MERIT Self-directed Joint Research

Verification of the stacking order of dipole layers at the interface of perovskite oxide multilayer films using photoemission electron microscopy (PEEM)

Atsushi Tamura[1], Yoichi Kageyama[2]
[1]Department of Materials Engineering, The University of Tokyo
[2]Department of Advanced Materials Science, The University of Tokyo

Authors

Atsushi Tamura He has been studying the control of the interfacial dipole effect by controlling the stacking sequence of dipole layers in perovskite oxides. In this study, he fabricated the sample.

Yoichi Kageyama He has been studying the observation of domains in ferroelectric materials using photoemission electron microscopy (PEEM). In this study, he performed PEEM measurements.

1. Introduction

The control of the dipole effect in perovskite oxide epitaxial stacked structures has been investigated [1,2]. One example is the dipole effect in $SrTiO_3$(STO) /$LaAlO_3$(LAO) /$SrRuO_3$(SRO) /STO subs. stacked structures. In order to control the dipole effect, the stacking sequence of the $(AlO_2)^-$ and $(LaO)^+$ layers in the dipole LAO layer was expected to be important. This is because the direction of the dipole effect is reversed depending on whether the $(AlO_2)^-$ or $(LaO)^+$ layer is grown first on SRO. The applicant's research using XPS has found that the macroscopic dipole effect is changed when $SrAlO_x$ (SAO) is inserted as a base layer of the dipole layer LAO [3,4]. The cause of this change in the dipole effect is expected to be the modulation of the stacking sequence of the dipole layers by SAO. In fact, lateral force microscopy (LFM) observations of LAO surface terminating atoms suggested that different regions of LAO surface terminating atoms are distributed like a patchwork in the sample without SAO, while in the sample with SAO, the surface-terminated atoms of

LAO are almost uniform [4]. LAO is composed of repeated structures of $(AlO_2)^-$ and $(LaO)^+$ layers, and if the number of layers is correctly controlled, the stacking sequence could be determined by observing the surface terminating atoms. However, LFM is affected by surface roughness and other factors, making it an indirect method for observing surface-terminating atoms; although XPS can be used for more direct observation, it is likely to be difficult to observe structures of several hundred nm even with μ-XPS, which has good spatial resolution. Therefore, we aim to reveal the differences in the distribution of surface-terminating atoms by experiments using photoemission electron microscopy (PEEM) [5]. Laser PEEM has a spatial resolution of several tens of nm and is considered suitable for observing changes in the distribution of surface terminating atoms associated with differences in the stacking sequence.

2. Method

Samples were prepared by pulsed laser deposition (PLD) using a KrF (248 nm) excimer laser. 65 nm of conductive oxide SRO as the bottom electrode and LAO as the dipole layer were deposited in sequence on a STO (001) single crystal substrate at 750°C. The laser energy density was 0.5 J/cm^2. In order to fabricate two different regions in the sample laterally and to modulate the stacking sequence of $(AlO_2)^-$ and $(LaO)^+$ monoatomic layers in one region, 0.2 nm of SAO was inserted between the SRO and LAO layers. Two specific sample structures were used: LAO/SRO/STO substrate stacking structure and LAO/SAO/SRO/STO substrate stacking structure. Based on previous studies, the stacking structure is assumed to be as shown in Fig.1, depending on the presence or absence of SAO.

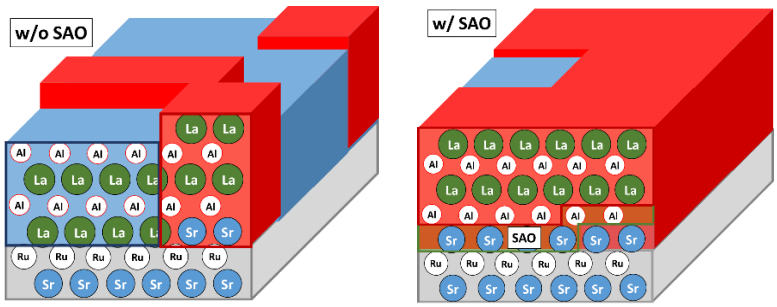

Fig. 1 . Predicted modulation of the stacking sequence of the dipole layer LAO with and without insertion of SAO. The left figure shows the case without SAO insertion and the right figure shows the case with SAO insertion.

As shown in Fig.1, in the sample without SAO insertion, the LAO growth is considered to be the growth of $(AlO_2)^-$ layers from (SrO) layers and $(LaO)^+$ layers from (RuO_2) layers. Therefore, two different directions of the dipole effect coexist in the sample plane. On the

other hand, for the sample with SAO insertion, the (SrO) or $(AlO_2)^-$ layer is on the surface of the SRO sample, so that the stacking always starts from the $(AlO_2)^-$ layer when LAO is grown. Therefore, the stacking order of LAO layers is expected to be aligned.

The laser energy of the PEEM used in the measurement is 2.44 eV. The cut-off energy is the point at which the kinetic energy of the photoelectrons is zero, which varies depending on the surface terminating atoms and the presence of the dipole effect. The spatial resolution of PEEM allows to observe the distribution on the sample surface and compare it with the LFM results to clarify the correlation between the macroscopic dipole effect and the modulation of the stacking sequence.

3. Results and Discussions

Figure 2(a) shows a PEEM image with a field of view of 50 μm observed by PEEM.

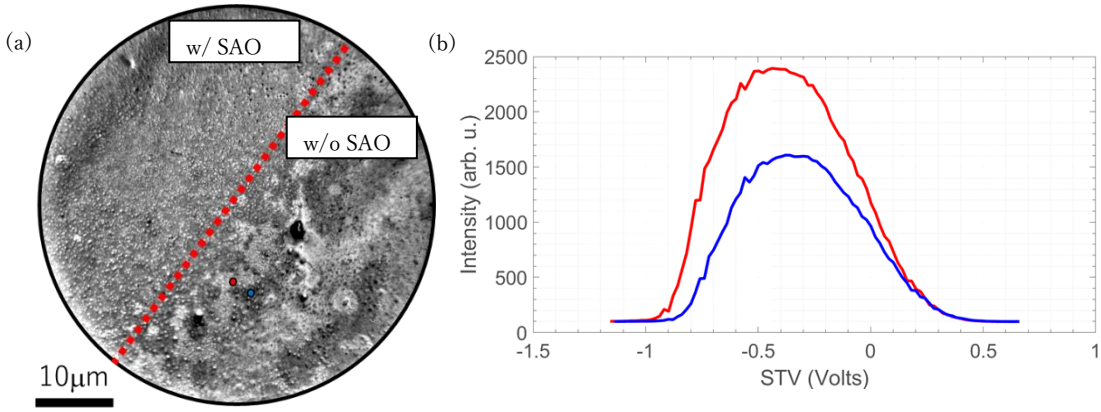

Fig. 2 (a). PEEM image of the LAO surface with a field of view of 50 μm. The left is the area with SAO inserted (w/ SAO) and the right is the area without SAO. (b). Voltage dependence of photoelectron intensity at the red and blue points shown in Figure 2(a).

However, Fig.2(a) is corrected for the potential distribution of photoelectron intensity affected by the measurement. This figure shows an image of the boundary between the area where SAO is inserted and the area where SAO is not inserted in the fabricated sample. The red line in the figure is the boundary. On the left side of the boundary, the intensity of photoelectrons is almost constant and uniform, while on the right side of the boundary, regions of strong intensity are distributed among regions of weak intensity of photoelectrons. This difference in intensity may be due to the difference in interfacial state density caused by the different stacking sequence of LAO.

Figure 2(b) shows the photoelectron spectra of the red and blue points in the figure when the voltage was swept. The spectral edge at the lower voltage corresponds to the cut-off energy, and the spectral edge at the higher voltage corresponds to the Fermi level. The

spectra of the Fermi level side are almost identical to those of the cut-off energy side, while the cut-off energy side is shifted by about 0.1 eV, taking into account the difference in the intensity. However, this shift is smaller than that observed in a previous study by XPS (about 0.5 eV). The reason for this is not necessarily clear, but it should be noted that we are not observing the same physical quantity, since both the dipole effect and the difference in the work function affect the difference in cut-off energy. In any case, the shift in cut-off energy implies differences in surface terminating atoms or dipole effects, indicating that regions with different stacking sequence are distributed in the sample without SAO insertion.

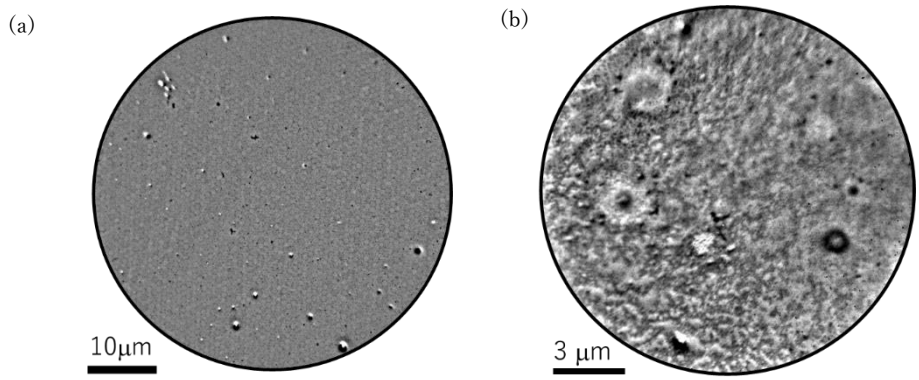

Fig. 3. PEEM images of (a) region w/ SAO and (b) region w/o SAO. The field of view is 50 μm in the w/ SAO region and 15 μm in the w/o SAO region.

Figure 3(a) shows PEEM image taken by moving to the area where SAO was inserted and there is no clear contrast difference. The particle-like structures on the surface are thought to be contamination, and the hexagonal structures are instrumental noise (noise from the MCP amplifying the photoelectron signal). In Fig.3(b), the field of view was narrowed to 15 μm to see the fine structures, and the contrast was clearly observed.

The AFM observations also reveal that the surface roughness of the surface w/o SAO is about 1 nm larger than that of the surface w/ SAO. However, it is assumed that the effect of surface morphology is not dominant, since the work function is not expected to change even if the surface is rough, as long as the surface terminating atoms are the same.

4. Conclusion

Without SAO insertion, the surface of LAO is non-uniform, while in the case of SAO insertion, the surface of LAO is almost uniform. When focusing on the regions without SAO

insertion, it is clear that there are regions with different work functions. This can be attributed to the difference in surface terminating atoms. In combination with the fact that the number of monoatomic layers of LAO can be precisely controlled, it is clear that the SAO insertion modulates the stacking sequence of LAO. These results for the LAO surface are consistent with the results of horizontal force microscopy, thus validating the model for the LAO stacking sequence using direct observation techniques.

5. Acknowledgement

We would like to express our sincere gratitude to our supervisors, Prof. Koji Kita and Prof. Takasada Shibauchi, for their great support and cooperation in conducting this research. We are grateful to Prof. Toshiyuki Taniuchi for PEEM measurement and Prof. Takeaki Yajima for sample fabrication by PLD, for their kind support to this research. In addition, we are grateful for the MERIT program to have the opportunity for this research.

References

[1] T. Yajima, Y. Hikita, M. Minohara, C. Bell, J. A. Mundy,L. F. Kourkoutis, D. A. Muller, H. Kumigashira, M. Oshima and H. Y. Hwang, Nat. Commun. 6, 6759 (2015).
[2] T. Yajima, M. Minohara, C. Bell, H. Y. Hwang and Y. Hikita, Appl. Phys. Lett. 113, 221603 (2018).
[3] A. Tamura S. Jang, Y. G. Park, H. Lim and K. Kita, Solid State Electronics 185, 108128 (2021).
[4] A. Tamura and K. Kita, J. Appl. Phys. 134, 235301 (2023).
[5] T. Taniuchi, Y. Motoyui, K. Morozumi, T.C. Rodel, F. Fortuna, A.F. Santander-Syro and S. Shin, Nat. Commun. 7, 1, 11781 (2016).