南京大学

研究生毕业论文

（申请　士学位）

论文题目 _____

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作者姓名 XXX

学科、专业名称 凝聚态物理学

研究方向 团簇物理学

指导教师 XXX　教授

2013 年 12 月 30 日

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Magnetoelectric coupling in oxide-based multiferroic composite film

by ×××

Supervised by Prof. ×××

Department of Physics, Nanjing University

National Laboratory of Solid State Microstructures

2010 硕

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$CoFe_2O_4/Pb(Zr_{0.52}Ti_{0.48})O_3$ (CFO/PZT)

0-3 CFO/PZT CFO PZT

CFO PZT

40nm CFO PZT CFO

CFO

CFO

CFO

PZT CFO

PZT

$SrTiO_3/(Co_{0.9}Zn_{0.1})Fe_2O_4$ (STO/CZFO)

$Pt/Ti/Si/SiO_2$ STO

STO/CZFO STO CZFO (002) (311) STO

0.7% CFO CZFO

Zn^{2+} Co^{2+}

P_r 5.3μC/cm^2

CZFO Fe^{3+} STO

CZFO STO STO/CZFO STO

CZFO STO STO/CZFO STO

$Pb(Zr_{0.2}Ti_{0.8})O_3/(La_{0.67}Ca_{0.33})MnO_3$ (PZT/LCMO)

PZT/LCMO/PZT/LCMO/PZT

PZT LCMO 20 nm 240 K

240 K

LCMO Curie 245 K PZT/LCMO

PZT/LCMO Mn^{3+} e_g PZT/LCMO

P_r 35 μC/cm^2

PZT

PZT

PZT-LCMO PZT

PZT PZT-LCMO

$Pb(Zr_{0.52}Ti_{0.48})O_3/CoFe_2O_4$ (PZT/CFO)

PZT/CFO/PZT

CFO PZT

Richter

CFO PZT CFO

CFO

THESIS: Magnetoelectric coupling in oxide-based multiferroic composite film

SPECIALIZATION: Condensed Matter Physics

POSTGRADUATE: ×××

MENTOR: Prof. ×××

The multiferroic composite film is comprised of magnetic component and ferroelectric component, which connect with each other in nanoscales. Besides of magnetism and ferroelectricity, obvious magnetoelectric coupling exists in multiferroic composite film, i.e., the response of ferroelectricity to magnetic field, or the response of magnetism to electric field. Due to the magnetoelectric coupling, the multiferroic composite film is helpful to achieve transferring electromagnetic signal, recording multi-state bit and so on, which is a hotspot of condensed matter physics recently. Therefore, our work is focused on the oxide-based multiferroic composite film. Firstly, we study the magnetoelectric coupling in graded $CoFe_2O_4$/$Pb(Zr_{0.52}Ti_{0.48})O_3$ (CFO/PZT) particulate composite film; secondly, we study the anisotropic magnetic-

in-plane, the Ampere circuit law requires the magnetic intensity is continuous in the whole film. The graded distribution of CFO particles enhances the ferroelectric polarization and dielectric constant of the composite film, which is attributed to the local concentration of electric field. Furthermore, the graded distribution of CFO particles enhances the magneto-dielectric effect on the composite film. Such enhancement results from two factors: under electric field, the graded distribution of CFO particles enhances the ferroelectric polarization and dielectric constant of PZT matrix, which consequently leads to the enhanced piezoelectricity in PZT matrix; under magnetic field, the graded distribution of CFO particles generates strain gradient in the PZT matrix, which consequently induces additional flexoelectricity in the PZT matrix. Because the sign of flexoelectric polarization depends on the gradient direction, the enhancement of magneto-dielectric effect relies on the gradient direction.

The 2-2 type STO/CZFO/STO composite film is fabricated by sol-gel method. The thickness of upper STO layer, CZFO layer and bottom STO layer is 60 nm, 120 nm, and 100 nm respectively. The STO layer and CZFO layer are grown along (002) direction and (311) direction, respectively, while the volume expansion of STO unit cell is 0.7%. Compared with CFO film, the CZFO layer displays stronger magnetization and lower coercive field, which is attributed to the partly substitute of Co^{2+} ion by Zn^{2+} ion. The heterostructure film displays room-temperature ferroelectricity, with P_r = 5.3 μC/cm^2; meanwhile the film is insulating. Such ferroelectricity results from defect dipole, which is generated as follow: during the annealing process, some Fe^{3+} ions in CZFO layer can immigrate into the STO layer and form the acceptor centre; when the oxygen vacancies combine with the acceptor centre, the defect dipole in generated. Under in-plane and out-of-plane magnetic field, the ferroelectric polarization is decreased and increased respectively, while the dielectric constant is also decreased and increased respectively. Such anisotropic magnetic-modulation of ferroelectric polarization is attributed to the coupling between magnetostriction and defect dipole. Under in-plane magnetic field, the magnetostrictive strain of CZFO layer can reduce the volume expansion of STO unit cell, consequently some defect dipole will degenerate to

expansion

The 2-2 type PZT/LCMO/PZT/LCMO/PZT composite film is fabricated by sol-gel method. Each layer is as thick as 20 nm. Only perovskite PZT phase and perovskite LCMO phase exist in the heterostructure film. Under 240 K, composite film displays anisotropic ferromagnetism; above 240 K, composite film displays isotropic ferromagnetism. Because the Curie temperature of pure LCMO film is 245 K, the room-temperature ferromagnetism should exist on the PZT/LCMO interface, which results from the coupling between magnetic polaron and ferroelectric domain. In detail, when the dipole moment of certain ferroelectric domain points toward the PZT/LCMO interface, the e_g electrons will be accumulated on the PZT/LCMO interface, which induces the room-temperature ferromagnetism of composite film. Composite film displays strong ferroelectricity, with P_r = 35 μC/cm^2. Due to the tunneling current, the conductance of composite film is much higher than that of pure PZT film. When the voltage is below coercive voltage, composite film displays evident magnetoresistance, and the magnetoresistance is reduced as increasing the voltage; when the voltage reaches coercive voltage, the magnetoresistance immediately vanishes. Such switchable electric-modulation of tunneling magnetoresistance is attributed to the rotation of ferroelectric domain. When the voltage is below coercive voltage, two separate ferroelectric domains in the PZT layer, with its dipole moment pointing toward upper PZT/LCMO interface and bottom PZT/LCMO interface respectively, will induce ferromagnetic LCMO clusters on the upper PZT/LCMO interface and bottom PZT/LCMO interface respectively. Consequently, PZT layer and the two ferromagnetic LCMO clusters will form tunneling junction, which allows the tunneling magnetoresistance. When the voltage reaches coercive voltage, all the ferroelectric domain will be polarized along electric field, and the ferromagnetic LCMO clusters only exist on one PZT/LCMO interface. Under this circumstance, there is no tunneling junction in the composite film, and the tunneling magnetoresistance vanishes.

The 2-2 type PZT/CFO/PZT composite film is fabricated by sol-gel method, and several magnetizing cycles are applied on the composite film. After the cycling, some oxygen vacancy has immigrated from CFO layer to PZT layer. After the cycling, the magnetization of CFO layer is enhanced obviously, which is in close relationship with the Richter delay. In detail, the Richter delay induces the immigration of oxygen vacancy during the cycling process, which enhances the double exchange strength of CFO layer. After the cycling, the ferroelectricity of PZT layer

keeps unchanged. After the cycling, both the magnetoelectric voltage and magneto-polarization is enhanced, which results from the enhanced double exchange of CFO layer. In detail, due to the enhanced double exchange, the quasi dipole-dipole interaction and quasi quadrupole-quadrupole interaction of CFO layer is enhanced, which results the enhanced magnetic anisotropy and magnetostriction of CFO layer.

Key Word: multiferroic composite film, magnetoelectric coupling, magneto-dielectric effect, magnetoresistance effect

(1) Journal of the American Ceramic Society, 2013

(2) Journal of Applied Physics, 2013 (accepted)

(3) Physical Review B, (under review)

(1) Nanotechnology, 2013

(2) Applied Physics Letters, 2012