution of the crystallites observed on the film surface, with the value of the root-mean-square-roughness, rms of 0.6, 1.5, 7.5, and 13 nm. The increase of the roughness values is directly proportional with the increase of the annealing temperature. At low temperatures (600 and 700 °C), AFM images indicate a crack-free and
homogeneous surface. With the increase in annealing temperatures (800 and 900 °C), the formation of outgrowth crystallites on the film’s surface is observed.

The morphology of the LNO layer was examined by an SEM micrograph (Figure 6). At 50 KX magnification, the film morphology has a plate-like aspect, but the surface of the film began to change with increase in annealing temperature. It is to be noted that the coalescence of the film is quite good without cracks and pores. In the case of the film annealed at 900 °C, the surface presents some nanosized particles, which do not appear in the case of 600 °C annealing temperature.

Figure 7a,b present the TEM cross-section images performed on the samples annealed at 600 and 900 °C, respectively. It can be seen that both the studied LNO films on STO substrates are compact and uniform without the presence of porosity along the cross-section.
direction. Generally, the films obtained by chemical methods present pores through the films thickness. The thickness, using a concentration of the precursor solution of 0.8 M, is about 50 nm.

![Figure 7. Cross-section of the TEM images of the LNO films annealed at (a) 600 and (b) 900 °C.](image)

3.1.2. Heating Ramp: 10 °C/min

Increasing the heating ramp at 10 °C/min, a similar crystallization study was performed in the temperature range of 600–900 °C, as well. The results of the XRD θ-2θ scans of the LNO films growth on STO substrates are shown in Figure 8a. The LNO films are well crystallized into single perovskite phase, and no other phase appears within the studied temperature range.

![Figure 8. XRD θ-2θ scans of LNO films on STO substrates at different crystallization temperatures using a heating of 10 °C/min (a); ω-scan through the (200) LNO (b).](image)

With respect to the films obtained with a lower heating ramp, no supplementary phases were observed at high crystallization temperatures. A similar behaviour was reported by Z. Duan et al. [30] in the case of the growth of LNO films on Si substrates coated with a thin layer of amorphous natural oxide-SiO₂ using different heating ramps.
They observed that the growth mechanism is controlled by thermodynamic nucleation: with the increase of the heating ramp, the c-axis of the LNO films is preferred, reaching a value of 99.57% orientation degree, while a low heating ramp leads to (110) orientation.

In order to investigate the degree of the preferred orientation, ω-scans analyses were performed. ω-scans around the (200) LNO peak demonstrate that these films have a good out-of-plane orientation. The values of the Full-Width-at-Half-Maximum (FWHM) of the rocking curve are situated in the range of 0.07°–0.4° (Figure 8b).

The surface morphology flattness of the thin films used as buffer layers in different functional devices is crucial for their integration into the superconducting architecture. The surface morphology of the LNO films obtained with a heating ramp of 10 °C/min were also characterized by AFM and is presented in Figure 9. The rms values of the studied thin films with a scan area of 5 µm × 5 µm are about 1.9, 2.4, 3 and 10 nm for LNO films crystallized at 600, 700, 800, and 900 °C, respectively. As compared with LNO films obtained with a lower heating ramp, it can be observed that the rms values (Figure 10) are closed. All these studied LNO films are dense and continuous. With the increase in crystallization temperature up to 900 °C, some outgrowths are present on the film surface.

![AFM images of the LNO thin films crystallized at different temperatures](image)

**Figure 9.** AFM images of the LNO thin films crystallized at different temperatures (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Figure 11 shows SEM micrographs of LNO thin films as a function of annealing temperature using 10 °C/min heating ramp. As can be seen in Figure 11a, the surface of the films annealed at 600 °C is crack-free and very smooth. However, some grain size is observed on the surface of the LNO films annealed at 900 °C (Figure 11b).
Figure 10. RMS roughness of LNO films using 5 and 10 °C/min heating ramp as the function of annealing temperature.

Figure 11. SEM images of the LNO films annealed at (a) 600 °C, (b) 900 °C.

Figure 12 shows the cross-sectional microstructure of the LNO films obtained with 10 °C/min heating ramp annealed at 600 and 900 °C, respectively. Figure 12 shows the TEM image of the cross-sectional area of the thin film indicating a dense film without pores and cracks. Based on the TEM data, the thickness of the epitaxial film was estimated to be around 55 nm.

Figure 12. Cross-section of the TEM images of the LNO films annealed at (a) 600 and (b) 900 °C.
Several groups have investigated the growth of LNO on different substrates (surface aspects) by using chemical methods. (i) modified Pechini method obtained LNO thin films with rms values of about 5.4 nm and 5.3 nm crystalized at 700 and 800 °C for one layer deposition [31]. On increasing the number of layers, the rms decreases to 2.9 nm for 700 °C and increases to 7.8 nm for the sample annealed at 800 °C. (ii) Using the CSD method [30], for a lower scan area of 1 µm × 1 µm, the rms values of the studied samples were in the range of 2.8–5.2 nm at a temperature of 750 °C. A detailed study of the morphology evolution using different single crystalline substrates (LAO, STO, MgO, sapphire) is presented in [32]. The best AFM rms values were obtained on LAO substrates, 5.7 nm. For LNO thin films on sapphire, the rms roughness increased to 42.8 nm. D.S.L. Pontes et al. [33] studied the growth of LNO on SrLaAlO$_4$ substrates at different thicknesses. All the thin films had smooth surfaces with rms roughness below 5 nm at a temperature of 700 °C. As compared with our results, at a same temperature, lower rms values were observed.

3.1.3. Electrical Characterization

The electrical properties of the LNO films were determined by performing R vs. T measurements using a four-point probe method. The results are presented in Figure 13a,b. The temperature dependence of electrical resistance shows a good metallic-like behavior for both heating ramps studied.

The temperature coefficient of resistivity was calculated as the average slope of the resistance in the temperature range from 200 to 300 K. The result is presented in Figure 14. The temperature coefficient decreases with increase in annealing temperature. It also strongly depends on the heating rate. Thus, the temperature coefficient for the sample annealed at 900 °C is $1.5 \times 10^{-3}$ and $5.5 \times 10^{-3}$ K$^{-1}$ for the heating ramp of 10 and 5 °C/min, respectively.

It is to be noted that these values are very close to those for pure metal (e.g., $3.86 \times 10^{-3}$ for pure Cu). For resistivity measurements, the samples were patterned using the standard UV photolithography and wet etching techniques in order to obtain 1 cm long and 100 µm wide strips.

Figure 15 exhibits a comparison of the resistivity values at 300 K of thin films deposited on STO substrates and using two different heating ramps. An increase in resistivity values with increase in the crystallization temperature of thin films was observed.
Resistance vs. temperature dependence of the LNO films using a heating ramp of (a) 5 °C/min and (b) 10 °C/min. TCR was obtained by linearly fitting the resistivity vs. temperature in the range 200–300 K.

Figure 15. Resistivity vs. temperature dependence of LNO films using 5 and 10 °C/min heating ramp.

For a heating rate of 5 °C/min, the electrical resistivity at 900 °C is about by three orders of magnitude greater with respect to the sample crystallized at 600 °C. This behavior is in a good agreement with XRD diffraction patterns, which indicated the presence of other phases at high annealing temperatures. The increase in resistivity with annealing temperature above 900 °C was attributable to the decomposition of LNO. Similar trends of the resistivity versus annealing temperature were also reported for LNO films fabricated on SiO$_2$/Si substrates [34] and on Si, SrTiO$_3$ and fused quartz substrates [17]. On a STO substrate, when the La$_2$NiO$_4$ phase appears in the film annealed at a high temperature, the valence state of a part of the Ni ions in the LNO films changes from Ni$^{+3}$ to Ni$^{+2}$. The reduction in numbers of free electrons in the LNO film causes an increase in resistivity of the film.

In this case of LNO thin films crystallized using a heating ramp of 10 °C/min, the effect of crystallization temperature is more reduced with respect to the film using a 5 °C/min heating rate. This may be due to the fact that short heating time leads to small grain size, whilst small grains possess large surface energy promoting grain growth of LNO.
during annealing. However, in this study, no peak generated by the decomposition of LNO is observed in the XRD results for the LNO films, even those annealed at a temperature of 800 °C (Figure 8a). This behavior could be explained by the fact that at low heating rates, the time to react is higher with respect to high heating rates.

4. Conclusions

Towards a better understanding of LNO thin films growth, the thermal decomposition of precursor powder was investigated. The thermal decomposition of the LNO precursor powder takes place in three main stages, indicating the LNO final compound as a single phase at 750 °C.

Regarding the films’ growth, epitaxial LNO thin films on (100)STO substrates were grown by chemical solution deposition using two heating rates (5 and 10 °C/min) and the crystallization temperature varying between 600–900 °C. For low heating ramps of LNO films (5 °C/min), XRD analysis indicated a high degree of crystallinity for the low crystallization temperatures confirmed by the present of diffraction fringes. The surface morphology of these films is smooth and without cracks. Furthermore, at high crystallization temperatures, the secondary phase was detected, meaning phase instability with the outgrowth presents on the films surface.

Increasing the heating ramps of the LNO films to 10 °C/min leads to epitaxial growth without the formation of any secondary phases. Surface images obtained by AFM exhibited low roughness values. Electrical resistance measurements demonstrated that the LNO film showed good metallic behavior with electrical resistivity of about 10^{-4} Ω·cm at room temperature and a temperature coefficient ranging from 1.5 × 10^{-3} to 5.5 × 10^{-3} K^{-1}, very close to that Cu. A potential limitation associated with the growth mechanism of oxides from the deposited layer of the precursor solution also emerges in the difficulty of texturing the phase: the textured target phase must grow from the interface with substrate in an existing precursor film, rather than growing epitaxially one monolayer at a time as is the case of some vapor methods.

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