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XPS STUDY OF SOL–GEL PRODUCED LANTHANUM OXIDE THIN FILMS

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La_2O_3 thin films were prepared by a sol–gel method and annealed in air and vacuum at various temperatures. The X-ray photoelectron spectroscopy (XPS) was used to investigate the properties and composition of films. The La 3d and O 1s spectra of films were analysed. It was shown that oxygen ions in La_2O_3 are in two states – O^{2-} anions connected with lanthanum, and oxygen in the $(OH)^-$ group. The thermal transformation of lanthanum hydroxide to oxide process was triggered by thermal treatment at temperatures above 600 K. It was shown that after annealing thin films for longer time intervals in vacuum the intensity of O^{2-} component increases and the intensity of oxygen in $(OH)^-$ decreases. The drop of oxygen in the $(OH)^-$ group was attributed to dehydration process.

Keywords: La_2O_3 thin films, sol–gel method, XPS, oxide materials

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1. Introduction

Lanthanum oxide (La_2O_3) has chemical and electronic properties that meet the requirements for applications in various fields. Currently, lanthanum containing compounds are studied very actively. The metal–insulator transition, high-temperature superconductivity, ferroelectricity, and colossal magnetoresistance compounds of perovskites are excellent materials for future technological application [1–4]. For example, $LaNiO_3$ is one of a few conductive oxides proper for integration in epitaxial heterostructures with perovskites [5, 6]. However, the rare earth oxides have a tendency to absorb water and carbon dioxide from the environment, so that any *ex situ* exposure of these films to ambient air will result in an uncontrolled reaction and surface stoichiometry variation [7].

In [5, 8, 9] La-Ni-O films were deposited onto $NdGdO_3$ monocrystalline (100)-plane oriented substrate using a DC magnetron sputtering system. Investigations on electronic structure and chemical composition of grown $LaNiO_{3-\delta}$ thin films after heating above dehydration temperatures in air and vacuum were performed. After investigation of O 1s spectra of films annealed at high temperatures using an XPS method no water traces were observed. Unfortunately, a comparison of O 1s spectra measurements *in situ* after annealing in super-high vacuum and after exposure to ambient air for a short (2 hours) time demonstrated a rapid water absorption and $LaNiO_{3-\delta}$ surface hydro oxidation. The hydro oxidation was likely caused by lanthanum oxide as it has a tendency to absorb water from ambient air. It confirms the results of [10–12] works, where the chemical composition of lanthanum oxide films was investigated using the XPS method. It was shown that independent of synthesis methods and various treatment of the samples (temperature annealing in air or NH_3 and N_2 plasma treatment) the hydro oxidation of pure La_2O_3 takes place. These results show that we must obtain new synthesis methods which let us produce the lanthanum oxide films without hygroscopic properties.

Recently, a series of experiments to synthesise La_2O_3 has been done at low temperatures by using the sol–gel method [13, 14]. The La_2O_3 sol was prepared from a lanthanum alkoxide precursor. However, the chemical composition and hygroscopic properties of the obtained thin films remained not covered. In [15] highly (100)-oriented $LaNiO_{3-\delta}$ thin films were prepared on amorphous SiO_2/Si (100) substrate by using the sol–gel method. In this case after annealing of films at high temperatures water traces in O 1s spectra were

not observed. It shows that the sol–gel method may be a promising solution to avoid water absorption in lanthanum oxide-based thin films.

The aim of this work is to investigate the properties and composition of La_2O_3 films prepared by the sol–gel method and to verify the absence of water.

2. Experiment

The powder of lanthanum oxide (99.9% purity, *SIGMA*) was dissolved in a 30% hydrogen peroxide solution at the temperature of 333 K, because at lower temperatures La_2O_3 does not dissolve in H_2O_2. However, the major part of lanthanum peroxide which appears during dissolving process dismantles at the given temperature of 333 K. The obtained gel was spread on the quartz glass substrate by a spin coating method and left to dry in ambient air for 24 hours. The thickness of produced films was ~10 μm. Finally, dehydration process was performed annealing samples at 773 K temperature for 2 hours. Later samples were annealed in vacuum using different temperatures at variable time intervals (see Table 1). After heat treatment in the air at 773 K (samples named A in Table 1) samples were annealed at 673 K in vacuum (samples named B in Table 1) and so on in accordance with temperature and vacuum regimes presented in Table 1.

Table 1. Conditions of annealing of samples.

Sample	Thermal treatment
A	773 K, air, 2 h
B	673 K, vacuum 10^{-7} Pa, 16 h
C	713 K, vacuum 10^{-7} Pa, 68 h
D	823 K, vacuum 10^{-7} Pa, 92 h

After each annealing the regions of La 3d and O 1s spectra were investigated using the XPS method. X-ray photoelectron spectra were recorded using an XSAM 800 (*KRATOS Analytical*, UK) spectrometer. The photoelectrons were excited using a non-monochromatized Al Kα (1486.6 eV) radiation source at 15 kV, 300 W. The analyser was used in a fixed retarding ratio mode with an energy resolution $\Delta E/E = 0.08\%$. The working pressure in the analysis chamber was maintained below 10^{-7} Pa during the spectrum analysis. Photoemission data were collected and processed by the *KRATOS* DS800 data system. After Al Kα satellites and background subtraction, the complex photoelectron spectra were decomposed into separate peaks by specifying the peak position – binding energy (BE), area, full width at half maximum (FWHM), and Gaussian / Lorentzian ratio. The adventitious carbon C 1s line was used for the fine correction of charging effects and binding energies calibration, supposing its (C 1s) binding energy is equal to 284.6 eV.

3. Results and discussion

The La 3d core level spectra of lanthanum compounds show results almost identical to [5, 6, 8–12, 15, 16]. It is known that the La 3d core level splits into $3d_{5/2}$ and $3d_{3/2}$ components. The satellite peak of the La 3d core level in insulating compounds on a higher binding energy side is separated from the main peak by about ~4 eV.

The overlap O 1s spectra of annealed La_2O_3 films are shown in Fig. 1 for A, B, C, and D samples. The O 1s peak consists of two components with binding energies ~528 and ~531 eV. Intensity of the last component is strongly affected by the heat treatment and decreases with the treatment time (component at ~531 eV in Fig. 1). The fitting results of XPS spectra of films La_2O_3 annealed in air (sample A) are presented in Fig. 2. The O 1s peak consists of two components

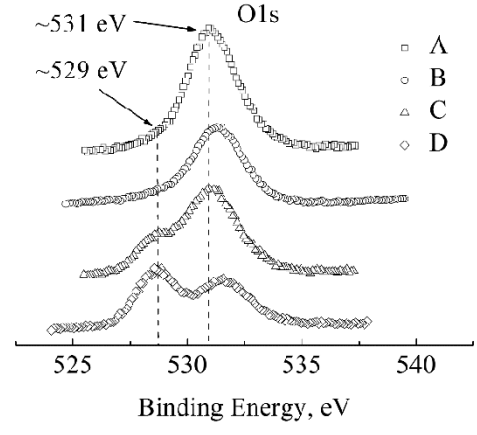

Fig. 1. Core level O 1s spectra of annealed La_2O_3 films for A, B, C, and D samples.

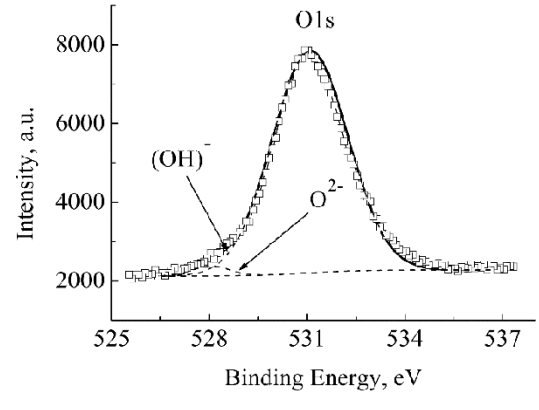

Fig. 2. O 1s region XPS spectra of sample A (annealed in air at 773 K for 2 hours).

with binding energies 528.0 and 531.1 eV that correspond to the oxygen ions O^{2-} in the crystalline network [17, 18] and the oxygen ions in the hydroxyl group [19], respectively. It must be noted that the character of O 1s spectra after heat treatment in vacuum is similar for all investigated samples (see Fig. 1). Consequently, we present a detailed O 1s spectrum only for the sample D which is shown in Fig. 3. In this case, as for all samples, the O 1s peak consists of two components with binding energies 528.6 and 531.6 eV that correspond to the oxygen ions in La_2O_3 and hydroxyl groups. The presence of water molecules (it can be indicated by the presence of the component with the binding energy >533 eV in the experimental O 1s peak [17–19]) in produced films was not indicated.

XPS investigation results of the samples A, B, C, and D are summarized in Table 2. It shows that intensity of O^{2-} component increases and intensity of oxygen in $(OH)^-$ group has a tendency to decrease for samples annealed for longer time intervals in vacuum. It can be related to the dehydration process of films.

The changes of the ratio of $O^{2-}/(OH)^-$ for all investigated samples were calculated using the data from Table 2 (Fig. 4). Going to higher annealing temperatures of thin films the tendency of increase of O^{2-} anions and decrease of oxygen in $(OH)^-$ groups is clearly visible. The ratio of sample A annealed in air at the temperature of 773 K is 0.022, and sample D annealed in vacuum at the temperature of 823 K gets a ratio of 0.889, which is more than forty times higher.

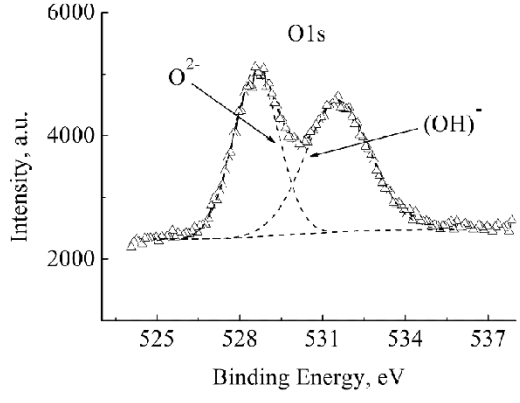

Fig. 3. O 1s region XPS spectra of sample D (annealed in vacuum at 823 K for 92 hours).

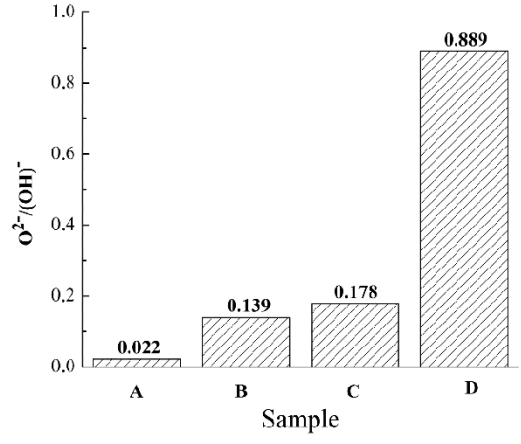

Fig. 4. $O^{2-}/(OH)^-$ ratio for investigated samples.

It is necessary to notice that XPS study results of all samples after their storage in the air during six months practically do not differ from the initial results.

Table 2. XPS investigation results of samples A, B, C, and D.

Sample	Peak	Binding energy, eV	FWHM, eV	Area a. u.
A	La $3d_{5/2}$	834.90 (La)	2.99	14998
		838.50 (Satellite)	2.75	9395
	O 1s	528.00 (O^{2-})	1.35	361
		531.10 ($(OH)^-$)	2.74	16521
B	La $3d_{5/2}$	834.30 (La)	3.02	24570
		837.80 (Satellite)	2.69	14888
	O 1s	528.60 (O^{2-})	2.31	1319
		531.30 ($(OH)^-$)	2.56	9481
C	La $3d_{5/2}$	834.10 (La)	2.99	16788
		837.98 (Satellite)	2.76	11114
	O 1s	528.30 (O^{2-})	1.64	2248
		530.90 ($(OH)^-$)	3.00	12652
D	La $3d_{5/2}$	833.70 (La)	2.88	14794
		837.90 (Satellite)	2.80	11424
	O 1s	528.60 (O^{2-})	1.99	5635
		531.60 ($(OH)^-$)	2.79	6340

4. Conclusions

Thin lanthanum oxide films were fabricated by sol–gel technology and investigated by the X-ray photoelectron spectroscopy method. After synthesis of the films they were thermally processed in vacuum at various temperatures and processing time intervals. Results of XPS spectra study of the samples have shown that irrespective of their thermal treatment lanthanum ions are in a stable La^{3+} state. The O 1s peak consists of two components with binding energies: ~528 eV, which corresponds to lattice O^{2-} anions of the crystalline network, and ~531 eV, which corresponds to oxygen ions in the hydroxyl group. Going to higher annealing temperatures and time intervals the tendency of increasing of O^{2-} anions and decreasing of oxygen in $(OH)^-$ groups was observed. The presence of water molecules in produced films was not indicated.

XPS study results of all (A, B, C, and D) thermally annealed samples after their storage in the air during six months practically do not differ from the initial results. The obtained decreasing of $(OH)^-$ groups after treatment of the samples in vacuum suggest that after selection of appropriate heat treatment regimes of the samples, the sol–gel method can be useful for receiving of non-hydroscopic films on the basis of lanthanum oxide.

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ZOLIŲ-GELIŲ METODU PAGAMINTŲ PLONŲJŲ LANTANO OKSIDO SLUOKSNIŲ XPS TYRIMAS

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Santrauka

Plonieji La_2O_3 sluoksniai pagaminti naudojant zolių-gelių technologijos metodus. Po sluoksnių sintezės jie buvo termiškai apdorojami oro atmosferoje ir vakuume (10^{-7} Pa) temperatūrų intervale 673–823 K nuo 2 iki 92 val. Po kiekvieno apdorojimo ciklo buvo matuojami bandinių rentgeno fotoelektronų spektrai (XPS).

Nustatyta, kad nepriklausomai nuo apdorojimo režimo (temperatūros ir laiko) lantano jonai bandiniuose yra stabilios La^{3+} būsenos. Visais atvejais deguonies O 1s RFS smailė turi savyje dvi dedamąsias su ryšio energijomis ~528 ir ~531 eV, kurios atitinka O^{2-} jonus oksido gardelėje ir deguonį, suištą hidroksilinėje grupėje $(OH)^-$. Didėjant bandinių apdorojimo temperatūrai ir laikui didėja O^{2-} jonų koncentracija bei mažėja deguonies kiekis $(OH)^-$ grupėje.

Visuose bandiniuose nepastebėta absorbuoto vandens. Po terminio bandinių apdorojimo vakuume aptikta mažėjanti $(OH)^-$ grupių koncentracija leidžia manyti, kad, tinkamai parinkus technologinius sluoksnių terminio atkaitinimo vakuume režimus (panaudojant zolių-gelių sintezės metodus), galima gauti nehigroskopinius lantano oksido sluoksnius.