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Epitaxial Growth and Oxygen Nonstoichiometry of Magnetron–Sputtered Conductive $LANIO_{3-\Delta}$ Thin Films

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$LaNiO_{3-\delta}$ thin films (d = 0.1÷0.2 μm) were grown heteroepitaxially by dc magnetron sputtering onto lattice–matched $NdGaO_3$ substrates. Oxygen content in the films was varied in a wide range (δ = 0÷0.5) by annealing at T_{ann} = 700÷900 K either in vacuum or pure oxygen. Resistance versus temperature of the nonstoichiometric films was measured in a wide temperature range (300÷1000 K). The metal-insulator (M–I) transition has been indicated for the films with δ increasing. Presence of composition-dependent energy gap has been indicated for oxygen-deficient films with $\delta \geq 0.25$.

Keywords: $LaNiO_{3-\delta}$ thin films, magnetron sputtering, annealing.

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Introduction

Mixed valence lanthanum-nickel oxide, $LaNiO_3$, is known as a conductive binary oxide exhibiting metallic-like conductivity in a wide temperature range. Low resistivity values (down to about ~ 34 μΩcm [1]) and high carrier density (up to ~ 1.7×10^{22} cm^{-3} [2]) have been indicated for the compound at T = 300 K.

Crystalline structure of $LaNiO_3$ characterized by a perovskite-related pseudocubic cell (a = 3.84 Å [3]) is matching well to those of various oxide materials. Therefore oxygen–saturated highly conductive $LaNiO_3$ films are frequently used as electrodes in various device structures containing perovskite-like ferroelectric, ferromagnetic and high T_c superconducting layers although it is well known that oxygen nonstoichiometry induced by film annealing under reduced oxygen pressure may result an increase of film resistance by several orders of magnitude.

Electrical and magnetic properties of nonstoichiometric $LaNiO_{3-\delta}$ (LNO) thin films were investigated by a number of authors [1-4]. It was found that resistance versus temperature of the oxygen-deficient compound changes from metallic-like (δ < 0.25) to a semiconductor-like ($\delta \approx$ 0.25÷0.5). However, up to now attention was only paid to low temperature region ($T \leq$ 300 K). It was established that at low temperatures resistivity of the metallic phase increases exponentially with δ. The metal-dielectric transition observed at δ = 0.25 has been explained assuming redistribution of electrons in the energy bands and by a change of both Ni ion valency (from 3+ to 2+) and symmetry of the crystal.

I. Experimental

Thin LNO films were deposited by a reactive d.c. magnetron sputtering on monocrystalline NGO(100) substrates. The sputtering was performed in Ar and O_2 mixture (1:1) at pressure of about 10 Pa. To prevent film bombardment by high energy oxygen ions occurring during deposition, NGO substrates were positioned in the *off-axis* configuration at a distance of 25 mm from the symmetry axis of the discharge and 10 mm over the target plane. The substrate temperature was set at 650 °C. Thickness of the sputtered films varied from about 0.1 μm to 0.3 μm.

Microstructure of the layers was investigated by means of X-ray diffraction, reflection high-energy electron diffraction and atomic force microscopy (AFM). Thermal stability of LNO thin films were investigated *in-situ* by measuring $R(T)$ dependencies during film annealing under various oxygen pressure conditions.

II. Results and discussion

Fig. 1 shows typical RHEED patterns demonstrating epitaxial quality of the prepared films. Relatively smooth surface of the LNO/NGO films can be seen from AFM image displayed in Fig. 2.

Curve 1 in Fig. 3 shows resistance versus temperature of oxygen saturated $LaNiO_3$ film measured during film heating (dT/dt = 9 K/min) from room temperature up to T = 1000 K in vacuum with residual oxygen pressure $p(O_2) \sim 10^{-3}$ Pa. Following this figure we point out three different regions in the presented R-T

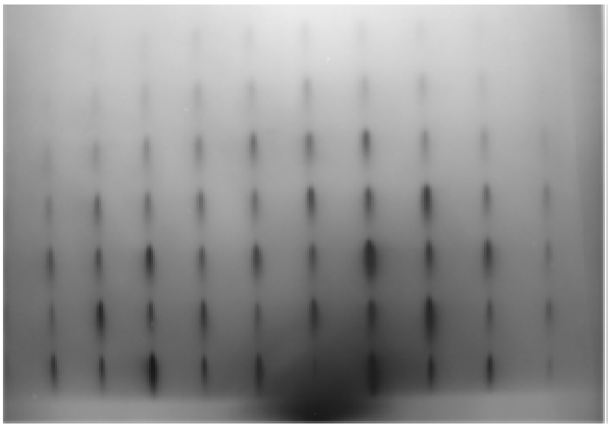

Fig.1. Typical RHEED pattern of epitaxial LNO thin film deposited at 650 °C

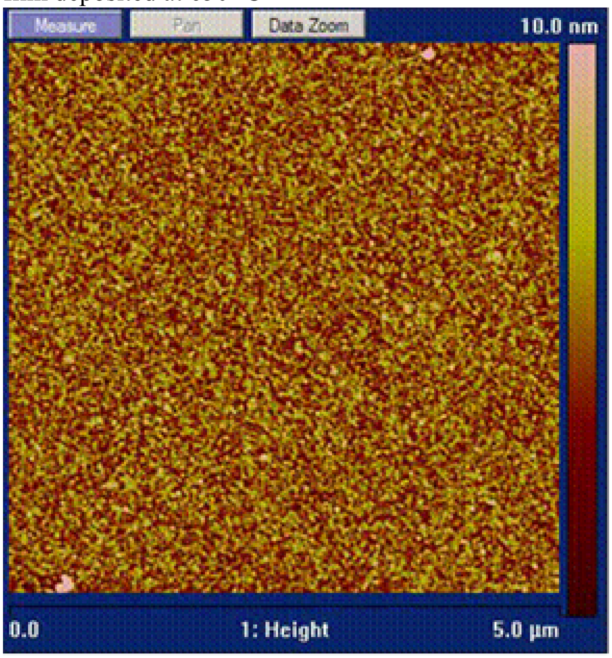

Fig.2. AFM images and surface roughness of LNO thin films on NGO substrate

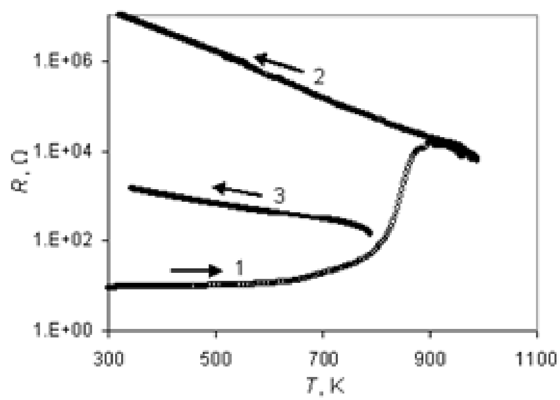

Fig.3. Resistance variation measured for $LaNiO_3$ film during heating with dT/dt = 9 K/min (1) and subsequent fast cooling in vacuum from T = 800 K (3) and 950 K (2)

curve. It can be seen from Fig. 3 that at low temperatures (up to T = 670 K), concentration of oxygen in the compound doesn't change with heating. Metallic-like conductivity observed in this case for the stoichiometric $LaNiO_3$ compound may be understood assuming presence of Fermi's level in a conduction band due to overlaping of O 2p6 and Ni 3d8 bands. Significant resistance increase at temperatures ranging from 670 to 870 K seen from the figure may be understood taking into account oxygen out-diffusion from the film to a gas ambient. Increase of R with film heating at these temperatures may be associated either to the localization of carriers, or appearance of gap between O 2p6 and Ni 3d8 bands at $\delta > 0.25$. At T = 870 K, symmetry of LNO cell changes, all Ni ions become bivalent, and resistance versus temperature of the films becomes semiconductor-like. Finally, with temperature increasing at T > 870 K, resistance of the film begins to decrease due to activation of carriers from the valence band to the conduction band. In this region the same R-T curve is reproduced either with increase or decrease of temperature. It means that all Ni ions should be bivalent (δ = 0.5) in this temperature region. The R-T curve in this region was found to follow the relationship: $(\rho/\rho_0) = \varepsilon_g/2kT$ with the band gap $\varepsilon_g \cong 1$ eV found as the best fitting parameter. This value is difficult to establish by applying direct optical methods as far as electronic transitions in Ni 3d9 band are overlapping with those related to La 5d band.

Curve 2 in the same figure was obtained for the same film with reduced oxygen content ($\delta \cong 0.5$) during film cooling from T = 950 K, while curve 3 corresponding to the same film with partially reduced oxygen content was measured during film cooling from T = 800 K.

The log$R$ = f(1/T) plots displayed for LNO films with various oxygen content (Fig.4) represent a set of lines demonstrating activation behaviour of electrical conductivity. The estimated activation energies of the material as a function of room temperature resistivity are shown in the inset to Fig.4. Thus, it leads from figure that both resistivity and activation energy of $LaNiO_{3-\delta}$ films ε_g (0÷1.0 eV) may be tuned in a wide range by changing oxygen content in the films.

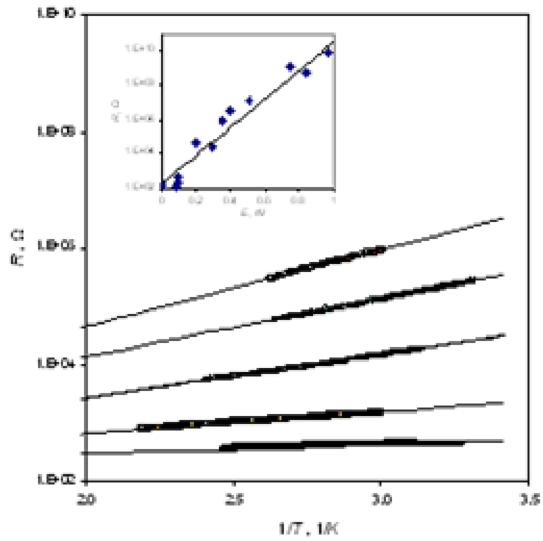

Fig.4. Electrical resistance versus $1/T$ of $LaNiO_{3-\delta}$ films with various oxygen contents measured during film cooling

Figure 5 depicts the R-T dependence of LNO film measured during annealing of $LaNiO_{3-\delta}$ films in an

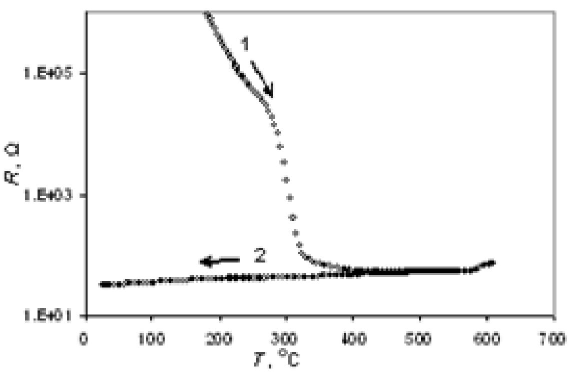

Fig.5. $R(T)$ dependencies of LNO films (d ≅ 0.1 μm) measured during heating (1) and following cooling (2) in pure oxygen ($p(O_2) = 5\times10^5$ Pa)

oxygen atmosphere (p $(O_2) = 1\times10^5$ Pa). Three different regions were found in this case in the R (T) dependencies, measured with temperature increasing. In the region of low temperatures, a comparatively slow decrease of resistance was observed. Similar $R(T)$ dependencies were measured either with temperature increasing up to 900 K or cooling down to 300 K. This means that the obtained $R(T)$ curves should be related to activation nature of conductivity rather than to a possible diffusion of oxygen in the film. Sharp resistance decrease occurring at $T \approx 600$ K is caused by penetration of oxygen into the film. In the region of higher temperatures the samples are saturated by oxygen and thus characteristic metallic-like conductivity is observed.

Conclusion

Electrical resistance of epitaxial $LaNiO_3$ films was measured in a wide temperature range (300÷1000 K) during their annealing in oxygen and vacuum. It was found from electrical measurements that both electrical resistance of the nonstoichiometric $LaNiO_{3-\delta}$ films and their activation energy (ε_g = 0÷1.0 eV) may be tuned by controlling oxygen out-diffusion from oxygen-saturated $LaNiO_3$ films with their annealing at T = 700÷900 K.

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Епітаксіальний ріст і нестехометрія за киснем тонких плівок магнетронно розпиленого провідного $LANIO_{3-\Delta}$

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Тонкі плівки $LaNiO_{3-\delta}$ (d = 0.1÷0.2 μm) Були вирощені гетероепітаксійним магнетронним розпиленням на підібрані підклідки субстраты $NdGaO_3$. Вміст кисню в плівках варіювався в широких межах (δ = 0÷0.5), відпалюючи при T_{ann} = 700÷900 K в вакуумі або чистому кисні. Стійкість протии температури нестехіометричних плівок булла виміряна в широкому діапазоні температур (300÷1000 K). Перехід метал-ізолятор (M–I) спостерігався в плівказ з збільшенням δ. Наявність композитно-залежного енергетичного кризесу було відзначене для бідних на кисень плівок з $\delta \geq 0.25$.