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SmNiO$_3$ layers epitaxially grown on (001) SrTiO$_3$ and LaAlO$_3$ substrates

Florine Conchon, Alexandre Boulle, René Guinebretière
SPCTS, CNRS-UMR 6638, Laboratoire Science des Procédés Céramiques et de Traitements
de Surfaces, ENSCI, 47 Avenue Albert Thomas, 87065 Limoges – France
Cécile Girardot, Stéphane Pignard, Jens Kreisel, François Weiss
LMGP, CNRS-UMR 5628, Laboratoire des Matériaux et du Génie Physique, INP Grenoble -
MINATEC - 3, parvis Louis Néel - BP 257, 38016 Grenoble – France
Schneider Electric, 160 rue des Martyrs - 38000 Grenoble - France
Eric Dooryhée, Jean-Louis Hodeau
IN, Institut Néel, CNRS-UPR 2940, 25 avenue des Martyrs BP 166– 38042 Grenoble –
France
ABSTRACT

This paper deals with the role of epitaxial strain on the structure and electronic transport properties of metastable SmNiO$_3$ layers grown by metal-organic chemical vapor deposition onto SrTiO$_3$ and LaAlO$_3$ substrates. The characterization of these layers is carried out by high-resolution X-ray diffraction and four-probes resistivity measurements. It is found that the SmNiO$_3$ phase is stabilized by in-plane compressive strain whereas in-plane tensile strain induces the creation of oxygen vacancies that induces an annihilation of the metal-insulator transition and a huge increase of the resistivity.
The stabilization in oxygen lattices of the highest oxidation states of transition metals is an important challenge for studying electronic phenomena in oxides such as low spin-high spin transition, metal-insulator (MI) transition or charge disproportionation. For instance, the +3 oxidation state of Ni was stabilized in the oxides RNiO₃ (R = rare-earth) with the perovskite type lattice using high temperatures and high oxygen pressures. Since rare-earth nickelates are among few perovskite oxides showing a very sharp MI transition much attention has been devoted to understand their physico-chemical properties. Nevertheless, the presence of the less stable +3 oxidation state of Ni implies the possibility of large oxygen deficiency for RNiO₃. Up to now, only few studies were devoted to analyze the effect of oxygen non-stoichiometry on the transport properties of RNiO₃ and all of them aimed to investigate bulk RNiO₃. In SmNiO₃₋δ and NdNiO₃₋δ ceramics it has been recently shown that the oxygen non-stoichiometry greatly influences transport properties. As a matter of fact, according to Nikulin et al., the sharpness of the MI transition strongly rises with the decrease of oxygen deficiency but without any change of the transition temperature. Besides, several authors made use of epitaxial strain in order to stabilize the RNiO₃ phase. Since future applications will extensively exploit thin films geometries the associated transport properties will strongly be determined by the strain misfit between the film and the substrate.

To date, the epitaxial stabilization mechanism of RNiO₃ phases and more particularly the stabilization of Ni³⁺ in RNiO₃ and the consequence on electronic properties remains unclear. In order to understand the role of epitaxial strain on this structural stabilization we deposited SmNiO₃ (SNO) layers epitaxially onto two single crystal substrates. On LaAlO₃ (LAO), the misfit (m) between the layer and the substrate is equal to m=-0.13%, the layer is subjected to in-plane compressive strain whereas on SrTiO₃ (STO), m=2.8%, the layer is subjected to in-plane tensile strain.
In the present study, we demonstrate the influence of a compressive and a tensile strain on the stabilization of the SNO phase and on the associated transport properties. As a matter of fact, we will prove that Ni$^{3+}$ is stabilized in the RNiO$_3$ structure by a compressive strain whereas the tensile strain induces the formation of oxygen vacancies in the structure and at the same time an annihilation of the MI transition of the SNO layer together with a huge increase of the resistivity. Moreover, in the case of the SNO layer deposited on STO we will show that the formation of oxygen vacancies acts as a strain relaxation mechanism as it increases the bulk (i.e. strain-free) lattice parameter of SNO.

SNO layers were grown by an injection metal-organic chemical vapor deposition (MO-CVD) process$^{12}$ on single crystal (001) LAO and STO substrates. We reported here the results obtained for two layers of the same thickness (17 nm), one is deposited on STO (sample 1) and the other on LAO (sample 2). For these two layers, the epitaxial relationships can be written as:

(001)STO//(001)SNO and [100]STO//[100]SNO for sample 1

(001)LAO//(001)SNO and [100]LAO//[100]SNO for sample 2 (schematic drawings of the heterostructures are given in figure 1).

Four probes resistivity measurements were carried out, in the temperature range 30°C-400°C, on a home made set up allowing the control of atmosphere. Finally, the layers were characterized by high resolution X-ray diffraction (HRXRD). A laboratory diffractometer ($\lambda_{CuK\alpha1} = 1.5406$ Å) was used to record asymmetrical (-103) reciprocal space maps (RSMs)$^{13}$ in the ($Q_x$, $Q_z$) plane, where $Q_x$ and $Q_z$ are the components of the scattering vector $Q$ ($Q = 4\pi \sin \theta / \lambda$) in the film plane and perpendicular to it, respectively. High resolution (002) $Q_z$ scans were carried out at the ESRF (Grenoble, France) on the BM2 beam-line$^{14}$. A single Si(111) crystal is used as an analyzing crystal. The wavelength was set to $\lambda = 0.613$ Å. (-103) RSMs and (002) $Q_z$ scans allowed us to derive the lattice parameters of the layers.
We report figure 1 the resistivity measurements as a function of temperature under oxygen for sample 1 and 2. It is obvious from figure 1 that the SNO layer deposited on LAO exhibits a sharp MI transition whereas the SNO layer deposited on STO exhibits only a smooth decrease of the resistivity. Furthermore, it can be seen that the resistivity is much higher in the latter case. These measurements simply indicates that the change of substrate and hence of misfit sign strongly affects the resistivity behavior of the SNO layers. We propose to explain this unexpected result with the help of epitaxial strain investigations. In this aim, we evaluated the lattice parameters of both layers using HRXRD. For sample 1, we recorded the (-103) RSM (figure 2a). From the relative position of the SNO (-103) RLP with respect to the position of the STO (-103) RLP, we calculated $a_{//}$ and $a_{\perp}$ respectively the pseudo-cubic in-plane and out-of-plane lattice parameters of the strained layer. We obtained $a_{//} = 3.903 \, \text{Å}$ and $a_{\perp} = 3.845 \, \text{Å}$ which correspond to averaged values for several (-103) and (002) RSMs (the uncertainty is $\sim10^{-4} \, \text{Å}$). $a_{//}$ being almost equal to the lattice parameter of STO (3.905 Å), we can conclude that the layer is strongly strained in the interface plane. For $a_{\perp}$, contrarily to what is expected the calculated value is much higher than the theoretical value of the bulk (i.e. strain-free) SNO pseudo-cubic lattice parameter ($a_{\text{thSNO}} = 3.795 \, \text{Å}$). The lattice spacing of STO being larger than the theoretical lattice parameter of SNO, the layer is subjected to in-plane tensile strain which should give rise to an out-of-plane contraction. The measurement of $a_{\perp}$ led us conclude that the actual lattice parameter of bulk SNO, $a_{\text{SNO}}$, must be higher than its commonly assumed value $a_{\text{thSNO}}$. To confirm this statement we calculated the actual lattice parameter as well as the strain relaxation of the SNO layer $^{15}$. For the relaxation rate we obtained $R = 3.8\%$ and for the bulk lattice parameter $a_{\text{SNO}} = 3.868 \, \text{Å}$. These results confirm on one hand that the layer is highly strained by the STO substrate and on the other hand that the actual lattice parameter of SNO is higher than its commonly assumed value. This latter effect has already been encountered and explained in bulk RNiO$_3$.
compounds (R = Sm and Nd)\textsuperscript{7,8} and results from the formation of oxygen vacancies during the deposition process. Nikulin\textsuperscript{7} demonstrates that in RNiO$_{3-\delta}$ compounds, the volume of the unit cell increases as $\delta$ increases. Indeed, the creation of oxygen vacancies comes from the reduction of a certain proportion of unstable Ni$^{3+}$ to Ni$^{2+}$, this latter having a larger ionic radius, the lattice parameters increase. It is then obvious from the calculation of $a_{\text{SNO}}$ of sample 1 that the SNO layer contains oxygen vacancies. While generally film materials adjust its lattice parameters to the substrate only by stretching or compressing its bond lengths, thereby paying a high energy penalty, RNiO$_3$ films may also use the creation of oxygen vacancies for strain accommodation. Here, the actual misfit between SNO and STO is reduced to 0.9\% instead of 2.8\%.

Due the well-known twinned structure of the LAO crystal\textsuperscript{16} a splitting of the reciprocal lattice points (RLPs) of LAO occurs that prevents us from using the asymmetrical RSMs to extract the lattice parameters of SNO. For sample 2, we derived $a_\perp$ from the (002) Qz scan (figure 2b), we obtained $a_\perp = 3.849$ Å. On LAO, the SNO layer is subjected to in-plane compressive strain, hence this gives rise to an out-of-plane expansion. The measured value of $a_\perp$ being much higher than the bulk SNO lattice parameter, this proves that the SNO layer is highly strained on LAO.

As the SNO layer is deposited on STO, the tensile strain within the interface plane appearing during growth induces an expansion of the NiO$_6$ octahedra. Due the small size of the Ni$^{3+}$ ions located at the center, such an expansion would be an unstable state for the octahedra\textsuperscript{17}. Similarly to what occurs in CaRuO$_3$ compounds\textsuperscript{17}, we propose that the tensile strain leads to the change in oxidation state of the nickel from Ni$^{3+}$ to Ni$^{2+}$ involving an out-of-plane expansion instead of the expected contraction. This phenomenon is accompanied by the formation of oxygen vacancies (for charge conservation). In turn, the lattice parameters of LAO being smaller than those of bulk SNO, the SNO layer is subjected to in-plane
compressive strain that stabilizes the 3+ oxidation state of the nickel by reducing the octahedral cavity. In this case, the in-plane strain avoids the formation of oxygen vacancies.

The structural difference between SNO/STO and SNO/LAO evidenced above directly affects the transport properties as it is shown figure 1. For NdNiO$_{3-\delta}$, Tiwari$^8$ highlights that the increase in oxygen vacancies increases the overall resistivity and induces a “flattening” of the resistivity curve, i.e., the transition becomes less sharp. This phenomenon appears also figure 1 where the in-plane tensile strain of sample 1 induces an increase of the overall resistivity of sample 1 which is two order of magnitude higher than for sample 2. Furthermore, whereas the MI transition is sharp as SNO is deposited on LAO, this MI transition is annihilated as SNO is deposited on STO.

In summary, we explain the role of epitaxial strain on the stabilization of SmNiO$_3$ layers grown on SrTiO$_3$ and LaAlO$_3$ substrates. We prove that an in-plane compressive strain stabilizes the 3+ oxidation state of the nickel in the SmNiO$_3$ phase whereas an in-plane tensile strain induces a change in oxidation state of the nickel from Ni$^{3+}$ to Ni$^{2+}$ that leads to the formation of oxygen vacancies. Finally, the formation of oxygen vacancies produces a flattening of the MI transition which disappears as SNO is deposited on STO and a strong increase of the resistivity.

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REFERENCES

FIGURE CAPTION

FIG. 1. Resistivity vs. temperature curves for the SNO layer grown on STO (filled circles) and on LAO (open circles) with corresponding schemes of the structures, the black arrows indicate the sign of the in-plane strain.

FIG. 2. (-103) RSM of sample 1 (a) and (002) Qz scan of the SNO layer of sample 2 (b).