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ARTICLE

Influence of Asymmetric Interface Coupling on Properties of $LaCoO_3/LaMnO_3$ Bilayers

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Abstract: The $LaCoO_3/LaMnO_3$ bilayers epitaxial film grown on (100) $SrTiO_3$ substrates were obtained by a simple polymer assisted sol-gel deposition method. Growing a $LaCoO_3$ layer on the top of $LaMnO_3$ leads to the asymmetric interface coupling at the interface layer due to their difference in strucural symmetry, and reduces the ferromagnetic transition temperature caused by the asymmetric interface coupling effect from 262 K to 200 K. In addition, compared with the coercive field of isolated $LaMnO_3$ film, the coercive field observed in the bilayers is increased by ~500% due to a strong ferromagnetic Mn-O-Co double exchange interaction at the interface. The results demonstrate that the recombination of multilayer films with different properties provides a new way to design functional materials for fundamental studies or demanding applications.

Key words: perovskite-type bilayers; ferromagnetic transition; coercive field; interface coupling effect

Fabrication and investigation of perovskite-type multifunctional thin films play an important role in lower power consumption and next generation electronic devices application[1,2]. Previous studies already show that the shape, size, and connection properties of BO_6 octahedron seriously affect the overlap of 3d orbit for transition metal ion and 2p orbit for O^{2-} in perovskite-type materials. Therefore, the electrical, magnetic, and thermal properties of these materials are determined not only by the filling of electron orbits for B-site ion, but also by the size or shape of BO_6 and the connection characteristics[3-8]. In thin film system, the epitaxial strain and multilayer structure effectively influence the B-O bond length (related to the BO_6 shape and size) and B-O-B bond angle (related to the BO_6 connection)[9-13].

Herein, a fabrication method of bilayer heterojunction film with the $LaCoO_3/LaMnO_3$ layers was proposed, and achieved a remarkable enhancement in coercivity at 10 K. The interface coupling effect in bilayers film system plays an important role in this research, providing an effective way to tune the structural characteristics and magnetic coupling of perovskite-based materials for fundamental studies or demanding applications.

1 Experiment

The $LaCoO_3$ (LCO)/$LaMnO_3$ (LMO) bilayers were synthesized by the polymer assisted deposition (PAD) method, as described in the previous literatures[14,15]. Briefly, the metal salts $La(NO_3)_3$ and $Mn(NO_3)_2$ were dissolved in deionized water with ethylene diamine tetraacetic acid (EDTA) and polyethylenimine (PEI) with molecular weight of 70 000 at mixture ratio of 1:1. Then the mixed solution was stirred and condensed to form a ~5 mL precursor in the oil bath at 60 °C. The LCO precursor solution was obtained through the same way. The LMO polymeric film was coated on the (100) oriented $SrTiO_3$ (STO) substrates by the dip-coating method, and then heated and calcined at 900 °C in air to form the solid film. The LCO polymeric film was coated on the LMO layer and annealed at 850 °C to obtain the LCO/LMO bilayers.

A Philip's X'Pert X-ray diffraction (XRD) system with a Cu Kα radiation source was used to characterize the crystallization and the epitaxial quality of the films. The morphological and microstructural properties of the deposited samples were observed by the atomic force microscopy (AFM) and an FEI Sirion 200 field emission scanning electron

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microscope (FESEM). In addition, the low-temperature magnetic properties were recorded by the superconducting quantum interference device magnetometer (Quantum Design MPMS XL-7) and a vibrating sample magnetometer (VSM, Quantum Design).

2 Results and Discussion

2.1 Structure and morphology of films

The XRD $\theta/2\theta$-scan, ω-scan (rocking curve), and φ-scan (asymmetric Bragg reflection) were carried out to detect the crystallinity and epitaxial quality of LCO/LMO bilayers. The typical XRD patterns for the bilayers grown on (100) oriented STO is shown in Fig. 1. Only the peaks of film and substrate are observed in Fig. 1a, indicating that the bilayer film is single phase and has a preferential *c*-axis orientation. The result of out-of-plane ω-scan for the LMO and LCO layer is shown in the inset of Fig. 1a. The small value of full widths at the half maximum (FWHM) for rocking curves indicates a good crystallization of the films. Besides, as shown in Fig. 1b, only one set of peaks spaced 90° apart indicates that there is a tetragonal symmetry in the in-plane texture for (100)-oriented LCO/LMO@STO. According to the XRD $\theta/2\theta$ scan spectrum, the (002) peak of LMO is located at 46.98°, while the (002) peak of LCO is located at 47.93°. Based on Bragg formula, the *c*-axis lattice parameter of LCO layer is 0.379(4) nm. Compared with the *c*-axis lattice parameter for LCO@STO film reported by Liu et al[15], the *c*-axis lattice parameter in this research is larger due to the smaller in-plane tensile strain (a_{LMO}=0.387 nm<a_{STO}=0.3905 nm) and out-of-plane compressive strain. This result suggests that the lattice parameters are sensitive to the epitaxial strain.

The two-dimensional (2D) and three-dimensional (3D) AFM images of surface morphology for LMO and LCO layers are shown in Fig. 2. The surface roughness is 1.9 and 2.1 nm for LMO and LCO layers, respectively. The cross-section image of LCO/LMO bilayers in Fig. 2c reveals that the thickness of LMO and LCO layers is ~20 nm. The AFM and SEM images indicate that the PAD is a simple and effective method to fabricate epitaxial multilayers.

2.2 Magnetic properties of films

The temperature-dependent magnetizations for the films are shown in Fig. 3. The isolated LMO film shows a magnetic

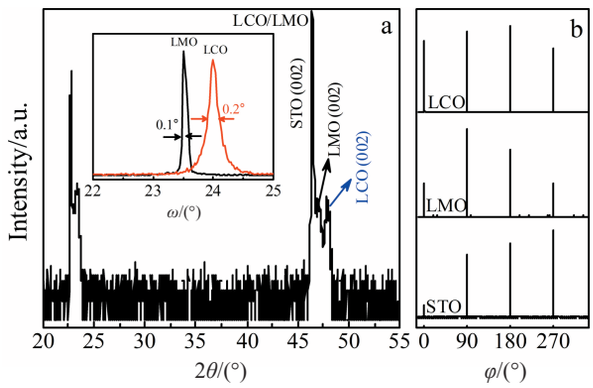

Fig.1 XRD patterns for LCO/LMO@STO: (a) $\theta/2\theta$-symmetric-scan; (b) in-plane φ-scan

transition at T_C=262 K. Growing a thin LCO layer (T_C≈85 K) on the LMO layer reduces the magnetic transition temperature to ~200 K. It is known that the bulk LMO shows orthorhombic symmetry with an O′-type structure (space group Pbnm) and the bulk LCO presents a rhombohedral distortion (space group R-3c). Considering that the octahedrons at interface of bilayers should meet the requirements in co-point and different structural symmetries between the LCO and LMO layers, the degree of tilt/rotation for MnO_6 near interface increases[16,17]. It is suggested that the MnO_6 near interface with more severe distortion is responsible for the decrease in magnetic transition temperature, which is caused by the decrease in Mn-O-Mn bond angle.

It is worth noting that the ferromagnetism (FM, T_C≈85 K) of the isolated LCO layer grown on STO is attributed to a spin-state transition of Co^{3+} induced by epitaxial tensile strain[18]. However, the LCO layer in LCO/LMO bilayers does not show a magnetic transition around 85 K, indicating that there is another factor to influence the magnetic exchange intensity. According to the previous studies, this phenomenon may be related to an interface FM coupling of the LMO and LCO layers[19-21]. In addition the coercive field (H_c) of the bilayers increases dramatically, compared with that of the isolated LMO film, as shown in Fig. 4. The increase in coercive field exceeds 500%. The results of high values of coercive field and T_C of ~200 K were reported for La_2MnCoO_6[22-24]. Due to the

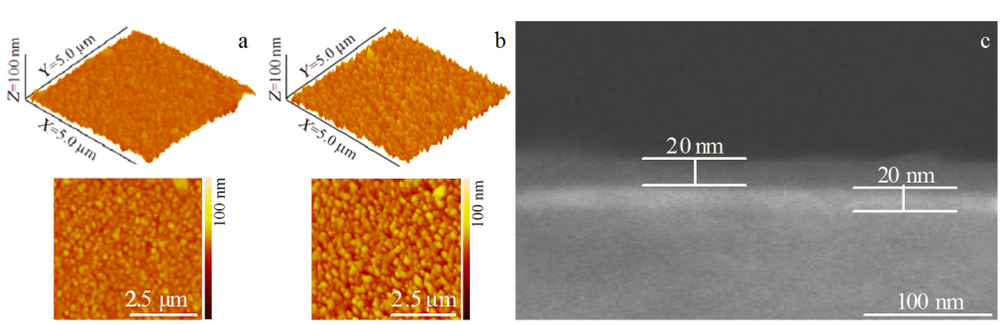

Fig.2 AFM images of LCO (a) and LMO (b) layers; SEM image of cross-sectional LCO/LMO bilayer (c)

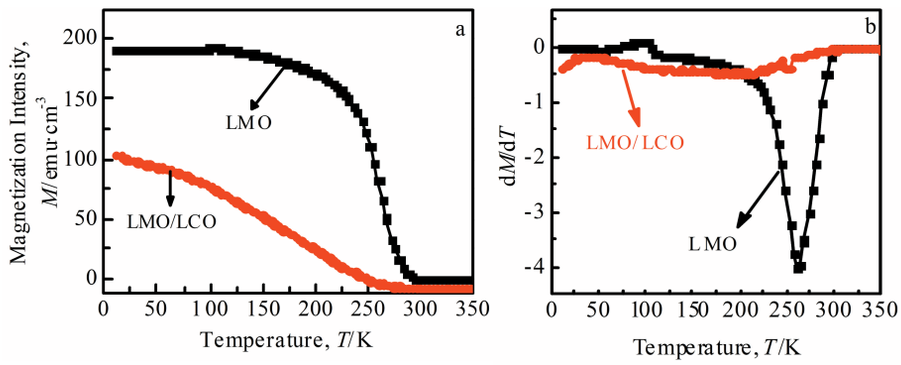

Fig.3 Magnetic properties of LMO single-layer and LCO/LMO bilayer: (a) *M-T* curves and (b) d*M*/d*T*-*T* curves

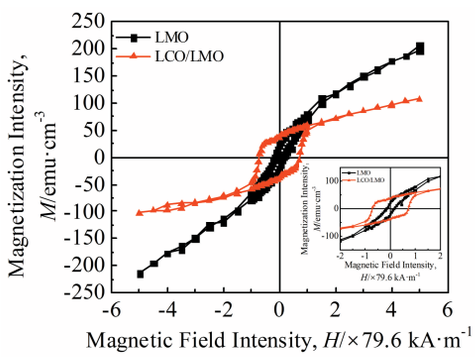

Fig.4 Hysteresis loops of LMO film and of LCM/LMO bilayer film

relative positions of the Mn^{4+}/Mn^{3+} and Co^{3+}/Co^{2+} redox pairs in an oxide atmosphere, the Mn^{3+} and Co^{3+} ions are unstable near the interface. A charge transfer between the Mn^{3+} and Co^{3+} occurs for the Mn^{4+}/Co^{2+} pair with the redox reaction of $Co^{3+}+Mn^{3+} \rightleftharpoons Co^{2+}+Mn^{4+}$. It is suggested that the strong ferromagnetic interaction originates from the Mn^{4+}-O-Co^{2+} double exchange interaction at the interface.

3 Conclusions

1) The high-quality epitaxial oxide heterointerfaces were fabricated by a simple polymer assisted deposition method.

2) The abrupt interfaces from $LaMnO_3$ to $LaCoO_3$ result in the interface charge transfer, which is responsible for the large increase in coercive field.

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非对称界面耦合对$LaCoO_3/LaMnO_3$双层膜性能调控研究

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摘　要：通过高分子辅助溶胶凝胶自旋涂沉积法在（100）取向的$SrTiO_3$衬底上制备出$LaCoO_3/LaMnO_3$双层膜。在$LaMnO_3$表面生长一层$LaCoO_3$膜后，由于二者结构对称性差异，最终会在膜层界面处形成非对称界面耦合。由于非对称耦合作用，双层膜的铁磁转变温度从单层$LaMnO_3$的262 K下降为200 K。此外，由于界面处Mn-O-Co的双交换作用，与单层$LaMnO_3$薄膜的矫顽场相比，双层膜的矫顽场增大了约500%。研究结果表明，不同结构和性质的薄膜重组为多层膜的基础研究和高性能功能材料的应用提供了一种新的结构设计途径。

关键词：钙钛矿型双层膜；铁磁转变；矫顽场；界面耦合作用

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