

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

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Thin $\text{LaNiO}_{3-\delta}$ 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 $\text{LaNiO}_{3-\delta}$ film surface after heat treatment.

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

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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 $\text{LaNiO}_{3-\delta}$ 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_α 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 $\text{LaNiO}_{3-\delta}$ surface may be restored by heating above dehydration temperature [6, 7]. Nickel hydroxide, in turn, decomposes at $T > 230^\circ\text{C}$ (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 ($h\nu \sim 30\text{--}90$ eV) or 4d–4f for rare-earth atoms ($\sim 100\text{--}200$ 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 ~ 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 $\text{LaNiO}_{3-\delta}$ thin films after heating above dehydration temperature of about 500°C .

2. Experiment

Thin $\text{LaNiO}_{3-\delta}$ films onto monocrystalline (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 $5 \cdot 10^8$ 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 $\sim 750^\circ\text{C}$. Under these conditions, the deposition rate was 25 nm/h, and the resultant thickness of $\text{LaNiO}_{3-\delta}$ film was about $0.1 \mu\text{m}$.

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 $0.5 \mu\text{A cm}^{-2}$ 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.

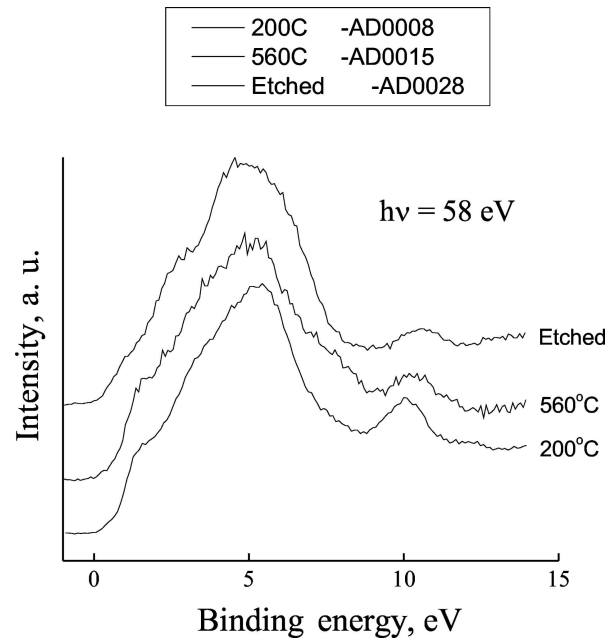


Fig. 1. Photoelectron spectra of $\text{LaNiO}_{3-\delta}$ thin film valence band region measured after annealing in UHV at 200 and 560°C and subsequent Ar^+ ion sputtering.

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 $\sim 1.24 \pm 0.08$ 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 from

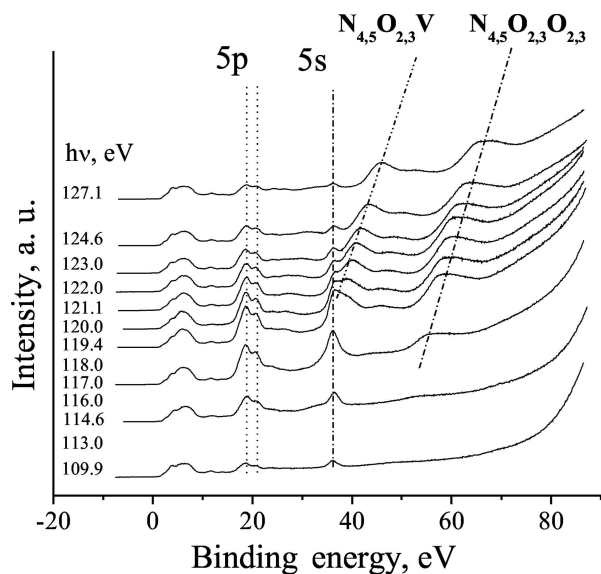


Fig. 2. Representative energy distribution curves for the core level (La 5s and La 5d) and Auger ($N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$) electrons in $LaNiO_{3-\delta}$ thin film recorded around the lanthanum $La[4d \rightarrow 4f]$ transition energy. Excitation energies are also shown.

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 $La\ 4d \rightarrow 4f$ 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 $4d \rightarrow 4f$ 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 $La\ 4d \rightarrow 4f$ threshold are displayed in Fig. 3. The relative intensities of these four lines have been determined by spectra fitting after Shirley background removal.

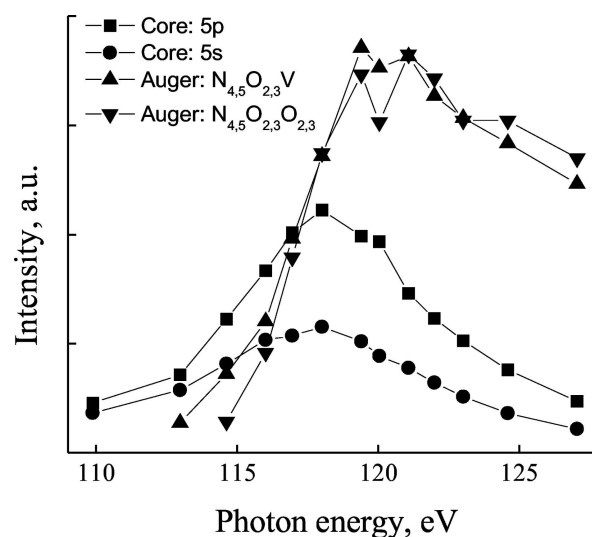
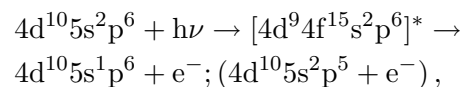


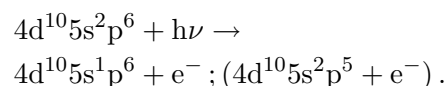
Fig. 3. Photon energy dependences of the relative intensities of lines corresponding to the Auger ($N_{4,5}O_{2,3}O_{2,3}$ and $N_{4,5}O_{2,3}V$) and photoelectron (5p and 5s) transitions for $LaNiO_{3-\delta}$ films in the vicinity of the $La\ [4d \rightarrow 4f]$ threshold.

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 $La\ 4d \rightarrow 4f$ excitation:



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



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 $4d \rightarrow 4f$ 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 $4d \rightarrow 4f$ 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

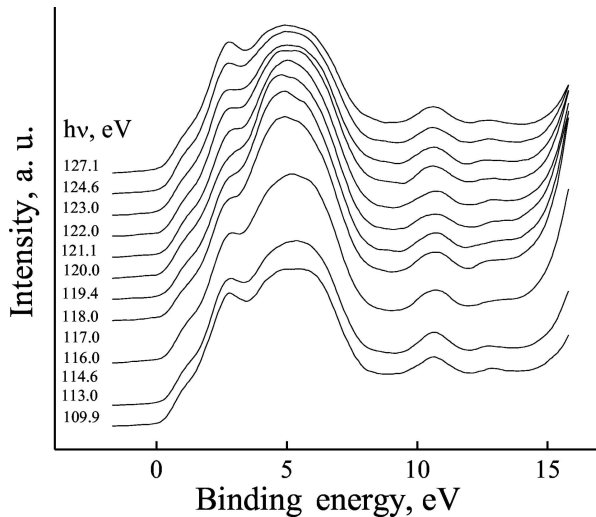


Fig. 4. Representative energy distribution curves for the valence-shell electrons in $\text{LaNiO}_{3-\delta}$ thin film recorded around the lanthanum $\text{La}[4d \rightarrow 4f]$ transition energies. Excitation energies are also shown.

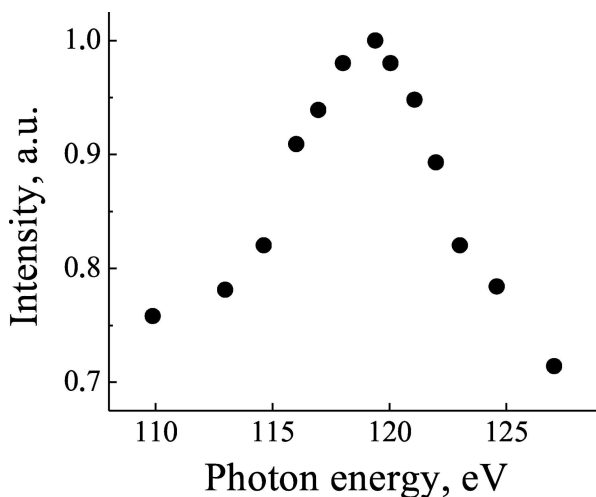


Fig. 5. Photon energy dependence of the photoelectron spectra intensity at valence band maximum in the vicinity of the $\text{La}[4d \rightarrow 4f]$ threshold.

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

Valence band energy-distribution spectra for various excitation energies near $\text{La}[4d \rightarrow 4f]$ 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 2p σ) states around 5–7 eV [11, 19] participate in the observed VB enhancement, while peak around 3 eV

corresponding to nonbonding O 2p π molecular orbital is actually insensitive to resonant $\text{La}[4d \rightarrow 4f]$ excitation.

Contrariwise, no changes were observed in VB spectra under Ni 3p \rightarrow 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 $\text{LaNiO}_{3-\delta}$ 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 $\text{La}[4d \rightarrow 4f]$ threshold ($h\nu = 119.5$ eV) is accompanied by a weak resonance of $\text{N}_{4,5}\text{O}_{2,3}\text{O}_{2,3}$ and $\text{N}_{4,5}\text{O}_{2,3}\text{V}$ 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 $\text{Ni}[3p \rightarrow 3d]$ excitation (escape depth $L \approx 2$ ML), indicating that nickel species are not present at the $\text{LaNiO}_{3-\delta}$ film surface after heat treatment.

Acknowledgement

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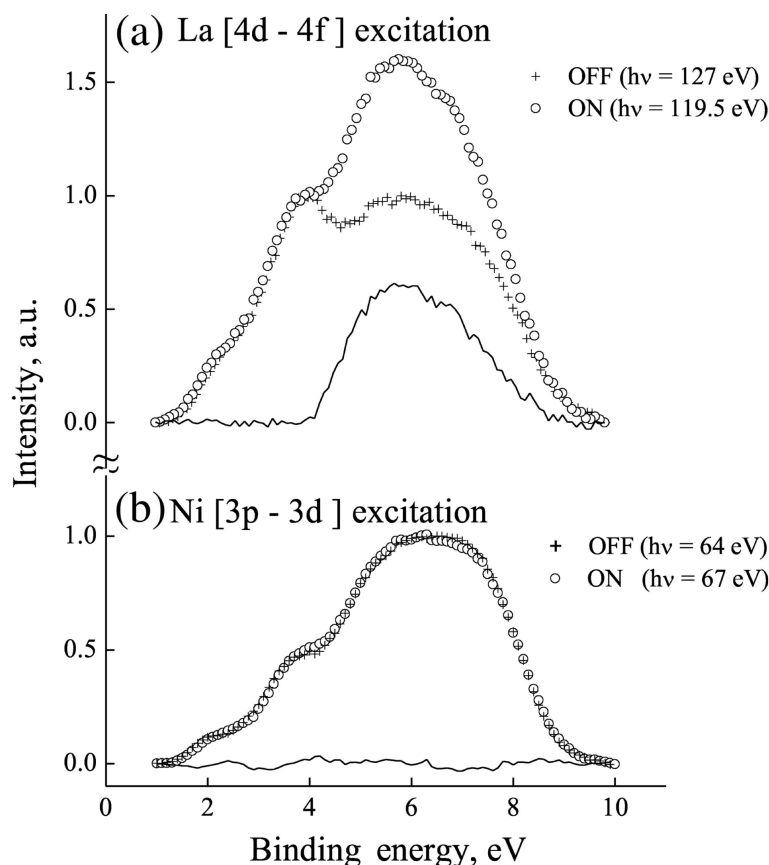


Fig. 6. EDCs showing the valence band of annealed at 560 °C thin $\text{LaNiO}_{3-\delta}$ film spectra after Shirley background removal at the $\text{La}[4d \rightarrow 4f]$ and $\text{Ni}[3p \rightarrow 3d]$ excitation for ON- and OFF-resonance photon energies. Lines correspond to the difference spectrum (ON–OFF).

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PLONŪJŲ $LaNiO_{3-\delta}$ SLUOKSNIŲ REZONANSINĖ FOTOEMISIJA

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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 kamie-

ninių lygmenų ir valentinės juostos fotoelektronų spektruose žadinant fotonais ties La 4d–4f šuolio slenksčiu, aiškintinos autojoniaciniais procesais ir lantano–deguonies valentinės juostos būsenų hibridizacija. Žadinant fotonais ties Ni 3p–3d šuolio slenksčiu, fotoelektronų spektruose rezonansas nestebimas. Tai rodo, kad tiriamo $LaNiO_{3-\delta}$ sluoksnio paviršiuje po terminio apdoravimo ni-kelio koncentracija tampa nykstamai maža.