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XPS STUDY OF EPITAXIAL $LaNiO_{3-x}$ FILMS

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X-ray photoelectron spectroscopy (XPS) was used to determine the composition and chemical structure of epitaxial $LaNiO_{3-x}$ films obtained by a reactive dc magnetron sputtering. It was found that, in contrast to the samples synthesized by using solid state chemical reactions, the surface Ni/La concentrations ratio is close to the stoichiometric bulk value. The existence of at least three different forms of oxygen in "as grown" films is shown by XPS characterization. XP spectra have also revealed that lattice oxygen and hydroxide species are in cooperation at the film surface. The significant dehydration of both La and Ni hydroxides to corresponding oxides was observed on cleaning film by Ar^+ ion bombardment.

Keywords: reactive dc magnetron sputtering, $LaNiO_3$, photoelectron spectroscopy

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1. Introduction

In recent years certain perovskite-related metallic oxides, such as high T_c superconductors, the compounds exhibiting giant magnetoresistance, and conductive oxides, are intensively studied. The current interest in thin films of high-temperature superconductors has posed the problem of a suitable substrate as an important point for epitaxial growth. A number of Ln-containing (Ln = La, Pr, and Nd) oxide crystals have been employed as the substrate material and many are under investigation now. There have been numerous studies on their morphology, structural, thermodynamic, magnetic, elastic properties and crystal growth [1, 2]. Even more attention is paid to multilayered structures consisting of several various metallic oxides. In many cases, the formation of these heterostructures on different type of substrates is curried out using dielectric buffer layers. The highly conductive films, which can be used both as the buffer layers and the interconnects or electrodes in hybrid devices, can be the promising alternatives for dielectrics.

In the previous papers [3, 4] it has been shown that epitaxial $LaNiO_{3-x}$ films prepared on mono-crystalline $NdGaO_3$ substrate demonstrate the excellent in-plane orientation. It is known that the considerable segregation of elements takes place in chemically synthesized $LaNiO_{3-x}$ samples, i. e. the surface concentrations of various species differ from the volume one. As a typical result, a systematic enrichment in La and O surface concentrations with respect to the bulk values is observed [5–7].

X-ray photoelectron spectroscopy (XPS) is known as the surface analysis method which provides the direct information on the species concentration and their valence states. So we use these features of the method for studies of the surface composition of $LaNiO_{3-x}$ thin films deposited by a magnetron sputtering.

2. Experimental

Thin $LaNiO_{3-x}$ films were deposited onto monocrystallyne (100)-plane-oriented $NdGaO_3$ substrate by using a reactive dc magnetron sputtering technique. The ceramic $LaNiO_3$ target (25 mm in diameter and 2.5 mm thick) was prepared by pressing at 5 t/cm^2 and after sintering in air at 1000 °C for 10 h the La_2O_3 and NiO powders (99.99% purity from Aldrich-Chemie) in stoichiometric ratio. The sputtering was performed in Ar and O_2 mixture (1:1) at a pressure of about 10 Pa. To prevent the film bombardment by high energy ions during deposition, $NdGaO_3$ substrates were positioned in "off-axis" configuration at a distance of 15 mm from the symmetry axis of the discharge and 20 mm over the target plane. The substrate temperature was 650 °C. Under

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these conditions the deposition rate was 25 nm/h and the resultant thickness of $LaNiO_{3-x}$ film was $\sim$0.1 μm.

X-ray photoelectron spectra were recorded using XSAM 800 (KRATOS Analytical, UK). The photoelectrons were excited using a non-monochromatized Mg Kα (1253.6 eV) radiation source at 15 kV, 300 W. The analyser was used in 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 have been collected and processed by using KRATOS DS800 data system. After the Mg K_α satellites and background subtraction the complex photoelectron spectra were decomposed into separate peaks by specifying the peak position – binding energy (BE), area (A), width (FWHM), and Gaussian/Lorentzian ratio (G/L). Because any mathematical operation (such as a data smoothing) on the raw data would distort the original physical picture, no such treatment was permitted in the quantitative data analysis. The accuracy of the measured lines BE and relative intensities were about 0.1 eV and 10%, respectively. The stoichiometry and chemical states of the oxide thin films were investigated by the standard quantification routine, including Wagner's energy dependence of attenuation length [8].

To control the sample contaminations, the survey spectra of an air-exposed, fresh sample have been studied. Only lanthanum, nickel, oxygen, and carbon lines were identified within the probing depth of XPS. No more contamination related to the sample preparation was detected by XPS within the accuracy of our measurements. The adventitious carbon C 1s line was used for the fine correction of the charging effects, supposing its BE should be equal to 284.6 eV.

The influence of ion sputtering on the chemical composition of investigated compounds was treated by using Ar^+ ion bombardment at 3 keV and current density of 10 μA·cm^{-2} for 15 min.

3. Results and discussion

The XPS spectra are analogous for both "as grown" (and exposed to atmospheric condition for a two hours) and Ar^+-etched samples and exhibit similar features.

Figure 1 presents the core-level O 1s spectra for the $LaNiO_{3-x}$ film before and after Ar^+ ion irradiation. The peaks are broad and asymmetric. This result is consistent with the presence of more than one type of oxygen species in the surface layer. This is clearly concluded from the peak deconvolution of O 1s spectra,

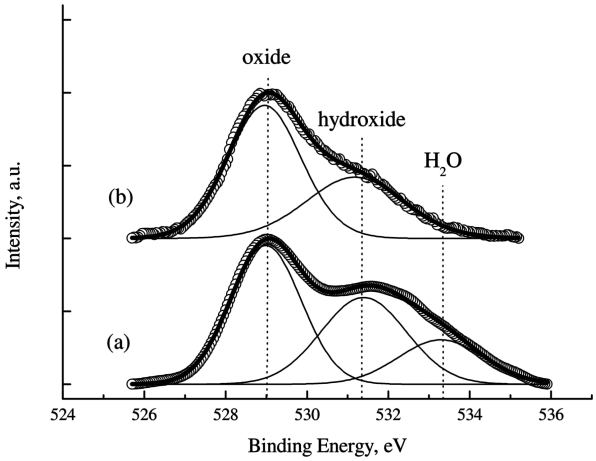

Fig. 1. Deconvolution analysis of O 1s signal of $LaNiO_{3-x}$ thin films: (a) "as grown", (b) Ar^+-etched film. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components, and the thick line is the spectral envelope.

which points to the existence of three and two peaks for "as grown" and Ar^+-etched films, respectively (Table 1). The low-energy peak at about 529.0 eV can be ascribed to a lattice O^{2-} anion. It is known that the rare earth oxides easily become hygroscopic after being exposed to atmospheric conditions [9]. Thus, an additional spectral component at 531.2 eV may be attributed to La and Ni hydroxides [10–12] for which O 1s BE is typically higher by (2.0–2.5) eV in respect to the associated lattice oxygen [13]. The supplementary peak at BE = 533.2 eV observed for fresh film may be attributed to the adsorbed water species [14]. On cleaning the film by argon ion bombardment this peak disappears, confirming that only thin adsorbed water layer is present at the sample surface.

The XPS spectra in the La 3d and Ni 2p binding energy regions are shown in Fig. 2. The analysis of the Ni $2p_{3/2}$ profile was difficult, due to overlapping of Ni $2p_{3/2}$ and La $3d_{3/2}$ peaks. The most intense Ni $2p_{3/2}$ peak was accompanied by a satellite line positioned at around (6–7) eV higher BE [7, 15]. This Ni $2p_{3/2}$ satellite component is complicated by a simultaneous presence of La $3d_{3/2}$ plasmon component [16, 17]. Thus, La 3d and Ni 2p regions cannot be analysed separately. Complex satellite structure of the La 3d spectra due to the electron transferred to the 4f level from a lower energy valence orbital of the anion [17, 18] complicate both La $3d_{5/2}$ and Ni $2p_{3/2}$ profile analyses.

To overcome these difficulties the whole La 3d and Ni 2p BE region was fitted to ten components. Two additional shake-up satellite components, corresponding to $J = 1$ and $J \neq 1$ [17], were used for the deconvolution of La 3d doublets, assuming the spin–orbit splitting

Table 1. Results of the fit of O 1s photoelectron spectrum. S is the relative area of the peak.

Peak	"As grown"			Ar^+-etched			Peak
	BE, eV	FWHM, eV	S, %	BE, eV	FWHM, eV	S, %	identification
A	528.96	2.07	45.9	528.97	2.06	64.5	O^{2-} lattice
B	531.35	2.67	35.8	531.15	2.57	35.5	OH groups
C	533.17	2.67	18.3	—	—	—	H_2O

Table 2. Results of the fit of La 3d and Ni 2p photoelectron spectrum.

Peak	"As grown"		Ar^+-etched		Peak identification		
	BE, eV	FWHM, eV	BE, eV	FWHM, eV	Line assignment	Process ascription	Species
A	835.44	3.2	834.69	2.1		Core level	La_2O_3
B	837.45	2.2	836.16	2.3	La $3d_{5/2}$	Satellite ($J \neq 1$)	and
C	839.53	3.3	839.18	3.2		Satellite ($J = 1$)	$La(OH)_3$
D	847.94	14.5	847.91	11.2		Plasmon	
E	—	—	854.19	2.1			Ni^{2+}
F	856.23	2.7	856.26	1.9	Ni $2p_{3/2}$	Core level	Ni^{3+}
G	858.7	3.1	—	—			Ni_{hydro}
H	863.2	9.0	862.8	13.1	La $3d_{3/2}$ Ni $2p_{3/2}$	Plasmon Satellite	Not
I	873.7	7.9	872.4	5.8	Ni $2p_{1/2}$	Core level	resolved
J	881.4	4.3	879.8	6.8	Ni $2p_{1/2}$	Satellite	

energy $\Delta_{SO} = 16.9$ eV [17, 18] and the theoretical intensity ratio $A_{5/2}/A_{3/2} = 1.5$ [18] for both the principal core-level and the satellite lines. The results are listed in Fig. 2 and Table 2. In spite of numerous assumptions the procedure appears to be reasonably accurate since the estimated values of BE for La and Ni peaks are in a good agreement with the data reported in literature.

The chemical state of La is revealed by a comparison of well resolved La $3d_{5/2}$ core-level spectrum and O 1s spectrum to the equivalent spectra for "standard" La_2O_3 and $La(OH)_3$ [8, 17, 18]. The core-level (*A*) La $3d_{5/2}$ peak after Ar milling shifts to lower BE indicating the decrease of relative $La(OH)_3$ concentration. The corresponding increase of satellite (*C*) and principal (*A*) peaks separation from 4.1 to 4.5 eV (Table 2) strongly confirm the decrease of lanthanum hydroxide at the film surface [7] after Ar^+ treatment. This result is in a good agreement with the significant decrease of the areas ratio for hydroxide S_{hyd} and lattice S_{lat} oxygen species, see Table 1 ($S_{hyd}/S_{lat} = 0.78$ and 0.54 for "as

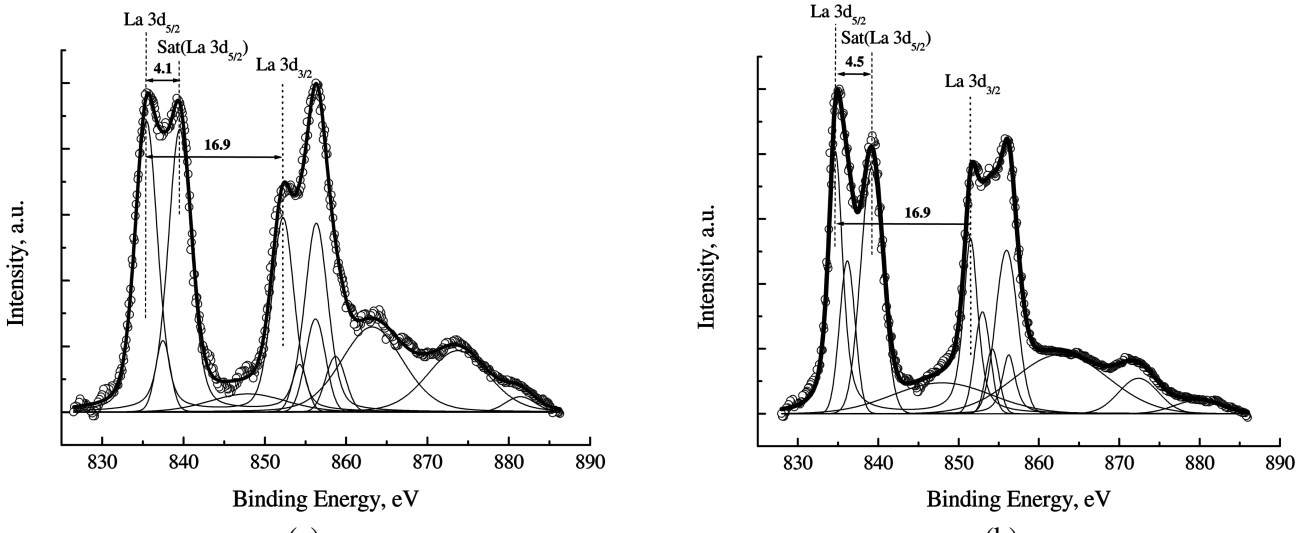

Fig. 2. Deconvolution analysis of La 3d and Ni 2p signal of $LaNiO_{3-x}$ thin films: (a) "as grown", (b) Ar^+-etched film. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components, and the thick line is the spectral envelope.

grown" and Ar^+-etched films, respectively). Note that the FWHM of principal (*A*) peak significantly decreases after Ar^+ bombardment, demonstrating that this peak is the superposition of La_2O_3 and $La(OH)_3$ core-level lines. Both changes in La $3d_{5/2}$ and O $1s$ spectra indicate dehydration from hydroxide to La_2O_3 on cleaning the film by argon bombardment.

The similar dehydrations were observed for Ni species, too (Table 2). The *D* peak, observed for a fresh film, may be assigned to nickel hydroxide [12] and disappears after Ar sputtering. After Ar bombardment the lattice Ni $2p_{3/2}$ line splits into two components (Ni^{3+} and Ni^{2+}) at BE 856.3 and 854.2 eV, respectively [12, 15]. The appearance of the additional Ni^{2+} species may be attributed to the preferential removing of oxygen under the surface cleaning.

The atomic surface concentrations in terms of Ni/La are equal to 0.92 and 1.03 for "as grown" and Ar^+-etched films, respectively, and within the experimental error correspond to the stoichiometric bulk composition (Ni/La = 1). Thus, it may be concluded that in contrast to the chemically synthesized $LaNiO_{3-x}$ samples, the surface composition of thin $LaNiO_{3-x}$ films deposited by a reactive dc magnetron sputtering corresponds to a bulk one.

4. Conclusions

The composition and chemical structure of $LaNiO_{3-x}$ films obtained by a reactive dc magnetron sputtering were determined by X-ray photoelectron spectroscopy. The existence of at least three different forms of oxygen in "as grown" films is shown by XPS characterization. XP spectra have also revealed a presence of lanthanum and nickel in oxide and hydroxide form at the film surface. The significant dehydration of both La and Ni hydroxides to corresponding oxides was observed on cleaning the film by Ar^+ ion bombardment. The surface Ni/La concentrations ratio is close to the stoichiometric volume one. Insignificant difference in the surface composition between the initial fresh and argon beam treated films has been observed.

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EPITAKSINIŲ $LaNiO_{3-x}$ SLUOKSNIŲ RÖNTGEN'O FOTOELEKTRONINIŲ SPEKTRŲ TYRIMAS

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Santrauka

$LaNiO_{3-x}$ epitaksiniai sluoksniai, gauti magnetroninio garinimo būdu, turi tobulą struktūrą bei didelį elektrinį laidumą. Šiame darbe pateikti minėtų sluoksnių cheminės sudėties bei galimos atskirų elementų segregacijos tyrimo rezultatai Röntgen'o fotoelektroninės spektroskopijos (RFS) metodu.

RFS spektrai buvo registruojami XSAM-800 spektrometru iki ir po bandinių bombardavimo argono jonais. La–Ni junginiuose Ni $2p_{3/2}$ smailė persikloja su La $3d_{3/2}$ smaile, todėl, interpretuojant RFS spektrus, reikia nagrinėti visą La $3d$ ir Ni $2p$ sritį ir, norint gauti informaciją apie atskirus elementus, reikia iš bendro spektro atiminėti arba nikelio, arba lantano dedamąsias.

Tiek iki bombardavimo, tiek ir po jo La/Ni santykis yra lygus $0{,}95 \pm 0{,}05$. Tai rodo, kad gauti kokybiški sluoksniai, atitinkantys reikiamą sudėtį. Pažymėtina, kad, sintetinant panašius sluoksnius kieto kūno cheminių reakcijų metodu, šis santykis lygus maždaug 2,5.