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Controlled B-site ordering in Sr_2CrReO_6 double perovskite films by using pulsed laser interval deposition

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We have investigated the effects of growth interval in pulsed laser deposition on structural, magnetic, and electrical transport properties of (111)-oriented Sr_2CrReO_6 double perovskite films. It was found that the degree of B-site ordering varied in a wide range by just changing the growth interval. Magnetization under 1 T and metallicity (the ratio of room-temperature resistivity to minimum resistivity at low temperatures) monotonically increased with increasing degree of ordering and reached values nearly identical to bulk. This technique, called pulsed laser interval deposition, may provide more efficient way to study relations between structural and physical properties in double perovskites than controlling growth parameters, such as temperature and oxygen partial pressure. © *2010 American Institute of Physics*. [doi:10.1063/1.3525578]

Oxide materials have attracted considerable attention because of their exotic properties.[1] Double perovskites are an important class of materials, in which the transition-metal sites are occupied alternately by two cations. After Sr_2FeMoO_6 was reported as a high Curie temperature (T_C) half-metal,[2] intensive research on double perovskite was triggered for engineering new materials with a wide spectrum of properties including multiferroic, spin-compensated antiferromagnetic half-metal, single spin superconductors, etc.[3,4] However, it is known that realization of perfect ordering in such materials is largely restricted. A number of attempts with different synthesis techniques have been made, but the amount of success is rather limited by intrinsic parameters, such as differences in formal valence and ionic radius of constituent transition-metal ions.[5]

One of the widely used synthesis techniques for the preparation of double perovskites thin films is pulsed laser deposition (PLD). PLD has a number of parameters that have to be adjusted, such as oxygen partial pressure (P_{O_2}), growth temperature (T_g), laser fluence, laser spot area, and target-substrate distance, to achieve the desired properties.[6–8] Usually, the first two (P_{O_2} and T_g) are systematically tuned as primary factors to survey an optimum condition, where oxidation states of B-site (transition-metal site) ions become favorable to the formation of the stoichiometric compound.[5,6] Such efforts so far have been put to maximize ordering,[6,9,10] but no attempt has been made with a technique so-called *pulsed laser interval deposition* (PLID) to control the overall growth dynamics.

The PLID technique has been proposed to impose layer-by-layer growth of homoepitaxial $SrTiO_3$ (STO) and other perovskites.[11] This protocol is the periodic triggering of laser ablation: fast deposition of the amount of materials needed to complete 1 ML, followed by a growth interval (t_w: waiting time) lasting long enough to allow the deposits to rearrange atomically flat surface. The essence of this technique is to promote interlayer mass transport, as well as surface diffusion of adatoms, before adsorbed species crystallize in multiterrace levels or a metastable phase. Therefore, similar technique may provide the ability to control the degree of ordering in double perovskite films, where the growth interval allows the B-site ions to rearrange themselves in ordered phase before the supplied species crystallize in disordered phase.

Here, we have employed PLD technique with interval to fabricate Sr_2CrReO_6 (SCRO), a high T_C half-metallic ferrimagnet,[12] on STO (111) substrates. This compound is suitable to a model experiment because well-ordered phases have already been realized both in bulk and thin film forms.[12–15] In this study, the structural, magnetic, and transport properties as a function of t_w have been investigated. The results clearly indicate that ordering of B-site cations is tuned in a wide range by changing t_w at a given T_g-P_{O_2} condition.

The SCRO films with a thickness of approximately 30 nm were grown at $T_g=850\ ^\circ C$ in $P_{O_2}=5\times10^{-4}$ Torr on atomically flat surface of STO (111) single crystal, (Shinkosha, Co., Ltd., Japan). KrF excimer laser pulses (248 nm, 4 Hz) were focused on a target (a SCRO ceramic tablet with single perovskite phase with no sign of B-site ordering) with a spot area of $0.35\times0.10\ cm^2$ at a constant fluence of $1.1\ J/cm^2$. These parameters were fixed for all experiments. In PLID mode, we used a mechanical shutter to regulate periods of growth (84 pulses) and interrupt ($t_w=13-20$ s). The entire growth was monitored by using *in situ* reflection high-energy electron diffraction (RHEED) along the $[11\bar{2}]$ direction. After the growth, the samples were annealed for 15 min, keeping T_g and P_{O_2} constant, then quenched to room temperature. The crystalline structure was investigated by using a four-circle x-ray diffractometer (XRD) (X'Pert MRD, PANalytical) with Cu $K\alpha$ radiation. The magnetic properties were measured under a magnetic field parallel to the film plane in a Quantum Design magnetic property measurement system operated with "reciprocating sample option" mode. Nonmagnetic tools were used to cut and handle the samples to avoid possible magnetic contamination. Using

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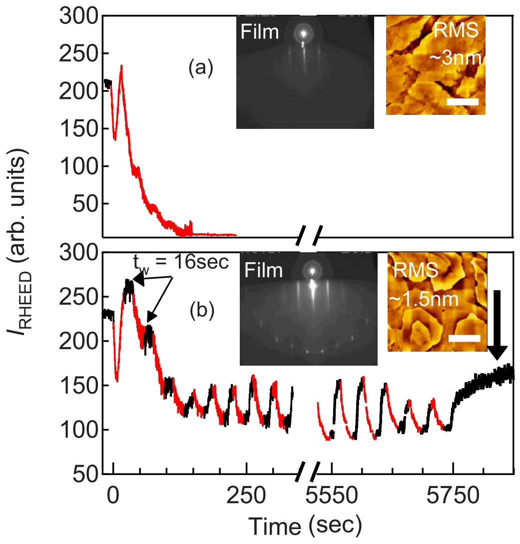

FIG. 1. (Color online) RHEED intensity oscillations for specular beam taken along the [11$\bar{2}$] direction (a) during continuous deposition and (b) interval deposition (t_w=16 sec). Insets depict RHEED patterns and the AFM images (scale bars are 0.5 μm) of the obtained SCRO films. Two representative interval periods (t_w=16 sec) are indicated in the figure. Regions between two intervals represent deposition of 84 pulses.

a physical property measurement system, the four-probe resistivity was measured for the samples having evaporated Au/Ti Ohmic contacts.

Figure 1(a) shows the temporal variation of the RHEED intensity (specular reflection) during continuous deposition (t_w=0 s). The number of laser pulses required for the completion of 1 ML (~0.23 nm) was estimated to be around 80 from the period of a few countable oscillations at the initial stage and also the absolute thickness measured by a surface profilometer. Quick damping of intensity indicates a transition to a three-dimensional growth mode and the obtained film exhibited a diffused streak pattern (see inset). In the case of PLID growth (84 pulses and t_w=16 s), the initial damping similar to the case of continuous deposition was observed [Fig. 1(b)], whereas the intensity at a steady state recovered immediately after the growth interruption. In addition, slow recovery behavior was seen at the very end (indicated by arrow). The highest amplitude of these recovery behaviors was achieved for t_w=16 s and, accordingly, a sharp streak pattern was observed, as shown in the inset of Fig. 1(b).

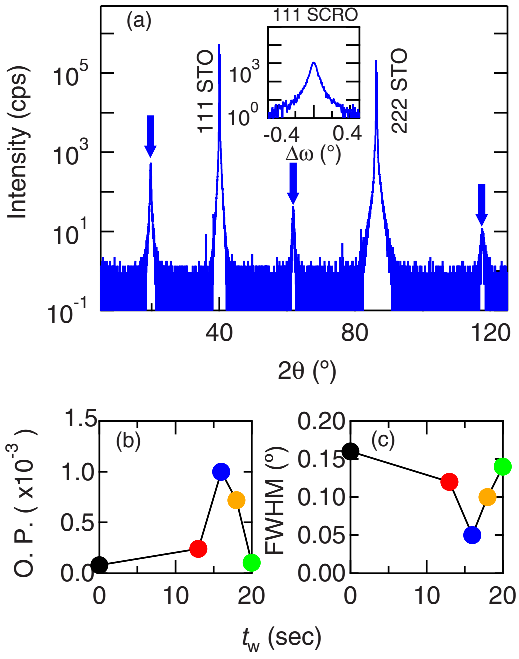

FIG. 2. (Color online) (a) X-ray diffraction pattern for the (111)-oriented highest ordered film prepared with t_w=16 s. Peaks due to the B-site ordering are indicated by blue arrows. The inset depicts rocking curve of SCRO 111 reflection (2θ~20°). [(b) and (c)] OP, defined as the ratio of peak intensity of SCRO 111 to STO 111, and FWHM of the rocking curve at SCRO 111 reflection as a function of t_w, respectively.

Figure 2(a) shows a wide range of XRD along the out-of-plane reflections for the sample prepared with t_w=16 s. Sharp peaks of the SCRO odd-*hhh* reflections were clearly observed (indicated by arrows). Note that the even-*hhh* reflections are not discernible from the STO 111 and 222 reflections. The full width at half maximum (FWHM) of SCRO 111 reflection was as small as 0.05°. This value is comparable to FWHM of STO 111 reflection (0.02°), indicating a good lateral coherency of B-site ordered domains. In order to evaluate the degree of ordering, we define an order parameter (OP) as the intensity ratio of SCRO 111 reflection to STO 111 reflection. As shown in Figs. 2(b) and 2(c), both OP and FWHM values indicate bell-shaped dependence on t_w. The highest B-site ordering and crystalline quality were simultaneously attained for the sample prepared with t_w=16 s. It is worth noting that the degree of ordering became lower as growth interval was extended longer than 16 s. A plausible explanation for this tendency is that longer interval might result in facilitating mass transport beyond two intact layers, thus increase of disorder. Despite this open question, we shall emphasize that close resemblance between dependencies of surface reconstruction (RHEED intensity recovery), degree of B-site ordering, and crystalline quality on

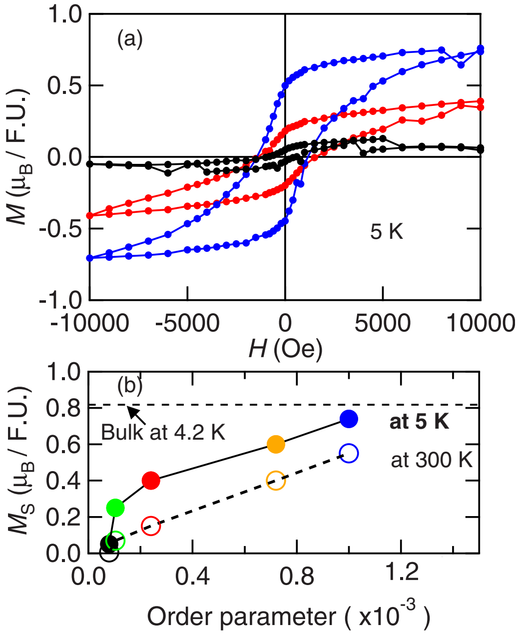

FIG. 3. (Color online) (a) Magnetic-field dependence of magnetization measured at 5 K for the highest ordered (t_w=16 sec), moderately ordered (t_w=13 sec), and the lowest ordered (t_w=0 sec) samples (higher to lower magnetization, respectively). (b) Magnetization under 1 T (M_s) as a function of order parameter at 5 K (closed circles) and 300 K (open circles). "Bulk" indicated by broken line refers to the data reported in Ref. 13.

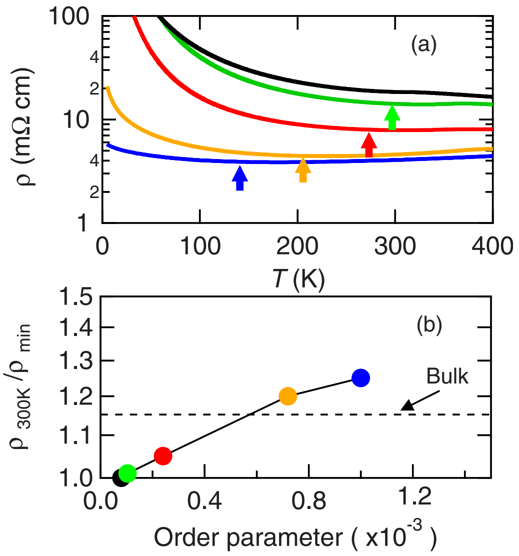

FIG. 4. (Color online) (a) Temperature dependence of resistivity for SCRO films. Arrows indicate metal-to-insulator transition temperatures for each sample. (b) Ratio of resistivity at 300 K to minimum resistivity at low temperatures ($\rho_{300\ \mathrm{K}}/\rho_{\mathrm{min}}$) as a function of the order parameter. Bulk indicated by broken line refers to data reported in Ref. 13.

t_w implies that there is a characteristic relaxation time associated with reconstruction dynamics during PLID.

In order to estimate the amount of antisite disorder defects (AS) in our samples, we investigate the low-temperature magnetization properties. All of the magnetization data presented here are after the correction of diamagnetic contribution of the STO substrate. Figure 3(a) shows the magnetic-field dependence of magnetization measured at 5 K for three representative samples [(t_w=16 s), 13 s, and 0 s (higher to lower magnetization respectively)]. The magnetization under 1 T (hereafter referred to as to M_s) systematically increased with increasing OP. The highest ordered sample indicated $M_s \sim 0.8\ \mu_B$/f.u. This value is comparable to 0.86 μ_B/f.u., measured for a bulk polycrystal ($AS = 16\%$) at 4.2 K under 7 T.[12] Assuming that M_s decreases linearly with increasing AS,[16] M_s at 5 K of our samples prepared with different t_w gives AS in a range from ~20% to ~50%. These AS values are considerably higher than those of the PLD-grown films reported by others.[13–15] Further optimization of T_g-P_{O_2}-t_w condition as well as growth rate might make AS much lower, although it is not the central focus of this study. To summarize the results of magnetization measurements, M_s at 5 K (closed circles) and 300 K (open circle) are plotted as a function of OP in Fig. 3(b).

In order to study the transport properties as function of the degree of ordering, we measured the temperature dependence of electrical resistivity ρ. A systematic decrease in ρ with increasing degree of ordering was seen at a temperature range from 2 to 400 K, as shown in Fig. 4(a). Room temperature ρ was ~4 mΩ cm for the highest ordered sample (t_w=16 s), which is comparable to 1–5 mΩ cm measured for high-quality bulk and thin films.[12,13,15] Another systematic dependence as a consequence of improved crystallinity was seen in a metal-to-insulator transition that has been previously observed at ~150 K.[12,13,15] In our samples, transition temperature (indicated by arrows) monotonically increased from 140 K with decreasing degree of ordering. In a viewpoint of metallicity, the ratio of room-temperature resistivity to minimum resistivity at low temperatures is plotted as a function of OP in Fig. 4(b). The decrease in metallicity with decreasing degree of ordering can be viewed as suppression of conduction channels due to disorder, which is essential to the spin polarized transport in SCRO.[17]

In summary, we have demonstrated new way to control the B-site ordering in Sr_2CrReO_6 double perovskite using pulsed laser interval deposition technique. The *in situ* RHEED diagnoses combined with XRD analyses revealed that tuning of growth interval significantly influenced the overall growth dynamics. Systematic dependencies of structural and physical properties on growth interval indicate that this approach is important to regulate the degree of ordering. In addition, transitions from disordered to long range ordered ferrimagnetic, as well as insulator to metal were clearly observed with increasing B-site ordering. This technique may turn out to be useful to enhance ordering of layered oxides.

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