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STEM Imaging and High-Resolution Elemental Mapping of La-doped $SrTiO_3$ Super Lattice Thin Film

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A layered perovskite-type Ruddlesden-Popper (RP) phase $Sr_{n+1}Ti_nO_{3n+1}$ compound is one of good candidates for a high T_c super conductor, a colossal magneto-resistive material and a next generation thermoelectric material[1]. The RP phase $Sr_{n+1}Ti_nO_{3n+1}$ compound exists as a stable mineral consisted of alternative stacking sequence of perovskite ($(SrTiO_3)_n$) units and a rock-salt (SrO) unit. With the recent improvement of a pulsed laser deposition (PLD) method, such a super lattice thin film growth and a dopant implantation into a target layer could have been artificially controlled on atomic scale[2]. It was reported that, based on the PLD method, the RP phase $(La_{0.5}Sr_{0.5}O)/(SrTiO_3)_5$ super lattice thin film could be synthesized, by accumulating the $(La_{0.5}Sr_{0.5})O$ mono layer and the n (n=5) unit cells of $SrTiO_3$ (STO) layers alternatively, and also by partially substituting Sr^{2+} of SrO mono layer with La^{3+}[2]. This thin film showed a metallic behavior and kept it even in low temperature region[2]. However, a mechanism of the metallic behavior still remains unclear. It is important to reveal a correlation between the electric properties and the micro structure of the super lattice.

In this work, analysis of the microstructure of the film was performed by using an aberration corrected scanning transmission electron microscope (STEM): JEOL JEM-2100F with CEOS corrector. We analyzed the location of La and Ti atoms using a high-resolution elemental mapping based on the 2-dimensional electron energy loss spectroscopy (EELS): Gatan Enfina. The energy loss near edge structure (ELNES) of Ti- $L_{3,2}$ edges were measured to examine electric states.

The bright-field (BF) STEM image of the La-doped RP-STO thin film taken along the $[100]_{STO}$ zone axis clearly showed super lattice structure with 5 times longer than primitive unit of STO. The high-angular annular dark-field (HAADF) STEM image (Z-contrast image[3]) shows that the positions of A-site (Sr) atoms with bright spots are displaced at SrO monolayer by $a/2$ (a: lattice constant of STO) toward the $[010]_{STO}$ direction compared to the positions of A-site in the neighboring STO blocks as shown in FIG. 1. This indicates that ideal RP phase structure can be formed. Unfortunately, it was difficult to identify distribution of La atoms only by using the HAADF-STEM image.

Therefore, we analyzed the location of La and Ti atoms using a high-resolution elemental mapping. Specimen drifts were corrected during the acquisitions. To reduce the delocalization in inelastic scattering, La-$M_{5,4}$ and Ti-$L_{3,2}$ core-loss edges were chosen[4,5]. This high-resolution elemental mapping (FIG. 2) revealed that the La and Ti atoms in the RP phase are distinguished clearly and the La atoms are localized not only at the Sr(A)-sites of the nominally doped layer but also at the neighboring A-sites (terminating Sr sites in the $(STO)_5$ blocks). It can be considered that the terminating Sr atoms in the $(STO)_5$ blocks are easily substituted with the doped La atoms.

The line analysis of energy loss near edge structure (ELNES) measured across the interface revealed that Ti atoms in close proximity to the SrO layer have tendency with mixed valence of Ti^{3+} and Ti^{4+}. This means that La atoms contribute to supply a carrier and to change electric state of Ti near the dopant element.

It can be concluded that localization of La atoms near the SrO monolayer may contribute to form 2 dimensional electron gas layer and metallic behavior of the super lattice thin film of RP-STO.

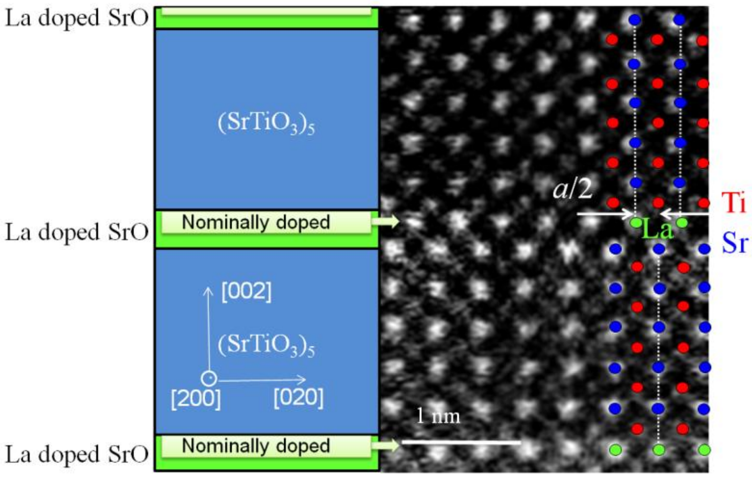

FIG. 1 High-angular annular dark-field STEM image.

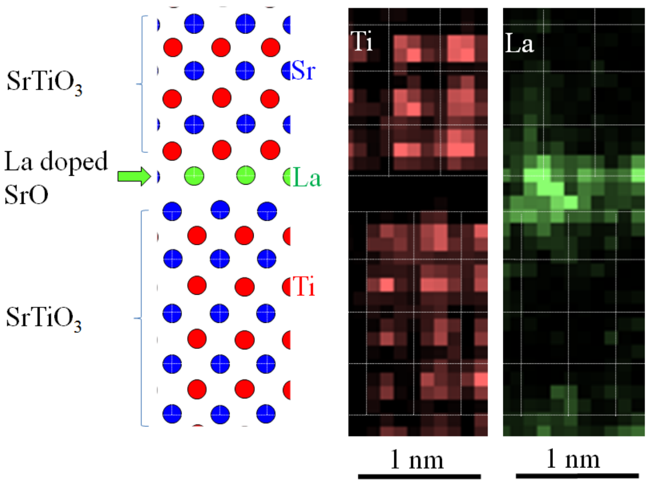

FIG. 2 High-resolution elemental mapping based on the 2-dimensional EELS.

References

[1] W. Tian, X. Q. Pan, J. H. Haeni, and D. C.Schlom, *J. Mater. Res.* **16**, (2001) 2013.
[2] M. Okude, A. Ohtomo, T. Kita, and M. Kawasaki, *Appl. Phys. Express* **1** (2008) 081201.
[3] S. J. Pennycook and D. E. Jesson, *Ultramicrosc*. **37** (1991) 14-38.
[4] K. Kimoto, T. Asaka, T. Nagai, M. Saito, Y. Matsui, and K. Ishizuka, *Nature* **450**, (2007) 702-704.
[5] R. F. Egerton, '*Electron Energy-Loss Spectroscopy in the Electron Microscope*', Plenum (1996).