Optica Applicata, Vol. XXXVI, No. 2–3, 2006

Investigation of the aging of epitaxial $LaNiO_{3-x}$ films by X-ray photoelectron spectroscopy

Sigitas MICKEVIČIUS[1*], Sergej GREBINSKIJ[1], Vladimiras BONDARENKA[1],
Henrikas TVARDAUSKAS[1], Bonifacas VENGALIS[1], Kristina ŠLIUŽIENĖ[1],
Bronisław A. ORŁOWSKI[2], Wolfgang DRUBE[3]

[1]Semiconductor Physics Institute, A. Gostauto 11, 01108 Vilnius, Lithuania

[2]Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, 02-668 Warsaw, Poland

[3]Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron DESY,
Notkestr. 85, D-22603 Hamburg, Germany

[*]Corresponding author: S. Mickevičius, sigism@pfi.lt

The X-ray photoelectron spectroscopy (XPS) was performed to study surface and volume composition, valence states and the concentration of hydroxyl groups in epitaxial $LaNiO_{3-x}$ thin films after aging in air. The existence of at least few different forms of oxygen as lattice oxide, hydroxyl groups and adsorbed water in the samples is shown by XPS characterization. The lanthanum and nickel exist in oxide and hydroxide chemical states. The concentration of hydroxyl groups increases at the surface but it is distributed through the volume as well. It was found that the surface Ni/La concentration ratio is close to the stoichiometric bulk value.

Keywords: reactive D.C. magnetron sputtering, $LaNiO_3$, photoelectron spectroscopy, synchrotron radiation.

1. Introduction

In recent years certain perovskite-related metallic oxides, such as high T_c superconductors, compounds exhibiting giant magnetoresistance and conductive oxides, are intensively studied. The current interest in thin films of high temperature superconductors has made the problem of a suitable substrate an important point for epitaxy to be successful. 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 types of substrates is carried 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], it was shown that epitaxial $LaNiO_{3-x}$ films prepared on mono-crystalline $NdGaO_3$ substrate demonstrate an excellent in-plane orientation. It is known that considerable segregation of elements takes place in chemically synthesized $LaNiO_{3-x}$ samples, *i.e.*, the surface concentration of various species differs from the volume one. As a typical result, a systematic enrichment of La and O surface concentrations with respect to the bulk values is observed [4–6].

X-ray photoelectron spectroscopy (XPS) using laboratory X-ray sources ($h\nu < 1500$ eV) is known as the surface analysis method (scanning depth ~3 nm), which provides direct information on the concentration of species and their valence states. So, we use these features of the method for studying the surface composition of $LaNiO_{3-x}$ thin films deposited by a magnetron sputtering after short time aging in atmosphere air. On the other hand, synchrotron X-rays at much higher energies are used to significantly enhance the volume sensitivity for core levels. In this paper, we utilize the volume sensitivity of tuneable high-energy X-ray photoelectron spectroscopy to study the epitaxial $LaNiO_{3-x}$ thin films after long time aging in air.

2. Experimental

Thin $LaNiO_{3-x}$ films were deposited onto monocrystalline (100)-plane oriented $NdGaO_3$ substrates by using a reactive d.c. magnetron sputtering technique. The ceramic $LaNiO_3$ target (25 mm in diameter and 2.5 mm in thickness) 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 (99.99% purity from Aldrich-Chemie) powders in stoichiometric ratio. The sputtering was performed in Ar and O_2 mixture (1:1) under 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 these conditions deposition rate was 25 nm/h and the resultant thickness of $LaNiO_{3-x}$ film ~ 0.1 μm.

X-ray photoelectron spectra for as-grown samples exposed to atmospheric conditions for two hours (short time aging) were recorded using XSAM 800 (KRATOS Analytical, UK). The photoelectrons were excited using a non-monochromatized Mg K_α (1253.6 eV) radiation source at 15 kV, 300 W. The analyser was used in fixed retarding ratio mode with the energy resolution $\Delta E/E = 0.08\%$. The working pressure in the 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 (G/L) ratio. Because any mathematical operation (such as 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 [7].

Using Ar$^+$ ions bombardment at 3 keV and current density 10 μA·cm^{-2} during a 15 min treatment the influence of ion sputtering on the chemical composition of compounds under investigation was determined.

The data of samples after long time aging in the atmosphere (about 1 year) were obtained with a tunable high-energy X-ray photoelectron spectrometer at the X-ray wiggler beam line BW2 of HASYLAB (Hamburg). The photon flux from the Si(111) double crystal monochromator typically amounts to 5×10^{12} s^{-1} on the sample. The electrons were measured using a hemispherical analyser with parallel detection capability (SCIENTA SES-200). Excitation energy was chosen (3000 eV) where the kinetic energy of the La and Ni levels do not overlap any of Auger electron emission peaks originating from the atoms of the layer. This was checked by EDC's covering a wide energy range. The total energy resolution at this photon energy is 0.6 eV. The binding energy scale was calibrated using the photoemission from gold reference sample. The angle dependent data were obtained by rotating the sample relative to the electron analyzer, which accepts electrons in the SR orbit plane at 45° relative to the incoming beam. The samples after long time aging in air were measured "as introduced", *i.e.*, without any surface treatment. The base pressure in the analyzer chamber was 5×10^{-10} mbar.

3. Results and discussion

The XPS spectra are analogous for both "as-grown" (and after short time aging in air, for two hours) and Ar$^+$-etched samples and exhibit similar features.

Figure 1**a** presents the core-level O 1*s* spectra for the LaNiO$_{3-x}$ film after short time aging and after successive 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. The low-energy peak at about 529.0 eV can be ascribed to lattice O^{2-} anion. It is known that the rare earth oxides are easily hygroscopic when exposed to atmospheric conditions [8]. Thus, an additional spectral component at 531.2 eV may be attributed to La and Ni hydroxides [9–11] for which O 1*s* BE is typically higher by 2.0–2.5 eV with respect to the associated lattice oxygen [12]. The supplementary peak at BE = 533.2 eV observed for fresh film may be attributed to the adsorbed water species [13]. On cleaning the film by argon-ion bombardment this peak disappears, confirming that only thin adsorbed water layer is present on the sample surface.

The core-level O 1*s* spectra for the LaNiO$_{3-x}$ film after long time aging for normal and grazing emission (89° angles are referred to the surface normal) angles are shown in Fig. 1**b** and collected in the Table [14]. As can be seen from Fig. 1**b**, the XPS spectra

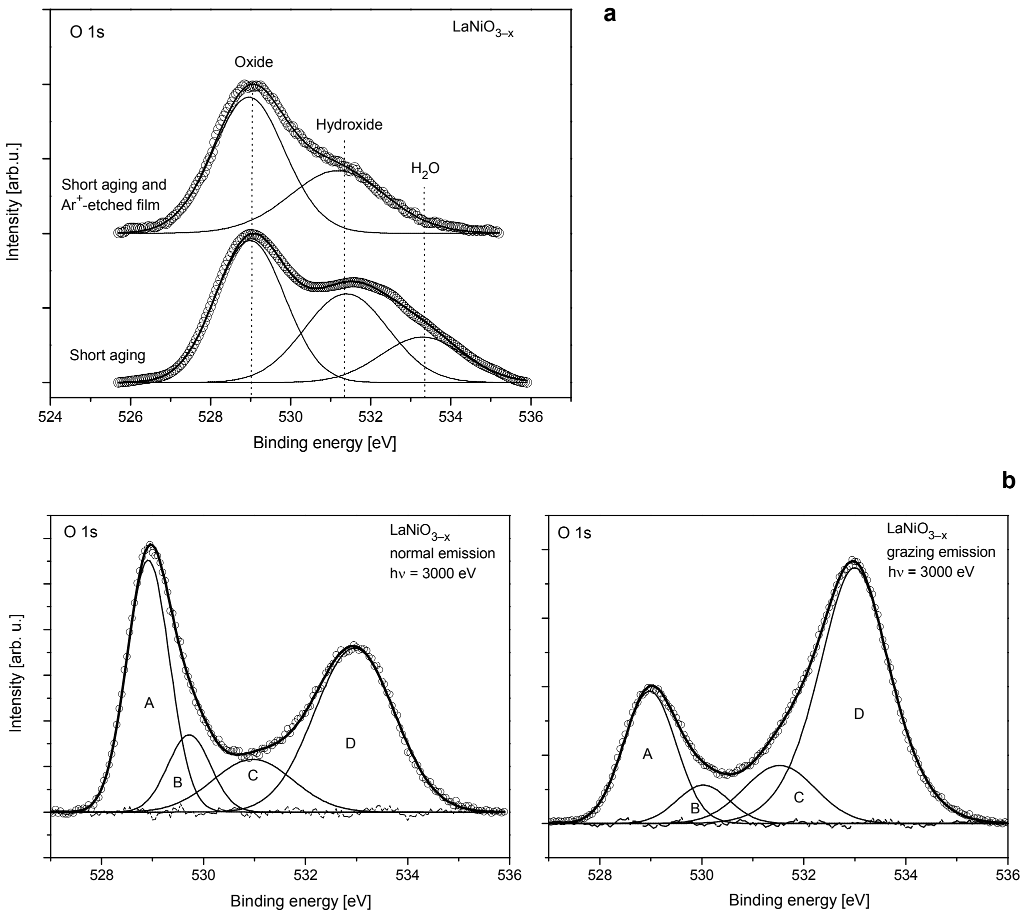

Fig. 1. Deconvolution analysis of O 1*s* signal of the $LaNiO_{3-x}$ thin films after short (**a**) and long (**b**) time aging taken at normal emission and grazing emission angle geometries using synchrotron radiation. Excitation energy $h\nu = 3000$ eV [14]. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and the thick line is the spectra envelope.

taken at different emission angles exhibit similar features. In the sample after long time aging the O 1*s* peaks are complex and can be deconvoluted into four peaks. The low-energy peak at about 529.0 eV can be ascribed to lattice O^{2-} anion in lanthanum oxides [15]. The peak B (see Fig. 1**b** and the Table) can be attributed to lattice O^{2-} anion in nickel oxides [15]. An additional spectral component *C* as in the case of short aging samples may be attributed to La and Ni hydroxides [9–11] and component *D* – the adsorbed water species [13].

The La 3*d* and Ni 2*p* core level photoemission spectra of $LaNiO_{3-x}$ film measured for samples after long time aging (curves 1 and 2) and after short time aging (curve 3) and sequential Ar ion etching (curves 4) are shown in Fig. 2. As can be seen from Fig. 2, the La 3*d* spectra are complex and exhibit fine structure beside the spin-orbit

Table. Results of the fit of O 1*s* photoelectron spectrum of LaNiO$_{3-x}$ after long time aging taken for normal emission and grazing emission angles.

	$\gamma = 45.0$			$\gamma = 89.3$			
Peak	BE [eV]	FWHM [eV]	A_{rel} [%]	BE [eV]	FWHM [eV]	A_{rel} [%]	Peak identification
A	528.92	0.99	34.25	528.98	1.21	21.55	O^{2-} in La oxide
B	529.72	0.99	10.51	530.03	1.21	6.25	O^{2-} in Ni oxide
C	530.97	1.85	13.45	531.53	1.64	12.86	$(OH)^-$ in La and Ni hydroxide
D	532.96	1.85	41.79	533.00	1.64	59.34	H_2O

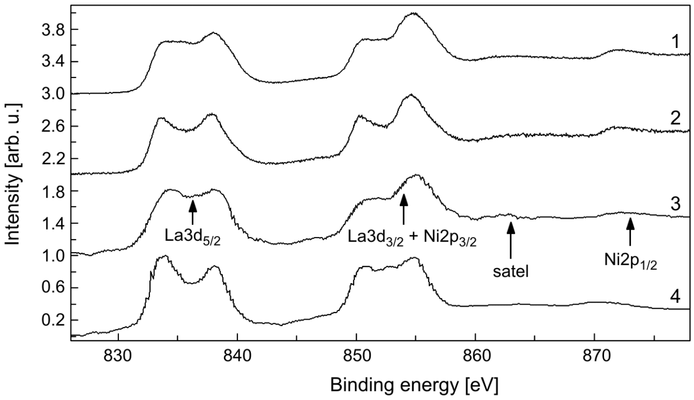

Fig. 2. La 3*d* and Ni 2*p* core level spectra of the LaNiO$_{3-x}$ thin films after aging in the atmosphere conditions: (1) long time aging taken at grazing emission and (2) normal emission angles using synchrotron radiation; excitation energy $h\nu = 3000$ eV; (3) short time aging and (4) short time aging and sequential Ar ion sputtering.

split peaks. As can be seen from Fig.2, each line is split to the main line ($3d^0 4f^0$ final state configuration) and satellite line ($3d^0 4f^1 \underline{L}$ final state configuration, $\underline{L}$ means the hole in the ligand). The satellite lines in the case of metallic or insulating lanthanum compounds have different nature and as a consequence the binding energy position with respect to the main peak is different [16–18]. In insulating compounds the nature of this satellite peak arises from an electron transfer from ligand to the lanthanum 4*f* state and this line is on the high binding energy side of the main peak. The situation is more complicated after aging procedures, because as was mentioned above the lanthanum oxide is easily hydroscopic. As is known, the surface oxide reacts with contaminant water and produces hydroxide, so lanthanum exists in chemical state after aging in the atmosphere. This confirms the investigation of La 3*d* core level spectra of the samples after aging.

Deconvolution analysis of La $3d_{5/2}$ signal of LaNiO$_{3-x}$ thin films obtained after the same aging procedures and taken at the same conditions as mentioned in Fig. 2, are shown in Fig. 3. The La $3d_{5/2}$ core level spectra, after short and long time aging

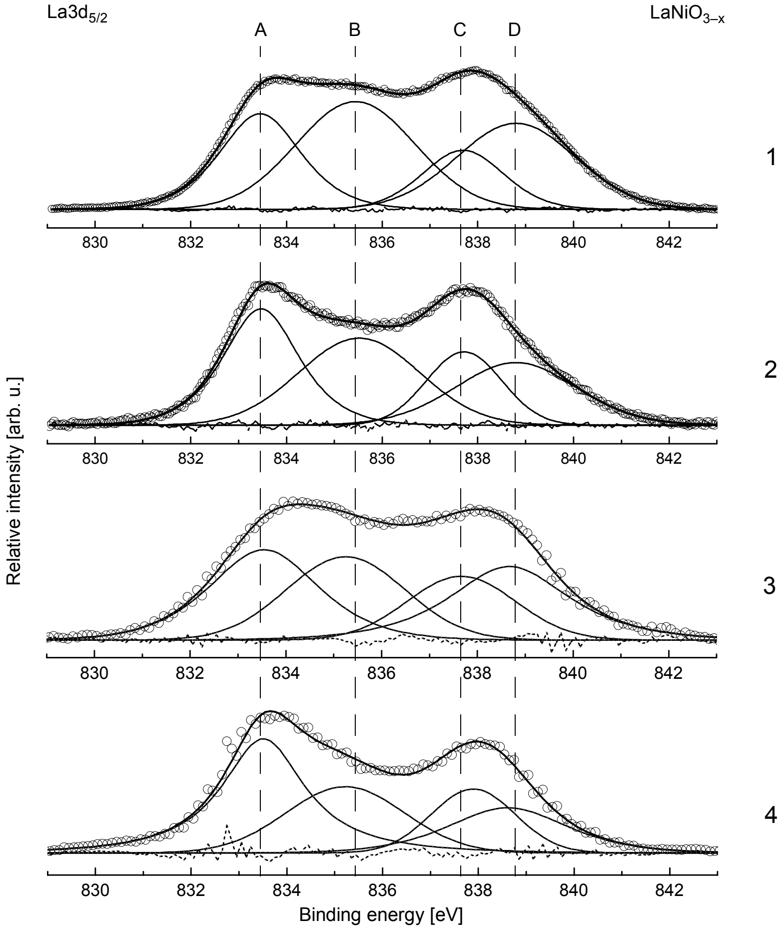

Fig. 3. Deconvolution analysis of La $3d_{5/2}$ signal of $LaNiO_{3-x}$ thin films obtained after the same aging procedures and taken under the same conditions as mentioned in Figs. 1 and 2. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and the thick line is the spectra envelope.

(Fig. 3) can be deconvoluted into two doublets, corresponding to oxide and hydroxide species. The oxide main line is at 833.47 eV binding energy (peak *A*) and satellite line at approximately 837.7 eV (peak *C*). The main line corresponding to the lanthanum bonding with hydroxyl group (peak *B*) lies at 835.3 eV and satellite peak at 838.85 eV (peak *D*). The ratio of hydroxide-oxide species decreases from 1.54 (1, long time aging, grazing geometry) to 0.66 (4, short time aging and sequential Ar ion sputtering). These changes in La $3d_{5/2}$ core level spectra as in O $1s$ spectra (see Fig. 1) indicate dehydration from hydroxide to La_2O_3 on cleaning the film by argon bombardment. A similar dehydration was observed for Ni species.

As can be seen from Fig. 2, the analysis of the Ni $2p_{3/2}$ core level is difficult, due to the partial overlapping of Ni $2p_{3/2}$ and La $3d_{3/2}$ peaks. For this reason, the Ni $2p_{3/2}$

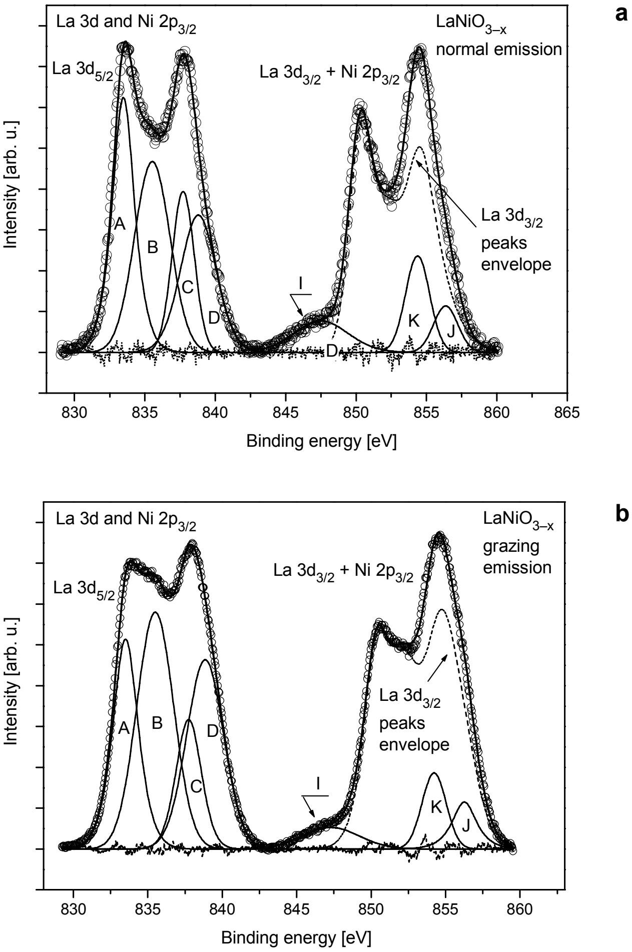

Fig. 4. Deconvolution analysis of La 3*d* and Ni $2p_{3/2}$ XPS signal of LaNiO$_{3-x}$ thin films after a long time aging taken at: normal emission (**a**) and grazing emission angles (**b**). Excitation energy $h\nu = 3000$ eV [14]. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and the thick line is the spectra envelope. The La $3d_{3/2}$ peaks are not designated, but their envelope is marked by dashed line.

regions cannot be analysed separately without La $3d_{3/2}$ core level spectra analysis. The results of the fit of the complex La 3*d* and Ni $2p_{3/2}$ region core level spectra of LaNiO$_{3-x}$ thin films obtained after long time aging procedure are presented in Fig. 4. The sign of La $3d_{5/2}$ peaks is the same as in Fig. 3 and peak *I* corresponds to the La $3d_{5/2}$ plazmon component [17]. As Figure 4 shows, the Ni $2p_{3/2}$ peaks correspond to different chemical states. As in the case of lanthanum, nickel in LaNiO$_{3-x}$ film after long time aging in the atmosphere exists as oxide (peak *K*) and hydroxide (peak *J*). The XPS spectra of nickel are analogous for both emission angle geometries (see Fig. 4). A similar view in XPS spectra of nickel was observed in the samples after short time aging procedures, too. After Ar ion sputtering procedure of these films, the nickel hydroxide disappears [11].

The atomic surface concentration obtained from XPS measurements of La 3*d* and Ni 2*p* spectra for the samples after short time aging and Ar-sputtered films in terms of Ni/La are equal to 0.92 and 1.03, respectively. This shows the stoichiometric bulk composition (Ni/La = 1) and 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 d.c. magnetron sputtering corresponds to a volume one.

A comparison of La 3*d* and Ni 2*p* and O 1*s* core level spectrum of $LaNiO_{3-x}$ film after long time and short time aging shows that hydroxide as a product of the reaction of water with the film is dominant at outermost surface but it is distributed throughout the reacted layer as well.

4. Conclusions

The composition and chemical structure of $LaNiO_{3-x}$ films obtained by a reactive d.c. magnetron sputtering after short and long time aging were determined by X-ray photoelectron spectroscopy. The existence of at least few different forms of oxygen as lattice oxide, hydroxyl groups and adsorbed water in both samples is shown by XPS characterization. XPS spectra have also revealed the presence of lanthanum and nickel in oxide and hydroxide form at the film surface. A significant dehydration of both La and Ni hydroxides to corresponding oxides was observed on cleaning film by Ar-ions bombardment. The surface Ni/La concentration ratio is close to the stoichiometric volume one. As a result of surface interaction with water vapors, hydroxyl group concentration increases at the surface but it is distributed through the whole volume, too.

Acknowledgement – This work was done in part within the research projects 72/E-67/SPB/DESY/P-03/DWM 68/2004-20061 and EC program G1MA-CT-2002-4017 (Center of Excellence CEPHEUS) and P03B 053 26.

References

[1] Pajaczkowska A., Gloubokov A., *Synthesis, growth and characterization of tetragonal $ABCO_4$ crystals*, Progress in Crystal Growth and Characterization of Materials **36**(1–2), 1998, pp. 123–62.

[2] Novosselov A.V., Zimina G.V., Filaretov A.A., Shlyakhtinb O.A., Komissarova L.N., Pajaczkowska A., *On the synthesis and thermodynamic properties of $SrLaGaO_4$-$SrLaAlO_4$ solid solutions*, Materials Research Bulletin **36**(10), 2001, pp. 1789–98.

[3] Vengalis V., Oginskas A.K., Lisauskas V., Butkut R., Maneikis A., Dapkus L., Jasutis V., Shiktorov N., *Growth and investigation of the $La_{1-x}CaxMnO_3/(LaNiO_3, RuO_2)$ heterostructures*, [In] *Thin Films Deposition of Oxide Multilayers. Industrial-Scale Processing: Proceedings of the International Conference*, Vilnius, Lithuania, 2000, pp. 45–8.

[4] Choisnet J., Abadzhieva N., Stefanov P., Klissurski D., Bassat J.M., Rives V., Minchev L., *X-ray photoelectron spectroscopy, temperature-programmed desorption and temperature-programmed reduction study of $LaNiO_3$ and $La_2NiO_{4+\delta}$ catalysts for methanol oxidation*, Journal of the Chemical Society Faraday Transactions **90**(13), 1994, pp. 1987–91.

[5] BARBERO J., PEÑA M.A., CAMPOS-MARTIN J.M., FIERRO J.L.G., ARIAS P.L., *Support effect in supported Ni catalysts on their performance for methane partial oxidation*, Catalysis Letters **87**(3–4), 2003, pp. 211–8.

[6] SIEGMANN H.S., SCHLAPBACH L., BRUNDLE C.R., *Self-restoring of the active surface in the hydrogen sponge LaNi$_5$*, Physical Review Letters **40**(14), 1978, pp. 972–5.

[7] WAGNER C.D., DAVIS L.E., RIGGS W.M., *The energy dependence of the electron mean free path*, Surface and Interface Analysis **2**(2), 1980, pp. 53–5.

[8] YAN-LI LI, NUO-FU CHEN, JIAN-PING ZHOU, SHU-LIN SONG, LI-FENG LIU, ZHI-GANG YIN, CHUN-LIN CAI, *Effect of the oxygen concentration on the properties of Gd$_2$O$_3$ thin films*, Journal of Crystal Growth **265**(3–4), 2004, pp. 548–52.

[9] BRUNDLE C.R., [In] *Electronic Structure and Reactivity of Metal Surfaces*, E.G. Derouane, A.A. Lucas [Eds.], Plenum, New York 1975, pp. 389–457.

[10] LU J.M., HWANG W.S., YANG J.S., *Effects of substrate temperature on the resistivity of non-stoichiometric sputtered NiO$_x$ films*, Surface and Coatings Technology **155**(2–3), 2002, pp. 231–5.

[11] LORENZ P., FINSTER J., WENDT G., SALYN J.V., ZUMADILOV E.K., NEFEDOV V.I., *ESCA investigations of some NiO/SiO$_2$ and NiO-Al$_2$O$_3$/SiO$_2$ catalysts*, Journal of Electron Spectroscopy and Related Phenomena **16**(4), 1979, pp. 267–76.

[12] DE ASHA A.M., CRITCHLEY J.T.S., NIX R.M., *Molecular adsorption characteristics of lanthanum oxide surfaces: the interaction of water with oxide overlayers grown on Cu(111)*, Surface Science **405**(2–3), 1998, pp. 201–14.

[13] MOULDER J.F., STICHLE W.F., SOBOL P.E., BOMBEN K.D., *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Inc., Eden Prairie, USA 1995.

[14] MICKEVIČIUS S., GREBINSKIJ S., BONDARENKA V., VENGALIS B., ŠLIUŽIENĖ K., ORLOWSKI B.A., OSINNIY V., DRUBE W., *Investigation of epitaxial LaNiO$_{3-x}$ thin films by high-energy XPS*, Journal of Alloys and Compounds **423**(1–2), 2006, pp. 107–11.

[15] BARR T.L., *An ESCA study of the termination of the passivation of elemental metals*, Journal of Physical Chemistry **82**(16), 1978, pp. 1801–10.

[16] SUZUKI C., KAWAI J., TAKAHASHI M., VLAICU A.-M., ADACHI H., MUKOYAMA T., *The electronic structure of rare-earth oxides in the creation of the core hole*, Chemical Physics **253**(1), 2000, pp. 27–40.

[17] MULLICA D.F., LOK C.K.C., PERKINS H.O., YOUNG V., *X-ray photoelectron final-state screening in La(OH)$_3$: a multiplet structural analysis*, Physical Review B: Condensed Matter **31**(6), 1985, pp. 4039–42.

[18] DALLERA C., GIARDA K., GHIRINGHELLI G., TAGLIAFERRI A., BRAICOVICH L., BROOKES N.B., *Charge-transfer excitations in lanthanum compounds measured by resonant inelastic X-ray scattering at the M$_5$ edge*, Physical Review B: Condensed Matter and Materials Physics **64**(15), 2001, pp. 153104/1–4.

Received December 15, 2006