論文の内容の要旨

論文題目 The Relationship between Structural and Electrical Properties in Complex Oxide Heterostructures

（複合酸化物ヘテロ構造における構造特性と電気特性との相関）

氏　　名　　佐藤　弘樹

1. Introduction

Complex oxide heterostructures have been attracting increasing interest for many years. This is first because of the rich variety of physical properties observed in bulk, particularly in perovskite oxides. Perovskites have a similar lattice structure with a small lattice mismatch to each other, which enables fabrication of high-quality epitaxial heterostructures. Thin films, superlattices, and interfaces show a wider range of properties that are often different from bulk, making the field of oxide electronics even more fascinating.

One of the most common fabrication techniques for complex oxide heterostructures is pulsed laser deposition (PLD). PLD is a versatile method with which a wide variety of nanostructures have been fabricated, including oxide thin films with atomic-length scale precision possible in the growth direction. It is also known, however, that the structural and electrical properties of PLD-grown films can vary greatly with growth conditions, due to growth induced defects, in particular off-stoichiometry. Therefore, in order to make a thorough investigation of complex oxide heterostructures, detailed knowledge of the relationship between growth and physical properties is necessary.

In this work, we study the relationship between structural and electrical properties, modulated by PLD growth conditions, for two complex oxide systems. The first is the $LaAlO_3/SrTiO_3$ (001) heterostructure. The quasi two-dimensional electron gas formed between the two band insulators [1] has been attracting extensive research. Yet, there remain many controversial issues, most notably the origin of the conductivity. In this study, we demonstrate that the electronic properties of this system can be controlled over a wide range by growth parameters. In particular, the enhanced mobility enables the observation of quantum oscillations at low temperatures, which gives important information about the electronic structure at the interface.

The second system is $SrMoO_3$ thin films. $SrMoO_3$ is known to have the highest conductivity among metallic oxides [2], which suggests that another electrically clean system may be realized using this material. However, due to the difficulty in growth that requires an extremely strong reducing condition, currently studies of this material are very limited. In this work we demonstrate the growth of high-quality $SrMoO_3$ thin films, by tuning the laser parameters and the argon partial pressure. In particular, the conductivity of the thin film grown in this study is improved from previous reports.

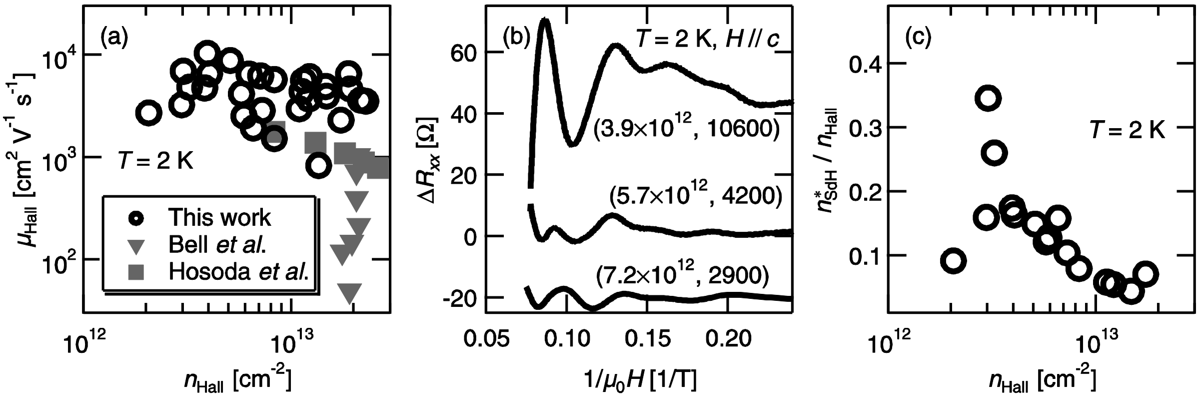

Fig. 1 (a) Summary of μ_{Hall} as a function of n_{Hall} at 2 K for $LaAlO_3/SrTiO_3$ samples grown at various conditions. Results of back-gating (by Bell *et al.* [3]) and top-gating (by Hosoda *et al.* [4]) are also included for comparison. (b) Magnetoresistance of three representative samples, after background subtraction, versus reciprocal magnetic field, measured at 2 K with magnetic field applied parallel to the substrate normal. Numbers in parentheses indicate n_{Hall} [in cm^{-2}], μ_{Hall} [in cm^{2}V^{-1}s^{-1}] for each sample. (c) Ratio of the carrier densities $n^*_{\mathrm{SdH}}/n_{\mathrm{Hall}}$ as a function of n_{Hall} at 2 K.

2. Mobility enhancement and quantum oscillations at the $LaAlO_3/SrTiO_3$ heterointerface

It has recently been reported that the low temperature mobility of the $LaAlO_3/SrTiO_3$ interface can be enhanced by optimizing the growth conditions, mainly the growth temperature. This provides a great opportunity to study the electronic structure at the interface in detail using quantum oscillations. However, previous studies found a discrepancy between the carrier densities estimated from the Hall effect (n_{Hall}) and from the Shubnikov-de Haas (SdH) oscillations (n_{SdH}). As the origin of this discrepancy is currently not well determined experimentally, it is important to compare the SdH oscillations of different samples with various n_{Hall} and Hall mobilities (μ_{Hall}).

In this study, we modulated the low-temperature transport properties of the $LaAlO_3$/ $SrTiO_3$ interface by growth conditions, in particular aiming to approach a very low-density high-mobility regime. Figure 1(a) summarizes μ_{Hall} as a function of n_{Hall}, evaluated by the Hall effect at 2 K, for $LaAlO_3$/ $SrTiO_3$ samples grown at various conditions. By tuning the growth temperature, the $LaAlO_3$ thickness and the laser parameters, both μ_{Hall} and n_{Hall} were modulated over a wide range, wider than that of conventional gating methods [3,4]. In particular, the highest mobility achieved is 10,600 cm^{2}V^{-1}s^{-1}.

As shown in Fig. 1(b), the high mobility achieved enabled the observation of SdH oscillations at low temperature. We estimated the carrier density using the SdH oscillations, assuming no valley or spin degeneracy, i.e., $n^*_{\mathrm{SdH}} = f \times e/h$ (f: frequency, e: elementary electric charge, h: Planck's constant, the superscript * emphasizes the assumption of no degeneracy). Figure 1(c) shows the ratio of the carrier densities evaluated by SdH and Hall, i.e., $n^*_{\mathrm{SdH}}/n_{\mathrm{Hall}}$, as a function of n_{Hall}. Down to $n_{\mathrm{Hall}} \sim 3 \times 10^{12}$ cm^{-2}, the $n^*_{\mathrm{SdH}}/n_{\mathrm{Hall}}$ ratio monotonically increases with decreasing n_{Hall}, and approaches ~0.4–0.5 (1/2). This can be understood that when the carrier density is relatively high, multiple subbands are occupied, and only a part of them contributes to the SdH oscillations. $n^*_{\mathrm{SdH}}/n_{\mathrm{Hall}} \sim 1/2$ at the lowest density regime suggests that either there still remain multiple subbands, or there is a two-fold degeneracy and nearly all of the electrons contribute to the oscillations.

In order to obtain more information from the quantum oscillations, a high-mobility $LaAlO_3/SrTiO_3$

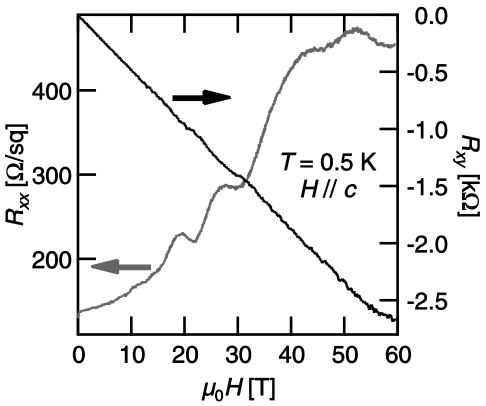

Fig. 2 Symmetrized magnetoresistance and antisymmetrized Hall resistance of a $LaAlO_3/SrTiO_3$ sample, measured at 0.5 K with magnetic field applied parallel to the substrate normal.

sample was characterized using a pulsed magnet, with which a maximum magnetic field of 60 T was available. Figure 2 shows the magnetoresistance and the Hall resistance of the sample. Clear SdH oscillations were observed, and the Hall resistance also showed small, but significant oscillation-like features. Additionally, there was a splitting of the SdH oscillation peaks at ~50 T, reminiscent of the Zeeman effect. This suggests that the spin degeneracy can be resolved only under very high magnetic fields, and thus the possible ~2-fold degeneracy discussed above could originate from the effective spin degeneracy under the relatively low fields.

3. Growth of high-quality $SrMoO_3$ thin films

$SrMoO_3$ is known to have the highest conductivity among metallic oxides, which suggests that another clean system may be realized using this material. In particular, ultrathin $SrMoO_3$ films may enable study on a different, high carrier density regime, contrasting to the $LaAlO_3/SrTiO_3$ interface, for which the low density regime is in particular interesting. However, since Mo^{4+} can be stabilized only under extremely low oxygen partial pressure, growth of $SrMoO_3$ is very difficult, and thus the study on this material is very limited. Most notably, the $SrMoO_3$ thin films grown previously have low conductivity (< 10^5 S cm^{-1}) [5,6] compared to the bulk single crystal (> 10^6 S cm^{-1} at low temperature) [2].

In this study, we modulated the structural and electrical properties of $SrMoO_3$ thin films using different growth conditions, mainly by the argon (inert gas) partial pressure. $SrMoO_3$ films were grown on $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) (001) substrates, first in the base pressure of the chamber. The properties of a representative $SrMoO_3$ thin film grown in vacuum are summarized in Fig. 3. The ultra-high vacuum enabled $SrMo^{4+}O_3$ to be stabilized, as confirmed by XRD [Fig. 3(a)]. However, the film surface imaged by atomic force microscopy (AFM) was found to be very rough [Fig. 3(b)]. As shown in Fig. 3(d), the conductivity of the film was, while comparable to that of the films grown by other groups, much lower than in bulk.

We next examined the effect of argon partial pressure, which can modulate the plume kinetics and stoichiometry by scattering the species in the plume, without affecting the reducing thermodynamic condition required. The properties of a representative $SrMoO_3$ thin film grown in argon are also summarized in Fig. 3. The XRD measurement again confirmed single-crystalline growth of $SrMoO_3$ [Fig. 3(a)]. Notably, the AFM surface topography [Fig. 3(c)] revealed that the film surface was much flatter, although the roughness was still significantly larger than the $SrMoO_3$ unit cell height. The resistivity of the film was found to be significantly lower than that of the films grown by other groups, but still considerably higher than in bulk, particularly at low temperatures [Fig. 3(d)].

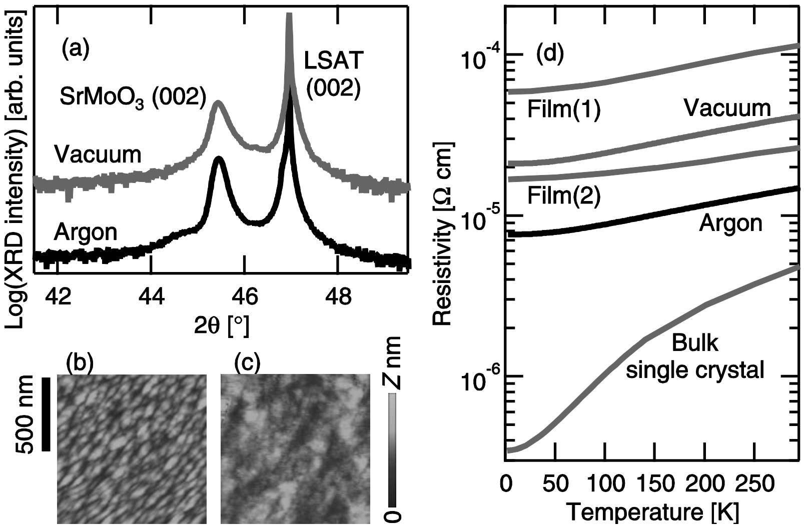

Fig. 3 (a) XRD θ–2θ pattern of the SrMoO$_3$/LSAT (001) samples grown in vacuum or argon. (b) AFM surface topography of the SrMoO$_3$ film grown in vacuum (height scale Z = 30 nm) and (c) in argon (Z = 5 nm). (d) Temperature dependence of the resistivity. Data of the films grown by other groups (Film(1): Ref. [5], Film(2): Ref. [6]) and the bulk single crystal (Ref. [2]) are also included for comparison.

These results demonstrate that the interaction of species in the plume with the ambient gas is another useful growth parameter to control the film properties. The high-quality SrMoO$_3$ film grown here will enable a more detailed study on this material, for example by photoemission spectroscopy, possibly also by transport measurements under high magnetic fields.

4. Conclusion

In this work, we presented fundamental growth studies on two representative oxide heterostructures. For the LaAlO$_3$/SrTiO$_3$ heterostructure, we demonstrated that the electronic properties at the interface can be widely tuned by the growth conditions, in particular by tuning the LaAlO$_3$ film stoichiometry. Combined with other growth parameters, the low-temperature mobility was greatly enhanced, which enabled the observation of quantum oscillations under high magnetic fields. These results help us to disentangle many conflicting studies on this popular system. For the SrMoO$_3$ thin films, we demonstrated that the plume–ambient gas interaction is a key growth parameter to realize a high conductivity and a flat surface. A high-quality SrMoO$_3$ film was successfully grown which has the highest conductivity among the films reported, which should enable a more detailed study on this material. We hope the results obtained in this work will play an important role as a basis for the study of complex oxide heterostructures. *Other studies on the film stoichiometry control and the ferromagnetism of the LaAlO$_3$/SrTiO$_3$ heterostructure are also presented in the Thesis.

References

[1] A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).

[2] I. Nagai *et al.*, Appl. Phys. Lett. **87**, 024105 (2005).

[3] C. Bell *et al.*, Phys. Rev. Lett. **103**, 226802 (2009).

[4] M. Hosoda *et al.*, Appl. Phys. Lett. **103**, 103507 (2013).

[5] H. H. Wang *et al.*, J. Vac. Sci. Technol. A **19**, 930 (2001).

[6] A. Radetinac *et al.*, Appl. Phys. Express **3**, 073003 (2010).