Strain-induced robust magnetic anisotropy and room temperature magnetoelectric coupling effect in epitaxial SmFeO_3 film

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ABSTRACT Rare-earth orthoferrite SmFeO_3 is an outstanding single-phase multiferroic material, holding great potential in novel low-power electronic devices. Nevertheless, simultaneous magnetic and ferroelectric orders as well as magnetoelectric (ME) coupling effect at room temperature (RT) in this system have not been demonstrated yet. In this study, epitaxial SmFeO_3 films were successfully prepared onto tensile-strain Nb-SrTiO_3 (Nb-STO) substrates by a pulsed laser deposition (PLD) method. Measurement results show that the films exhibit obvious ferromagnetic and ferroelectric orders at RT. Meanwhile, the magnetic anisotropy gradually changes from out-of-plane (OP) to in-plane (IP) direction with increasing film thickness, which is attributed to the variations of O 2p-Fe 3d hybridization intensity and Fe 3d-orbit occupancy caused by the strain-relaxed effect. Moreover, electrically driven reversible magnetic switching further proves that the SmFeO_3 films exhibit the RT ME coupling effect, suggesting promising applications in new-generation electric-write magnetic-read data storage devices.

Keywords: SmFeO_3 film, multiferroicity, magnetoelectric coupling, magnetic anisotropy

INTRODUCTION

Single-phase multiferroics, presenting the coexistence of ferroelectric and magnetic orders simultaneously, have been considered as one class of the most promising materials because of their vast application potential in spintronic devices, information storage, sensors, etc. [1–

6]. However, traditional theory holds that the two orders have incompatible occupation rules and thus lead to extremely rare multiferroic materials in nature [7]. Recently, spin-induced improper ferroelectricity has been widely explored in some oxide materials [8–11]. In such systems, the ferroelectric and magnetic orders bind each other and may exhibit strong magnetoelectric (ME) coupling effect. In order to explain the origin of the magnetically induced ferroelectricity, a large number of theoretical models were proposed one after another, such as reverse Dzyaloshinskii-Moriya (D-M) interaction [12], spin-dependent p - d hybridization and exchange striction mechanism [13,14]. So far, numerous single-phase multiferroic materials have been found, such as (Y, Sr, Gd, Dy, Tb, Ho, Lu) MnO_3 films [15–18], (Dy, Gd, Tb, Ho, Er, Lu) CrO_3 films [19–23], (Gd, Dy, Yb) FeO_3 films [24–26], EuTiO_3 films [27], hexaferrite $\text{Ba}_{2-x}\text{Sr}_x\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ single crystal [28], and LaFeO_3 polycrystal [29]. Despite rich characteristics and fascinating physics, the low working temperature and weak saturation magnetization (M_s) restrict the practical applications of these materials. In addition, some nanocomposite single-phase systems were also studied. For example, room temperature (RT) multiferroic properties were found in the PbTiO_3 - SmFeO_3 film and BiFeO_3 - PbTiO_3 single crystal [30,31], but the ME coupling effect was rather weak because the magnetic and ferroelectric orders respectively arose from different ions. Therefore, exploring new single-phase multiferroic materials with high temperature, large M_s as well as strong

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ME coupling effect have become a topical research field.

Parts of rare-earth orthoferrite materials, possess high Neel temperature (T_N) of around 700 K and large ME coupling effect at RT, making them the most potential candidates in the microelectronic field. As a typical representative, the hexagon-strained LuFeO_3 film with a $P6_3cm$ structure has been reported, revealing that the polar structure could persist up to 1050 K, and an anti-ferromagnetic order was also observed below 440 K, the mechanism might be related to strain-induced asymmetric $\text{Lu } 5d_z^2\text{-O } 2p_z$ hybridization [32]. However, bulk- LuFeO_3 single crystal with an orthorhombic-stabilized $Pbnm$ structure lacked such properties. Additionally, orthorhombic SmFeO_3 (SFO) was also studied and its bulk single crystal had no ferroelectric order [33], but the film revealed an obvious multiferroic characteristic [34]. Regrettably, the magnetic transition temperature was around 185 K and below RT, which is the only report on the multiferroic property of the film-style SFO until now to the best of our knowledge. Subsequently, a large number of models have been proposed to explain the ferroelectricity of SFO. Johnson *et al.* [35] concluded that the exchange striction mechanism was relevant to the manifestation of the improper ferroelectricity. Lee *et al.* [36] illustrated that the reverse D-M interaction dominated over the exchange striction mechanism in the realization of the improper ferroelectricity. However, recent studies have confirmed that the ferroelectricity should originate from structural distortion [34]. Although many reasonable explanations have been considered, the physical mechanism of ferroelectricity in SFO is still controversial and needs to be further explored.

In this work, we choose SFO material as an object and prepare the films of different thicknesses on the 0.7 wt% Nb-SrTiO₃ (Nb-STO) substrates which are subjected to an in-plane (IP) tensile strain. The RT ferromagnetic order appears and the magnetic anisotropy gradually transforms from out-of-plane (OP) to IP direction with increasing film thickness. Combining O *K*-edge X-ray absorption spectra (XAS) with Fe *L*-edge X-ray linear dichroism (XLD) analyses, we propose that the changes of occupancy state of Fe-3d orbits together with O 2p-Fe 3d hybridization intensity caused by the strain-relaxed effect, force a tremendous manipulation in the magnetic anisotropy of SFO films. Moreover, the ferroelectricity of the films is confirmed *via* polarization-electric field (P-E) loops and piezoresponse force microscopy (PFM) phase images. Furthermore, the electrically driven reversible magnetic switching demonstrates an obvious RT ME coupling effect in the SFO films, implying a broad application prospect in

the novel generation of magnetoelectricity devices.

EXPERIMENTAL SECTION

Orthorhombic SFO films with various thicknesses were fabricated onto atomically flat Nb-STO substrates (denoted as Nb-STO/SFO film) by a reflection high-energy electron diffraction-assisted pulsed laser deposition (PLD) system using a KrF excimer laser ($\lambda=248$ nm). During the deposition, the laser energy was stabilized at 350 mJ and the frequency was repeated at 10 Hz. The dynamic flowing oxygen pressure and substrate temperature were kept at 30 mTorr (1 Torr $\approx$ 133.3 Pa) and 725°C, respectively. Subsequently, the films were annealed *in-situ* at the same temperature and an oxygen pressure of 700 Torr for 1.5 h to further reduce oxygen vacancies and then cooled to RT at a rate of 15°C/min. The crystal orientation and microstructure of the films were determined by X-ray diffraction (XRD) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The magnetic characterization was performed by using a Quantum Design vibrating sample magnetometer in physical property measurement system (PPMS-VSM). The magnetization-magnetic field (*M-H*) loops were obtained with an applied magnetic field of $|H| \leq 15$ kOe after the diamagnetic background of the substrates was subtracted. The macroscopic *P-E* loops were measured by Radiant Precision Multiferric II with a test frequency of 1 kHz. All measurements were carried out at RT. Before testing, Au electrodes with a diameter of 300 μm were deposited on the films by a magnetron sputtering system using a standard shadow mask, accompanied with optimal sputtering pressure and power of 8 Pa and 5 W, respectively. The local ferroelectric (magnetic) domain textures were measured using an atomic force microscope (AFM, Bruker, Dimension Icon) equipped with PFM and magnetic force microscopy (MFM) test modules. O *K*-edge and Fe *L*-edge XAS were performed at beamline 08U1A of Shanghai Synchrotron Radiation Facility (SSRF) in a total electron yield mode. All the O *K*-edge XAS were collected at an X-ray incident angle perpendicular to the surface of the film. The Fe *L*-edge XAS were measured by selecting two different incident angles of 90° ($E//a$, I_{ab}) and 30° ($E//c$, I_c) with respect to the film surface, respectively. The XLD corresponds to the difference between IP ($E//a$) and OP ($E//c$) XAS ($I_{ab}-I_c$), providing a signal of the preferential orbital occupancy.

RESULTS AND DISCUSSION

Fig. 1a shows the XRD data of the SFO film deposited on

Figure 1 (a) XRD pattern for the SFO film grown on (00 l)-oriented Nb-STO single crystal substrate. (b) The orthorhombic crystal structure for bulk SFO unit cell and corresponding perovskite pseudocell. (c) Cross-sectional STEM image of the Nb-STO/SFO 90 nm film. (d, e) Cross-sectional HAADF-STEM images of the Nb-STO/SFO interface and SFO top surface, respectively.

the (00 l) Nb-STO (cubic, $a=3.905$ Å) single crystal substrate. The only perovskite-like pseudocell (002) diffraction peak appears, indicating perfect epitaxial growth along the OP (00 l) orientation. For bulk SFO unit cell, as shown in Fig. 1b, the lattice constants $a=5.400$ Å, $b=5.597$ Å and $c=7.711$ Å, correspond to $b'=3.856$ Å, $a'=c'=3.889$ Å of a perovskite pseudocell structure. Thus, it is easy to conclude that the SFO film deposited on the Nb-STO substrate is subjected to the IP tensile strain, which may elongate the IP lattice constant and contract the OP lattice constant of SFO at the interface. As the depositing thickness increases, the restriction of substrate to film gradually weakens due to the strain-relaxed effect, probably causing the lattice constant of SFO to gradually recover the value of the bulk. Fig. 1c presents a low-magnification cross-sectional STEM image of the as-fabricated Nb-STO/SFO film, suggesting that the thickness is about 90 nm. In addition, HAADF-STEM images at the film and substrate interface as well as the top surface in Fig. 1d and e further demonstrate the perfect epitaxial growth of SFO with consistent orientation along the Nb-STO (00 l) direction.

As far as we know, most of the single-phase multiferroic materials that have been found at present reveal weak M_s , which strongly limits their applications. After that, a large number of studies have focused on exploiting

new ways of improving the magnetism, such as strain-induced displacement of ions or oxygen vacancy ordering [37,38], electrical manipulation of orbital occupancy or spin-orbital coupling [39,40], and element doping-driven change of exchange constant [41], among which the strain effect has proven to be a very powerful approach. Hence, we prepared a series of SFO films with different thicknesses on Nb-STO substrates and measured the IP and OP M - H loops so as to investigate the relationship between magnetism and epitaxial strain, the results are shown in Fig. 2a–c. It is obvious that both M_s and magnetic anisotropy of the SFO films display a strong dependence on the film thickness.

For the SFO 30 nm film, see Fig. 2a, the OP M - H loop exhibits a large M_s value of around 67 emu cm^{-3} . In contrast, the IP direction displays rather weak ferromagnetism, indicating that a robust perpendicular magnetic anisotropy is produced. Previous report also prepared the Nb-STO/SFO 450 nm film and obtained the OP M - H loop [34]; however, the ferromagnetic transition temperature was only 185 K (below RT) due to serious structural distortion. As the film thickness reaches up to 60 and 90 nm (Fig. 2b and c), the OP M_s decreases from 44 to 9 emu cm^{-3} and the IP M_s increases from 16 to 43 emu cm^{-3} , respectively. It is illustrated that a strong magnetic anisotropy rotates from perpendicular to par-

Figure 2 IP (dark line) and OP (red line) M - H loops for the Nb-STO/SFO films with different thicknesses of (a) 30, (b) 60 and (c) 90 nm. The insets illustrate the direction of magnetic anisotropy. (d) IP and OP M_s values as a function of different thicknesses of 30, 60 and 90 nm for the Nb-STO/SFO films.

allel film direction. Fig. 2d summarizes the M_s values of all the SFO films, which exhibits a rapid variation along both the IP and OP directions, suggesting that the magnetic moment distributions are indeed sensitive to the film thickness.

To elucidate the influence of thickness on magnetic anisotropy, Fe L -edge XLD spectra were measured in all the SFO films at RT. With reference to our previous work [42], we selected the area of $L_{2,3}$ peaks (marked as A_{XLD}) to determine the relative orbital occupancy. Negative and positive A_{XLD} values represent a preferential occupancy of IP x^2-y^2 orbits and OP $3z^2-r^2$ orbits, respectively. Fig. 3a–c show Fe XLD spectra with different SFO thicknesses grown on Nb-STO substrates. For the SFO 30 nm film, the negative A_{XLD} is remarkable, implying that the IP x^2-y^2 orbit occupancy is stable through a strong tensile strain exerted by the substrate. With the film thickness varying from 30 to 60 and to 90 nm, as shown in Fig. 3b and c, negative A_{XLD} still exists and just the absolute value relatively reduces, which illustrates that preferential occupancy of x^2-y^2 orbits gradually weakens owing to the strain-relaxed effect. Correspondingly, O K -edge XAS were also measured and provided in Fig. 3d. It is obvious that the intensities of O 2p-Fe 3d hybridization peaks located at the vicinity of 529.6 eV are considerably re-

duced as the film thickness increases. Based on the above results, we can conclude that both Fe x^2-y^2 orbital occupation and O 2p-Fe 3d hybridization intensity are obviously enhanced (weakened) as the film becomes thinner (thicker). Namely, the changes of Fe 3d-orbital occupation together with O 2p-Fe 3d hybridization may lead to a switch of the magnetic anisotropy from OP to IP direction for the SFO film.

In addition, Fe L -edge XAS test was also performed to further confirm the origin of weak ferromagnetism in the SFO film, which shows that the L_3 peak position of Fe ion located at 708.86 eV (Fig. S1), assigning to an Fe³⁺ state [43]. This indicates that the SFO films prepared using the PLD method have fewer oxygen vacancies after annealing at a high oxygen pressure of 700 Torr. Therefore, combining with the HAADF-STEM image and XRD pattern, we consider that the weak ferromagnetism of the SFO films is majorly attributed to D-M interaction [36].

Besides the magnetic properties discussed above, macroscopic ferroelectric measurements of Nb-STO/SFO films with different thicknesses were also collected. Fig. S2 displays a simple schematic for measuring the P - E loop and time dependence of the applied voltage-current ($I(V)$ - t) curve. One of the advantages for the Nb-STO/SFO film is that the Nb-STO substrate can directly serve

Figure 3 Fe *L*-edge XLD spectra of Nb-STO/SFO films with different thicknesses of 30 (a), 60 (b) and 90 nm (c), respectively. (d) O *K*-edge XAS as a function of the SFO film thickness. The light red, blue and white areas are linked to the O 2p hybridizing with Fe 3d, Sm 5d, and Fe 4sp state, respectively.

as a bottom electrode, wherein Au electrode with a diameter of 300 μm is used as a top electrode. The *P*-*E* loops of the SFO 30 nm film with different maximum test voltages are revealed in Fig. S3a–c, which indicate that all the loops are shown as round whether a small or large voltage is provided. The corresponding triangular-wave *I* (*V*)-*t* curves in Fig. S3d–f imply that an obvious resistance behavior appears instead of ferroelectric behavior because of the huge leakage current. As the film thickness increases to 60 nm (Fig. S4a–c), all the *P*-*E* loops exhibit a cone-shaped form. Although the corresponding *I*(*V*)-*t* curves (Fig. S4d–f) reveal slight hysteresis phenomenon, a large leakage current still exists. When the thickness reaches up to 90 nm (Fig. 4a), a quasi-rectangular *P*-*E* loop with a remanent polarization of 1.1 $\mu\text{C cm}^{-2}$ and a coercive field of 0.2 MV cm^{-1} can be observed. Meanwhile, the *I*(*V*)-*t* curve (Fig. 4b) exhibits obvious switching and hysteresis characteristics, indicating a clear signal of ferroelectricity. Fig. S5 presents the relationship between the leakage current and applied voltage. The test result shows that the leakage current density remains less than $10^{-5} \text{ A cm}^{-2}$ even if it provides a high voltage of 2.5 V. An increasing maximum test voltage such as 3 V will lead to a large leakage current, which in turn affects

the authenticity of the ferroelectric measurement (Fig. S6). To further provide a proof of the local ferroelectricity, OP PFM phase image was characterized by applying a pair of opposite polar voltages. During the measurement, the 4- μm^2 square inside was poled by +7 V direct current (DC) voltage after the 16- μm^2 square region outside was poled by –7 V DC voltage first, and the result is displayed in Fig. 4c. It is clear that the positive and negative polarized areas show a sharp contrast, suggesting the realization of opposite domain switching. Furthermore, phase-voltage and amplitude-voltage curves were also tested and shown in Fig. 4d, indicating an almost 180° ferroelectric polarization switching and obvious piezoelectric signal, respectively. Although the explanation has been inconclusive till now, in our case, we suppose the ferroelectricity of SFO film more likely come from the exchange striction mechanism [35].

The RT ME coupling effect is one of the important characteristics for multiferroic materials, as well as the desired goal of our work. To realize the reversible switching of magnetic domains merely by voltage, we applied a series of DC voltages of 0 V → –1 V → –2 V → –3 V → +0.5 V on the SFO 90 nm film *via* a conductive Co/Cr-coated tip in AFM. Before the measurement, an

Figure 4 (a) P - E loop and (b) $I(V)$ - t curve of the SFO 90 nm film. (c) The OP PFM phase image of the two boxes after a pair of opposite polar voltages were applied. (d) Phase-voltage and amplitude-voltage curves of the SFO 90 nm film. The local ferroelectricity of (c) and (d) were measured by using a Pt/Ir-coated conductive tip in the AFM.

oscillation demagnetization treatment was applied to the film. Then, the magnetic domain distributions of the same area were characterized after different voltages were applied. Fig. 5a shows the surface morphology over a $500 \text{ nm} \times 500 \text{ nm}$ scan range and proves a high-quality film with a root-mean-square coarseness of around 0.26 nm. Fig. 5b presents the corresponding MFM phase image of the SFO film at a demagnetization state, which

shows that the downward-oriented (yellow regions) and upward-oriented (blue regions) mosaic domains are randomly distributed. As the applied voltage varies from 0 to -2 V , the magnetic domain orientation has some slight variation, but it is not obvious (Fig. 5c and d). With further increasing voltage to -3 V , the blue area suddenly increases (Fig. 5e), which means that the majority of downward-oriented magnetic domains reverse to upward

Figure 5 (a) Surface morphology over a $500 \text{ nm} \times 500 \text{ nm}$ scan range in the Nb-STO/SFO 90 nm film. (b-f) MFM phase images of the SFO film after being subjected to different voltages of $0 \text{ V} \rightarrow -1 \text{ V} \rightarrow -2 \text{ V} \rightarrow -3 \text{ V} \rightarrow +0.5 \text{ V}$.

Figure 6 (a) Surface morphology over a 260 nm $\times$ 260 nm scan range in the Nb-STO/SFO 90 nm film. (b) MFM phase image after applying a -3 V voltage. (c) The MFM phase image which was measured by reversing the tip magnetization at 0 V after the manipulation of (b).

direction at this critical voltage. However, when a small voltage of $+0.5$ V is provided again (Fig. 5f), most of the magnetic domains that have been polarized upward reverse to downward direction. It is worth mentioning that the above manipulation shows an asymmetric critical switching voltage, which is probably attributed to the pinning effect of the residual antiferromagnetic-SFO part or different work-function of the used electrodes [44]. Fig. S7 displays the OP PFM phase images of the SFO film with box-in-box patterns written with different voltages and corresponding MFM phase images in the same area. A clear contrast of the ferroelectric and ferromagnetic phases illustrates the ferroelectric domains and the corresponding ferromagnetic domains being electrically switched simultaneously, demonstrating an obvious ME coupling effect.

To verify the authenticity of ME coupling, we also scanned the film by applying the same tip with opposite magnetization. Fig. 6a shows the surface morphology over a 260 nm $\times$ 260 nm range in the SFO 90 nm film. When providing a -3 V voltage in this area, as revealed in Fig. 6b, the majority of magnetic domains are forced to orientate upward. A pronounced difference in the magnetic domain orientation is observed compared with the same area when measured by reversing the tip magnetization at 0 V (Fig. 6c). This method can effectively exclude the influence of electrostatic interactions between the film and conductive tip and really prove the electrical control of magnetic phenomenon.

Overall, the present research verifies a controllable magnetic anisotropy by utilizing the epitaxial strain. On the basis of the changes of O 2p-Fe 3d hybridization intensity and Fe 3d-orbital occupation, we can get a reasonable explanation for the magnetic anisotropy of the SFO film which gradually varies from OP to IP direction with increasing film thickness. A series of ferroelectric tests and electrically controlled magnetic switching give a

direct experimental evidence for the existence of multiferroicity as well as ME coupling effect at RT.

CONCLUSIONS

Fully epitaxial Nb-STO/SFO films were successfully prepared by using the PLD method. Measurement results illustrate that the SFO films exhibit obvious ferromagnetic and ferroelectric orders at RT, and the magnetic anisotropy gradually changes from OP to IP direction with increasing film thickness. We propose that the variation of magnetic anisotropy direction is attributed to the changes of Fe 3d-orbital occupation and O 2p-Fe 3d hybridization intensity due to the strain-relaxed effect. Moreover, macroscopic P - E loop, local PFM phase image as well as phase (amplitude)-voltage curves simultaneously show that the films are ferroelectric. Furthermore, electrically driven reversible magnetic switching further confirms that the films exhibit RT ME coupling effect, which is promising for applications in ferroelectric random access memory (FeRAM) and other electronic devices.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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应力诱导外延 SmFeO_3 薄膜强烈的磁各向异性以及室温磁电耦合效应

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摘要 稀土正铁氧体 SmFeO_3 由于在低能耗自旋电子学器件领域的潜在应用,被认为是一种杰出的单相多铁材料.然而,至今尚未证明该体系在室温下兼具磁性、铁电性以及磁电耦合效应.本文使用脉冲激光沉积法在可以提供拉应力的Nb-SrTiO₃基片上成功外延了倾斜反铁磁 SmFeO_3 单层薄膜.测量结果显示薄膜具有明显的室温铁磁和铁电序.同时,随着厚度的增加,薄膜的磁各向异性逐渐从面外转移到面内方向,这是由应力释放效应导致的O 2p-Fe 3d杂化强度和Fe-3d轨道占据变化同时引起的.另外,电压驱动可逆磁畴反转进一步证明 SmFeO_3 薄膜具有明显的室温磁电耦合效应.本工作对设计新一代电写磁读数据存储器件具有一定的推动作用.