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Original Research

Transport dynamics analysis in ferromagnetic heterojunction using Raman spectroscopy and magnetic force microscopy

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ABSTRACT

The ZnO/$La_{0.7}Sr_{0.3}MnO_3$ thin film was epitaxially fabricated on $LaAlO_3$ (100) by pulse laser deposition. The Raman scattering on the single layer LaSrMnO and junction ZnO/$La_{0.7}Sr_{0.3}MnO_3$ was investigated in a giant softening by 490 cm^{-1} John-Teller, 620 and 703 cm^{-1} optical phonon modes. The Raman spectra LaSrMnO and ZnO/$La_{0.7}Sr_{0.3}MnO_3$ were observed with distinct features, i.e., the thickness was in dependent of frequency and intensity. The dynamics results showed that the spin–orbital coupling was caused by anomalies tilt of MnO_6 octahedron. The LSMO/ZnO junction exhibited excellent junction positive magneto-resistance behavior in the temperature range of 77–300 K. The kinetic energy gain was achieved by orbital competition, strong crystal field and charge order of energy band splitting. The transport orbits were in the environment of the ferromagnetic-orbital ordering. The structures of barriers could be adjusted by junction interface and domain boundary condition in terms of the presence of spin–orbital fluctuating.

1. Introduction

The doped manganese oxides $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) shows competition coupling of spins, charge, orbital, and lattice order of freedom, and leads to a mount of phase transition [1–2,4–7]. The single layer $La_{0.7}Sr_{0.3}MnO_3$ is an ideal candidate because of its pronounced two-dimensional structure and magnetoresistance (MR) effect [3]. The orbital transport is coupled to lattice in a low dimensionality. ZnO simultaneously with a wide band gap (3.37 eV) and large exciton binding energy (60 meV) potentially possesses the characteristics of ultraviolet wavelength, high efficiency, lower power, light emitting and laser diodes. This can generate either more promising function or orbital degeneracy. The heterojunction ZnO/$La_{0.7}Sr_{0.3}MnO_3$ nanostructure is a good candidate for fabrication of nanometer-sized optoelectronic devices in ferromagnetic semiconductor [8,9], multilevel resistive switching [10], positive colossal magnetoresistance [11,12], colossal electroresistance [13], manganite tunnel junctions [14], high magnetic sensitivity [15], and ultraviolet fast-response [16]. Moreover, the oxides ZnO/$La_{0.7}Sr_{0.3}MnO_3$ with different carrier transfer and doping lever has recently been carried out.

In this paper, the transfer of $d_{x^2-y^2}$ orbits dynamics coupled to ferro-orbital order state of crystal and carrier transport near the Curie temperature Tc were studied. We measured the SERS (Surface-enhanced Raman scattering spectrum) of LSMO and ZnO thin films. The depletion layer of heterojunction controlled the interface properties. The lattice vibration was observed, and the Raman spectra of crystal lattice vibration modes could reveal ferroelectric transition phase of spin polarization and dielectric properties information. The La/Sr doping ratio, gain size of film and micros-powder, calcined condition, and lattice matching in the LSMO and ZnO thin films heterojunction took effect on phonon frequencies and the direction of lighting. The crystal lattice vibration modes of Raman spectra can reveal the ferroelectric phase transition of spin polarization and dielectric properties information. By changing temperature, film thickness and area, we measured the soft mode frequency to determinate lattice vibration modes, and studied temperature-resistance and the critical size of grain boundary of the heterojunction.

2. Experimental

The crystals of $La_{0.7}Sr_{0.3}MnO_3$ and ZnO were prepared from the analytically pure oxides appropriate stoichiometric proportion by solid state reaction, respectively. The multilayer thin films were annealed at 800 °C with an oxygen pressure 6 Pa for 5 h in order to get better epitaxial character and oxygen doped deposit. The substrate was maintained at 700 °C during the deposition process and then cooled down to room temperature. The LSMO and ZnO layers were successively deposited on the single-crystal LAO (100) substrate by pulse laser deposition. The heterojunction thin film

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was placed in a JanisCCS-300 closed-circuit refrigerator cryostat and the measured temperature ranged from 50 to 350 K. The magnetic field of 0.1, 0.3, and 0.5 T was supplied perpendicularly to the heterostructure. Raman spectra were measured in a quasi-back scattering with the excitation line $\lambda = 514$ nm of Ar laser, 325 nm of solid-state laser, the power of 8 MW. The spectrums were collected by Raman spectrometer (HR800, HORZBA, Jobin Yvon) and a nitrogen cooled charge-coupled device detector. The ZnO film about 75 nm (estimated by profilometer) was masked on $La_{0.7}Sr_{0.3}MnO_3$ (100). The heterojunction had been extensively characterized using XRD, neutron, magnetization, thermal expansion, and magnetoresistivity measurements. The phase structures of the target and orientation of the deposited film were studied by x-ray diffraction.

3. Results and discussions

According to previous researches [17–24] the LSMO has a rhombohedral structure with the R3C space group with O(1) in-plane and O(2) apical oxygen sites as some high-Tc cuprates. The LaO_2 and SrO_2 planes are stacked along a-b axis and separated by the MnO_2 planes as the result of a ferromagnetic-orbital ordering of orbital d_3z^2-r^2 and C-type anti-ferromagnetic (AF) spin ordering below $T = 117$–127 K. Ferroelectric ZnO contains transition metal ions with unpaired *d* electrons. The presence of the *d* electrons can result in a relatively small gap and give rise to a concentration of charged impurities and defects [25]. The question is whether the spin–orbital degrees of freedom are a relevant parameter to describe the properties of $ZnO/La_{0.7}Sr_{0.3}MnO_3$ characteristics.

The LSMO/ZnO heterojunction was characterized by x-ray diffraction pattern, and the results are shown in Figs. 1 and 2. For the LSMO space group R3C, the factor group analysis conformed four Raman-active phonon modes. The Mn^{3+}–O–$Mn^{4+}$and $La(Sr)O_2$ extending modes stretched along the c axis with A_{1g} symmetry. The laser confocal micro Raman spectrometer (HR800 HORZBA, Jobin Yvon), laser light source, were used for the tests with the 325 nm UV laser and optical laser of 514 nm, respectively. The O (2) and La(Sr) vibrations were measured by shifting along the *a* and *b* axis with E_g symmetry.

The spin polarization transport of double exchange mechanics was observed in metal insulate transition, where the substitution

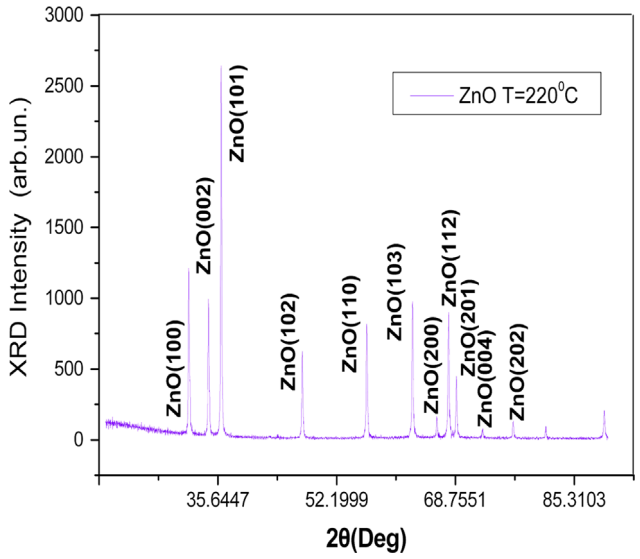

Fig. 1. X-ray diffraction of ZnO.

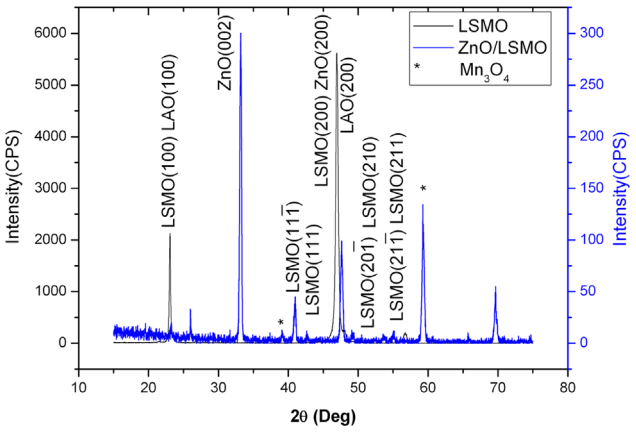

Fig. 2. X-ray diffraction of $ZnO/La_{0.7}Sr_{0.3}MnO_3$/LAO. X-ray diffraction pattern of $ZnO/La_{0.7}Sr_{0.3}MnO_3$/LAO heterostructure. The insets show the (100) and (200) peaks of the LSMO film and LAO substrate.

of divalent alkaline earth element leads to the mixed valence state of Mn:$Mn^{3+}t_{2g}$ 3d and $Mn^{4+}t_{2g}$ 3d. The orbital occupation of diluted $d_{x^2-y^2}$ driven by temperature was in the background of crystal field $d_{3z^2-r^2}$. It is so called spin coupling strongly to the lattice. Moreover, the Mn^{3+}–O^{2-}–Mn^{4+} coupling generates strong ferromagnetic correlation through the charge hopping leading to the anomalous magnetization. The coupled JT effect blurs e_g bands and allows the $Mn^{3+}e_g$ electrons to hop into the empty orbital states [10].

The diffraction peaks of $La_{0.7}Sr_{0.3}MnO_3$/ZnO were matched with the LAO substrate (lattice constant 0.38769 nm) when the lattice constants are 0.386 and 0.379 nm respectively. The LSMO/ZnO structure was characterized by x-ray diffraction pattern shown in Figs. 1 and 2. The inset indicates that the $La_{0.7}Sr_{0.3}MnO_3$ (100) and (200) diffraction peaks occurred at $2\theta = 23°$ and $2\theta = 47°$, while the ZnO (002) (102) (004) diffraction peaks occur at $2\theta = 34°$, $2\theta = 47°$ and $2\theta = 69.7°$, respectively. The results indicate that both the $La_{0.7}Sr_{0.3}MnO_3$ and ZnO thin films both have better epitaxial character. The ZnO film is $2\theta = 34°$ for the (002) orientation with the structure of a hexagonal wurtzite at 220 °C.

Fig. 3 displays AFM results of $ZnO/La_{0.7}Sr_{0.3}MnO_3$/LaAlO. Fig. 4 shows the phonon modes dependence of frequencies and number at 192, 210, 325, 430, 649 cm^{-1}, which rule out impurities and defects as a possible origin. The force microscopy image and further magnetic force microscopy image indicate the interface effect and small effect sizes. The gain size and phase gain boundary take effects to the ferroelectric coupling and mechanical–electrical coupling properties. From LaSrMnO and ZnO of Raman spectra shift, Raman scattering spectrum has four peak at 150, 220, 490, 620 and 703 cm^{-1} in situ growth of LSMO films. The group analysis yields four Raman active phonon modes: Mn–O(2) and (La, Sr)–O(2) stretching modes have shifted along the *c* axis with A_{1g} symmetry, and O(2) and (La,Sr) vibrations displace along the *a* and *b* axes with Eg symmetry. It is shown that LaSrMnO E (TO_1) soft mode is in the first Brillouin zone. LaSrMnO Raman spectrum contains ten kinds of typical single mode E (TO_1), E (LO_1), B_1+E, E

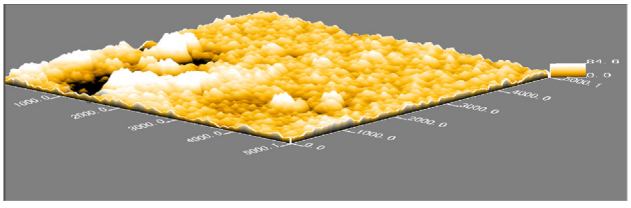

Fig. 3. The atom force microscopy image of surface morphology $ZnO/La_{0.7}Sr_{0.3}MnO_3$/LAO.