Growth Temperature Dependence of the LaAlO$_3$/SrTiO$_3$ Interfacial Structure

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Abstract. The growth temperature dependence of the interfacial structure of LaAlO$_3$ thin films on SrTiO$_3$ substrates is clearly observed by means of surface x-ray diffraction, combined with a holographic analysis. Although the interfacial structure that is tuned by the fabrication condition is known as a key to the control of various film properties, such a minute change in structure has not been studied in detail. Our observations show that a microscopic evaluation of the interfacial structure, as a function of the growth conditions, is achievable.

Transition metal oxide thin films are widely studied for their possible use in applications. In some cases, the interface between the substrate and the film possesses electronic or magnetic properties that are very different from that of either the film or the substrate. One of the most famous examples is the interface between two band insulators with the perovskite ABO$_3$ structure, LaAlO$_3$ and SrTiO$_3$.[1, 2] With certain growth conditions, this interface exhibits metallic conduction to low temperatures, showing a surprisingly large carrier mobility.[1, 3] Various groups have reported wide range of properties of the interface, and the differences are attributed to the film thickness[4] and the growth conditions such as the oxygen pressure and the temperature for the pre-anneal, growth, and post-anneal processes for pulsed laser deposition (PLD).[2] In other words, films fabricated under different condition provide different conductivity. This implies that the seeds of these differences must be in the film structure. However, the structural features as a function of growth conditions have not been studied in detail.

Structural characterization for transition metal oxide films has been mostly made by reflection high-energy electron diffraction (RHEED) during the film growth process and atomic force microscopy (AFM) measurements, post-fabrication, to observe the surface topography. X-ray diffraction is also often used to obtain the in-plane and out-of-plane lattice parameters and the homogeneity of the thickness of the film. Less is known about the detailed atomic distributions, and chemical intermixing at the interface. To clarify the interfacial structure, only a limited numbers of studies have been made by scanning transmission electron microscope (STEM) or similar electron microscopy on thinned section.[5] Recent developments in the analysis techniques of x-ray diffraction make it possible to observe the detailed atomic arrangements at the interface.
Figure 1. X-ray scattering intensity profiles along (00ζ) for two 600°C-samples, one 700°C-sample and two 800°C-samples. Right hand panel shows a magnified view around the (004) Bragg reflection of the substrate.

of ultrathin films[6, 7, 8]. In this paper, we demonstrate that it is possible to observe minute structural differences caused by variations in the growth temperature of LaAlO$_3$ film by means of the surface x-ray diffraction, which is a nondestructive technique.

The LaAlO$_3$ ultrathin films were fabricated by means of PLD, using 7.5 mm by 7.5 mm TiO$_2$ terminated (001) SrTiO$_3$ substrates. Following a pre-anneal at 950°C in 5×10$^{-6}$ torr of oxygen for 30 minutes, the LaAlO$_3$ deposition was carried out at a growth pressure of 10$^{-5}$ torr of oxygen with a total laser energy of 40 mJ, (spot size at the target = 2.5 mm$^2$), using a laser repetition rate of 2 Hz. The thickness of the films were monitored by RHEED oscillations and controlled to 5 unit cells. The samples were cooled to room temperature at the deposition pressure. During the deposition, the temperature of the substrate was set to 600, 700 or 800°C. In the following, we refer to the samples using this temperature label. Five films were prepared: two 600°C-samples, one 700°C-sample and two 800°C-samples. X-ray diffraction measurements were performed at BL-3A of the Photon Factory, KEK, Japan. A standard four-circle diffractometer equipped with a scintillation counter is installed in this beamline. The x-ray energy for the measurements was 14 keV.

The structure of a ultrathin film made on a (001) substrate is reflected in the x-ray scattering intensity profile along the c*-direction.[9] One of the simplest examples is the scattering intensity profile along (00ζ), which includes the reflectivity profile. This profile is given by the absolute-square of the Fourier transformation of the electron density along the depth direction. In normal reflectivity measurements, only a limited part of q-space is analyzed, resulting in a poor spatial resolution. In order to achieve atomic resolution, we measured a larger range of q-space including several Bragg reflections in this study. This method is known as crystal truncation rod scattering.

X-ray scattering intensity profiles along (00ζ) up to ζ=5.2 were obtained by performing rocking curve measurements at various ζ positions. Throughout this paper, we use the reciprocal
lattice defined by the substrate crystal lattice. Figure 1 shows the scattered intensity per unit illuminated area for all of the five samples. The results clearly show that the intensity profiles of the two 600°C-samples are similar to each other, and the two 800°C-samples are also similar, while the 600°C-samples data can be clearly distinguished from the 800°C-samples. Moreover, the intensity profile for the 700°C-sample is intermediate between the higher and lower growth temperature data. Since the intensity profile is directly connected to the structure, these results clearly indicate that the film structure changes with growth temperature.

An important question is what structural feature is controlled by the growth temperature? To answer this question, we utilized a recently developed analyzing method for surface x-ray diffraction data: coherent Bragg rod analysis[6, 7]. This method is a kind of holography, and has been utilized to analyze not only oxide films[8] but also an extremely complicated organic semiconductor structure[10]. In this method, the electron density of the unknown structure around the surface is obtained as the difference from that of a reference structural model. Therefore, this method is ideal to find minute changes between films having very similar structures. The data for samples 600°C-1 and 800°C-1 in Fig. 1 are processed with this method. Since an electron density analysis requires quasi-continuous intensity data, we interpolated the experimental results. For the regions with no intensity data available because of low intensity or too close proximity either to the direct beam or substrate Bragg reflections, we used the calculated intensity profile for the reference structure model that reproduces the experimental result rather well. This analysis procedure follows that of our previous report on an organic semiconductor[10].

The resultant depth (z) profiles of the electron densities for the two samples are shown in Fig. 2. The alternating peaks in the electron density, corresponding to the AO and BO₂ planes, are clearly visible. The flat and very low electron density in the region z > 23Å, corresponding to the vacuum beyond the sample, ensures that the electron density given by this analysis is correct. The peaks close to the surface, i.e., those between 17Å and 23Å, show significant suppression, meaning that there is some surface roughness as well as the miscut of the substrate. Although the profiles shown in Fig.2 look very similar to each other at the first sight, there are some differences in interfacial atomic mixing. In order to present the differences more clearly, we plot the ratio of the electron number in the AO planes and the averaged electron number in the neighboring BO₂ planes in Fig.3. This ratio should be 1.2 in SrTiO₃ (electron number of [Sr²⁺+O²⁻]/[Ti⁴⁺+2O²⁻]=[36+10]/[18+20]) and 2.1 in LaAlO₃ ([La³⁺+O²⁻]/[Al³⁺+2O²⁻]=[54+10]/[10+20]). For both the 600°C-1 and 800°C-1 samples, these ratios are 1.2 inside the substrate, and more than 2 in the film, indicating good stoichiometry of the films. The depth profile of the ratio shows the interfacial structure including the atomic mixing. According to Ref.[8], the interface between LaAlO₃ and TiO₂-terminated SrTiO₃ has one layer of LaTiO₃; this structure is schematically shown in the inset of Fig. 3. The open triangles in the main
Figure 3. Depth dependence of the ratio of the electron number in the AO planes and the averaged electron number in the neighboring \( \text{BO}_2 \) planes. Closed squares and circles show the results for the 600°C-1 and 800°C-1 samples, and the open triangles show the values for the model interface that has one layer of \( \text{LaTiO}_3 \) at the interface. Inset: (inset) Schematic view of the model structure, which is made by a simplification simplified version of the result of Ref.[8].

Panel show the calculated electron number ratio for an interface having such a structure, i.e., the \( \text{(SrTiO}_3/\text{SrO/\text{TiO}_2/\text{LaO/\text{TiO}_2/\text{LaO/AlO}_2/\text{LaAlO}_3})} \) interface. Note that our surface x-ray scattering result supports the structural model. The slope of the ratio at the interface for the model structure is steeper than the experimental values, meaning that the experimental results show some interfacial roughness. In order to quantify this interfacial roughness, these profiles were fitted using the error function. As a result, we obtained interfacial r.m.s. roughness of 4.5Å, 5.4Å, and 3.4Å for the 600°C-1 sample, the 800°C-1 sample and the model structure, respectively, which are very close to the interfacial roughness reported by STEM measurements[5]. Our results allows us to find minute changes in structure caused by the deposition condition, and this increase in interfacial roughness for the higher growth temperatures may be related to the adatom mobility and thermodynamic driving force towards intermixing.

To summarize, surface x-ray diffraction experiments combined with the coherent Bragg rod analysis make it possible to clarify minute changes in the interfacial structure caused by changes in the film growth conditions. This method provides an opportunity to study the growth condition dependence of the film properties in detail.

Acknowledgement
This work was supported by the TORAY science foundation and the support center for advanced telecommunications technology research. This work was also supported by KAKENHI (21740274,19052002) and Global COE Program (G10).

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