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Highly insulating ferromagnetic cobaltite heterostructures

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ABSTRACT

Ferromagnetic insulators are rather rare but possess great technological potential in, for example, spintronics. Individual control of ferromagnetic properties and electronic transport provides a useful design concept of multifunctional oxide heterostructures. We studied the close correlation among the magnetism, atomic structure, and electronic structure of oxide heterostructures composed of the ferromagnetic perovskite $LaCoO_3$ and the antiferromagnetic brownmillerite $SrCoO_{2.5}$ epitaxial thin film layers. By reversing the stacking sequence of the two layers, we could individually modify the electric resistance and saturation magnetic moment. The ferromagnetic insulating behavior in the heterostructures was understood in terms of the electronic reconstruction at the oxide surface/interfaces and crystalline quality of the constituent layers.

1. Introduction

Ferromagnetic exchange interactions in transition metal oxides have been interpreted predominantly as double exchange or Stoner type [1–4]. In perovskite manganites, for example, double exchange occurs between two magnetic manganese ions linked by an oxygen ion. Electron hopping is considered between the two neighboring sites, and it proceeds without spin-flip of the hopping electron. Therefore, metallic conduction is inevitable in a conventional double exchange scheme as well as in itinerant ferromagnetism, which explains why ferromagnetic insulators are not very common.

Although quite rare, ferromagnetic insulating transition metal oxides do exist, and they possess great potential for spintronic applications, including spin valves [5–13]. For example, ferromagnetic insulators can serve as spin filters, while simultaneously acting as a tunneling barrier, within a metal-insulator-metal heterostructure. To properly employ the ferromagnetic insulating property, however, independent control of the electronic and magnetic characteristics is required. In particular, it would be interesting to search for ways to decouple the magnetic property from the insulating behavior so as to realize magnetic heterostructure devices based on transition metal oxides.

Both lanthanum and strontium cobalt oxides are great platforms for the study of magnetism, because they exhibit intriguing spin state and ordering resulting from the coupling among charge, spin, lattice and orbital. While bulk $LaCoO_3$ reveals an antiferromagnetic ordering with spin state transition from low-spin (LS) to high-spin (HS) states as temperature decreases [14,15], epitaxial $LaCoO_3$ thin films under tensile strain exhibit a robust ferromagnetic long-range ordering with an insulating behavior [16–18]. Microscopic and spectroscopic studies have shown a close correlation between the strain state and spin ordering in $LaCoO_3$ thin films [19–26]. On the other hand, $SrCoO_x$ undergoes a topotactic phase transformation from a ferromagnetic metallic phase ($x = 3.0$, perovskite) to an antiferromagnetic insulating phase ($x = 2.5$, brownmillerite) [27–29]. The large deviation in oxygen stoichiometry modifies the local electronic environment of the Co ions and their valence states from 4+ to 3+ [30]. Such diversity in magnetic properties and the compatibility of the building blocks allow us to examine cobaltite heterostructures as a candidate for tunable ferromagnetic insulators.

In this work, we studied structural, electrical, and magnetic properties of oxide heterostructures composed of $LaCoO_3$ (LCO) and $SrCoO_{2.5}$ (SCO) to show that insulating and ferromagnetic behaviors can be tuned by heterostructuring. In particular, we changed the

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stacking sequence between LCO and SCO on (001) $SrTiO_3$ (STO) substrates, to control the ferromagnetic insulating characteristics in the resulting heterostructures. While both LCO/SCO//STO and SCO/LCO//STO heterostructures exhibit a robust ferromagnetic and insulating behavior, the SCO/LCO//STO heterostructure shows a higher magnetization as well as a higher resistivity compared with the LCO/SCO//STO heterostructure. This result contradicts the conventional double exchange model of ferromagnetism in transition metal oxides, even more so because both heterostructures consist of exactly the same constituent layers with the same degree of epitaxial strain. We propose that the stacking sequence and resultant modifications at the interface, possibly based on electronic reconstruction at a polar/nonpolar interface, are responsible for the modified ferromagnetic insulating characteristic in cobaltite heterostructures.

2. Experimental methods

The high-quality epitaxial LCO and SCO thin films were grown on atomically flat single crystalline STO (001) substrates using pulsed laser epitaxy at 750 °C [23,30]. A KrF excimer laser ($\lambda = 248$ nm) with a laser fluence of 1.0 J cm^{-2} at a repetition rate of 10 Hz was used. The oxygen partial pressure during the growth was 100 mTorr. The crystal structure and epitaxial relations of the thin films were characterized using high-resolution X-ray diffraction (XRD). The thickness of each layer was 5 ± 1 nm, as determined by X-ray reflectometry.

The resistivity as a function of temperature $\rho(T)$ was measured using a physical property measurement system using the Van der Pauw geometry with In electrodes and Au wires. The magnetization as functions of temperature $M(T)$ and magnetic field $M(H)$ was measured using a superconducting quantum interference device. The magnetic field was applied to the in-plane direction of the thin films.

3. Results and discussions

In order to examine the coupling between the ferromagnetic and insulating properties in cobaltite heterostructures, we designed two heterostructures using ferromagnetic LCO and antiferromagnetic SCO, as schematically shown in Fig. 1. Fig. 1(a) (Fig. 1(b)) shows the LCO/SCO//STO (SCO/LCO//STO) heterostructure, where the SCO (LCO) layer was first deposited on STO, followed by the LCO (SCO) layer deposition. Note that it is not trivial to predict whether the octahedral CoO_2 layer or the tetrahedral CoO layer will be first deposited on top of the surface. In the schematic, we follow a recent observation by Meyer et al., where they confirmed that the tetrahedral CoO layer comes first on top of the TiO_2-terminated STO surface based on scanning transmission electron microscopy [31]. Another point worth mentioning is the difference in the *A*-site and *B*-site networks within the perovskite ABO_x framework of the heterostructures. For LCO/SCO//STO, the *A*-site network is not disturbed at the SCO//STO interface. Furthermore, only the *A*-site network is disturbed at the LCO/SCO interface, preserving the *B*-site network. On the contrary, for SCO/LCO//STO, both *A*-site and *B*-site networks are discontinuous at the LCO//STO interface.

Based on the discussion regarding the atomic layers sequence, further differences between the heterostructures can be implied regarding the valence states of Co. The nominal valence states of Co ions are 3 + for both the LCO and SCO layers. However, we could consider a charge transfer near the interface between polar (LCO) and nonpolar (STO) oxides, which might result in the polar catastrophe. It should be noted that LCO thin films on STO substrates reveal an insulating behavior [32]. Therefore, we can conclude that

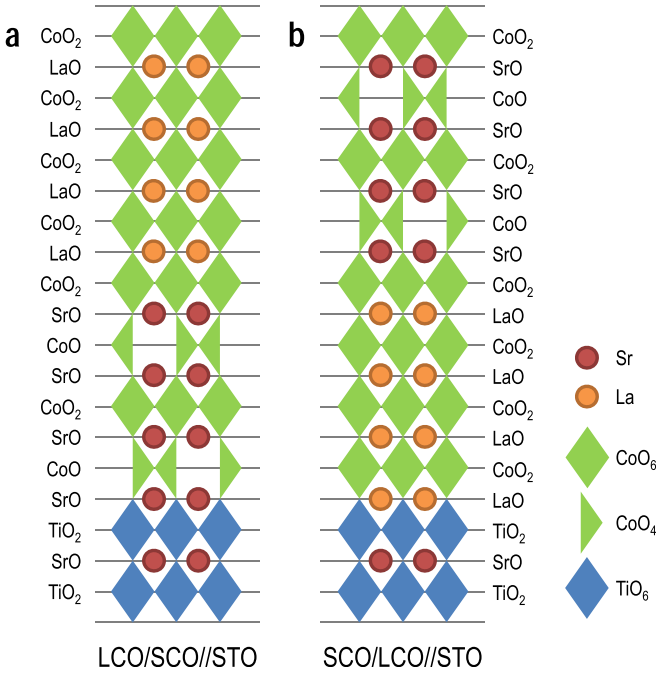

Fig. 1. Schematic diagrams of cobaltite heterostructures seen along the [110] direction of the STO substrate. (a) LCO/SCO//STO heterostructure. For the SCO//STO interface, only the *B*-site network is disturbed (Ti → Co), while the *A*-site network (Sr) is not disturbed. On the other hand, for the LCO/SCO interface, only the *A*-site network is disturbed (Sr → La), while the *B*-site network (Co) is not disturbed. (b) SCO/LCO//STO heterostructure. For the LCO//STO interface, both *A*-site and *B*-site networks are disturbed (Sr → La and Ti → Co, respectively). On the other hand, for the SCO/LCO interface, only the *A*-site network is disturbed (La → Sr), while the *B*-site network (Co) is not disturbed. All Co ions are considered to have nominal 3 + valence state.

the Ti valence state in LCO//STO does not change (from 4+ to 3.5+) as efficiently as in the prominent case of a $LaAlO_3$ thin film on a STO substrate [33,34]. Instead, we might expect an increase in the Co valence state from 3+ to 3.5+ at the interface although Co^{4+} is rather unstable [35,36]. If this were the case, Co^{4+} within the perovskite framework with Sr as the *A*-site cation could further stabilize the ferromagnetism in the heterostructure as in ferromagnetic $SrCoO_{3-\delta}$.

Fig. 2 manifests the high-quality crystalline structure of our heterostructures, characterized by XRD. LCO has a pseudocubic lattice constant $a_c = 3.8029$ Å and experiences tensile strain when grown on STO (a = 3.905 Å) [23]. On the other hand, SCO has pseudo-tetragonal lattice constants $a_t = 3.905$ and $c_t/2 = 3.936$ Å, and therefore, has a larger out-of-plane lattice compared with STO [30]. This is clearly observed in the XRD results of the single-phase thin films (~40 nm) as shown in Fig. 2(a) and (b). Compared with LCO, the SCO thin film shows additional half-order peaks in-between the perovskite peaks, indicating the presence of ordered oxygen vacancies in the brownmillerite structure, as mentioned in the discussion of Fig. 1 [37]. The magnified region in Fig. 2(b) also indicates the high quality of the film with Laue fringes originating from the sharp interfaces and surfaces.

Based on the phase-pure crystalline thin films of LCO and SCO, we constructed heterostructures by stacking each layer with a 5-nm thickness in reverse sequences. The low angle X-ray reflectometry in Fig. 2(c) shows that the total thicknesses of the heterostructure films were close to the intended thickness of ~10 nm. In addition, both of the heterostructure films showed the expected peak features, from both the LCO and SCO layers, as shown in Fig. 2(d). Both heterostructure films were also epitaxially strained revealing the coherent lattice with the substrate one, without any