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MS-3-P-2393 Phase Control of Transition-Metal Oxide Films through Interfacial Octahedral Connections

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The octahedral distortions in perovskite transition-metal oxide thin films strongly correlate with the functional properties. The control of such octahedral distortions is crucial for designed fabrication of oxide heterointerfaces with desired properties. However, identification of the controlling parameter for the octahedral distortions associated with the oxygen displacements has remained elusive because of the experimental difficulties in observing oxygen atoms.
In this work, we investigate $SrRuO_3$ (SRO) thin films grown on the $GdScO_3$ (GSO) substrates using high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging in aberration-corrected scanning transmission electron microscopy (STEM) (JEM-9980TKP1). We found that while the SRO films below 16 nm thickness have the monoclinic structure with the bulk-equivalent tilted octahedra, the SRO films above 16 nm have the tetragonal one with negligibly tilted octahedra [1,2]. We further reveal that the in-plane displacement of the oxygen atoms shared between the RuO_6 and ScO_6 octahedra at the interface for the monoclinic SRO is larger than that for the tetragonal SRO. The correlation between the interfacial oxygen displacement and the SRO structural phase raises the possibility for controlling film phases by interface engineering of oxygen displacements.
To demonstrate this, we inserted the one unit-cell-thick $BaTiO_3$ (BTO) layer between the 10 nm-thick SRO film and GSO substrate. The bulk BTO with relatively large A-site cation (Ba) has non-tilted octahedra, allowing for minimizing the in-plane oxygen displacements at the interface and thus for blocking the octahedral tilt propagation from the GSO substrate to the SRO film. Figure 1 shows HAADF-STEM image and its intensity profiles in the SRO/BTO/GSO heterostructure, confirming the coherent growth with the chemically sharp interface across the entire heterostructure. The ABF-STEM analyses shown in Fig. 2 reveal that the octahedral tilts in the GSO substrate are drastically suppressed in the BTO layer and that the octahedral tilts in the SRO film are negligibly small. This indicates that while the 10 nm-thick SRO films directly grown on the GSO substrate have the monoclinic structure, the SRO film on the BTO/GSO has the tetragonal one, which is stabilized by the suppression of interfacial oxygen displacements. The results demonstrated that the film structure can be manipulated by adjusting the oxygen displacements through the interfacial octahedral connections.
[1] R. Aso, D. Kan, Y. Shimakawa, H. Kurata, *Sci. Rep.* **2013**, *3*, 2214.
[2] D. Kan, R. Aso, H. Kurata, Y. Shimakawa, *Adv. Funct. Mater.* **2013**, *23*, 1129.

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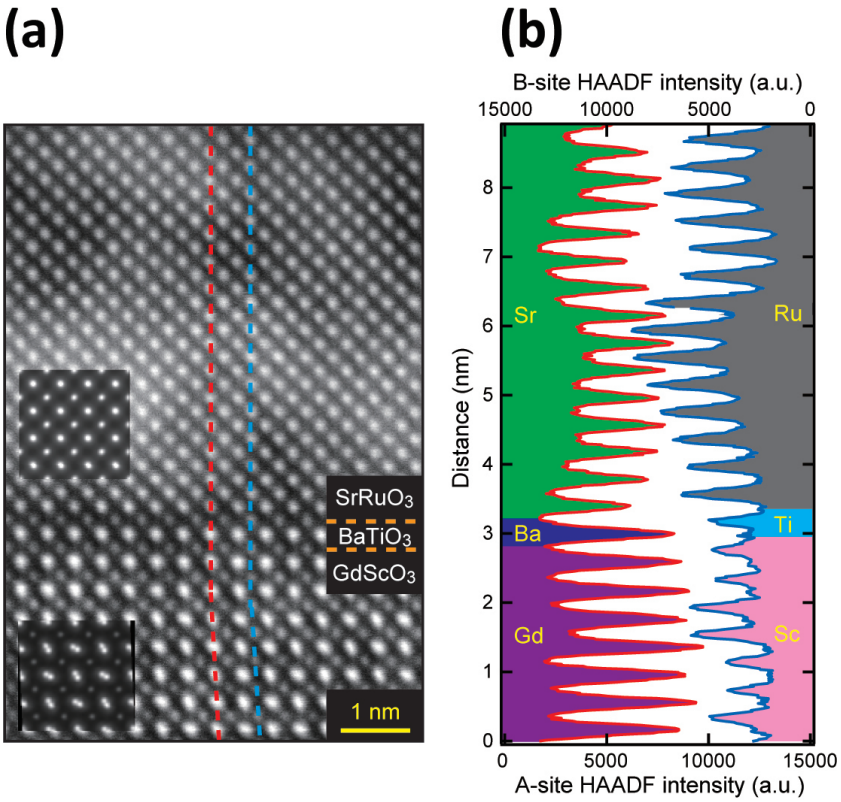

Fig. 1: (a) HAADF-STEM image and (b) HAADF intensity profiles of the A- and B-site cations in the $SrRuO_3/BaTiO_3/GdScO_3$ heterostructure. The orange dashed lines also indicate the heterointerfaces.

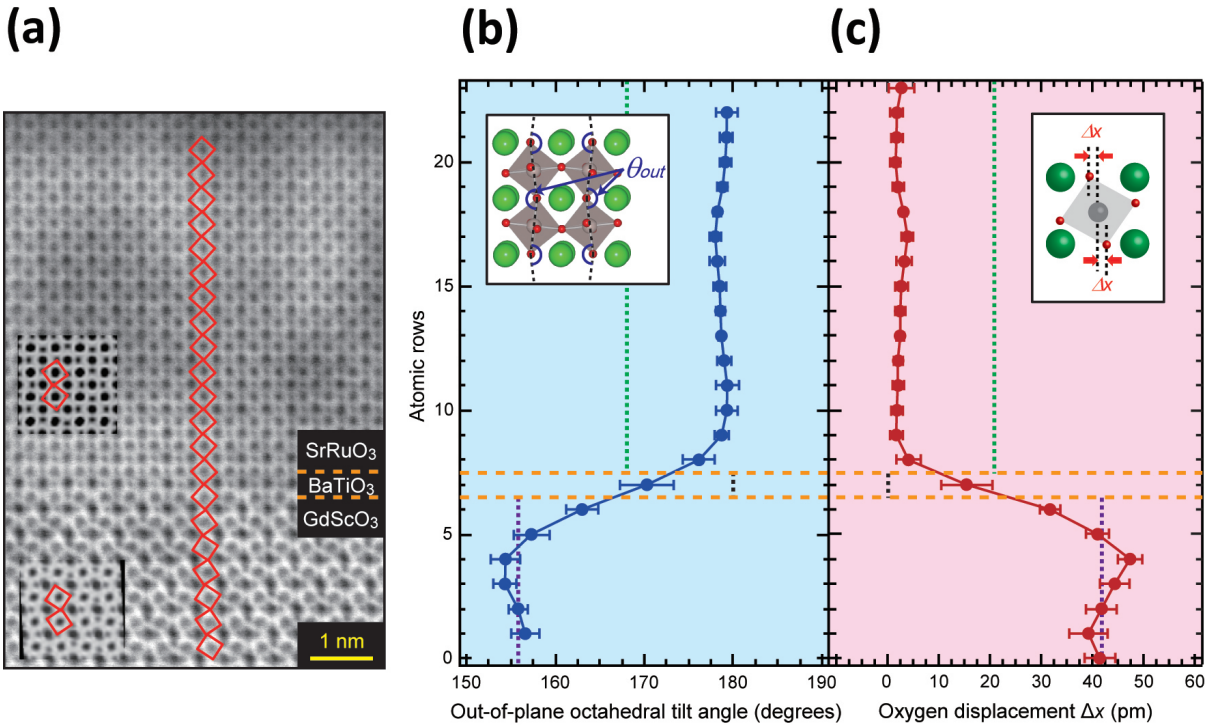

Fig. 2: (a) ABF-STEM image, (b) octahedral tilt angle θ, and (c) in-plane displacements Δx of oxygen atoms in the $SrRuO_3/BaTiO_3/GdScO_3$ heterostructure. The green and purple dotted lines represent the bulk counterparts of $SrRuO_3$ and $GdScO_3$, respectively. The orange dashed lines also indicate the heterointerfaces.