RESONANT PHOTOEMISSION OF LaNiO$_{3-\delta}$ THIN FILMS

S. Mickevičius [a], S. Grebinskij [a], V. Bondarenka [a], H. Tvardauskas [a], M. Senulis [a], V. Lisauskas [a], K. Šliužienė [a], B. Vengalis [a], E. Baškys [a], and R.L. Johnson [b]

[a] *Semiconductor Physics Institute, Center for Physical Sciences and Technology, A. Goštauto 11, LT-01108 Vilnius, Lithuania*
E-mail: sigism@pfi.lt

[b] *Hamburg Synchrotron Radiation Laboratory HASYLAB at German Electron Synchrotron DESY, Notkestrasse 85, D-22603 Hamburg, Germany*

Thin LaNiO$_{3-\delta}$ films with pseudocubic (100) preferred orientation were prepared by reactive DC magnetron sputtering and annealed at ultra high vacuum above dehydration temperature. The resonant photoemission spectroscopy was used to study the surface composition and electronic structure under La 4d→4f and Ni 3p→3d photoexcitation. The resonance features observed in core level and valence band spectra under La 4d→4f transition were explained in terms of autoionization process and lanthanum–oxygen valence band states' hybridization. No resonant features were observed in the valence band spectra under Ni 3p→3d excitation indicating that nickel species are not present at the LaNiO$_{3-\delta}$ film surface after heat treatment.

Keywords: rare earth alloys and compounds, oxide materials, resonant photoelectron spectroscopy

PACS: 68.47.Gh, 81.15.Cd, 82.80.Pv

1. Introduction

LaNiO$_3$ is one of the few conductive oxides with a crystal structure suitable for integration in epitaxial heterostructures with perovskites of enormous technological potential such as colossal magnetoresistance materials, high-temperature superconductors, and ferroelectrics.

It is known that a considerable surface segregation of elements may take place in LaNiO$_{3-\delta}$ samples [1]. Another factor to be considered is the tendency of rare earth and nickel oxides to absorb water vapour and carbon dioxide from air, so that any *ex situ* exposure of these films to air will result in an uncontrolled reaction and surface stoichiometry variation [2]. Thus the knowledge of the surface composition is extremely important because it is directly related to the heterostructure properties.

In the previous paper [3] by means of X-ray photoelectron spectroscopy (XPS) using Mg K$_\alpha$ excitation ($h\nu = 1253.6$ eV) it was shown that even a short time (of about two hours) exposure to an outside ambient leads to the formation of the hydroxide layer on the film surface. The escape depth at these conditions is about 4 monolayers (ML) [4] for the La 3d and Ni 2p spectra of interest.

Angle dependent spectra, obtained with synchrotron X-rays at much higher energies ($h\nu = 3000$ eV, escape depth about 10 ML) reveal that significant variations in oxide versus hydroxide concentrations occur within the relatively thin surface layer even after long-term (one year) exposure to the atmosphere. Estimated thickness of this hydroxide enriched layer is about 6±1 ML [5].

The initially hydrated LaNiO$_{3-\delta}$ surface may be restored by heating above dehydration temperature [6, 7]. Nickel hydroxide, in turn, decomposes at $T > 230\,^\circ$C (melting point) [8]. When heated to decomposition it emits toxic fumes of metallic nickel, and one would expect a decrease of Ni-species relative concentration in the previously hydrated surface layer.

A powerful tool to investigate the electronic properties of d- and f-metals' compound surface is resonant photoemission. In this technique the radiation energy $h\nu$ is tuned to reach the resonant electron transition, e. g. 3p–3d for transition metal ($h\nu \sim 30$–90 eV) or 4d–4f for rare-earth atoms ($\sim$100–200 eV), to excite locally and selectively the electrons in the particular chosen atom. The escape depth of electrons leaving the crystal depends strongly on their kinetic energy and reaches a minimum value of $\sim$2 ML in the case when kinetic energy of escaping electron is about 90 eV [4]. That is the reason why the resonant photoemission spectra

become a powerful tool for studying surface electronic structure.

The aim of our work is to investigate the surface electronic structure and chemical composition of $LaNiO_{3-\delta}$ thin films after heating above dehydration temperature of about $500\,°C$.

2. Experiment

Thin $LaNiO_{3-\delta}$ films onto monocrystallyne (100)-plane oriented $NdGaO_3$ substrate were deposited by using a reactive DC magnetron sputtering technique. The ceramical $LaNiO_3$ target (25 mm in diameter and 2.5 mm thick) was prepared by pressing at $5·10^8$ Pa 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 the stoichiometric ratio. The sputtering was performed in Ar and O_2 mixture (20:1) at pressure of about 15 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 $\sim750\,°C$. Under these conditions, the deposition rate was 25 nm/h, and the resultant thickness of $LaNiO_{3-\delta}$ film was about 0.1 μm.

The film was annealed at $560\,°C$ under ultra-high vacuum (UHV, 10^{-10} torr) conditions for 10 hours. Additional Ar^+ ion sputtering at 600 V and current density 0.5 $\mu A\,cm^{-2}$ during 15 min were used to remove surface contamination. The resonant photoemission experiments were performed in the synchrotron radiation laboratory HASYLAB, Hamburg (Germany). Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER II plane grating vacuum monochromator designed for the photon energy range of 15–200 eV. The spectrometer was equipped with a CMA electron energy analyzer. The total energy resolution was kept at 0.1 eV. The origin of the energy axis was set at the Fermi energy as measured for a reference Au sample [9].

After Shirley background [10] subtraction, the complex photoelectron spectra were decomposed into separate peaks by specifying the peak position – binding energy (BE), area, width, and Gaussian / Lorentzian ratio. The accuracy of the measured lines BE and relative intensities were about 0.1 eV and 10% respectively.
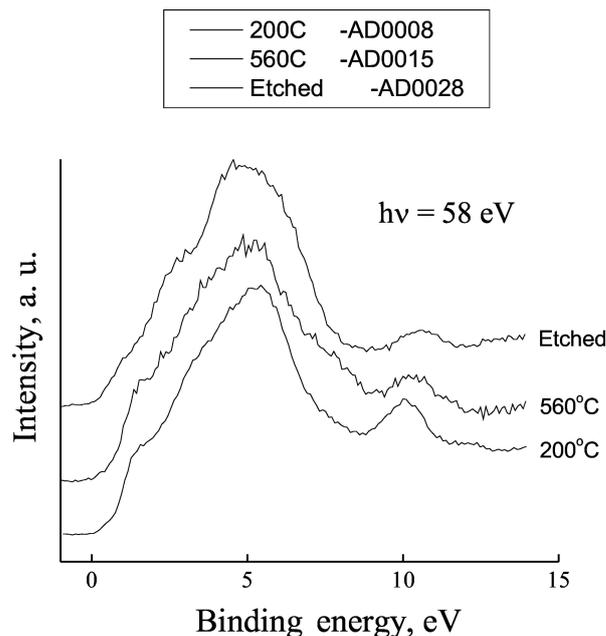
Fig. 1. Photoelectron spectra of $LaNiO_{3-\delta}$ thin film valence band region measured after annealing in UHV at 200 and $560\,°C$ and subsequent Ar^+ ion sputtering.

3. Results and discussion

3.1. Spectra normalization procedure

To compare photoelectron spectra obtained at different excitation photon energies one needs an appropriate normalization procedure to adjust measurements. In the absence of data required for normalization to the photon flux, the adventitious contamination peaks such as O 2p signal of surface oxygen (at about 6 eV binding energy) in the case of metallic lanthanum [10] or contaminations peaks from carbon monoxide around ~10 eV for metal oxides may be used for normalization [11]. The photoelectron spectra measured at $h\nu = 58$ eV, i. e. far from both La 4d$\rightarrow$4f and Ni 3p$\rightarrow$3d resonance are presented in Fig. 1 after different treatments. All spectra are normalized to the valence-band (VB) maximum. The relatively thin (FWHM $\sim 1.24\pm0.08$ eV) peak at BE ~ 10 eV may be attributed to carbon monoxide contamination [11]. A sequential decrease in this peak intensity after annealing in UHV at $560\,°C$ for 10 hours and Ar^+ ion sputtering confirms that it may be associated with surface contamination resulting from CO absorption.

The photon energy dependence of adventitious peak intensity includes not only the intensity of the monochromatized photon flux, but also the cross-section and escape depth spectral distribution and may be used as a reference for the spectra normalization. This procedure is reasonable since the peak around ~10 eV arises
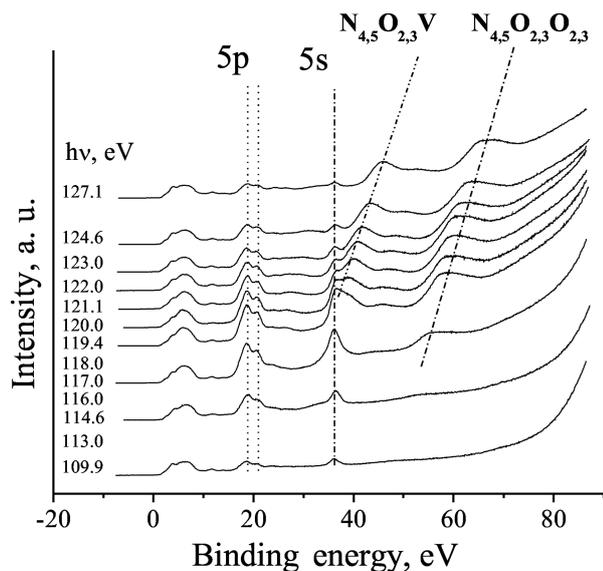
Fig. 2. Representative energy distribution curves for the core level (La 5s and La 5d) and Auger ($N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$) electrons in $LaNiO_{3-\delta}$ thin film recorded around the lanthanum La[4d→4f] transition energy. Excitation energies are also shown.

from the binding state 5σ of oxygen 2p and carbon 2s/2p orbitals in CO, their photon energy dependence of the cross-section is similar to that of oxygen 2p [12–14].

3.2. Core-level spectra

A set of energy distribution curves (EDCs) of a $LaNiO_{3-\delta}$ film for the photon energy range covering the energy of the La 4d→4f transition are shown in Fig. 2. In the photoelectron spectra there are three different line groups: 5s photoemission with binding energy of around 36.2 ± 0.3 eV; 5p doublet being at La $5p_{3/2}$ BE = 18.3 ± 0.3 eV (spin splitting = 2.2 ± 0.1 eV), and the main Auger peaks at kinetic energies (KE) of 62.3 ± 0.1 and 81.5 ± 0.1 eV corresponding to $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ Auger peaks respectively [15, 16]. These results are in agreement with the data reported for 4d→4f excitations in metallic lanthanum [10]. Slight (of about 1.2 eV) BE shift for La 5s and 5p lines towards higher energies may be attributed to Coulomb interaction in ionic compounds. The Coulomb interaction also leads to a slight energy shift of 0.7 eV towards lower KE in the case of $N_{4,5}O_{2,3}V$ transition, while KE for $N_{4,5}O_{2,3}O_{2,3}$ transition is actually the same as for metallic lanthanum.

Photon energy dependences of the relative intensities of the different Auger and photoelectron lines observed for $LaNiO_{3-\delta}$ films in the vicinity of the La 4d→4f threshold are displayed in Fig. 3. The relative intensities of these four lines have been determined by spectra fitting after Shirley background removal.
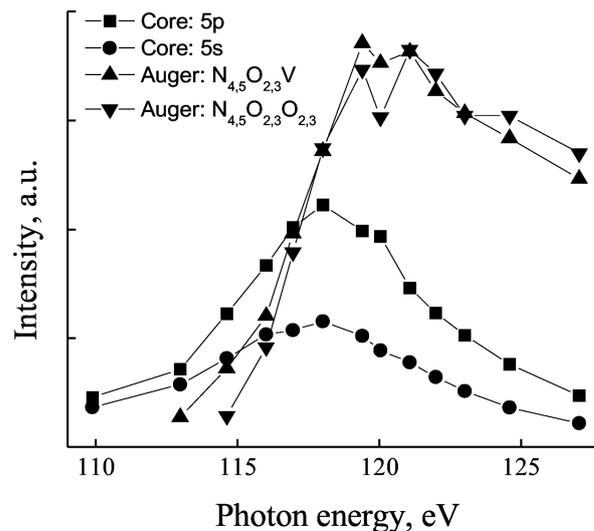
Fig. 3. Photon energy dependences of the relative intensities of lines corresponding to the Auger ($N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$) and photoelectron (5p and 5s) transitions for $LaNiO_{3-\delta}$ films in the vicinity of the La [4d→4f] threshold.

The giant resonance observed for lanthanum 5s; (5p) core levels may be explained by an autoionization process [10] leading to the emission ejected electron after the resonant La 4d→4f excitation:

$$4d^{10}5s^2p^6 + h\nu \rightarrow [4d^9 4f^{15}5s^2p^6]^* \rightarrow$$
$$4d^{10}5s^1p^6 + e^-; (4d^{10}5s^2p^5 + e^-),$$
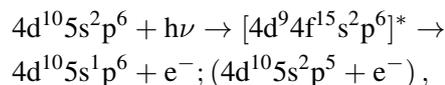
where * denotes the excited state.

In this process the energy of additional electron is the same as it were when produced by direct photoemission of an electron from the 5s; (5p) orbital expressed by formula

$$4d^{10}5s^2p^6 + h\nu \rightarrow$$
$$4d^{10}5s^1p^6 + e^-; (4d^{10}5s^2p^5 + e^-).$$
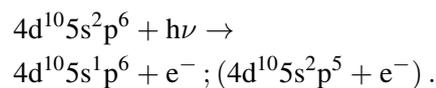
The direct photoemission occurs in a wide range of $h\nu$ energies, while the additionally ejected electrons are excited in the resonant photoemission energy region corresponding to 4d→4f threshold and in photoelectron spectra these processes are seen as enhanced intensity of corresponding photopeaks.

The resonant structure also appears in Auger $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ transitions (Fig. 3) in agreement with an autoionization model of resonance process after 4d→4f excitation [17, 18].

3.3. Valence band spectra

Apart from the giant resonance observed for lanthanum 5s and 5p core levels, a relatively weak resonance structure is also observed for valence-band
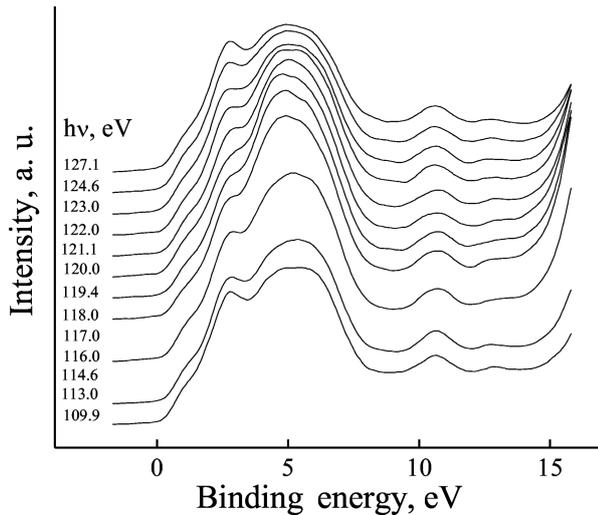
Fig. 4. Representative energy distribution curves for the valence-shell electrons in $LaNiO_{3-\delta}$ thin film recorded around the lanthanum La[4d→4f] transition energies. Excitation energies are also shown.
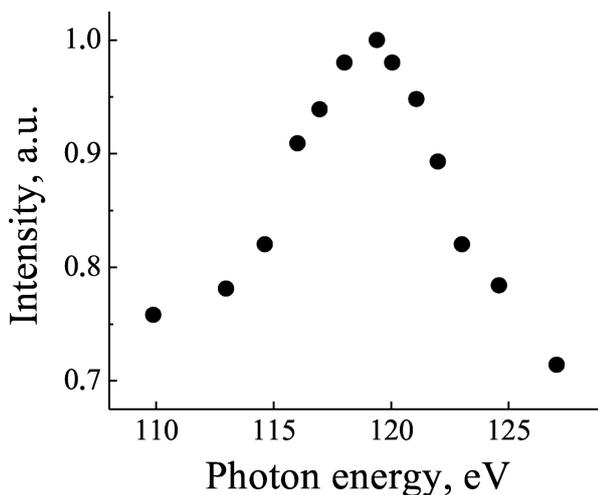
Fig. 5. Photon energy dependence of the photoelectron spectra intensity at valence band maximum in the vicinity of the La[4d→4f] threshold.

photoemission (Fig. 2). In this section results of detailed study of VB photoelectron spectra in the vicinity of La[4d→4f] and Ni[3p→3d] resonant transitions are presented.

Valence band energy-distribution spectra for various excitation energies near La[4d→4f] transition are shown in Fig. 4. The relatively weak resonance observed in the VB maximum (Fig. 5) may be related to a small admixture of La 5d character to O 2p valence band. The difference between ON ($h\nu = 119.5$ eV) and OFF ($h\nu = 127$ eV) resonance photoemission spectra (Fig. 6(a)) clearly indicates that only bonding (i. e. O 2pσ) states around 5–7 eV [11, 19] participate in the observed VB enhancement, while peak around 3 eV cor-

responding to nonbonding O 2pπ molecular orbital is actually insensitive to resonant La 4d→4f excitation.

Contrariwise, no changes were observed in VB spectra under Ni 3p→3d excitation (Fig. 6(b)). This result means that only traces of the nickel species may be present at the film surfaces within the escape depth (of about 2 ML) after the heating above dehydration temperature of 550 °C.

4. Summary and conclusions

In summary, we studied the surface electronic structure and chemical composition of $LaNiO_{3-\delta}$ thin films after heating above dehydration temperature. The experimental method used in this study was resonant photoemission spectroscopy using tunable synchrotron radiation.

The giant resonance in La 5p and La 5s peaks' intensity observed at excitation energy corresponding to a La[4d→4f] threshold ($h\nu = 119.5$ eV) is accompanied by a weak resonance of $N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$ Auger peaks. The obtained results are in agreement with the model of an autoionization process after resonant excitation.

The relatively weak enhancement of the intensity of valence band maxima (at about 6 eV) may be explained by the small mixing of the La 5d ionic character to the O 2p valence band. No resonant features were observed in the VB spectra under Ni[3p→3d] excitation (escape depth $L \approx 2$ ML), indicating that nickel species are not present at the $LaNiO_{3-\delta}$ film surface after heat treatment.
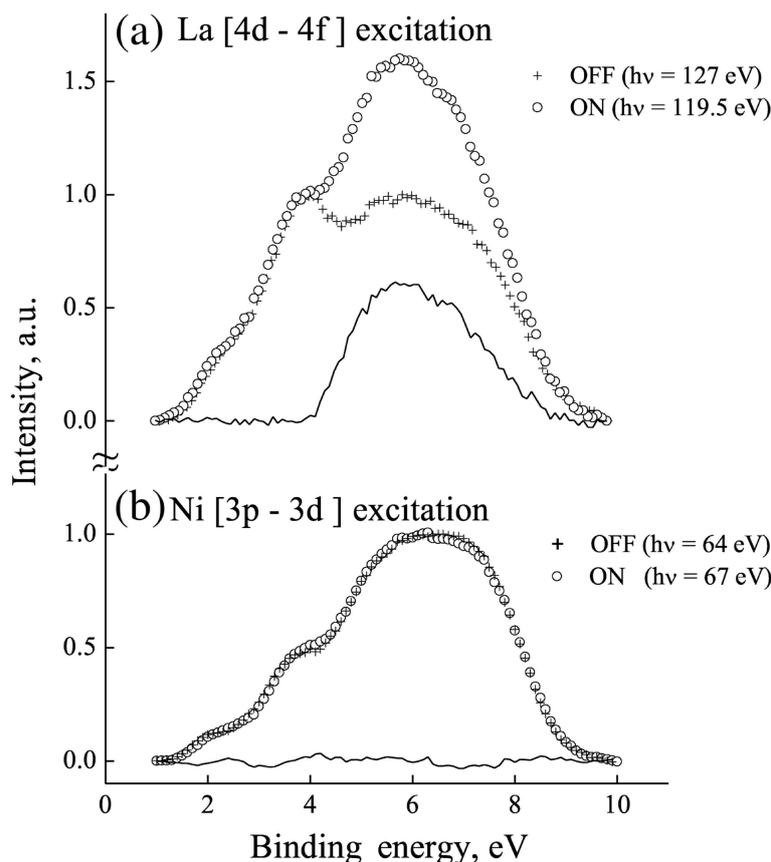
Fig. 6. EDCs showing the valence band of annealed at 560 °C thin LaNiO$_{3-\delta}$ film spectra after Shirley background removal at the La[4d→4f] and Ni[3p→3d] excitation for ON- and OFF-resonance photon energies. Lines correspond to the difference spectrum (ON−OFF).

References

[1] J. Choisnet, N. Abadzhieva, P. Stefanov, D. Klissurski, J.M. Bassat, V. Rives, and L. Minchev, X-ray photoelectron spectroscopy, temperature-programmed desorption and temperature-programmed reduction study of LaNiO$_3$ and La$_2$NiO$_{4+\delta}$ catalysts for methanol oxidation, J. Chem. Soc. Faraday Trans. **90**, 1987–1991 (1994).

[2] Y. Li, N. Chen, J. Zhou, S. Song, L. Liu, Z. Yin, and C. Cai, Effect of the oxygen concentration on the properties of Gd$_2$O$_3$ thin films, J. Cryst. Growth **265**, 548–552 (2004).

[3] V. Bondarenka, S. Grebinskij, V. Lisauskas, S. Mickevičius, K. Šliužienė, H. Tvardauskas, and B. Vengalis, XPS study of epitaxial LaNiO$_{3-x}$ films, Lithuanian J. Phys. **46**, 95–99 (2006).

[4] D. Briggs and M.P. Seach, *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (John Wiley & Sons Ltd, Chichester–New York, 1996).

[5] S. Mickevičius, S. Grebinskij, V. Bondarenka, V. Lisauskas, K. Šliužienė, H. Tvardauskas, B. Vengalis, B.A. Orlowski, V. Osinniy, and W. Drube, The surface hydro-oxidation of LaNiO$_{3-\delta}$ thin films, Acta Phys. Pol. A **112**, 113–120 (2007).

[6] H. Samata, D. Kimura, Y. Saeki, Y. Nagata, and T.C. Ozawa, Synthesis of lanthanum oxyhydroxide single crystals using anelectrochemical method, J. Cryst. Growth **304**, 448–451 (2007).

[7] V.G. Milt, C.A. Querini, and E.E. Miro, Thermal analysis of K(x)/La$_2$O$_3$, active catalysts for the abatement of diesel exhaust contaminants, Thermochim. Acta **404**, 177–186 (2003).

[8] M. Sakashita and N. Sato, The structure and reactivity of nickel hydroxide, Bull. Chem. Soc. Jpn. **46**, 1983–1987 (1973).

[9] D.A. Shirley, High-resolution X-ray photoemission spectrum of the valence bands of gold, Phys. Rev. B **5**, 4709–4714 (1972).

[10] O.-P. Sairanen, S. Aksela, and A. Kivimaki, Resonace Auger and autoionization processes in solid lanthanum after 4d→4f resonant excitation by synchrotron radiation, J. Phys. Cond. Matter **3**, 8707 (1991).

[11] J. Park, S.-J. Oh, J.-H. Park, D.M. Kim, and C.-B. Eom, Electronic structure of epitaxial (Sr,Ca)RuO$_3$ films studied by photoemission and X-ray absorption spectroscopy, Phys. Rev. B **69**, 085108-1–6 (2004).

[12] J.J. Yeh and I. Lindau, Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leq Z \leq 103$, At. Data Nucl. Data Tables **32**, 1–155 (1984).

[13] I. Wilhelmy, A. Lutz, A. Görling, and N. Rösch, Molecular photoionization cross sections by the Lobatto technique. I. Valence photoionization, J. Chem. Phys. **100**, 2808–2820 (1994).

[14] E.W. Plummer, T. Gustafsson, W. Gudart, and D.E. Eastman, Partial photoionization cross sections of N_2 and CO using synchrotron radiation, Phys. Rev. A **15**, 2339–2355 (1997).

[15] J.C. Riviere, F.P. Netzer, G. Rosina, G. Strasser, and J.A. Matthew, The 4d Auger, Coster–Kronig and recombination spectra of the lanthanides, J. Electron Spectrosc. Relat. Phenom. **36**, 331–375 (1985).

[16] M. Richter, T. Prescher, M. Meyer, E. von Raven, B. Sonntag, H.E. Wetzel, and S. Aksela, Solid-state binding, recombination and Auger energy shifts of rare-earth metals, Phys. Rev. B **38**, 1763–1772 (1988).

[17] S. Aksela, O.-P. Sairanen, H. Aksela, G.M. Bancroft, and K.H. Tan, Normal and resonance LVV Auger spectra of gas-phase SiC_4 molecules, Phys. Rev. A **37**, 2934–2940 (1988).

[18] G.M. Bancroft, K.H. Tan, O.-P. Sairanen, S. Aksela, and H. Aksela, Decay processes after resonant excitation of S 2p and F 1s electrons in SF_6 molecules, Phys. Rev. A **41**, 3716–3722 (1990).

[19] D.F. Mullica, H.O. Perkins, C.K.C. Lok, and V. Young, The X-ray photoemission of $La(OH)_3$, J. Electron Spectrosc. Relat. Phenom. **61**, 337–355 (1993).

PLONŲJŲ LaNiO$_{3-\delta}$ SLUOKSNIŲ REZONANSINĖ FOTOEMISIJA

S. Mickevičius [a], S. Grebinskij [a], V. Bondarenka [a], H. Tvardauskas [a], M. Senulis [a], V. Lisauskas [a], K. Šliužienė [a], B. Vengalis [a], E. Baškys [a], R.L. Johnson [b]

[a] *Fizinių ir technologijos mokslų centro Puslaidininkių fizikos institutas, Vilnius, Lietuva*
[b] *Hamburgo sinchrotroninės spinduliuotės laboratorija HASYLAB prie Vokietijos elektronų sinchrotrono DESY, Hamburgas, Vokietija*

Santrauka

Plonieji (100) orientacijos LaNiO$_{3-\delta}$ sluoksniai buvo pagaminti nuolatinės srovės magnetroninio dulkinimo būdu ir atkaitinti ultraaukštame vakuume virš dehidracijos temperatūros. Sluoksnio elektroninė struktūra ir cheminė sudėtis tirti rezonansinės fotoemisinės spektroskopijos metodu, žadinant fotonais ties La 4d–4f ir Ni 3p–3d šuolio slenksčiu. Rezonansinės savybės, stebimos kamieninių lygmenų ir valentinės juostos fotoelektronų spektruose žadinant fotonais ties La 4d–4f šuolio slenksčiu, aiškintinos autojonizaciniais procesais ir lantano–deguonies valentinės juostos būsenų hibridizacija. Žadinant fotonais ties Ni 3p–3d šuolio slenskčiu, fotoelektronų spektruose rezonansas nestebimas. Tai rodo, kad tiriamo LaNiO$_{3-\delta}$ sluoksnio paviršiuje po terminio apdorojimo nikelio koncentracija tampa nykstamai maža.