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Journal of the European Ceramic Society 27 (2007) 3819–3822

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Tailoring of morphology and orientation of $LaNiO_3$ films from polymeric precursors

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Abstract

The aim of this work was to prepare lanthanum nickel oxide ($LaNiO_3$, LNO) thin films of different morphology and orientation. The precursor solutions were prepared by a chemical method from citric salts of lanthanum and nickel. Films were deposited using spin-on technique on Si (1 0 0) substrates. Tailoring of the films orientation and morphology has been attained through two thermal treatment processes with different heating devices: tubular furnace (process 1) and hot plate (process 2). Films were annealed at 600 and 700 °C, with heating rates: 20 °C/min (process 1) and 1 °C/min (process 2). Annealing times were from 30 min to 20 h. LNO films were characterized by AFM and X-ray diffraction analysis. Depending on the heating process applied, the obtained films showed very different structures, from completely amorphous to well crystallized and highly oriented. Films treated by process 1 were polycrystalline, had smaller oval grains and lower roughness parameters than films heated on a hot plate. Due to the low heating rate and heating from the substrate side, films obtained through process 2 were highly (1 1 0) oriented with elongated grains aligned along one direction.

Keywords: Precursors-organic; Films; $LaNiO_3$

1. Introduction

Among perovskite oxides with one lanthanide and one transition metal atom, $LaNiO_3$ stands out, because of its electric,[1] magnetic[2] and catalytic[3] properties. This oxide has very high conductivity which makes it suitable replacement for platinum electrodes in ferroelectric devices. Similarity of cell parameters of LNO and the ferroelectric layer enables better adhesion of ferroelectric layer on LNO.

Different methods are used for preparation of LNO thin films. Physical methods, such as PLD[4] or RF sputtering,[4] are more suitable for growing epitaxial films, but these methods require very expensive and sophisticated experimental conditions. On the other hand, chemical methods are simpler but they require further improvement for obtaining thin films with satisfactory properties. Methods for deposition of thin films from the solutions are especially interesting because they enable good control over the stoichiometry of prepared oxide films and do not require high working temperature. Also, they are reproducible and make easier the deposition of thin films over the larger surface. Optimization of precursor solutions' parameters (such as concentration, viscosity, pH, etc.), type of substrates,[5] as well as optimization of thermal treatment conditions[6] enables better control over the microstructure and therefore, over the electric properties of the deposited film.

The aim of this work is to investigate the dependence of crystallinity and microstructural properties of LNO thin films (grain size, roughness and homogeneity) on thermal treatment conditions, such as heating rate and construction of the heating devices. The main idea was to prepare LNO films of different orientation and morphology on Si substrates.

2. Experimental procedure

LNO precursor solution was prepared by modified Pechini method.[7] Citric acid was added into a water suspension of lanthanum-oxide (La_2O_3); the molar ratio of La^{3+} and citric acid was 1:4. After refluxing for 2 h at 120 °C, an amorphous lanthanum citrate was obtained, and then dissolved in aqueous ammonia, until pH of the solution was around 7. Nickel citrate

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doi:10.1016/j.jeurceramsoc.2007.02.052

was prepared by heating the water solution of nickel acetate [$Ni(CH_3COO)_2 \cdot 4H_2O$] and citric acid. Molar ratio of Ni^{2+} and citric acid in this solution was 1:4. In both citrate solutions ethylene glycol was added in molar ratio 60:1 with respect to metal ions. These two solutions were mixed, with La:Ni molar ratio equal to 1, to make the final precursor solution. The viscosity of final precursor solution was adjusted to 30 cP.

Precursor solution was deposited on Si (1 0 0) substrates by spin-on technique (3000 rpm, 30 s) and thermally treated under different conditions. In a tubular furnace, the films were slowly heated up to 300 °C (heating rate was 1 °C/min) and then they were heated up to 600 and 700 °C (heating rate was 20 °C/min) where they were annealed for 30 min (process 1). On a hot plate, films were constantly heated with the heating rate of 1 °C/min, up to 700 °C, where they were annealed for 1, 10 and 20 h (process 2).

Microstructure of thin films was analyzed by AFM (AutoProbe CP Research, TM microscopes). 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 micrographs. Elongation factors (f) of the grains were calculated from the equation: $f = D_1/D_2$. X-ray diffraction measurements (θ–2θ) were performed on Bruker D8-Advance diffractometer using Cu Kα radiation.

3. Results and discussion

The microstructure of the thin film thermally treated by process 1 and annealed at 600 °C is shown on Fig. 1. From the XRD pattern shown on Fig. 2a it can be seen that the surface of the film is amorphous, and that annealing temperature is too low for complete crystallization. That is the reason for increasing the final annealing temperature in both processes to 700 °C.

All the films, obtained by both processes, and annealed at 700 °C, are smooth, uniform, without cracks or pores, which is the result of well optimized synthesis conditions (composition of precursor solution, method of deposition, annealing temperature). Anyway, microstructure, i.e. shape and size of the grains strongly depend on the thermal treatment.

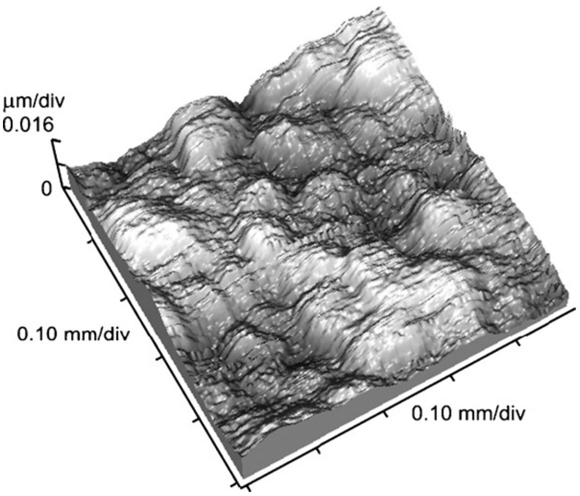

Fig. 1. AFM micrograph of amorphous LNO thin film obtained by process 1 and annealed at 600 °C.

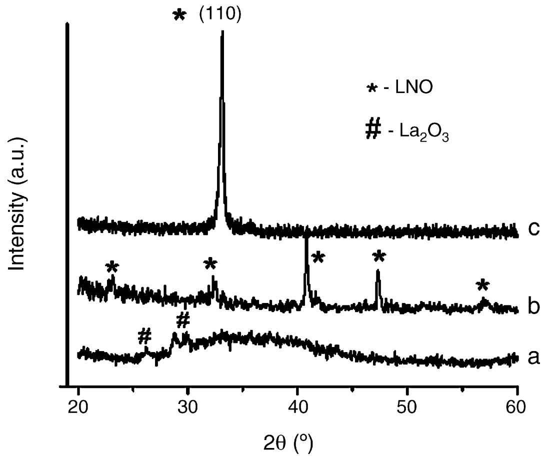

Fig. 2. XRD pattern of LNO thin film (a) amorphous, (b) polycrystalline and (c) (1 1 0) oriented.

During the thermal treatment of each deposited layer, different processes take place on particular temperatures: evaporation of water and ethylene glycol, structural rearrangements inside the layer, pyrolysis of organic material, etc.[8] All these processes lead to densification of the film, formation of crystallization cites and the grain growth. First phase of the heating treatment (up to 300 °C) for both processes is the same: that is the temperature range in which solvents evaporate, and structure of polyester matrix changes through rearrangements of the ions inside of it. At the temperatures above 300 °C the process of formation and crystallization of the oxide film begins.

The microstructure of the polycrystalline LNO thin film obtained by process 1 and annealed on 700 °C is shown in Fig. 3. Grains are oval ($f = 1.6$), densely packed and homogenously distributed on the film's surface. Its roughness is very low: $R_a = 2.9$ nm and Rms = 3.5 nm. Average grain size is around 49 nm ($D_1 = 82$ nm, $D_2 = 50$ nm). However, the grains are not all of the same size, which can be result of several factors. Large number of the smaller grains is a result of formation of more nucleation cites, which means that the process of nucleation is more favorable than the grain growth process. The number of formed crystallization centers depends on the heating rate,[9] temperature on the substrate/film interface, temperature of the film layer but also on the temperature of the film's surface. With increase of heating rate from 1 to 20 °C/min temperature of crystallization is reached faster, which leads to the multiplication of nucleation cites and therefore of the number of the grains. Above 300 °C, the pyrolysis of organic material begins. Gasses released through this process can be left "trapped" during the faster densification of the film and form pores which can act as additional nucleation cites.[10] The XRD analysis (Fig. 2b) showed that films annealed in tubular furnace, i.e. films uniformly heated in all directions, are polycrystalline with randomly oriented grains.

The construction of heating device can also influence the microstructure of the film.[6] The films treated by process 2 were heated only from the bottom, i.e. from the substrate side, so the temperature on the film's surface was considerably lower.

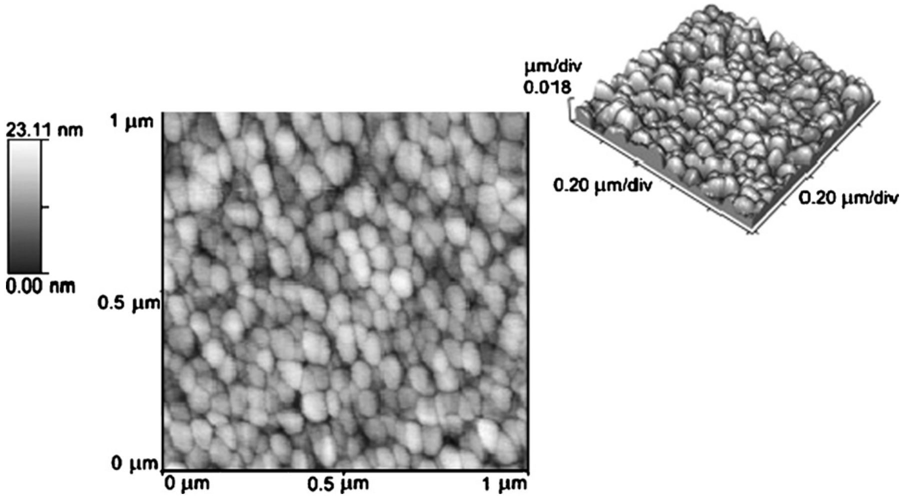

Fig. 3. AFM micrograph of polycrystalline LNO film obtained by process 1 and annealed at 700 °C.

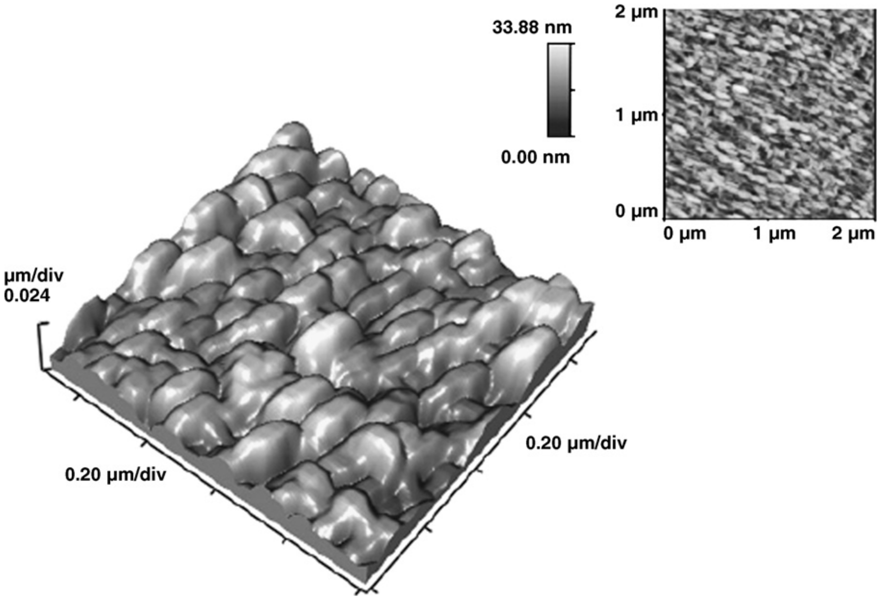

Fig. 4. AFM micrograph of oriented LNO thin films obtained by process 2 and annealed at 700 °C for 10 h.

Regardless its low thickness, the temperature difference existed through the film, leading to formation of majority of nucleation cites on the substrate/film interface, while less cites are formed on the surface[11] of the film.

Surface microstructure of the films obtained by process 2 is shown in Fig. 4. Their morphology is completely different to those obtained by process 1: grains are oval, flat, very elongated and aligned along certain direction. Based on literature data,[9] it would be expected for process 2 to result in even broader grain size distribution than process 1. Still, grain size distribution is homogenous for all annealing periods and grain size increased with increasing annealing time, while the roughness of these films is very low (Table 1.).

Fig. 2c shows the XRD pattern of the LNO thin film obtained by process 2. The existence of only one peak on $2\theta = 33.02^\circ$ indicates that the film is highly (1 1 0) oriented. Some authors[1,12] reported on obtaining films with highly (1 0 0)-orientation by chemical methods. LNO thin films with (1 1 0) preferred orientation were already obtained by pulsed laser deposition[4] on Si (1 0 0) substrates. The key similarity between our process 2 and PLD could be the heating of the films from the substrate side which is present in both methods.

Low heating rate during thermal treatment of the film enables slower realization for all processes. It leaves enough time for complete pyrolysis and better rearrangement of metal ions

Table 1
Grain size and roughness of LNO thin films thermally treated by the process 2, annealed for different times at 700 °C

Annealing time (h)	Grain size (nm)	R_a (nm)	Rms (nm)	f
1	115	2.7	3.6	2.6
10	134	4.3	5.5	2.3
20	148	2.17	2.8	2.4

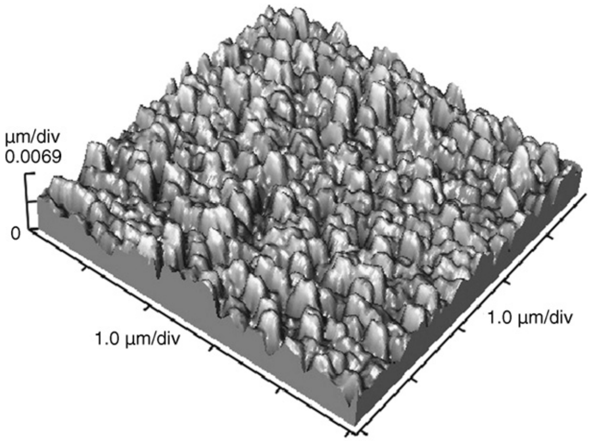

Fig. 5. AFM micrograph of columnar growth of two-layered LNO thin film obtained by process 2.

within the formed gel. Consequently it leads to formation of smaller number of crystallization centers at lower temperatures. The energy released through pyrolysis of the organic material may not be enough for forming other crystallization cites, but it could be sufficient for growth of the grains over the existing ones. Also, the process of densification is slowing down, leaving enough time for all gasses to leave the film without making any cracks or pores.[11]

Increase in the number of layers on the films treated by process 2, led to "columnar growth" of LNO films,[8] i.e. grains grew intensively in the z-direction, where z-direction refers to z axis of AFM micrograph, not crystallographic z axis (Fig. 5). This is in accordance with the idea of influence of the temperature gradient through the film on the grain growth from the substrate direction, considering the fact that grains formed in the first layer act as nucleation cites for the second layer.

Similarities of cell parameters of Si[13] and LNO[5] make easier adhesion between the substrate and the film which leads to the formation of highly oriented and even epitaxial thin films. Obviously, the heating of the films from the substrate side (process 2) and the existence of thermal gradient through the film, enables the formation of LNO films on Si substrates with (1 1 0) preferred orientation by chemical method. Several authors who used similar heating conditions reported on obtaining epitaxial LNO films of different orientation even on amorphous substrates.[10]

4. Conclusion

In this paper, smooth, crack-free LNO thin films were successfully prepared from polymeric citrate precursors on Si substrates. Using a conventional heating treatment polycrystalline films were obtained. Highly (1 1 0) oriented thin films, with very elongated grains, were obtained by decreasing the heating rate of the treatment from 20 to 1 °C/min and by heating from the bottom of the substrate. Nucleation and crystallization mechanisms were discussed. Given results proved that the morphology of LNO thin films strongly depends on heating conditions and that orientation and crystallinity of the films deposited by chemical solution deposition can be controlled and tailored by changing of thermal treatment conditions.

Acknowledgment

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

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