Investigation of epitaxial LaNiO_{3-x} thin films by high-energy XPS

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Abstract

Epitaxial thin films of LaNiO_{3-x} were deposited by using a reactive d.c. magnetron sputtering technique. High-energy X-ray photoelectron spectroscopy was used to analyze the composition and valence states of La and Ni in the films after long time aging in atmosphere. The obtained results show the existence lanthanum and nickel in oxide and hydroxide chemical states. The oxygen exists in four chemical states: lattice oxides, hydroxyl groups and in adsorbed water. Comparison of the spectra recorded at normal emission and grazing emission angle revealed that the hydroxyl group's concentration is mostly present at the surface of the film.

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1. Introduction

Recently, the great interest in thin films of ferroelectrics, high temperature superconductors or semiconductors for group III nitrides (such as GaN or AlN) epitaxial layers has made the problem of a suitable substrate an important and a lot of studies have been undertaken to find a suitable substrate [1,2]. Lanthanide oxide materials ($\text{Ln} = \text{La}, \text{Pr}$ and Nd) have shown promise due to lattice matching and have been employed as the substrate layers. There have been numerous studies on their morphology, structural, thermodynamic, magnetic, elastic properties and crystal growth [3,4]. 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 carried out using dielectric buffer layers. The highly conductive films, which can be used both as the buffer layers and interconnects or electrodes in hybrid devices, can be the promising alternatives for dielectrics. One of them – LaNiO_{3-x} films has been successfully fabricated by various methods such as d.c. Sputtering, pulsed laser deposition (PLD), sol–gel method, metalorganic decomposition (MOD), metalorganic chemical vapor deposition (MOCVD) or mist plasma evaporation (MPE) [5–10].

In order to probe bulk properties or to access buried structures, high-energy photoemission can be effectively used. It offers additional advantages to distinguish features of the surface electronic structure from those related to the volume or originating from buried species. Because at high kinetic energies the electron mean free path is large, the probing depth can be varied by measuring EDCs versus the photoelectron exit angle. This can also be done using laboratory X-ray sources ($h\nu < 1500 \text{ eV}$), although the energies are often too low to reach true bulk sensitivity. In this study, synchrotron X-rays at much higher energies (3000 eV) are used to significantly enhance the volume sensitivity for shallow core levels. At the same time, also deeper atomic levels can be accessed to obtain additional information on the electronic structure. Using synchrotron X-rays, the excitation energy may be varied over a large range. This is also advantageous in the study of high-Z materials, like rare earth, because it allows to discriminate the core level photoemission from the rich structure of lines originating from Auger cascades.

In this paper we utilize the volume sensitivity of tunable high-energy X-ray photoelectron spectroscopy to study the epitaxial LaNiO_{3-x} thin films deposited on NdGaO_3 substrate by a reactive d.c. magnetron sputtering after long time aging in air atmosphere.

2. Experimental

Thin LaNiO_{3-x} films onto monocrystalline (1 0 0)-plane oriented NdGaO_3 substrates were deposited by using a reactive d.c. magnetron sputtering tech-

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nique. 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 powders (99.99% purity from Aldrich) in stoichiometric ratio. The sputtering was performed in Ar and O_2 mixture (1:1) at 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 $\sim 0.1 \mu\text{m}$.

The data were obtained with the tunable high-energy X-ray photoelectron spectrometer at the X-ray wiggler beam line BW2 of HASYLAB (Hamburg). The photon flux from the Si (1 1 1) double crystal monochromator was about $5 \times 10^{12} \text{ s}^{-1}$ amounts on the sample. The base pressure in the analyzer chamber was 5×10^{-10} mbar. The electrons kinetic energy was measured using a hemispherical analyzer with parallel detection capability (SCIENTA SES-200). Excitation energy (3000 eV) was chosen where the kinetic energy of the La and Ni levels are not overlapping any of Auger electron emission peaks originating from the atoms of layer. This was checked by energy distribution curve (EDC) 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 synchrotron radiation orbit plane at 45° relative to the incoming beam. The samples after long time (about 1 year) aging in air atmosphere were measured “as introduced”, i.e. without any surface treatment.

3. Results and discussion

The La 3d core level spectra of lanthanum compounds show very complicated multi-component structures. It is well known that La 3d core level split into $3d_{5/2}$ and $3d_{3/2}$ components due to a spin–orbit interaction. Additionally each line split to main line ($3d^0 4f^0$ final state configuration) and a satellite line ($3d^0 4f^1 L$ final state configuration) [11,12]. The latter final state has different nature in the case of metallic or insulating lanthanum compounds [12,13]. For the metals and intermetallics it is due a charge fluctuation from $4f^0$ to $4f^1$ occupation, while in the insulating compounds such oxides, halides and sulfides it arises from an electron transfer from the ligand to the lanthanum 4f state. The satellite peak of the La 3d core level in insulating compounds on the higher binding energy side is separated from the main peak by about $\Delta E_{\text{sat}} \approx 4 \text{ eV}$.

It is known that the rare earth oxides are easily hygroscopic when they were exposed to atmospheric conditions [14,15]. The study of interaction of water with lanthanum oxide by XPS, UPS and TDS study show that La_2O_3 films rapidly adsorb water in a dissociate fashion, with an accompanying conversion of surface ions, to give a high concentration of surface hydroxyl groups [14]. Wandelt and Brundle [15] have studied the interaction of oxygen with evaporated Gd films at room temperature by Al K α XPS and HeI and HeII UPS techniques. They show that surface oxide reacts with contaminant water to produce hydroxide.

The La 3d and Ni 2p photoemission spectra of LaNiO_{3-x} film after long time aging in atmosphere are shown in Fig. 1 (curve 1 corresponds for the normal emission $\gamma = 45.0^\circ$ and curve 2 for the grazing $\gamma = 89.3^\circ$ emission, respectively). It is known that the La $3d_{3/2}$ peak overlap Ni $2p_{3/2}$ peak [16]. The most intense Ni $2p_{3/2}$ peak is accompanied by a satellite line, which positioned at ca. 6–7 eV higher binding energy (BE) (see Fig. 1) [17,18]. This Ni $2p_{3/2}$ satellite component is overlapping with existing

Fig. 1. La 3d and Ni 2p core level spectra of the LaNiO_{3-x} thin films taken at: (1) normal emission and (2) grazing emission angles.

of La $3d_{3/2}$ plasmon component (see Fig. 1) [11,19]. Thus Ni $2p_{3/2}$ core level spectra cannot be analyzed separately without La $3d_{3/2}$ core level spectra analysis. The complex structures of the La $3d_{3/2}$ spectra complicate Ni $2p_{3/2}$ profile analyses.

To eliminate the above mentioned difficulties it was assumed that the shape of synthetic lanthanum spectra is the same for both La $3d_{5/2}$ and La $3d_{3/2}$ lines. At the first stage measured spectra—Fig. 2 was analyzed in the La $3d_{5/2}$ BE region (828–843 eV). Later than the B, C and D peaks were linked to A peak (Fig. 2), thus making the shape of La $3d_{5/2}$ invariant on the A—peak position and intensity. This synthetic peak was used for further analysis in the whole La 3d and Ni $2p_{3/2}$ BE region (828–860 eV). The La $3d_{5/2}$ versus La $3d_{3/2}$ spin–orbit splitting (SOS) is equal to 16.8 eV [16] and the theoretical relative intensity ratio (RIR) for La $3d_{5/2}$ and La $3d_{3/2}$ = 1.5 were used as a starting approximation. After that, the common peak fitting procedure was used to obtain the parameters corresponding to various lanthanum and nickel species. After comparing SOS energies (16.79 and 16.80 eV for $\gamma = 45.0^\circ$ and 89.3° , respectively) and RIR (1.42 and 1.40 for $\gamma = 45.0^\circ$ and 89.3° , respectively) of La $3d_{5/2}$ and La $3d_{3/2}$ peaks in this work with those reported in literature (SOS = 16.9 eV [12,19]; RIR = 1.41 [12]), it is seen that our experimental values are in good agreement with experimental values presented in literature. It can be concluded with confidence that our fitting model accurately describe the physical events. For cleanliness only La $3d_{3/2}$ synthetic spectra envelope was presented in Fig. 2 by dashed line.

The La 3d and Ni $2p_{3/2}$ region core level spectra and its deconvolution parameters for LaNiO_{3-x} film are presented in Fig. 2 and Table 1. The La $3d_{5/2}$ core level spectra, taken at normal emission (Fig. 2a) and grazing emission angle (Fig. 2b) can be deconvoluted into two doublets, corresponding to oxide and hydroxide species. The oxide main line is at 833.5 eV binding energy and satellite line at 837.7 eV. The main line corresponding to the lanthanum bonding with hydroxyl group lies at 835.5 eV and satellite peak – 838.8 eV. The satellite separation $\Delta E_{\text{sat}} = 4.2$ and 3.3 eV for oxide and hydroxide species, respectively. For comparison the literature date of binding energy shifts

Fig. 2. Deconvolution analysis of La 3d and Ni 2p_{3/2} XPS signal of LaNiO_{3-x} thin films taken at normal (a) and grazing emission (b) angles. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and thick line is the spectra envelope. The sign of spectra components correspond the marking in Table 1. The La 3d_{3/2} peaks (see Table 1, peaks: E, F, G, H) did not sign, but shown these peaks envelope by a dashed line. The dotted line corresponds to the fitting residuals.

Table 1
Fitting results of La 3d and Ni 2p_{3/2} photoelectron spectra of LaNiO_{3-x}

Peak	Peak parameters						Peak identification		
	$\gamma = 45.0^\circ$			$\gamma = 89.3^\circ$			Species	Line	Assignment
	BE (eV)	RA (%)	FWHM (eV)	BE (eV)	RA (%)	FWHM (eV)			
A	833.47	14.70	1.86	833.50	12.10	2.00	La ₂ O ₃	3d _{5/2}	Core
B	835.52	16.23	2.97	835.50	18.67	2.93	La(OH) ₃		
C	837.71	8.56	1.86	837.74	7.15	2.00	La ₂ O ₃		
D	838.79	11.86	2.97	838.85	15.01	2.93	La(OH) ₃	3d _{3/2}	Core
E*	850.26	10.36	1.86	850.30	8.68	2.00	La ₂ O ₃		
F*	852.31	11.44	2.97	852.29	13.38	2.92	La(OH) ₃		
G*	854.50	6.04	1.86	854.54	5.13	2.00	La ₂ O ₃	3d _{3/2}	Satellite
H*	855.58	8.36	2.97	855.65	10.76	2.92	La(OH) ₃		
I	847.52	4.14	4.60	847.28	2.57	4.50	La ₂ O ₃ and La(OH) ₃	3d _{5/2}	Plazmon
J	856.37	2.70	2.02	856.26	2.69	1.92	Ni(OH) ₂	2p _{3/2}	Core
K	854.37	5.61	2.02	854.23	3.85	1.92	Nickel oxide		

RA: relative area of peak; FWHM: full width at half maximum. The asterisk signs the peaks of La 3d_{3/2} which envelope is presented in Fig. 2.

Table 2

XPS binding energy separation between the main and satellite peak in La spectra for various lanthanum compounds

Peak	Species	ΔE_{sat} (eV)	Ref.
La 3d _{5/2}	La ₂ O ₃	3.9	[19]
		4.27	[20]
		4.5	[17]
La 4p _{3/2}	La ₂ O ₃	3.9	[19]
		3.62	[21]
		3.7	[17]
La 3d _{5/2}	La(OH) ₃	3.5	[22]
		3.37	[21]

ΔE_{sat} is the BE difference between the main and the satellite peaks.

between the main peak and the satellite one: ΔE_{sat} for La₂O₃ and La(OH)₃ are presented in Table 2 [17,19–22].

In Fig. 2 are shown the envelope of La 3d_{3/2} deconvoluted peaks and two Ni 2p_{3/2} peaks corresponding different chemical states. Lanthanum and nickel in LaNiO_{3-x} film after long aging in atmosphere exists as oxide (peak K, Fig. 2) and hydroxide (peak J, Fig. 2). The XPS spectra of nickel are analogous for normal and grazing emission angle geometry's (see Fig. 2a and b). 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 a data reported in literature [16].

The core-level O 1s spectra for the LaNiO_{3-x} film are shown in Fig. 3. As can be seen from Fig. 3 the XPS spectra measured at different emission angles exhibits similar features. The O 1s peaks are complex and 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 into four peaks. The results of the deconvolution for normal and grazing emission angles are collected in Table 3. The low-energy peak at about 529.0 eV can be ascribed to a lattice O²⁻ anion in lanthanum oxides [23]. The peak B (see Fig. 3, Table 3) can be attributed to a lattice O²⁻ anion in nickel oxides [23]. The fully oxidized, Ni³⁺ containing LaNiO₃ sample exhibits a slightly distorted perovskite-like rhombohedral cell [24]. It is

Table 3

Fitting results of O 1s photoelectron spectrum of LaNiO_{3-x} , taken at normal and grazing emission angles

Peak	$\gamma = 45.0$			$\gamma = 89.3$			Peak identification
	BE (eV)	FWHM (eV)	RA (%)	BE (eV)	FWHM (eV)	RA (%)	
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	$(\text{OH})^-$ in La and Ni hydroxide
D	532.96	1.85	41.79	533.00	1.64	59.34	H_2O

The abbreviations are the same as in Table 1.

known that the chemical bonding in LaNiO_3 is not purely ionic, but exhibits covalent (Ni–O and La–O) and metallic (Ni–O–Ni) parts [25] that can explain the presence of two different oxides in the sample.

As was mentioning above, the rare earth oxides are easily hygroscopic when they were exposed to atmospheric conditions [14]. Thus, an additional spectral component C at approximate 531 eV may be attributed to La and Ni hydroxides [23,26,27] for which O 1s BE is typically higher by a 2.0–2.5 eV in respect to the associated lattice oxygen [14]. The supplementary peak at

BE = 533.2 eV may be attributed to the adsorbed water species [16].

4. Conclusions

The composition and chemical structure of LaNiO_{3-x} films obtained by a reactive d.c. magnetron sputtering after long time aging in atmosphere were investigated by using high-energy XPS synchrotron radiation at 3000 eV. XPS spectra have revealed a presence of lanthanum and nickel in oxide and hydroxide states. The oxygen O 1s core level spectra analysis show the existence of at least four different forms of oxygen in LaNiO_{3-x} films: lanthanum and nickel oxides, hydroxides and adsorbed water. The concentration of hydroxide species decreases going from the surface to the volume of the films.

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Fig. 3. Deconvolution analysis of O 1s signal of taken at normal (a) and grazing emission (b) angles. The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and thick line is the spectra envelope. The dotted line corresponds to the fitting residuals.

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