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Synthesis of infinite-layer $LaNiO_2$ films by metal organic decomposition

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ABSTRACT

We report the synthesis of infinite-layer $LaNiO_2$ thin films by metal organic decomposition. Our work is aimed to synthesize perovskite-like oxides with $3d^9$ electronic configuration, which high-T_c copper oxides commonly take. The $3d^9$ configuration is very rare in oxides other than cuprates. Ni^{1+} oxides, even though Ni^{1+} is an unusual oxidation state, may be one of very few candidates. One example is infinite-layer $LaNiO_2$. The bulk synthesis of $LaNiO_2$ is difficult, but we demonstrate in this article that the thin-film synthesis of $LaNiO_2$ by metal organic decomposition is rather easy. This is due to the advantage of thin films with a large-surface-to-volume ratio, which makes oxygen diffusion prompt. Although superconductivity has not been observed yet, resistivity measurements indicate that $LaNiO_2$ is conductive.

1. Introduction

More than two decades have passed since the discovery of high-temperature superconductivity in cuprates, and many (more than 100) superconducting cuprates have been synthesized. However, this fascinating phenomenon remains confined only to cuprates, and has not been extended even to neighboring nickelates. At the extreme forefront of research in superconductivity is to explore the possibility of high-temperature superconductivity in non-copper oxides, which will also be quite important for understanding the superconducting mechanism yet unexplained. The common features shared by all high-T_c cuprates are: (1) two-dimensional CuO_2 planes in crystal structure and (2) $3d^{9\pm\delta}$ configuration in electronic structure. The former feature can be found in other "layered" perovskite (K_2NiF_4 structure, etc.) oxides whereas the latter is very rare in ionic solids except for divalent Cu^{2+}. The formal similarity between Ni^{1+} and Cu^{2+} seems to suggest that Ni^{1+} compounds might be one possibility. Ni^{1+} is an unusual oxidation state, but Crespin et al. reported the monovalent nickel oxide, $LaNiO_2$, in 1983 [1,2]. $LaNiO_2$ 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. Hence this compound might provide a platform for possible high-temperature superconductivity. According to the original report by Crespin et al., $LaNiO_2$ can be synthesized by a special synthetic route, namely a topotactic reduction with H_2 of perovskite $LaNiO_3$ at low temperatures (250–450 °C). The synthesis by Crespin et al., however, involves complicated steps in a hydrogen recirculating system. In fact, several unsuccessful attempts by other researchers to reproduce their experiments cast some doubt on the existence of the $LaNiO_2$ phase [3]. Later, in 1999, Hayward et al. succeeded in reducing $LaNiO_3$ into $LaNiO_2$ with NaH, the most powerful reducing agent, at lower reduction temperatures (~200 °C) to avoid the decomposition [4]. Their experiments revealed that the Ni^{1+} (d^9) two-dimensional sheets behave quite differently from their isoelectronic Cu^{2+} counterparts, and show no antiferromagnetic long range order. They suggested that this difference may be due to reduced covalent mixing of Ni3*d* and O2*p* orbitals.

$LaNiO_2$ is an interesting compound and may shed some light on the superconducting mechanism of high-T_c cuprates. However, its synthesis is not as easy as the synthesis of cuprates, and only powder samples are available so far, which prevents detailed measurements of physical properties. In this article, we report the synthesis of epitaxial $LaNiO_2$ thin films by metal organic decomposition (MOD) and subsequent hydrogen reduction. Our synthesis process is much easier than those employed by Crespin et al. and Hayward et al. This is because of the advantage of thin films with a large-surface-to-volume ratio, which makes oxygen diffusion prompt. Furthermore resistivity measurements were performed on $LaNiO_2$ for the first time, which indicated that $LaNiO_2$ is conductive although superconductivity has not been observed yet.

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2. Experimental

We have attempted both vacuum and hydrogen reduction of perovskite $LaNiO_3$ films toward the synthesis of infinite-layer $LaNiO_2$. The starting materials, $LaNiO_3$ films, were prepared by MOD, using La and nickel 2-ethylhexanoate solutions. The stoichiometric mixture of solutions was spin-coated on various substrates, including $SrTiO_3$(1 0 0), $LaAlO_3$(1 0 0), $DyScO_3$(1 1 0), and $YAlO_3$(1 1 0) (abbreviated below as STO, LAO, DSO, and YAO, respectively) [5]. Table 1 summarizes the lattice constants of $LaNiO_3$, $LaNiO_2$, and those substrates. The coated films were first calcined at 450 °C in air for 10 min to obtain precursors, then fired at 900 °C for 3 h in a tubular furnace under pure O_2 ($P(O_2) = 1$ atm). One cycle of spin-coating and calcination gives a film with thickness of ~800 Å after firing. Thicker films were produced by repeating the cycle before final firing. After firing, the films were furnace-cooled in oxygen, and underwent a subsequent reduction process in another tubular furnace. The reduction was made either in vacuum (<10^{-4} torr) or in pure hydrogen ($p(H_2) = 1$ atm) with the reduction temperature (T_{red}) and reduction period (t_{red}) varied. After reduction, the films were furnace-cooled in the same atmosphere as during reduction. The crystal structure of the films was determined by $\theta-2\theta$ scans using a powder X-ray diffractometer, and resistivity was measured by a 4-probe method.

3. Results and discussion

3.1. Properties of $LaNiO_3$ films grown by MOD

Fig. 1a shows the XRD patterns around the (2 0 0) reflection of the starting $LaNiO_3$ films on different substrates. All the observed peaks between $2\theta = 5°$ and 90° can be indexed as the (h 0 0) reflection lines of the perovskite structure, indicating single-crystalline films achieved by solid-state epitaxy. With regard to the substrate dependence, we have observed a noticeable change in the peak positions on different substrates, and also found that the peak intensities of the films are the strongest with best lattice-matched LAO (see Table 1). A similar trend is also observed in the resistivity. Fig. 1b shows the temperature dependence of resistivity ($\rho(T)$) for $LaNiO_3$ films on different substrates. The resistivity is the lowest on LAO and the highest on DSO. The resistivity value of $LaNiO_3$ films on LAO is ~100 μΩ cm at 300 K and ~10 μΩ cm at 4.2 K, which is comparable to the best value reported for bulk samples [6]. Both of the XRD and resistivity data indicated that high-quality epitaxial thin films of $LaNiO_3$ can be obtained by MOD, especially with LAO substrates. Therefore we performed subsequent reduction experiments mostly for films on LAO.

3.2. Vacuum reduction

We first attempted vacuum reduction. Fig. 2 shows the XRD patterns of the films after vacuum reduction at $T_{red} = 400$ °C with different t_{red} from 13 to 56 h. The film thickness before reduction was ~800 Å. With $t_{red} = 13$ h, the $LaNiO_3$ peaks shift to lower angles, then with $t_{red} = 26$ h, the original peaks of $LaNiO_3$ disappear (may be buried under the substrate peaks) and new peaks appear at $2\theta = 11.6°$ and 35.3°, which arise from double-perovskite $La_2Ni_2O_5$. This suggests that oxygen is gradually removed from the perovskite structure, resulting initially in the formation of oxygen-deficient $LaNiO_{3-\delta}$ with no oxygen order, and then in the formation of $La_2Ni_2O_5$ with the double-perovskite structure. In $La_2Ni_2O_5$, the chains of NiO_6 octahedra lying along the c axis and

Table 1
Lattice constants of $LaNiO_3$, $LaNiO_2$, and substrates used. The lattice constants of $DyScO_3$, $LaAlO_3$, and $YAlO_3$, which have distorted perovskite structures, are given by regarding these substrates as the pseudo-cubic structure.

	Lattice constant (Å)
$LaNiO_3$	3.817
$LaNiO_2$	$a = 3.959$, $c = 3.375$
$DyScO_3$	3.944
$SrTiO_3$	3.905
$LaAlO_3$	3.790
$YAlO_3$	3.715

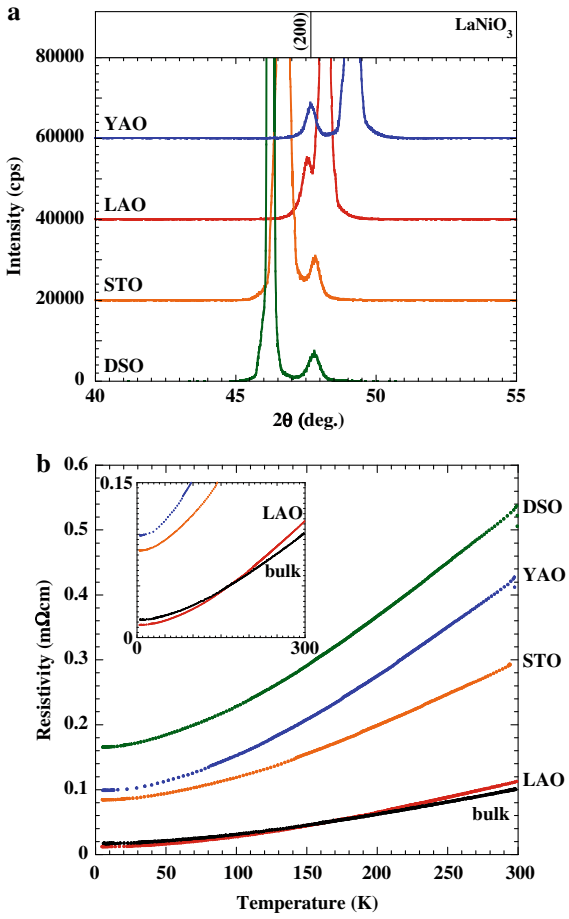

Fig. 1. (a) XRD patterns and (b) $\rho(T)$ curves of $LaNiO_3$ films prepared by metal organic decomposition on different substrates. The inset in (b) is an enlarged view to compare the $\rho(T)$ curves of a best bulk specimen [6] and our MOD film on LAO.

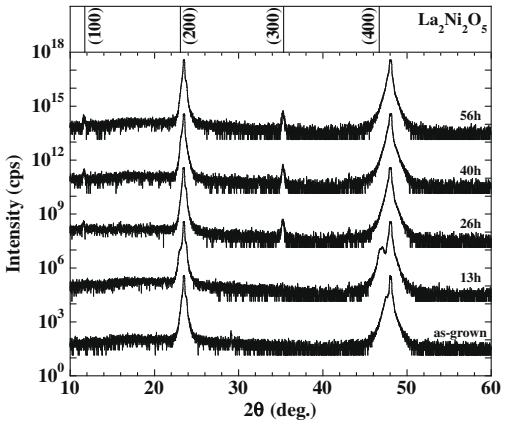

Fig. 2. XRD patterns of the films after vacuum reduction at $T_{red} = 400$ °C with different reduction periods (t_{red}) from 13 to 56 h.