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Thickness-dependent charge ordering state in Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO₃ thin films under the anisotropic strain

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We have achieved clear charge ordering (CO) state in Ca doped $Bi_{0.4}Sr_{0.6-x}Ca_xMnO_3$ (BSCMO) films on (110)-orientated SrTiO₃. The BSCMO film's CO transition temperature (T_{CO}) was tuned to room temperature (RT) by optimum doping Ca (x = 0.32). Asymmetric x-ray reciprocal space mapping was used to determine the structure evolution of the films with thickness, in detail, under the anisotropic stress in films. We found that the CO phase only appears in thicker films, accompanied by an unique distortion in structure, in which twin-domains structure occurs with the [110] axis slightly tilting toward [1–10] and [–110] directions. The results demonstrate the effects of anisotropic stress on the structure and electronic phases in BSCMO films as thickness increases. Our works are valuable for allowing a RT study in the CO film and further operation of the devices for a practical use. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4913295]

INTRODUCTION

Perovskite manganites with charge/orbital ordering (COO) have attracted much attention not only due to physics interests but also the amazing magnetic/transport properties under external perturbations. For bulk material, the bismuthbased manganite $Bi_{1-x}Sr_xMnO_3$ (BSMO) with a doping range from x = 0.5 to 0.8 is a typical COO manganite.^{1,2} The charge ordering (CO) transition in Bi_{1-x}Sr_xMnO₃ takes place against a paramagnetic (PM) background and the CO transition temperature T_{CO} is generally higher than other manganites, i.e., the T_{CO} locates at \sim 370 K for bulk Bi_{0.4}Sr_{0.6}MnO₃. High-T_{CO} manganite is not suitable for room temperature (RT) operation of correlated electron devices for a practical use. So, it will be found more great use by tuning the T_{CO} near RT. For the above manganites, which involve a network of corner-sharing MnO₆ octahedra, doping A-site is an effective methods to tune the T_{CO} by tuning the e_g bandwidth.³ In this paper, through tuning the concentration of Ca^{2+} replacing Sr^{2+} ions, we have tuned the T_{CO} of bulk Bi_{0.4}Sr_{0.6-x}Ca_xMnO₃.

In addition, the epitaxial growth of manganite films can also reduce the T_{CO} , due to the lattice strain in the films.^{4,5} However, the CO transition is usually depressed by the tetragonal lattice stability in manganite thin films grown on (001)oriented substrates.⁶ For instance, bulk Nd_{0.5}Sr_{0.5}MnO₃ and Bi_{0.4}Ca_{0.6}MnO₃ show an antiferromagnetic-charge ordering insulated (CAF)-COI ground state. However, it is difficult to realize the COI transition in epitaxial films unless an anisotropic strain filed is introduced.⁷ Also, Ogimoto *et al.* have found a clear MI transition arising from the COO in Pr_{0.5}Sr_{0.5}MnO₃ films utilizing (110)-orientated substrates.^{8,9} In the case of (110)-orientated films, anisotropic stress causes more complicate lattice distortion, since the two in-plane crystallographic directions [001] and [1–10] are no longer equivalent and lattice constants b and c can vary freely. The anisotropic stress and the low-symmetry structure have stabilized the Jahn-Teller distortion, triggering a clear COI transition in the films. In the CO phase, films behave amazing magnetic and transport properties.

In our work, we have tuned the T_{CO} of $Bi_{0.4}Sr_{0.6}MnO_3$ compound by doping Ca and found that $Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO_3$ was optimally doped for achieving a CO transition near RT. A series thickness of $Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO_3$ films were grown on (110)-orientated $SrTiO_3$ (STO). The electronic transport properties of films were studied and a detailed structural study was performed using X-ray diffraction (XRD) reciprocal space maps (RSMs). Clear RT-CO transition occurs in films upon the critical thickness ~40 nm. It is interesting to note an unusual splitting of the X-ray Bragg reflections in these films, suggesting a twin-domains structure existing. We attribute the CO transition to the twin-domains in films under the anisotropic stress.

EXPERIMENT

A series of Ca²⁺ doped stoichiometric Bi_{0.4}Sr_{0.6}MnO₃ $(Bi_{0.4}Sr_{0.6-x}Ca_xMnO_3, x = 0.25, 0.3, 0.32, 0.34, 0.35, and$ 0.4) targets have been synthesised by a standard solid reaction technique using high-purity powdered Bi₂O₃, SrO₂, CaO, and MnO₂ in stoichiometric ratio. Choosing the most optimal doping ratio x = 0.32, we have grown Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO₃ films with thicknesses ranging from 19 to 200 nm on (110)-orientated STO substrates by pulsed laser deposition method. During deposition, the substrate temperature and O² pressure were 650 °C and 70 Pa, respectively. Then, we have performed a systematic study on the evolution of the structure and electronic transport behaviors of the films. The surface morphology of the films was investigated by atomic force microscopy (AFM). The magnetization (M) was measured on Quantum Design superconducting quantum interference device (SQUID). The structures of the films were checked by XRD including 2θ - ω linear scan, and RSMs using Cu K α 1

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radiation ($\lambda = 1.5406$ Å, Bruker Discover). Transport properties were measured by the standard four-point method.

RESULTS AND DISCUSSIONS

XRD investigations of Bi_{0.4}Sr_{0.6-x}Ca_xMnO₃ targets were performed (not shown), revealing no secondary phase emerging and a monoclinic crystal structure. Fig. 1(a) shows the temperature dependence of magnetization plots for those Bi_{0.4}Sr_{0.6-x}Ca_xMnO₃ targets. A wide CO transition region is observed in all the samples. The T_{CO} is found to decrease with the increasing Ca content. This behavior is different from the general size effects at rare earth site, since for the Ln_{1-x}A_xMnO₃ (Ln-Rare earth elements, A-alkaline earth elements) compounds, the substitution of large ions at rare earth site always causes a decrease T_{CO} , by tuning the one electron bandwidth.3 A mechanism based on the manifestation of a Bi³⁺ lone pair 6s² character is proposed for the bismuthdoped manganites to justify the strong tendency of the charges to localize and order.² In Fig. 1(b), noting that the T_{CO} range of $Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO_3$ is tuned to 310–365 K, slightly above RT. For Bi_{0.4}Sr_{0.6-x}Ca_xMnO₃ compounds, 0.32 should be the most optimal doping ratio to achieve a RT-CO transition in films.

The (110)-Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO₃/STO (BSCMO) films display clear Kiessig oscillations (not shown), giving qualitative proof of high quality of these unique orientation films. The lattice constants are 3.815 Å and 3.905 Å, for bulk BSCMO and STO, respectively. Thus, the -2.3% mismatch of coherently grown (110)-BSCMO/STO film could take an anisotropic in-plane compressive strain. The XRD 2θ - ω scans (not shown) confirm the epitaxial growth of the BSCMO films, and the out-of-plane pseudo-cubic lattice vector, $d_{[110]}$, relaxed gradually in films with the increasing thickness. From the AFM morphology result, the growth direction changes gradually, form first along the [1-10] direction, then go through a transitional rectangular grains, and finally reorientate to be as rectangular stripes toward the [001] direction. The result is also observed in others' work,¹⁰ evidencing the influence of the anisotropic stress on the anisotropic plastic deformation in our (110) films.

The detailed structure and strain states of the films were characterized by the RSMs, as shown in Fig. 2. In order to determine the length of the in-plane lattice vectors, RSMs of asymmetric reflections around the (222) and (130) reflections were collected, and the angle between an in-plane and the

FIG. 1. (a) The temperature dependence of magnetization (*M-T*) for Ca doped $Bi_{0.4}Sr_{0.6}MnO_3$ targets: $Bi_{0.4}Sr_{0.6-x}$ Ca_xMnO_3 . (b) $Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO_3$ is optimally doped for achieving T_{CO} near RT. The shaded area represents the CO phase transition zone.

out-of-plane lattice vector can be obtained from the difference between an asymmetric reflection with a positive and one with the same negative in-plane contribution.¹¹ In Figs. 2(a), 2(c), 2(e), and 2(g), the q_{001} value of (222) reflection is nearly equal for both film and substrate, proving the coherently strained growth of BSCMO film on STO along [001] (tensile-strained direction), and the q_{1-10} value of (130) reflection gradually relaxed in films along [1-10] (tensilerelaxed direction). Most notably is the splitting of (130) reflection of films upon 40 nm in Figs. 2(f) and 2(h), which exists even in 200 nm thick film! The splitting of (130) reflection indicates that the film has twin-domains structure with the [110] axis oppositely tilts toward the [1-10] and [-110] directions slightly, shown in Fig. 2(i). The twindomains structure should be attributed to the anisotropic stress relaxation mechanism, especially the shear stress. Similar twin-domains structure has been observed in many other experiments to be a shear-mode lattice distortion.^{7,12} It is generally believed that the properties of 200 nm thick film have recovered to the bulk material, that is, twin-domains should exist in bulk BSCMO. In fact, previous study has



FIG. 2. RSMs of the $Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO_3$ films on (110)-STO. (a) 19 nm (222), (b) 19 nm (130), (c) 33 nm (222), (d) 33 nm (130), (e) 40 nm (222), (f) 40 nm (130), (g) 55 nm (222), and (h) 55 nm (130). (i) The schematic of the twinned structure containing two domains with [110] axis tilting toward [1–10] and [–110] directions.



FIG. 3. (a) The temperature dependence of the magnetization (*M*-*T*) and resistivity (*R*-*T*) of the 100 nm BSCMO film. The shaded area is the CO phase transition zone. (b) The $Ln\rho - 1000/T$ curves of BSCMO films with different thicknesses, 50 nm, 100 nm, and 350 nm. (c) The $\frac{d(Ln\rho)}{dT} - T$ plot of Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO₃ film with different thicknesses. The shaded area expresses the CO transition degree.

shown that the structure of bulk $Bi_{0.5}Sr_{0.5}MnO_3$ consists of double stripes of two different types of manganese octahedra, different from the structural model of "Mn³⁺" and "Mn⁴⁺" single stripes alternating in the COO manganites $La_{0.5}Ca_{0.5}MnO_3$.^{1,13,14}

Fig. 3 shows the temperature dependence of the magnetization (M) and resistivity (R) of the BSCMO films. All the films are insulating over the whole temperature range. Distinct transport behaviors are observed in films upon 40 nm. Take, for example, the film of 100 nm, in Fig. 3(a), *R*-*T* curve exhibits a kink near 320 K. A phase transition also shows up at 280–340 K (in shadow) on the M-T curve. These features are the signature of the CO transition, and the kink on the R-T curve indicates the onset of the carrier localization. T_C of these films was near 300 K, \sim 30 K lower than that in bulk BSCMO. To investigate the electronic transport mechanism, we have fitted the R-T data and found that variable range hopping (VRH) model was responsible for the transport properties below T_{CO} as well as above T_{CO}. In Fig. 3(b), knee points near T_{CO} exist in films of 50 nm, 100 nm, and 350 nm. We have examined the thickness dependence of the CO transition degree by giving the $\frac{d(Ln\rho)}{dT} - T$ plots in Fig. 3(c). The area of the shade part in Fig. 3(c) expresses the CO transition degree. We can see that the CO transition exists upon 40 nm and increases slightly with the increasing thickness.

Comparing the *R*-*T* and *M*-*T* results with the corresponding structure of BSCMO films, the CO phase transition should correlate with the unique twin-domains structure in thicker films. The large in-plane lattice mismatch introduces a large anisotropic stress in films and induces [110] axis tilting, forming twin-domains structure. In the strongly correlated systems, the different lattice parameters with the longest a-axis lattice parameter suggest the anisotropic crystal field acting on the Mn site. CO transition associated with the e_g orbital states was influenced through the coupling between orbital and lattice degrees of freedom. For the epitaxial (110)-films, the OO plane is expected to lie out of the film plane.⁹ Surely, in our work, research on the COI distributed image and titled MnO_6 octahedra needs to be carried out, as all the unique properties should be understood in the light of titled MnO_6 octahedra.

SUMMARY

We have synthesised a series of Ca²⁺ doped Bi_{0.4}Sr_{0.6}MnO₃ $(Bi_{0.4}Sr_{0.6-x}Ca_xMnO_3, x = 0.25, 0.3, 0.32, 0.34, 0.35, and 0.4)$ samples, and tuned the T_{CO} near RT by optimally doping of x = 0.32. This doping way provides a suitable temperature range to allow us to study the properties of the manganites across the CO transition near RT. CO transition near RT was observed in Bi_{0.4}Sr_{0.28}Ca_{0.32}MnO₃ films on (110)-STO substrates only above the critical thickness of 40 nm, accompanied with a twin-domains structure, in which [110] axis tilted slightly toward [1-10] and [-110] directions. All these results indicate that the anisotropic stress induced by substrate plays a crucial role in tuning the inhomogeneous structure, which further influences the electronic and magnetic properties in epitaxial manganite thin films. Our works are valuable in order to understand the role of anisotropic epitaxial strain in microscopic origin of the CO phase in doped manganite films and allow studying and designing correlated CO electron devices in RT range for a practical use.

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