TEM and FESEM investigation of lanthanum nickelate thin films obtained by chemical solution deposition

Milica Počuča-Nešić[1,*], Goran Branković[1], Slavko Bernik[2], Aleksander Rečnik[2], Dana Vasiljević-Radović[3], Zorica Branković[1]

[1]*Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, 11000 Belgrade, Serbia*
[2]*Jožef Stefan Institute, Department for Nanostructured Materials, Jamova 39, 1000 Ljubljana, Slovenia*
[3]*IHTM - Institute of Microelectronic Technologies and Single Crystals, Njegoševa 12, 11000 Belgrade, Serbia*

Received 30 March 2012; received in revised form 5 May 2012; accepted 15 May 2012

Abstract

Lanthanum nickelate (LNO) is a perovskite oxide material with metallic conductivity in a wide temperature range which makes it suitable for application as electrode material for thin films. In this paper LNO thin films were prepared by polymerizable complex method from the diluted citrate solutions. Precursor solutions were spin coated onto Si-substrates with amorphous layer of SiO_2. Deposited layers were thermally treated from the substrate side with low heating rate (1 °/min) up to 700 °C and finally annealed for 10 hours. Results of AFM and FESEM showed that films are very smooth (Ra = 4 nm), dense, crack-free and with large square-shaped grains (170 nm). According to FESEM and TEM results the obtained four-layered film was only 65 nm thin. EBSD and XRD analyses confirmed polycrystalline microstructure of the films without preferential orientation. It was concluded that the presence of SiO_2 layer on Si substrate prevents epitaxial or oriented growth of LNO.

Keywords*: lanthanum nickelate, films, electron microscopy, microstructure*

I. Introduction

Because of their simple ABO_3-type structure and possibility of various cations occupying A and B sites, perovskite oxides show great diversity about their chemical and physical properties which is very important for their technological applications. They can reveal piezoelectric ($Pb(Zr,Ti)O_3$), relaxor ferroelectric ($(Pb(Nb,Mg)O_3$), dielectric ($BaTiO_3$), electro-optic ($(Pb,La)(Zr,Ti)O_3$), magneto-resistive ($LaMnO_3$) or catalytic properties ($LaCrO_3$) [1]. When conductivity of perovskite oxides is considered, they can be superconductors ($(K,Ba)BiO_3$), insulators, ionic ($BaInO_{2.5}$) or metallic conductors ($CaRuO_3$, $LaNiO_3$, $La_{0.5}Sr_{0.5}CoO_3$, $(La,Pr)_{0.7}(Sr,Ca)_{0.3}MnO_3$).

Lanthanum nickelate ($LaNiO_3$, LNO) can be used as an oxygen sensor or catalyst for the combustion of lower hydrocarbons but its major application derives from its metallic conductivity in wide temperature range [2]. This feature makes LNO a candidate for the bottom electrode material for ferroelectric thin films. For this purpose LNO films have to be very thin, dense, with homogenous surface without cracks or pores. These requirements can be fulfilled by means of physical methods for the preparation of thin films, but also by chemical methods under appropriate processing conditions.

Chemical solution deposition (CSD) methods are very attractive as a low-cost alternative for the expensive physical methods. CSD methods are very flexible concerning precursors and solvents used in the preparation route, coating techniques and thermal treatment of the deposited layers [3]. Polymerizable complex method, one of the CSD methods, derives from the Pechini patent [4] and it uses multifunctional organic acids as chelating agents for cations present in the solution. In this method, diols are also used, firstly as solvents and later in the polyesterification reactions with free carboxylic groups of organic acid. During this reaction polyester network is formed with metal ions distributed on atomic level inside.

In our previous investigation we showed that it is possible to prepare highly oriented LNO thin films on Si

* Corresponding author: tel: +381 11 208 5032
fax: +381 11 208 5038, e-mail: *milicaka@imsi.rs*

monocrystal using CSD and appropriate thermal treatment [5]. Gradient thermal annealing was applied, in which the deposited layer is heated from the substrate side at a very low heating rate. Slow heating reduces the defect formation by providing enough time for pyrolysis of the organic material and diffusion of species existing in the film. Also, during this kind of treatment, a temperature gradient is formed inside the film with the lowest temperature on the film's surface and the highest on the substrate/film interface where the nucleation takes place. A long annealing time is used to obtain a larger grain size of the films.

In this work the similar method was applied, but on amorphous SiO_2 substrate. The crystallinity, orientation and microstructure of the obtained films were investigated.

II. Experimental

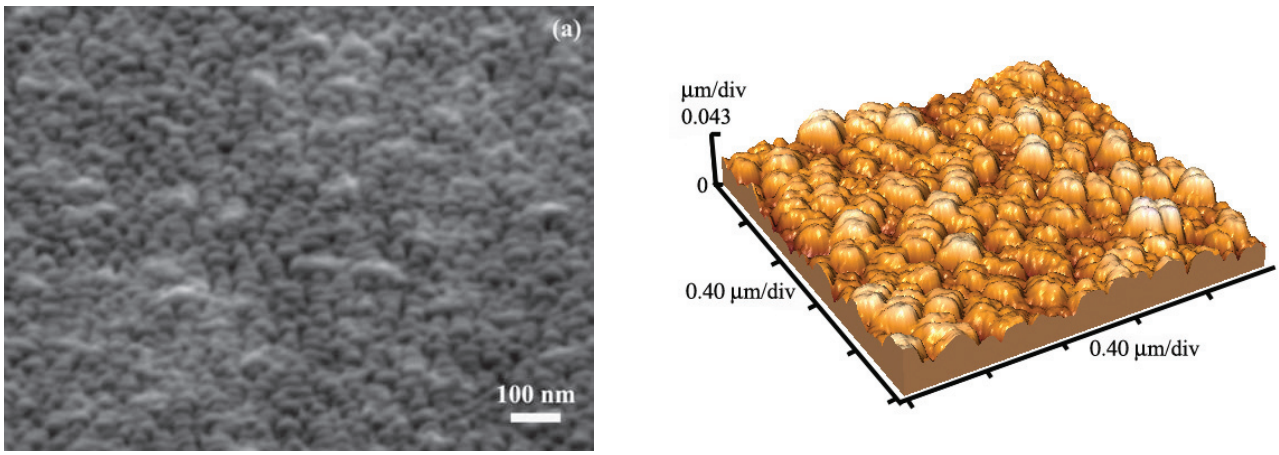
In this paper LNO thin films were prepared by polymerizable complex method from the citrate precursors. Lanthanum oxide (La_2O_3, Alfa Aeser, 99.99 %, USA), nickel acetate ($Ni(CH_3COO)_2 \times 4H_2O$, Fluka, 98 %, USA) and citric acid (CA, $C_6H_8O_7$, Lach-Ner, 99.8 %, Czech Republic) were used as starting materials for the preparation of LNO precursor solution. The water suspension of La_2O_3 and CA, with molar ratio La^{3+} : CA = 1 : 4, was refluxed for 2 hours at 120 °C. White precipitate of lanthanum citrate was obtained and further dissolved with aqueous ammonia (Hemos, Serbia). The pH value of the final solution was 7. Nickel citrate was prepared by heating the water solution of nickel acetate and citric acid. The molar ratio of Ni^{2+} and citric acid in this solution was 1 : 4. In both citrates solutions ethylene glycol (EG, $C_2H_2(OH)_2$, Lach-Ner, 99 %, Czech Republic) was added in excess with molar ratio CA : EG = 1 : 15. Final precursor solution was prepared by mixing lanthanum and nickel citrate solutions in an equimolar ratio. The viscosity of the precursor solution was adjusted to 30 mPa×s using a Haake Rotovisco RV 20 viscometer (Haake, Germany).

Precursor solution was spin-coated onto amorphous SiO_2/Si (111) substrate (3000 rpm, 30 s) to obtain single layer of LNO film. The spin-coater used was SCS G3P-8 Spinocoat Specialty Coating Systems (Cookson Electronics Equipment, USA). The as-deposited layer was thermally treated in the following manner: the coated substrate was slowly heated on a hot alumina plate only from the substrate side. The heating rate was very low: 1 °/min, from room temperature up to 700 °C where deposited film was annealed for 10 hours. A new layer of precursor solution was spin-coated only after the whole thermal treatment of previous layer was completed. Samples with two and four layers of LNO were prepared.

The microstructure of thin films was analyzed by the following methods: atomic force microscopy, AFM (AutoProbe CP Research, TM microscopes, USA), field emission scaning electron microscopy, FESEM (JEOL 6500S, Japan) equipped with EBSD system (Oxford Instruments Inca Crystal 400, UK) and high-resolution transmission electron microscopy, HRTEM (JEM-2100, JEOL, Japan). In order to study the interface and crystallinity of the LNO layers, the samples were prepared by a cross-section technique. The TEM specimens were ion-milled until perforation using Ar^+ ions at energy of 4 kV (RES 010, Bal-Tec AG, Balzers, Liechtenstein). X-ray diffraction (XRD) analysis was performed on four layered film using a Rigaku RINT 2000 diffractometer (Japan), with Ni filtered CuK_α radiation (λ = 1.54178 Å).

III. Results and discussion

The surface microstructure of the four layered LNO thin film deposited on SiO_2/Si (111) is shown on Fig. 1. From these micrographs it can be seen that the surface of the prepared film is very dense, smooth and uniform without any cracks or pores. AFM micrograph show that LNO thin films deposited on SiO_2/Si (111) substrates had homogenous surface with tetragonal grains and uniformly distributed grain size. The mean size of these grains was 180 nm.



a) b)

Figure 1. FESEM and AFM micrographs of LNO thin films: a) 4-layered, b) 2-layered

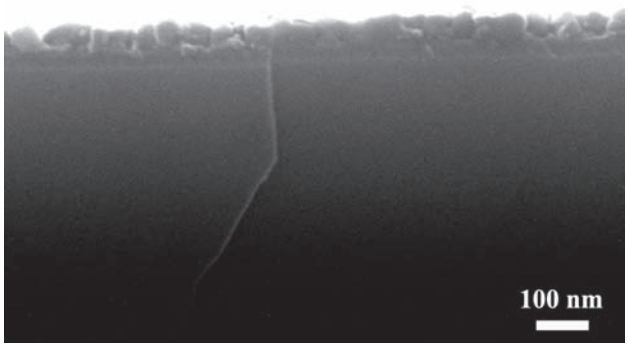


Figure 2. Cross-section of LNO thin film on amorphous SiO_2 layer

RMS roughness values of these samples were around 4.5 nm, which is lower value than reported one obtained by metalorganic decomposition method [6]. The thin films with RMS roughness values below 5 nm are considered to be smooth enough to be used as bottom electrode [7] in ferroelectric devices. Low roughness values were expected since we used CA : EG ratio which is close to the one proposed in the literature data for the preparation of smooth thin films [8].

Ethylene glycol in precursor solution serves not only as the polymerization agent but also as the solvent. Its large quantity in the precursor solution can significantly reduce solution's concentration. Having in mind that decreasing the concentration of the precursor solution leads to the formation of the films with lower thickness values [9] we expected the obtained LNO thin films to be very thin. This assumption was proved by measuring the thickness of the obtained films by SEM and HRTEM (Figs. 2 and 3). The thickness of the four layered LNO thin film determined from the cross section of the films was 65 nm and the thickness of amorphous layer of SiO_2 formed on Si (111) substrate is around 28 nm. Also, the mean crystallite size of LNO thin films is less than 10 nm.

From these figures it can be seen that deposited film consisted of columnar grains and each grain was grown through the whole width of the film. This microstructure is expected in CSD derived perovskite films where heterogeneous nucleation occurs at the substrate/film interface [3]. In our investigation thin films were heated from the substrate side, at a very low heating rate, to avoid the situation of typical heat scenarios where the probability for bulk and interface nucleation is equal, and to promote nucleation at the substrate/film interface by providing a thermal gradient inside the film. Grain growth from nuclei proceeds from the substrate towards the surface of the film resulting in coarse crystallinity in the resulting film. As already mentioned, the apparent mean grain size derived from the surface analyses of the films is 180 nm, which is almost 3 times of the film's thickness. Nevertheless, from the 3D AFM micrograph it can be recognized that each of these grains is composed of four smaller, round shaped grains, as the result of the long annealing period during which coalescence of smaller grains occurs. Also, from the molar ratio between citric acid and metal ions (*Rc* value) employed in this experiment larger grain size is expected. It is known that grain size increases with the increasing *Rc* value, and that higher citrate and lower metal ion concentrations in the precursor solutions is more favorable for crystallization and grain growth [8].

The existence of columnar grains suggests some kind of oriented structure of the investigated thin films which could be expected since the growth of oriented LNO thin films on amorphous substrates was previously reported in literature [10,11]. In our case a large amount of ethylene glycol present in the solution could reduce tensile stress on the substrate/film interface and combined with very low heating rate leaves enough

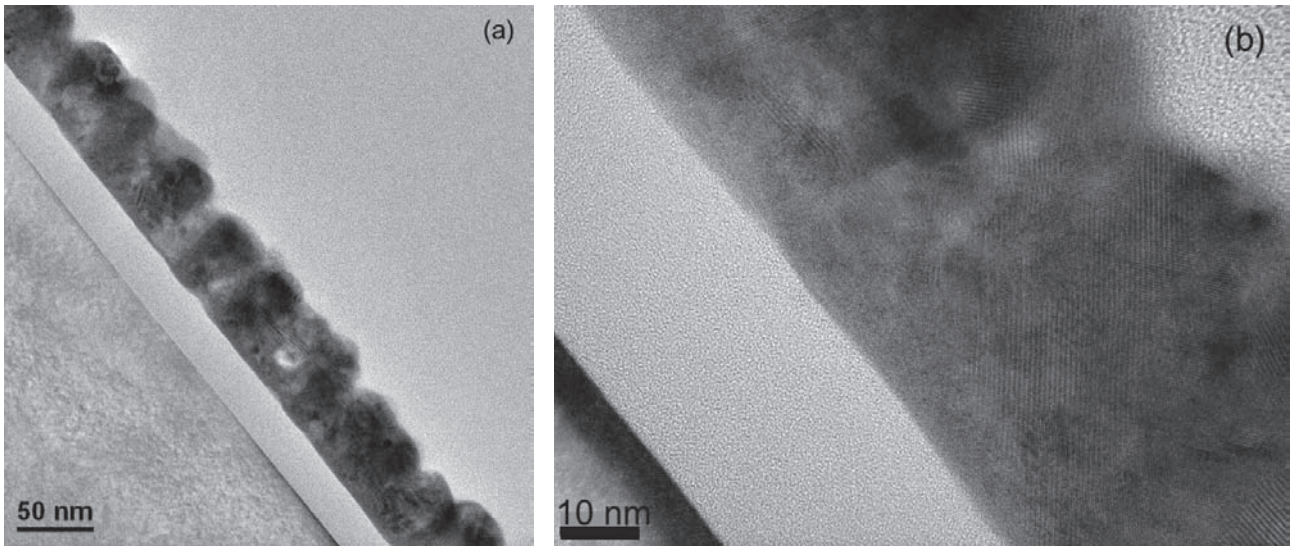


Figure 3. Cross-section HRTEM micrographs of 4-layered LNO thin film

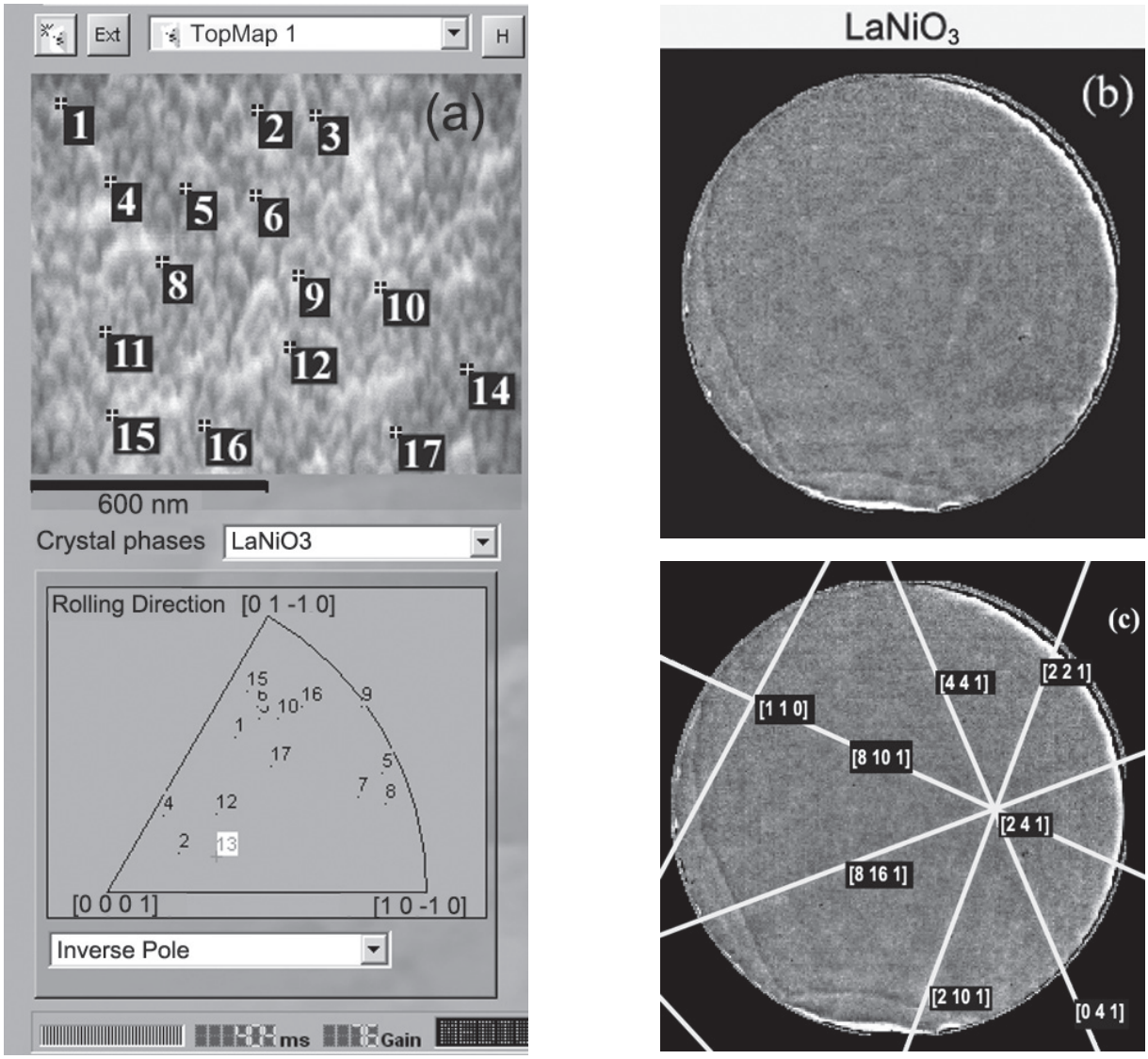


Figure 4. a) SEM micrograph with points in which diffraction analysis was done and corresponding Inverse pole figure; b) Kikuchi pattern at point 13; c) Kikuchi pattern at point 7

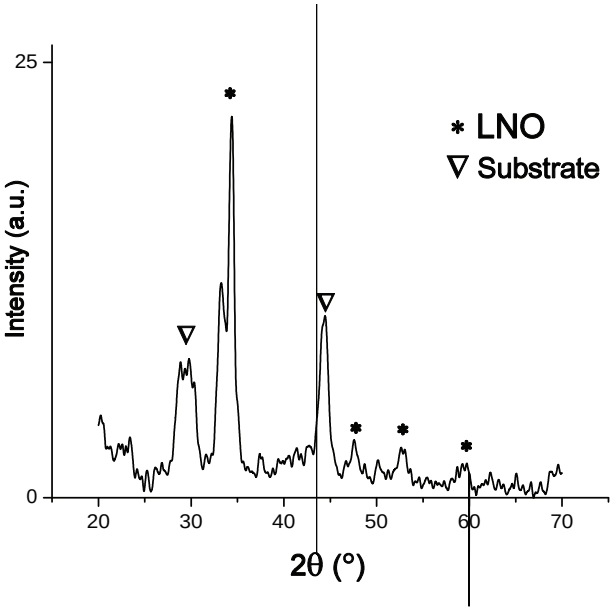


Figure 5. XRD pattern of the four layered LNO thin film

time for the volume reduction and rearrangement processes in the film [3]. The films consist of single columnar grains, which are crystallographically oriented but not necessarily show an in-plane orientation or a relation to the lattice of the underlying substrate [12].

In order to further investigate orientation and crystallinity of the obtained LNO thin films EBSD analyses on more than 20 different points on the film's surface and XRD were performed. The results of these analyses show that the films are polycrystalline without preferred in-plane orientation (Figs. 4 and 5).

Thin film microstructure and orientation depend on several different parameters: solution properties, thermal treatment conditions and the substrate used. It is known from the literature data that combination of the low solution's concentration and the thermal treatment conditions where each layer is annealed before the next layer is coated, heterogeneous nucleation is promoted and the chanc-

es for the preparation of epitaxial thin films significantly increase [3]. Although low concentration of solution and special thermal treatment conditions enabled columnar grain growth, the preparation of highly oriented films requires an appropriate substrate, for example Si (100) or Si (111), as reported in our previous investigation [5]. It is clear that in our experiment the choice of the substrate used is the crucial parameter for the observed orientation and structural properties of LNO thin films.

IV. Conclusions

LNO thin films were prepared by chemical solution deposition method on amorphous silica substrates. Even though our previous results showed the possibility of preparation of highly-oriented thin films on *monocrystal substrates* using the same thermal treatment method, in this investigation the LNO films deposited on *amorphous substrate* were polycrystalline. Obviously the presence of SiO_2 layer on Si substrate prevents epitaxial or oriented growth of LNO. Nevertheless, the films are of very good quality: four layered LNO film has thickness of 60–65 nm, they are very smooth (*Ra* = 4 nm), homogeneous, dense, crack-free and with large square-shaped grains (170 nm).

Acknowledgements: This work was financially supported by the Ministry of Education and Science of the Republic of Serbia through the project III45007.

References

1. L.Q. Jiang, J.K. Guo, H.B. Liu, M. Zhu, X. Zhou, P. Wu, C.H. Li, "Prediction of lattice constant in cubic perovskites", *J. Phys. Chem. Solids*, **67** (2006) 1531–1536.
2. D.P. Norton, "Synthesis and properties of epitaxial electronic oxide thin-film materials", *Mater. Sci. Eng. R*, **43** (2004) 139–247.
3. R.W. Schwartz, T. Schneller, R. Waser, "Chemical solution deposition of electronic oxide films", *C.R. Chimie*, **7** (2004) 433–461.
4. M.P. Pechini, "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor", U.S. Patent 3 330 697, July, 1967.
5. M. Počuča, G. Branković, Z. Branković, D. Vasiljević-Radović, M Mitrić, "Tailoring of morphology and orientation of $LaNiO_3$ films from polymeric precursors", *J. Eur. Ceram. Soc.*, **27** (2007) 3819–3822.
6. 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.
7. J. Zhu, L. Zheng, Y. Zhang, X.H. Wei, W.B. Luo, Y.R. Li, "Fabrication of epitaxial conductive $LaNiO_3$ films on different substrates by pulsed laser ablation", *Mater. Chem. Phys.*, **100** (2006) 451–456.
8. S. Saka, *Handbook of Sol-Gel Science and Technology, Processing, characterization and applications*", Vol. 1. Sol-gel Processing, Kluwer Academic Publishers, 2005.
9. 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** (2005) 48–52.
10. S. Miyake, K. Yamamoto, S. Fujihara, T Kimura, "(100)-Orientation of pseudocubic perovskite-type $LaNiO_3$ thin films on glass substrates via the sol-gel process", *J. Am. Ceram. Soc.*, **85** (2002) 992–994.
11. Z.J. Wang, T. Kumagai, H. Kokawa, "Microstructure and electrical properties of lanthanum nickel oxide thin films deposited by metallo-organic decomposition method", *J. Cryst. Growth*, **290** (2006) 161–165.
12. R.M. Waser, "Microstructure of ceramic thin films", *Curr. Opin. Solid State & Mater. Sci.*, **1** (1996) 706–714.