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Mini Review

Thin Films and Heterojunctions Composed with Electron Doped $La_{1-X}Hf_xMnO_3$ Manganite

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Abstract

All oxide heterojunctions have been fabricated with electron doped $La_{1-x}Hf_xMnO_3$ manganite. The sole tetravalent state of Hf^{4+} ensures a n-type conductive mechanism in $La_{1-x}Hf_xMnO_3$ manganite. $La_{1-x}Hf_xMnO_3$/Nb-$SrTiO_3$ heterojunctions were fabricated. These junctions showed excellent rectifying characteristics in a wide temperature range. Their transport properties are tunable electrically and magnetically. Such heterojunctions may be of potential in developing functional field-effect transistors of manganites.

Keywords: Heterojunctions; Manganite; Field effects; Thin films

Introduction

Most perovskite manganite's are known as p-type conductors which showed variety of features such as colossal magnetoresistance (CMR) and electro resistance (ER) effects [1-5]. A few cases of n-type manganite, substitution of tetravalent ions (e.g. Sn^{4+}; Ce^{4+}; Sb^{4+}; Te^{4+}) for trivalent La ions in $LaMnO_3$ were reported [6-8]. However, there are also arguments on whether it is intrinsically n-type conductive mechanism in these systems due to the existence of multi-valence of these doping elements. To prevent such problems, we tried to dope tetravalent hafnium ion (Hf^{4+}) into manganite oxides to form the n-type manganite [9,10]. The sole tetravalent state of Hf ensures a reliable n-type conductivity in $La_{1-x}Hf_xMnO_3$ (LHMO). XPS and Hall measurements confirmed that a mixed Mn^{2+}/Mn^{3+} state was formed in LHMO film, implying an electron-type conductive mechanism. We further fabricated heterojunctions composed with such a n-type LHMO and Nb-$SrTiO_3$ perovskites.

Heterojunctions were formed by growing LHMO on single crystal of 0.05%Nb-STO (NSTO) using pulsed laser deposition [11-13]. Excimer laser operated at KrF model with a wavelength of 248 nm was employed. The laser frequency was 2 Hz and output energy density were ～2 J/cm^2 [14]. During the deposition the substrate temperature and oxygen pressure were kept at 700 °C and 0.5 mbar, respectively. To avoid possible deficiency of oxygen, the as-grown films were in situ annealed in pure oxygen of 1 atm for a duration of 30 min [15].

The phase structures and epitaxy of the heterostructures were investigated by X-ray diffraction (XRD) including θ-2θ scan and rocking curve measurements [16]. No reflections from the randomly oriented gains and secondary phases like HfO_2 were visible, implying that the grown films were of single phase. Rocking curve of the *(002)* reflection presented a very small value of the full width at half maximum, typically <0.2 degree, indicating a highly epitaxial growth and excellent crystallinity. XPS studies show that the binding energies of the 4f-Hf are nearly identical to the 4f binding energies of HfO_2 and are ~2 eV higher with respect to that of Hf-metal. It clearly reveals that the Hf ions are indeed tetravalent in LHMO film.

Similar to those p-type manganite's, the electron-doped LHMO also demonstrated colossal magnetoresistance (CMR) effect (Figure 1). When the sample is placed in a magnetic field of 2 T, the peak resistance decreased remarkably, leading to a MR~-40% (defined as MR= $[R_H-R_0]/R_H$ 100%). Meanwhile, the M-I phase transition shifted to a higher temperature. Such observations are quite similar to those observed in hole-doped $LaMnO_3$ manganite's, implying a change of magnetic and electronic structure of LHMO in magnetic fields. It shows that the CMR effect is a common feature for both p-type and n-type manganites.

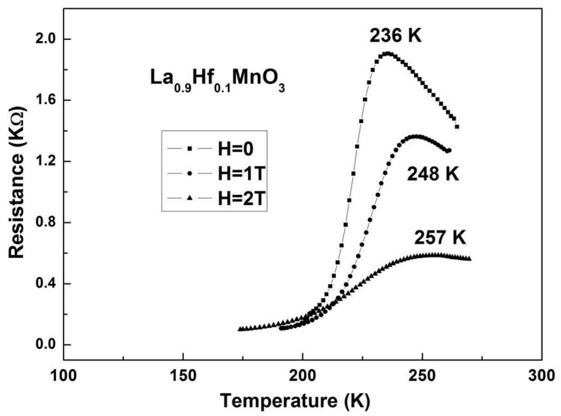

Figure 1: Typical resistance-temperature dependences for LHMO films with or without magnetic fields (B = 0, 1, 2 T).

A typical resistance-temperature dependences for a thin film of LHMO with or without magnetic fields is shown in Figure 1. In the absence of a magnetic field, a metal-insulator (M-I) phase transition took place at ~236 K (Figure 1). Such a M-I phase transition is believed to be close to the PMI-FMM transition temperature (Curie temperature T_C). The R-T curves of this sample in presence of magnetic fields (B = 1, 2 T) are also presented in Figure 1. The M-I transition temperature T_C increases from 236 K to 257 K as the magnetic fields increases from 0 to 2 T. The maximum value of magnetoresistance [MR% = $(R_0—R_H)$ / R_H × 100%] under a magnetic field of 2 T is 303% (as can be seen in Figure 1). The results show that the CMR effect is also a common feature for the n-type manganite [17].

We found that the M-I phase transition can be greatly affected by oxygen deficiency. The MR-T dependence (H = 9 T) for as-grown and annealed LHMO films are shown in Figure 2. The value of MR [We define the magneto resistance as MR = $(R_0–R_H)/R_H$×100%] at the Curie temperature is 350% and 520%, respectively. It clearly reveals that the post-annealing can enhance the CMR effect, indicating the influence of oxygen deficiency. Similar phenomena were also observed in other doped manganites. The inset of Figure 2 shows a typical X-ray diffraction spectrum.

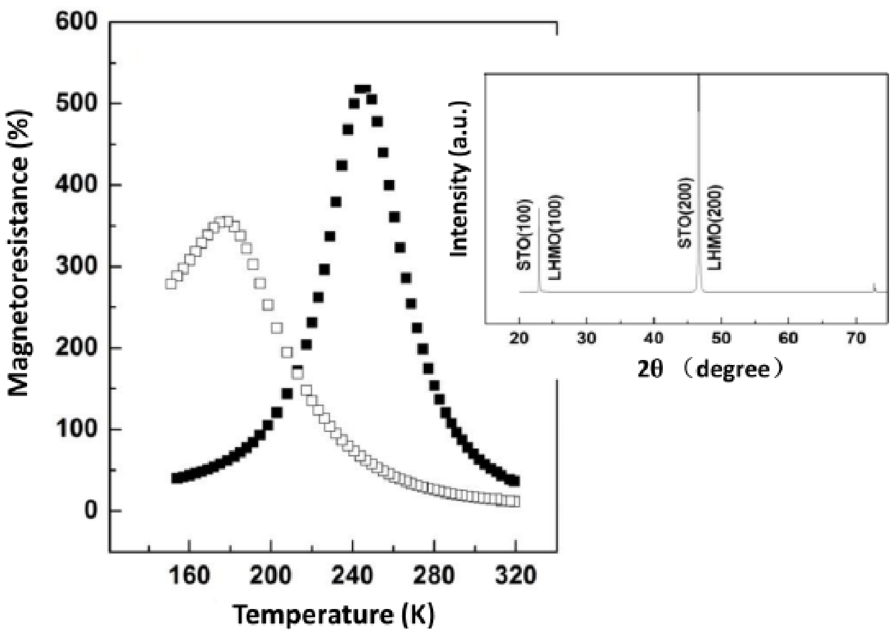

Figure 2: Temperature dependence of magnetoresistance (at H=9 T) for the as-grown (open circle) and annealed (solid circle) 400 nm LHMO films. The inset is the X-ray diffraction spectrum.

The current-voltage (I-V) dependences of the LHMO/STON heterojunction at different temperatures are presented in Figure 3. We defined the positive bias for a current flowing from LHMO film to STON substrate. The *I-V* curves presents a good rectifying behavior for temperature from 60 to 300 K. The observed *I-V* relation mimics that of conventional bipolar junctions. The breakdown voltage (V_b) and diffusion voltage (V_d) increase monotonously as temperature is decreased, indicating that the junction resistance ($R_j = V/I$) depressed as the temperature increased. These are similar to the previous studies on the manganite-based heterojunction. At this moment detailed mechanism for manganite-based heterojunctions is still unclear. Previous studies indicated that the *I-V* relations and transport of these heterojunctions may be interpreted with model of a *p-n* junction or a Schottky junction, i.e. the thermionic emission mechanism. More systematical investigations of the n-type LHMO-based heterojunctions could benefit our understanding of manganite compounds and promote the application of such heterojunctions.

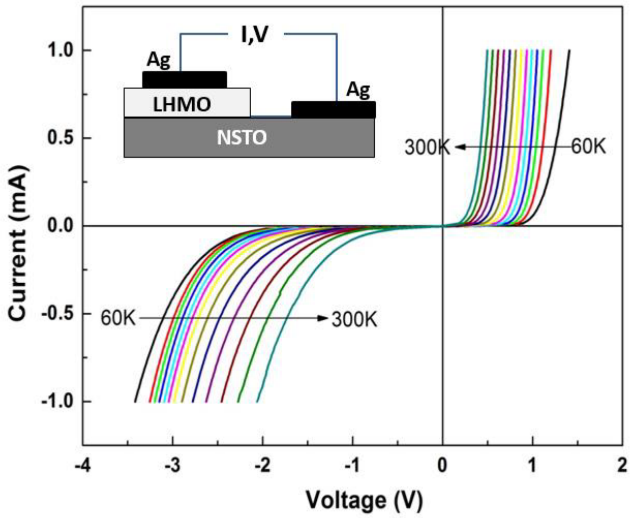

Figure 3: Current-voltage relations of LHMO/STON heterojunction in a wide temperature range from 60 to 300 K at a 20 K interval. The inset is schematic diagram of our heterojunction.

In summary, thin films and heterojunctions of Hf^{4+} doped $LaMnO_3$ manganite have been fabricated and investigated. Such n-type LHMO also showed remarkable CMR effect and M-I phase transition. The oxygen deficiency may play an important role for their CMR effect and phase transition. Heterojunctions composed with the n-type LHMO demonstrated excellent rectifying characteristics.

Acknowledgment

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Conflict of Interest

No conflict of interest.

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