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Improved conductivity of infinite-layer $LaNiO_2$ thin films by metal organic decomposition

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ABSTRACT

Infinite-layer $LaNiO_2$ thin films were synthesized by metal organic decomposition and subsequent topotactic reduction in hydrogen, and their transport properties were investigated. $LaNiO_2$ is isostructural to $SrCuO_2$, the parent compound of high-T_c $Sr_{0.9}La_{0.1}CuO_2$ with T_c = 44 K, and has $3d^9$ configuration, which is very rare in oxides but common to high-T_c copper oxides. The bulk synthesis of $LaNiO_2$ is not easy, but we demonstrate in this article that the thin-film synthesis of $LaNiO_2$ is rather easy, thanks to a large-surface-to-volume ratio, which makes oxygen diffusion prompt. Our refined synthesis conditions produced highly conducting films of $LaNiO_2$. The resistivity of the best film is as low as 640 μΩ cm at 295 K and decreases with temperature down to 230 K but it shows a gradual upturn at lower temperatures.

1. Introduction

More than 25 years have passed since the discovery of high-T_c superconductivity in cuprates. However, this fascinating phenomenon remains confined only to cuprates, and has not spread even to neighboring nickelates. The common features shared by all high-T_c cuprates are: (1) two-dimensional CuO_2 planes in crystal structure and (2) $3d^9$ configuration in electronic structure. The former can be found in other "layered" perovskite oxides whereas the latter is practically nonexistent in ionic solids except for divalent Cu^{2+}. Ni^{1+} compounds might be another possibility, but this valence state of nickel has scarcely been observed in mineral compounds. In 1983, the synthesis of $LaNiO_2$ with formally monovalent Ni^{1+} ions was reported by Crespin et al. [1,2]. After the discovery of high-T_c cuprates, $LaNiO_2$ was revisited because it has not only $3d^9$ configuration but also the so-called infinite-layer structure, isostructural to $SrCuO_2$, the parent compound of superconducting $Sr_{0.9}La_{0.1}CuO_2$ with T_c = 44 K. According to the original report by Crespin et al., $LaNiO_2$ can be synthesized by topotactic reduction of perovskite $LaNiO_3$ with hydrogen at low temperatures (~300 °C). Topotactic reduction of complex metal oxides allows low temperature transformation to structures in which ordered arrays of anion vacancies can enforce metal coordination environments and oxidation states inaccessible to a conventional high temperature route. The synthesis by Crespin et al., however, required complicated and delicate steps in a hydrogen recirculating system. In fact, several unsuccessful attempts to reproduce the experiments of Crespin et al. have blown some doubt on the existence of the $LaNiO_2$ phase. Later, in 1999, Hayward et al. succeeded in transforming $LaNiO_3$ to $LaNiO_2$ employing NaH [3], one of the most powerful reducing agents known. The use of NaH allows one to isolate the $LaNiO_2$ phase at lower reduction temperatures (~200 °C) than the use of H_2. Recently we have shown that thin films of $LaNiO_3$ can be topotactic-transformed to $LaNiO_2$ by simple hydrogen reduction owing to the large surface-to-volume ratio [4].

In this article, we report the synthesis and characterization of $LaNiO_2$ thin films. We have optimized the synthesis conditions such as substrate choice, firing and reducing conditions. Our refined synthesis conditions produced highly conducting films of $LaNiO_2$.

2. Experimental

Infinite-layer $LaNiO_2$ thin films were prepared by hydrogen reduction of perovskite $LaNiO_3$ thin films. The starting $LaNiO_3$ films were prepared by metal organic decomposition (MOD) using La and Ni 2-ethylhexanoate solutions. The stoichiometric mixture of 2-ethylhexanoate solutions was spin-coated on various substrates listed in Table 1. The lattice constant (a_s) of substrates ranges from 3.68 Å to 3.95 Å. The substrate influences the crystallinity of starting $LaNiO_3$ films and the preferred orientation of resultant $LaNiO_2$. The films were first calcined at 400 °C in air to obtain precursors, and then fired at 850 °C in a tubular furnace under oxygen

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Table 1
In-plane lattice constant (a_s) for the substrates used in this work. The in-plane lattice constants (a_0) for $LaNiO_3$ [5,6] and $LaNiO_2$ [3] are also included. The a_s for the substrates with the $GdFeO_3$ structure is for the pseudo-perovskite (001) face. Rhombohedral $LaAlO_3$ and $LaNiO_3$ are also indexed as pseudo-cubic systems.

Substrate	Abbreviation	Structure	a_s or a_0 (Å)
$DyScO_3$ (110)	DSO	$GdFeO_3$	3.944
$SrTiO_3$ (001)	STO	perovskite	3.905
$NdGaO_3$ (110)	NGO	$GdFeO_3$	3.858
$LaAlO_3$ (001)	LAO	rhombohedral	3.790
$LaSrAlO_4$ (001)	LSAO	K_2NiF_4	3.756
$YAlO_3$ (110)	YAO	$GdFeO_3$	3.715
$NdCaAlO_4$ (001)	NCAO	K_2NiF_4	3.688
$LaNiO_3$		rhombohedral	3.830
$LaNiO_2$		infinite-layer	3.959

(p_{O2} = 1 atm) and furnace-cooled in pure oxygen down to 300 °C for t_{cool} = 1–20 h. Finally the films were given topotactic reduction in pure hydrogen (p_{H2} = 1 atm). The process parameters in reduction are reduction temperatures (T_{red}) and reduction time (t_{red}). Typically we varied T_{red} from 350 °C to 450 °C and t_{red} from 10 min to 90 min. After reduction, the films were furnace-cooled under hydrogen. The film thickness was typically 800 Å although it may vary film by film to some extent. Films with no reduction are referred to "as-grown" in this article. The crystal structure and lattice parameters of the films were determined by a standard $2\theta/\omega$ X-ray diffractometer (XRD) (Rigaku, Smart Lab). The resistivity and Hall coefficients were measured by the standard four- and six-probe methods.

3. Results and discussion

3.1. Synthesis of $LaNiO_3$ films on various substrates

Highly crystalline starting $LaNiO_3$ films are prerequisite to obtain reproducible results in the subsequent hydrogen reduction process. Therefore in this subsection we describe the growth optimization of $LaNiO_3$ films. We prepared $LaNiO_3$ films on various substrates listed in Table 1. The XRD patterns showed that all the observed peaks between 2θ = 5° and 85° can be indexed as the (00l) reflections of the perovskite structure, indicating that single-crystalline films are grown by solid-state epitaxy. Fig. 1(a) shows the XRD patterns around the (002) reflection of films on (110)$DyScO_3$ (DSO), (001)$SrTiO_3$ (STO), (110)$NdGaO_3$ (NGO), and (001)$LaAlO_3$ (LAO). In this figure, one can see a noticeable change not only in the peak intensity but also in the peak position. Fig. 1(b) is a plot of the (002) peak intensity against the substrate a_s. The peak intensity is stronger for the films on substrates better lattice-matched with $LaNiO_3$ (3.830 Å) [5,6] and the strongest on NGO (3.858 Å), the best lattice-matched substrate in Table 1. Fig. 1(c) is a plot of the (out-of-plane) lattice constant (c_0) of the film evaluated from the XRD peak positions against the substrate a_s. The film on LAO has the longest c_0 and the film on STO has the shortest c_0. The substrate dependence of the film's c_0 appears to arise from epitaxial strain and the Poisson effect. The film on LAO has in-plane compressive and concomitant out-of-plane tensile strain whereas the film on STO has in-plane tensile and out-of-plane compressive strain.

Fig. 2 is the corresponding resistivity data of the films presented in Fig. 1. Fig. 2(a) shows the temperature dependence of resistiviy (ρ–T), and Fig. 2(b) is a summary of the substrate dependence: ρ(295 K) and the residual resistivity ratio RRR = ρ(295 K)/ρ(4.2 K) plotted as a function of the substrate a_s. There is a clear correlation between the crystallinity and transport properties, namely films with higher crystallinity have lower ρ(295 K) and higher RRR. The films on lattice matched LAO and NGO have ρ(295 K) ~ 140–

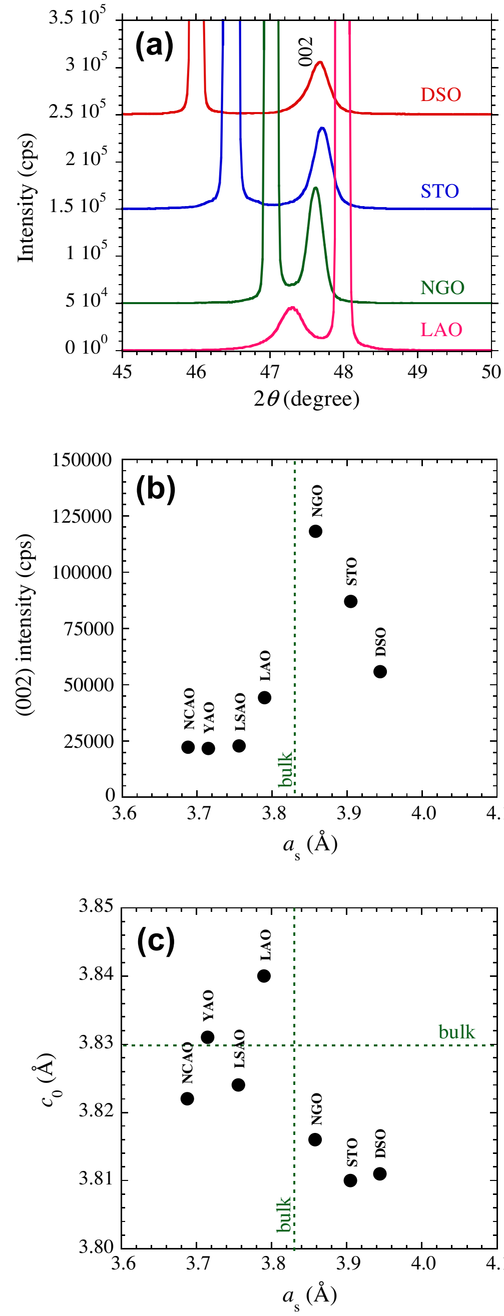

Fig. 1. XRD data for starting $LaNiO_3$ films on various substrates. (a) XRD patterns around the (002) reflections of $LaNiO_3$ films on DSO, STO, NGO, and LAO. The (002) peak intensity and c_0 are plotted as a function of a_s in (b) and (c). In order to see the lattice matching of each substrate with $LaNiO_3$, the pseudo-cubic lattice constant reported for $LaNiO_3$ bulk samples is indicated by the broken line in (b) and (c).

180 μΩ cm and RRR > 10. These values are comparable to the best values reported for bulk samples [7]. Both of the XRD and transport data indicate that high-quality epitaxial films of $LaNiO_3$ can be obtained by MOD, using lattice-matched substrates such as LAO, NGO, STO. Therefore subsequent topotactic reduction experiments were performed mainly for films on these substrates.

3.2. Topotactic reduction

Next the experimental results of hydrogen reduction are presented. Fig. 3(a) shows the evolution of the XRD patterns of films on NGO with increasing T_{red} from 370 °C to 450 °C. In this