Microscopic Observation of Degradation of LaNiO_3 Ultrathin Films Caused by Air Exposure*

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Sample degradation of LaNiO_3 ultrathin films on SrTiO_3 (001) substrate caused by air exposure is examined by means of crystal truncation rod (CTR) scattering method. Although the film is conductive right after the sample deposition, long term storage makes it insulating. CTR measurements were performed on three- and four-unit cell-thick samples just after the sample deposition and after six months of storage in air. The results show that the storage induced a significant increase in the lattice spacing along the surface normal direction with keeping in-plane periodicity. Such a structural change can be caused by escaping oxygen atoms by the thermal fluctuation. [DOI: 10.1380/ejsnt.2016.14]

Keywords: X-ray scattering, diffraction, and reflection; Oxidation; Nickel oxides; Heterojunctions

I. INTRODUCTION

Transition metal oxides show various properties such as ferroelectricity, superconductivity, colossal magnetoresistance, metal-insulator transition, and so on. One of the typical structures of transition metal oxides is perovskite structure. The lattice parameter of perovskite oxides is similar to each other. As a result, various combination of epitaxial interface, such as ferromagnet/superconductor interface [1], can be fabricated to explore new functionality. The most famous example is the interface between two band insulators, $\text{LaAlO}_3/\text{SrTiO}_3$ interface. It exhibits anomalous conductivity [2], ferromagnetism [3], and superconductivity [4]. SrVO_3 film is presented to show quantum well states [5]. Epitaxial LaNiO_3 films are one of the well studied interfaces. Since bulk LaNiO_3 is a simple paramagnetic metal, films have been studied to control the band structure by using the epitaxial strain [6–8]. Interestingly, LaNiO_3 film with tensile strain is expected to have electronic structure similar to high- T_C cuprates [9].

One of the significant differences between bulk materials and thin films is the stability. Usually, metal oxide single crystals are extremely stable, whereas those in the thin film form are sometimes easy to change. In most cases, experimental studies on films are made on fresh samples, and the time evolution is just labeled “degradation” without clarifying the origin of the change. How-

ever, the knowledge of the degradation is required to control it.

As-grown LaNiO_3 films on SrTiO_3 (001) surface are metallic when they are thicker than 4 unit cells thick. However, after keeping them for several months, they turn into insulating. In this work, we have examined a structural change in LaNiO_3 thin films caused by long-term exposure to air by means of the x-ray crystal truncation rod (CTR) scattering method. The CTR scattering method is a non-contact, non-destructive method that allows us to detect atomic positions around the surface and interface [10, 11]. As a result, we found significant expansion of the interplanar spacing perpendicular to the surface, which indicates the change in the degree of oxidation of Ni ions.

II. EXPERIMENTAL

The CTR scattering measurements were performed at the SPring-8, BL15XU and the Photon Factory, BL-3A. The energy of the X-ray used was 12.4 keV. Typical beam size is 0.5 mm $\times$ 0.5 mm. During the measurements, the samples were kept in 1 atm He gas or in 10^{-5} torr vacuum chamber.

The three- and four- unit cell thick LaNiO_3 thin films (we call them 3 u.c. and 4 u.c. samples, respectively) were grown on the atomically flat (001) surface of Nb-doped SrTiO_3 by means of a pulsed laser deposition method. During deposition, the substrate temperature was maintained at 450°C under an oxygen pressure of 10^{-3} Torr. The film thickness was precisely controlled on the atomic scale by monitoring the intensity oscillation of reflection high-energy electron diffraction. The films were subsequently annealed at 400°C for 45 min under an atmospheric pressure of oxygen to fill residual oxygen vacancies. Each sample was measured twice; just after the sample growth, and after 6 months of storing in air. We call

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FIG. 1. CTR profiles of a 3 u.c. sample for 0 m.o. and 6 m.o. measurements. Closed and open symbols show the results of 0 m.o. and 6 m.o. measurements, respectively. The relative scale among the rods are shifted for presentation.

the measurements 0 months old (m.o.) measurement and 6 m.o. measurement, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the CTR profile along (00ζ) , (01ζ) and (02ζ) -rods of the 3 u.c. sample. Closed symbols show the results of the 0 m.o. measurement. Apart from the Bragg peaks, observed strong oscillation in the intensity profile is a hallmark of the homogeneous film thickness over all illuminated area. While the area depends on the diffractometer angle, the typical dimension of the illuminated area is $\sim 0.5 \text{ mm} \times 2.0 \text{ mm}$. The open symbols show the results of the 6 m.o. measurement. It is clear that the CTR profile, and therefore the film structure, of the 3 u.c. film is changed during the storage in air for 6 months. The CTR profiles of 6 m.o. measurement show less-significant oscillations, which means the thickness of the “film” is non-uniform. Here, the term “film” means significantly different scattering object than the substrate. The lattice spacing, or d -value, can be derived from the Bragg angle. In case of ultrathin films, however, the Bragg angle is ill-defined because of the interference between the scattering amplitude from the film and the CTR from the substrate as well as the broad peak width of the film. In the present case, the intensity around the substrate 001 Bragg peak is examined. The 6 m.o. profile shows a hump in the lower scattering angle side, while the broad maximum in the 0 m.o. profile is on the higher angle side of the substrate 001 Bragg peak. This means that the 6 m.o. sample has a longer d -value than substrate, whereas the 0 m.o. sample has a shorter d -value than substrate.

Among various $(hk\zeta)$ rods, (00ζ) -rod (specular rod) has unique information. The structure without the periodicity of the in-plane lattice parameter can be seen only in the specular rod, whereas other rods reflect only the structure having the periodicity of the in-plane lattice parameter. In other words, off-specular rods reflect the film

FIG. 2. Calculated CTR profiles along the (00ζ) -rod for the 3 u.c. sample. The black curve shows the result of the fit to the 0 m.o. profile presented in Fig. 1. The red curve shows the calculated profile for a modulated structure. The modulation assumed here is 4% of expansion and $6\text{\AA}^2$ of atomic displacement parameter of the entire film in addition to 20% and 50% of reduction of apical and in-plane oxygen sites.

FIG. 3. CTR profiles of a 4 u.c. sample for 0 m.o. and 6 m.o. measurements. Closed and open symbols show the results of 0 m.o. and 6 m.o. measurements, respectively. The relative scale among the rods are shifted for presentation.

structure having the same in-plane periodicity with the substrate. The results of both 0 m.o. and 6 m.o. measurements show that the 3 u.c. sample has the same in-plane periodicity with the substrate.

In order to clarify the structure change caused by the storage, quantitative analysis was made. At first, structure model of the 0 m.o. sample was constructed by means of the least-squares method. The resulting (00ζ) profile is presented in Fig. 2 with the black curve. For the 6 m.o. sample, one cannot perform simple least-squares analysis because of the non-uniformity. Here, we performed a model calculation for a modulated structure. We assumed (1) 4% of expansion, (2) $6\text{\AA}^2$ of atomic displacement parameter, and (3) 20% and 50% of reduction of apical and in-plane oxygen sites of the entire film. The result qualitatively reproduces the experimental result of 6 m.o. sample presented in Fig. 1. Note that each one of the modulation is insufficient to reproduce the experimental results; The combination of them is needed. Therefore, we con-

cluded that the microscopic structure of degraded sample has longer inter-plane distance, large positional fluctuation and oxygen deficiency in the LaNiO_3 region.

Figure 3 shows the results for 4 u.c. sample. It also shows the time evolution very similar to the 3 u.c. sample. Both the 3 u.c. and 4 u.c. samples increase their d -value perpendicular to the surface by exposure to the air.

LaNiO_3 thin films on SrTiO_3 substrate elongate their d -value with losing some oxygen ions during the storage. While the structural change is limited to a few unit cells thick, entire LaNiO_3 film is affected. The time constant is slower than a week, and faster than a year. Such time scale is usually seen in the phenomena involving atomic diffusion. In this case, the time constant relates with the escape of oxygen ions from the film due to the thermal fluctuation. In $\text{LaNiO}_{3-\delta}$, the valence of the Ni ion is $3 - 2\delta$. The charge neutrality is kept by the flexibility of the Ni valence. The oxygen deficiency makes a cation face another cation, which results in a large repulsive interaction. This is the origin of the large lattice expansion. The

oxygen deficiency causes strong disorder in the film, which can be the cause of the loss of the conductivity by the sample degradation. Since the in-plane periodicity survives, fresh state is expected to recover by annealing the film in oxygen. Theoretical calculation of the oxygen binding energy in the film would help to understand the stability of the Ni oxide film samples on various substrates.

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