Growth-Orientation Dependent Charge- and Orbital-Ordering in Epitaxially-Grown Thin Films of $Pr_{0.5}Ca_{0.5}MnO_3$

The effect of growth-orientation dependent epitaxial strain on charge- and orbital-ordering (CO-OO) was studied for thin films of half-doped perovskite manganite, $Pr_{0.5}Ca_{0.5}MnO_3$, fabricated on $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate. Synchrotron x-ray diffraction revealed a drastic difference between the two films grown on [011]- and [001]-oriented substrates [(011)-film and (001)-film, respectively] in the transition temperature and the domain size of CO-OO. While the (011)-film showed CO-OO transition at 220 K, similarly to a bulk sample, the CO-OO transition temperature of the (001)-film was greatly enhanced to 300 K. Furthermore, the domain size of CO-OO was three times as large in the (011)-film as in the (001)-film. These results demonstrate that the CO-OO in manganites can be affected by the growth orientation via the epitaxial strain from the substrate.

The colossal magnetoresistive (CMR) effect has been attracting interest as a promising candidate for application to resistance-switching nonvolatile memories. Especially, half-doped perovskite manganites have been extensively studied, because of their gigantic responses to various kinds of stimuli [1]. A plausible origin of the gigantic responses in half-doped manganites is that the external stimuli melt the insulating CO-OO, and induce a metallic state. In this report, we demonstrate that the growth orientation of the epitaxial film can modulate the insulating CO-OO state.

To observe the CO-OO state, we performed synchrotron X-ray diffraction and resistivity measurements. The target material was a typical CMR manganite, $Pr_{0.5}Ca_{0.5}MnO_3$. (011)- and (001)-films of $Pr_{0.5}Ca_{0.5}MnO_3$ with 40 nm thickness were grown by the pulsed laser deposition method. X-ray diffraction experiments were performed with four-circle diffractometers installed at BL-3A and 4C.

Schematic views of the relation between the film and the LSAT substrate are shown in Figs. 1 (a) and (b). In the (001)-film, both of the a- and *b*-lattice constants are locked to those of the substrate. In contrast, the a-lattice constant and [01-1] axis are locked in the (011)-film, while the lengths of *b* and *c*, and the angle between them, are partly variable. Schematic pictures of the stripe-type CO-OO are also shown. Blue lobes and red circles schematically indicate the e_g-orbitals in Mn^{3+} and Mn^{4+} ions, respectively. The lobes represent the occupied $(3x^2\text{-}r^2)$- or $(3y^2\text{-}r^2)$-type orbital.

Figure 2 (a) shows the temperature dependence of resistivity in the (001)- and (011)-films. The (011)-film shows a clear anomaly near 220 K, similarly to a bulk behavior [2]. In contrast, the (001)-film does not show any clear anomaly. The origin of the difference in resistivity data was clarified by using X-ray diffraction. The superlattice (1/4 7/4 2) was observed in both films, as shown in Fig. 2(b), which indicates the emergence of the CO-OO [3]. The superlattice reflection in the (011)-film begins to grow at 220 K in accord with the anomaly in resistivity. In contrast, the superlattice reflection in the (001)-film subsists at higher temperature than that of the (011)-film and a bulk sample [4], and disappears near room temperature. One can also see a difference in the temperature dependence of lattice constants in Fig. 3. In the (011)-film, the qualitative behavior of elongated

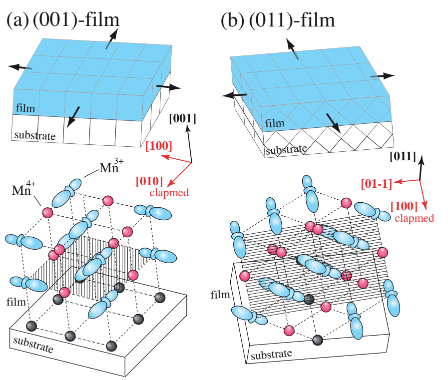

Figure 1
Schematic views of $Pr_{0.5}Ca_{0.5}MnO_3$ thin films fabricated on (a) LSAT(001) [(001)-film] and (b) LSAT(011) [(011)-film], respectively. The directions of tensile strain from the substrate are represented by the black arrows. Schematic pictures of charge- and orbital-ordering states are also depicted. Red circles and blue lobes indicate Mn^{4+} and Mn^{3+} ions with one occupied e_g-orbital, respectively. (Reproduced from Ref. [6].)

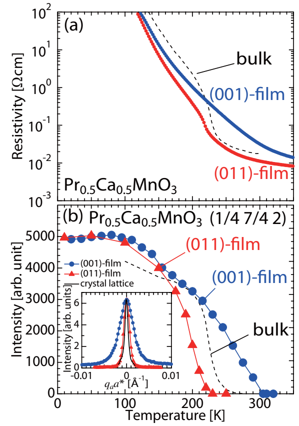

Figure 2
Temperature dependence of (a) the resistivity and (b) the (1/4 7/4 2) superlattice reflection by using synchrotron x-ray diffraction in $Pr_{0.5}Ca_{0.5}MnO_3$ films. In the inset, the x-ray diffraction profiles of (1/4 7/4 2) at 50 K are shown. Blue circles and red triangles are the data of the (001)- and (011)-films, respectively. The black dashed line is that of bulk sample [2, 4]. The black solid line in the inset indicates the profile of (0 2 2) of the film. (Reproduced from Ref. [6].)

b- and shortened *c*-lattice constants is similar to that of a bulk sample [5], in marked contrast with the (001)-film. In the inset of Fig. 2(b), the peak profiles of (1/4 7/4 2) and (0 2 2) at 50 K are shown. From these data, the domain size of CO-OO is estimated to be about 30 and 75 nm for the (001)- and (011)-film, respectively, while that of the crystal lattice is 160 nm. The CO-OO domain of the (001)-film is about three times as larger as that of the (011)-film.

A plausible origin of the drastic changes in the transition temperature and the domain size of CO-OO for the two films is the tensile-epitaxial strain from the substrate. The *a*- and *b*-lattice constants of a bulk sample become longer in the CO-OO phase while the c-lattice constant becomes shorter. A similar distortion is embedded in the (001)-film. The *a*- and *b*-lattice constants of the (001)-film are extended by the tensile strain, and the *c*-lattice constant is reduced so as to satisfy Poisson's ratio. As a result, the stable configuration of CO-OO forms in the (001)-film. Nonetheless, the locking of the *a*- and *b*-axes to the substrate imposes the constraint that the orbital-ordering plane should maintain tetragonal symmetry. As a result, a fine structure of domains with different direction of orbital stripe would form. In contrast, in the (011)-film, the CO-OO which is analogous to the bulk can be achieved. This is the reason for the similar transition temperature to the bulk sample [3]. The orbital-ordering plane is partly free from the locking of the substrate, which would make the domain size in the (011)-film larger than in the (001)-film. In this manner, the growth orientation highly affects the CO-OO state via the epitaxial strain.

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3A and 4C

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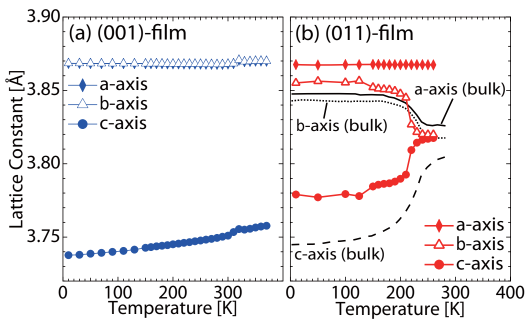

Figure 3
Temperature dependence of the lattice constants of (a) the (001)-film and (b) the (011)-film. The black lines indicate the lattice constants of bulk $Pr_{0.5}Ca_{0.5}MnO_3$ [5]. (Reproduced from Ref. [6].)