XPS STUDY OF $LaNiO_{3-x}$ LAYERS

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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. Even more attention is paid to multilayered structures consisting of several various metallic oxides. 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.

It was shown [1] 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. 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.

Thin $LaNiO_{3-x}$ films onto monocrystallyne (100)-plane oriented $NdGaO_3$ substrate were deposited by using a reactive d.c. magnetron sputtering technique.

X-ray photoelectron spectra were recorded using XSAM 800 (KRATOS Analytical, UK). The photoelectrons were excited using a non-monochromatized Mg K_α (1253.6 eV) radiation source.

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 influence of ion sputtering on the chemical composition of investigated compounds was treated by using Ar^+ ions bombardment at 3 keV and current density 10 $\mu A \cdot cm^{-2}$ by a 15 min.

The results of the O 1s spectra analysis are presented in Table 1. On cleaning the film by argon-ion bombardment H_2O peak disappears and the intensity of the hydroxide peak decreases.

Table 1. Results of the fit of O 1s photoelectron spectrum.

Peak	"As grown"			Ar^+- etched			Peak identification
	BE, eV	FWHM, eV	A_{rel}, %	BE, eV	FWHM, eV	A_{rel}, %	
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

The XPS spectra in the La 3d and Ni 2p binding energy regions are shown in Figure 1. The most intense Ni $2p_{3/2}$ peak was accompanied by a satellite line positioned at (6 -7) eV higher BE [2]. Thus, La 3d and Ni 2p regions cannot be analyzed separately.

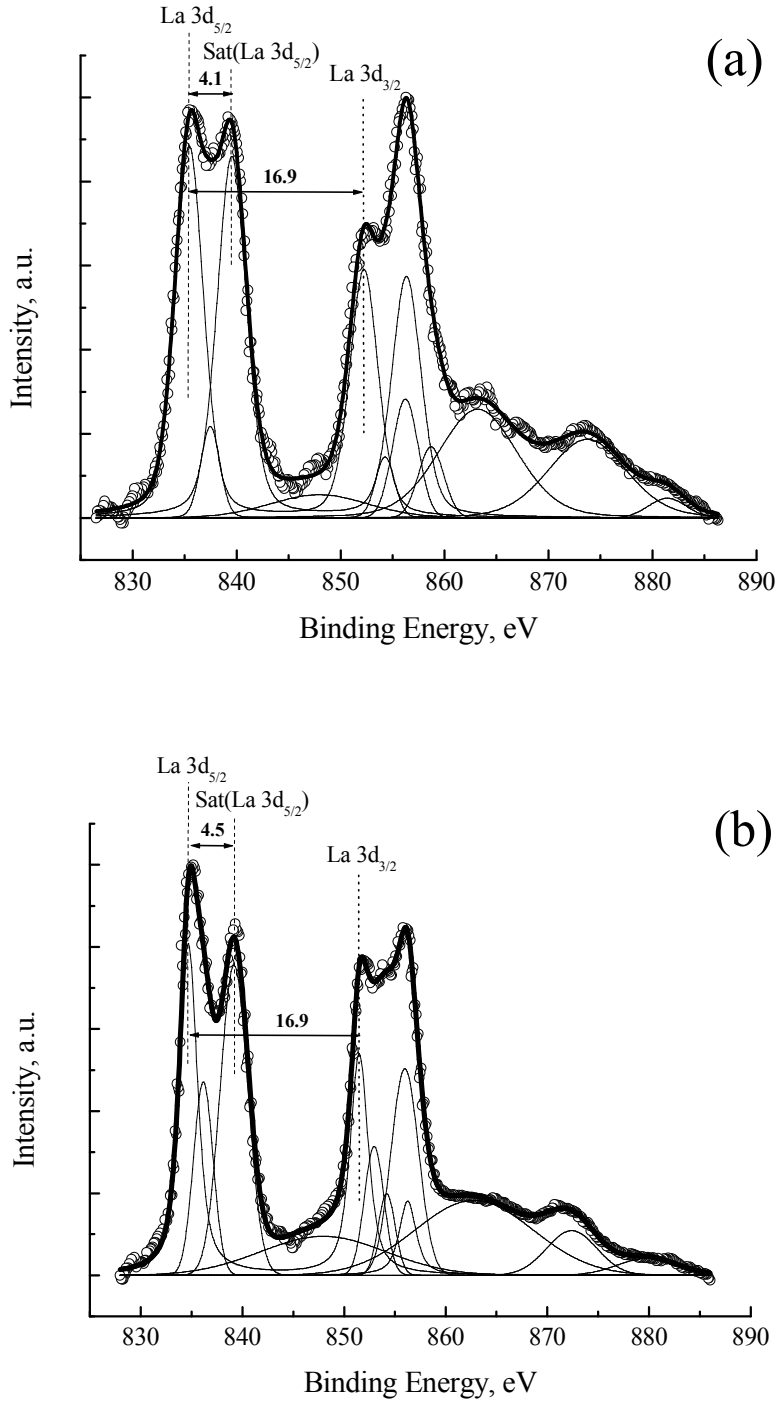

Figure 1. Deconvolution analysis of La 3d and Ni 2p signal of $LaNiO_{3-x}$ thin films. (a) – "As grown";(b) – Ar^+ etched film.The scattered points refer to the raw data, the thin solid lines correspond to the spectral components and thick line is the spectra envelope.

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 $La(OH)_3$ [3,4]. The core-level 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 and principal peaks separation from 4.1 to 4.5 eV (Fig.1) strongly confirm the decrease of lanthanum hydroxide at the film surface [5] after Ar^+ - treatment. This result is in a good agreement with the significant decrease of the areas ratio for hydroxide A_{hyd} and lattice A_{lat} oxygen species - Table 1 (A_{hyd}/A_{lat} = 0.78 and 0.54 for "as grown" and Ar-etched films, respectively.

The atomic surface concentration in terms of Ni/La are equal 0.92 and 1.03 for "As grown" and Ar-etched films, respectively and within the experimental error corresponds 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 D.C. magnetron sputtering corresponds to a volume one.

Conclusions

The composition and chemical structure of $LaNiO_{3-x}$ films obtained by a reactive d.c. 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 were observed on cleaning film by Ar-ions 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.

References

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