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南京大学硕士学位论文

多铁氧化物复合薄膜的磁电耦合特性及其调控

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Magnetoelectric coupling in oxide-based multiferroic composite film

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南京大学研究生毕业论文中文摘要首页用纸

毕业论文题目：多铁氧化物复合薄膜的磁电耦合特性及其调控

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多铁复合薄膜是由磁性体和铁电体在介观尺度上通过一定连通方式复合而成的薄膜。由于磁性相与铁电相之间较强的耦合作用，多铁复合薄膜一般呈现出较强的磁电耦合效应，因而在电-磁信号/能量变换、多态信息存储等电磁集成器件中具有广阔的应用前景，是当前多铁性材料学和凝聚态物理学等领域的前沿研究方向之一。但是，由于衬底约束等因素，目前多铁复合薄膜的磁电耦合作用普遍较弱，这是一个亟需解决的问题。

本论文拟针对若干种多铁氧化物复合薄膜，在制备方法、微结构表征、磁学、电学以及磁电耦合特性测量的基础上，系统研究相关复合薄膜的磁电耦合效应及其调控。全文的主要研究内容和结果如下：

$\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (CFO/PZT)梯度复合薄膜的制备与磁电耦合特性。采用共沉淀法和溶胶-凝胶法，成功制备出 0-3 型 CFO/PZT 梯度复合薄膜，其中 CFO 粒子在 PZT 基体中沿薄膜厚度方向呈现出梯度分布。复合薄膜中只存在尖晶石 CFO 相和钙钛矿 PZT 相。直径为 40nm 的 CFO 粒子均匀分布在结构致密的 PZT 基体中。CFO 粒子的梯度分布导致复合薄膜出现磁各向异性，且易磁化方向在面内。CFO 粒子的梯度分布还明显提高了复合薄膜的铁电极化和介电常数。最重要的是，CFO 粒子的梯度分布增强了复合薄膜的磁介电效应。这种磁介电效应的增强源于两个因素：一方面，CFO 磁性粒子的梯度分布造成 PZT 基体中电场的不均匀分布，从而导致其铁电极化的增强；另外一方面，CFO 粒子的应变梯度导致了在磁场作用下 PZT 基体的弯电铁电极化效应。此外，还发现磁介电效应的增强幅度与梯度方向密切相关，这主要是因为弯电铁电极化的方向与应变梯度的方向有关。

$\text{SrTiO}_3/(\text{Co}_{0.9}\text{Zn}_{0.1})\text{Fe}_2\text{O}_4$ (STO/CZFO)异质结薄膜的制备以及磁场对其铁电极化各向异性的调制。采用溶胶-凝胶法，在 Pt/Ti/Si/SiO₂ 晶片上成功制备出以 STO 层为缓冲层的 STO/CZFO 异质结薄膜。STO 层和 CZFO 层分别沿(002)和(311)方向择优取向，同时 STO 晶胞的体积扩张率为 0.7%。观察到异质结的磁化强度高于 CFO 薄膜，这主要归结为 CZFO 晶胞中 Zn²⁺离子对 Co²⁺离子的部分取代。观察到异质结薄膜呈现出明显的室温铁电性，其

剩余极化 P_r 值约为 $5.3\mu\text{C}/\text{cm}^2$ 。异质结薄膜的铁电极化起源于 $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ 缺陷偶极子，其形成机制是：在高温热退火过程中 CZFO 层的少量 Fe^{3+} 离子扩散到 STO 层中而形成 Fe'_{Ti} 受体中心，当氧空位与 Fe'_{Ti} 受体中心结合时即可构成 $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ 缺陷偶极子。观察到异质结薄膜的铁电极化在不同方向的外磁场作用下呈现出不同的变化规律：在面内磁场和离面磁场下，异质结薄膜的电极化值分别表现出减小和增大，同时其介电常数也分别减小和增大。这种外磁场对电极化值的各向异性调制作用起源于缺陷偶极子与磁致伸缩的相互作用。在面内磁场作用下，从 CZFO 层传递到 STO 层的应变会减小 STO/CZFO 界面上的 STO 晶胞体积扩张率，从而导致部分 $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ 缺陷偶极子分解为自由氧空位与 Fe'_{Ti} 受体中心；在离面磁场作用下，从 CZFO 层传递到 STO 层的应变会增大 STO/CZFO 界面上的 STO 晶胞体积扩张率，从而导致部分自由氧空位与 Fe'_{Ti} 受体中心结合成 $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ 缺陷偶极子。

$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3/(\text{La}_{0.67}\text{Ca}_{0.33})\text{MnO}_3$ (PZT/LCMO) 异质结薄膜的制备以及电场对其隧道磁电阻的调控。采用溶胶-凝胶法制备了 PZT/LCMO/PZT/LCMO/PZT 多层异质结薄膜，每一 PZT 层和 LCMO 层的厚度均为 20 nm。磁性测量结果表明：在 240 K 以下，异质结薄膜表现出各向异性的铁磁性；在 240 K 以上，异质结薄膜表现出各向同性的铁磁性。由于纯 LCMO 薄膜的 Curie 温度为 245 K，异质结薄膜的室温铁磁性只存在于 PZT/LCMO 界面上。这种室温铁磁性起源于磁极化子与铁电畴的相互作用，即：当铁电畴的极化方向指向 PZT/LCMO 界面时，由于电荷屏蔽作用， Mn^{3+} 离子的 e_g 电子在 PZT/LCMO 界面上积累，进而导致室温铁磁性。异质结薄膜表现出明显的铁电性，其 P_r 值为 $35\mu\text{C}/\text{cm}^2$ 。另外，当电压高于一定值时，由于隧穿电流的影响，异质结薄膜的电导率明显高于纯 PZT 薄膜。观察到异质结的磁电阻呈现出明显的电场开关效应，这种电压对磁电阻效应的开关调制作用来源于铁电畴对磁隧道结的影响：当电压低于铁电矫顽电压时，PZT 层中向上极化和向下极化的铁电畴分别导致上端和下端 PZT-LCMO 界面附近的铁磁性簇，相应地 PZT 层与其两端的铁磁性簇将形成磁隧道结结构，进而导致其磁电阻效应；当电压高于铁电矫顽电压时，PZT 层中沿电场方向极化的铁电畴只能导致一端 PZT-LCMO 界面附近的铁磁性簇，此时磁隧道结无法形成，因此异质结的磁电阻效应趋于零。

循环磁化过程对 $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/\text{CoFe}_2\text{O}_4$ (PZT/CFO) 异质结薄膜磁电耦合特性的调控。采用溶胶-凝胶法制备了 PZT/CFO/PZT 异质结薄膜，并对异质结薄膜进行循环磁化处理。结果表明，循环磁化可导致部分氧空位从 CFO 铁磁层迁移到 PZT 铁电层。在经历一定次数的循环磁化后，铁电性并没有发生明显变化，但是其磁性有明显增强，同时其磁电电压输出和磁致铁电极化均表现出明显增强。基于 Richter 磁后效机制，我们对此实验结果进行

了合理解释：当部分氧空位从 CFO 层迁移到 PZT 层时，CFO 层的双交换作用被增强，进而增大了 CFO 层的磁各向异性度和磁致伸缩应变。

关键词：多铁复合薄膜、磁电耦合效应，磁介电效应、磁电阻效应

南京大学研究生毕业论文英文摘要首页用纸

THESIS: Magnetolectric 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 magnetolectric 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 magnetolectric 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 magnetolectric coupling in graded $\text{CoFe}_2\text{O}_4/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (CFO/PZT) particulate composite film; secondly, we study the anisotropic magnetic-modulation of ferroelectric polarization in $\text{SrTiO}_3/(\text{Co}_{0.9}\text{Zn}_{0.1})\text{Fe}_2\text{O}_4$ (STO/CZFO) heterostructure film; thirdly, we study the switchable electric-modulation of tunneling magnetoresistance in $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3/(\text{La}_{0.67}\text{Ca}_{0.33})\text{MnO}_3$ (PZT/LCMO) heterostructure film; finally, we study the influence of magnetizing cycles on magnetolectric coupling in $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/\text{CoFe}_2\text{O}_4$ (PZT/CFO) heterostructure film.

The graded CFO/PZT particulate composite film is fabricated by coprecipitation method and sol-gel method, where the distribution of CFO particles in PZT matrix is graded along the thickness direction. Only the perovskite PZT phase the spinel CFO phase exist in the composite film. The CFO particles with diameter = 40 nm are clearly dispersed in the compact PZT matrix. The graded distribution of CFO particles induces magnetic anisotropy in the composite film, with the easy axis along in-plane direction. Such magnetic anisotropy is explained by the magnetic continuous rule: when the magnetic field is out-of-plane, the magnetic Gauss law requires the magnetic induction is continuous in the whole film; when the magnetic field is

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 $P_r = 5.3 \mu\text{C}/\text{cm}^2$; meanwhile the film is insulating. Such ferroelectricity results from $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ 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 Fe'_{Ti} acceptor centre; when the oxygen vacancies combine with the Fe'_{Ti} acceptor centre, the $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ defect dipole is 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 $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ defect dipole will degenerate to Fe'_{Ti} acceptor centre and oxygen vacancy. Under out-of-plane magnetic field, the magnetostrictive strain of CZFO layer can enhance the volume expansion of STO unit cell, consequently some Fe'_{Ti} acceptor centre and oxygen vacancy will integrate to $\text{Fe}'_{\text{Ti}} - \text{V}_\text{O}$ defect dipole.

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 $P_r = 35 \mu\text{C}/\text{cm}^2$. 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

正文部分

已发表与待发表的论文

第一作者论文:

(1) Journal of the American Ceramic Society, 2013

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

(3) Physical Review B, (under review)

第二作者论文:

(1) Nanotechnology, 2013

(2) Applied Physics Letters, 2012

致谢（盲审阶段，暂时隐去）