VALENCE BAND STUDY OF $LaNiO_{3-\delta}$ THIN FILMS

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$LaNiO_3$ 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 the considerable surface segregation of elements may place in $LaNiO_{3-x}$ samples and is the tendency of rare earth and nickel oxides to absorb water vapor 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 [1-2]. Thus the knowledge of the surface composition is extremely important because it is directly related to the heterostructures properties.

The initially hydrated $LaNiO_{3-\delta}$ surface may be restored by heating above dehydration temperature. Nickel hydroxide, in turn, decomposes at $T > 230$°C (melting point). 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. The aim of this work is to investigate the valence band electronic structure and chemical composition of $LaNiO_{3-\delta}$ thin films after heating above dehydration temperature about 500°C.

Thin $LaNiO_{3-x}$ films onto monocrystallyne (100)-plane oriented $NdGaO_3$ substrate were deposited by using a reactive DC magnetron sputtering technique. 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 ~ 750ºC and the resultant thickness of $LaNiO_{3-x}$ film was about 0.1 μm.

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 metallic sample.

The giant resonance in La 5*p* and La 5*s* peaks intensity observed at excitation energy corresponding to a La[$4d \rightarrow 4f$] 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 an agreement with the model of an autoionization process after resonant excitation. The relatively week enhancement of the intensity of valence band maxima (at about 6 eV) may be explained by the small mixing of the La 5*d* ionic character to the O 2*p* valence band. No resonant features were observed in the VB spectra under Ni[$3p \rightarrow 3d$] excitation (escape depth $L \approx 2$ ML), indicating that nickel species are not presented at the $LaNiO_{3-\delta}$ film surface after heat treatment.

References

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