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Oxygen-vacancy-induced atomic and electronic reconstructions in magnetic Sr(Ti$_{0.875}$Fe$_{0.125}$)O$_3$-$\delta$ thin films

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Abstract

The atomic and electronic structures have been investigated for the multiferroic behavior in the perovskite oxides, which also can be tuned by oxygen vacancy for enhancing properties. Here epitaxial Sr(Ti$_{0.875}$Fe$_{0.125}$)O$_3$-$\delta$ thin films were deposited on (001) SrTiO$_3$ substrates by pulsed laser deposition and were post-annealed in an oxygen atmosphere. We found that the oxygen vacancies formed in high vacuum are the source of the macroscopic crystal distortion as the growth strain along out-of-plane. Moreover, it was determined that the full-filled Fe 3$d$ states induced by oxygen vacancy effect are responsible for the decreased magnetization. This work demonstrates that the oxygen vacancy can both lead to atomic and electronic reconstructions in the perovskite films for manipulating ferroic properties.

1. Introduction

Perovskite oxides have been broadly investigated in the ranges of physical research and devices as magnetoelectrics, vortex, solid oxide fuel cell and photoelectrochemical water splitting [1–4]. During the fabrication, the point defects like the cation impurity and oxygen vacancy ($V_O$) have always been formed in such oxides and display a significant impact on the improved and crucial functionalities. Compared with the other cation nonstoichiometry, the $V_O$ benefited from the lower formation energy and double donor nature can be a remarkable candidate for the multiferroic and conductivity enhancement [5–9]. Especially in the epitaxial films, the $V_O$ concentration coupled to the microcosmic changes in bond length or octahedral rotation can be significantly associated with the biaxial strain, confirmed that a tensile strain should increase the amount of $V_O$ and a compressive strain lead to decrease [10–14]. On the other hand, with a massive increase in the $V_O$ concentration arising from high-vacuum, an unexpected expansion of the out-of-plane crystal lattice has been reported in the homoepitaxial SrTiO$_3$ and heteroepitaxial EuTiO$_3$ thin films, ranging from 0.4% to 2%, depended on the oxygen pressure during the deposition process [15, 16]. However, the local unit-cell distortion alone is insufficient to explain the large macroscopic uniaxial strain on the films. Furthermore, it also has been proven that the $V_O$ effect have an opposite impact on the ferromagnetic behavior of the different perovskites, such as the enhanced ferromagnetic in the Eu$_{0.3}$Ba$_{0.7}$TiO$_3$ and weakened in the La$_{2/3}$Sr$_{1/3}$MnO$_3$ thin films [17, 18]. These complex tuning effects on the physical properties are directly related to the electronic structure of specific material systems.

To further reveal the role of $V_O$ in the crystal and electronic structures, we report experimental and computational comparison between as-deposited and annealed Sr(Ti$_{0.875}$Fe$_{0.125}$)O$_3$-$\delta$ (STF) thin films. In contrast to the various Fe-doped concentration [19–21] - in this particular model system the equivalent hole carriers provided by 12.5% Fe-doping level can contribute to absolutely compensate the double electrons.
donated by $V_{O}$, which can certain the stabilized Fe$^{4+}$ and reduced $V_{O}$ in the stoichiometric STF films. The crystal structure and valence band of the both films have been investigated, providing that the continuous SrO planes induced by $V_{O}$ leads to the expanded lattice spacing and growth-related strain. Then the first-principles calculations and magnetic measurement have been performed to demonstrate the relationship between the ferromagnetic and electronic reconstructions, which present the enhanced ferromagnetic depends on the half-filled Fe 3$d$ states.

2. Methods

The STF films were prepared on atomically flat SrTiO$_3$ (STO, 001) substrates via pulsed laser deposition (PLD, Lambda Physik, 248 nm, 3 Hz, 2 J cm$^{-2}$). A ceramic pellet with a ratio of STF was used as the composite target. The deposition temperature was maintained at 700 °C under an oxygen pressure of $5 \times 10^{-5}$ mbar. After deposition, the films were post-annealed at 1000 °C in an oxygen atmosphere (500 mbar) for 6 h to relax the growth-related strain and reduce the amounts of $V_{O}$ (Discussed later) [22]. X-ray diffraction (XRD) was used to investigate the lattice structure by Burkerc D8 diffractometer. Magnetic measurements were performed by a physical properties measurement system (PPMS-9, Quantum Design), and the valence states of the films confirmed by x-ray photoemission spectroscopy (XPS) at PHI5000 VersaProbe. And in theory the structure and electronic structure of the doped system have been studied via the generalized gradient approximation (GGA) with on-site Coulomb correlation corrections (GGA + U) [23, 24], within the frame work of density functional theory. A $8 \times 8 \times 8$ Monkhorst Pack sampling of the Brillouin zone [25] are used for the self-consistent calculations with a plane-wave cutoff energy of 600 eV. The orbitals of Sr(4$s^2$4$p^6$5$s^2$), Ti(3$p^6$3$d^2$4$s^2$), Fe(3$p^6$3$d^2$4$s^2$) and O(2$s^2$2$p^4$) are treated as valence states and taken as the basis set in the calculations. Based on Dudarev method [26], $U = 3.0$ eV and $J = 0.6$ eV [27](only $U_{ctf} = U - J$ is meaningful) are adopted to include the strong correlation effect between Fe 3$d$. The optimized geometries of the doped system under various strain can be obtained by full relaxation of the atomic positions and the lattice constants until the Hellmann-Feynman forces are less than 0.01 eV/Å.

3. Results and discussion

3.1. Atomic reconstruction

The crystal structures of the as-deposited (STF-D) and annealed (STF-A) films have been observed by XRD $\theta - 2\theta$ scans, which both show only (00) peaks of the films and substrates in figure 1(a). Obviously, the reflections from the STF-A film are buried by the substrate reflections due to the small amount of the doped. Based on the STO (002) peak selected as the reference for sample alignment, the out-of-plane lattice constants of the STF-D and STF-A films are estimated to be 3.93 ± 0.01 Å and 3.91 ± 0.01 Å, respectively. To further find out the in-plane lattice, X-ray reciprocal space mapping (RSM) was measured for the both films. Compared to the overlapped STF-A film and STO substrate peaks (not shown), two distinct Bragg spots from film and substrate are observed in the STF-D film around the (003) (figure 1(b)) and (003) (figure 1(c)) reflections. It is found that a and b lattice constants are both identical to that of the STO substrate, owing to the same $q_x$ in the perpendicular planes. In addition, a 4-fold symmetry is observed in the $\varphi$ measurements to confirm the epitaxial relationship between STF-D and STO (figure 1(d)), showing that the STF-D films grow on the STO (00 1) substrate in a tetragon-on-cube mode and the epitaxial relationships are (002)$_{STF-D}$ // (002)$_{STO}$ and [200]$_{STF-D}$ // [100]$_{STO}$. Hence, it was determined that the STF-D films have the growth-related strain of +0.51% unidirectionally along out-of-plane and been restricted along in-plane, while the STF-A films are fully relaxed by the postannealing.

3.2. Valence change

XPS measurement in figure 2 was focused on the valence states of the component elements in two films, which has provided routine for the determination of the different defects, as $V_{O}$ and extended defects [28]. In order to confirm the place of the Fe dopant, the results can be obtained from the valence state of the 2+$+$ and 4+$+$ components, which present the A-site (Sr$^{2+}$) or B-site (Ti$^{4+}$) substituting respectively. Figures 2(a) and (b) represent the comparison of the fitting Fe 2p$_{3/2}$ - 2p$_{1/2}$ peaks between STF-D and STF-A films, both show a clear contribution at binding energy (BE) doublet of 711.4 eV–725.4 eV. According to the previous studies of the Fe 2p spectra of oxides [29], the peaks at these BEs correspond to Fe$^{4+}$ give a direct evidence that the dopants are placed in the center of an octahedron. Based on the similar lattice substituting, the difference in deposition pressure between two films can only cause the change of oxygen content as shown in the different O 1$s$ lines (figures 2(c) and (d)). Like the typical O 1$s$ spectra in the perovskite films [30], it contains three components in the STF-A film as the 1$s$ peak position (529.0 eV), hydroxyl groups (530.3 eV) and O-C groups (531.9 eV).
representing the amount of \( V_O \) in the STF-A film can be neglected, due to the annealing in the oxygen atmosphere. However, the enhanced peak from oxygen vacancies (531.8 eV) has been observed in the STF-D film apart from the above three components \[31\], and the peak of O-C groups is superimposed on the enhanced peak in figure 2(c). As a result, the \( V_O \) can be formed during the high-vacuum deposition and almost decreased by the annealing in oxygen.

To investigate the relationship between the growth-related strain and \( V_O \), the microstructure modification induced by \( V_O \) need to be found out. We further performed Sr 3d XPS core-level scans in both films and obtained some appreciable changes in the spectra. First, the Sr 3d peaks of two films can be fitted by one set of Sr 3d\(_{5/2}\) and Sr 3d\(_{3/2}\) with a splitting energy of 1.8 eV named the ‘lattice’ Sr contribution, as shown in figures 2(e) and (f) \[28\]. After annealing, the STF-A film has a lower energy doublet (3d\(_{5/2}\) at 131.8 eV and 3d\(_{3/2}\) at 133.6 eV) than that in STF-D film (132.5 eV and 134.3 eV) by around 0.7 eV. According to the above discussion on the reduced \( V_O \), this chemical shift in the Sr 3d component could arise from the compensate charges of oxygen vacancy (2+) for the charge balances. Second, other than the similar ‘lattice’ contribution, there are an obvious different ‘surface’ component between the two films and an additional SrO secondary phase in STF-D film. It is interesting to note that the contribution from the ‘surface’ component correspondingly decrease by 50%, reconfirmed that the nearly stoichiometric property and reduced \( V_O \) can be obtained in STF-A film after thermal treatment. Moreover, the enrichment of ‘surface’ component in the STF-D film may drive additional SrO layers toward the surface, as the evidence of the peak belong to SrO secondary phase (~137.2 eV) \[32\]. These inserted SrO layers can break the successive (Sr-O)/(Ti-O) layers and stretch the vertical lattice constant. In addition, the same Ti\(^{4+}\) 2p peaks have been observed for the both films (not shown). Hence, the oxygen vacancy can cause the Sr surface enrichment and vertical growth strain in the as-deposited STF films.

### 3.3. First-principles calculation

Next, we investigated the dominated tuning effect on the electronic structures and magnetic behavior in the STF films, through the first-principles calculations and magnetic measurement. As mentioned above, the growth strain and \( V_O \) effect coexist in the STF films and need to be determined which plays the dominated role in the enhanced magnetic properties. Figure 3(a) illustrates that the magnetization density of unstrained STF is mainly distributed around the Fe atom and the adjacent O atoms, which is in good agreement with the previous
investigation regarding the ferromagnetic properties are mainly derived from the doped Fe \([\text{Fe}^{19}]\). Meanwhile, the different atoms' \(l\)-dependent partial density of states (PDOS) in figure 3(b) also present that the contribution of Fermi energy (\(E_F\), marked as magenta dashes) are mostly from Fe atoms and slightly from O atoms, rather than that from Sr and Ti atoms (not shown). In particular, the O atoms can be divided into two categories by the ionic positions, labeled as \(O_5\) (in-plane, IP) and \(O_{13}\) (out-of-plane, OP). To further determine the dominated mechanism between the vertical strain and VO effect, the \(l\) and \(m\)-dependent PDOS of Fe \(t_{2g}(d_{3z^2-r^2}, d_{3x^2-y^2})\), \(e_g(3d_{yz}, 3d_{xy}, 3d_{xz})\) and O 2\(p\) are calculated as shown in figures 3(c) and (d). It is found that the strong hybridization occurs between \(d_{3z^2-r^2}/O_5\) and \(d_{3x^2-y^2}/O_{13}\) with the different color lines. Hence, a change in the IP and OP oxygen atoms can be both used for tuning effect on the magnetic properties of STF films through the alteration in the hybridization, such as the position distortion and vacancy (discussed later).

### 3.4. Magnetic behavior

Then, we make a comparison on the magnetic character of two films by magnetic measurement on the physical properties measurement system (PPMS). Figure 4(a) describes the magnetic field dependence of the magnetization (M-H) curve in the STF-D (Black dotted) and STF-A (Red dotted) films at 300 K. Obviously, two films are both ferromagnetic at room temperature as shown by the well-saturated magnetic hysteresis loops with the approximate coercive field (\(H_C\)) of 200 Oe. In addition, the saturation magnetization (\(M_S\)) of STF-D and STF-A samples are 0.19 \(\mu B/Fe\) and 0.65 \(\mu B/Fe\), respectively, which means the postannealing process have improved the magnetic properties and the one of vertical strain and VO effect have an opposite effect. The reduced magnetic behavior presents a competition between the oxygen vacancy and strain effect, which is similar with that in the EuTiO\(_{3-\delta}\) films \([33]\). Therefore, we begin by the vertical strain effect on the magnetic behavior, performed as the stretched unit-cell along \(c\)-axis and slight squeezed in-plane. The calculated magnetic moment of the STF (marked as Strained) are shown as a function of the uniaxial strain along with out-of-plane in figure 4(b), ranging between +2.5% and −2.5% (positive for tension and negative for compression). We found that the total magnetic moment (magenta line) is higher than that from Fe ions (black line) under the whole range of vertical strain. The decreased magnetic moment demonstrates the O atoms also have a positive influence on the magnetic behavior, which is consistent with the above calculation. And a monotonic increasing

![Figure 2. The peak fittings in STF-D and STF-A films are performed on the upper panel and lower panel, which show the (a), (b) Fe 4p, (c), (d) O 1s and (e), (f) Sr 3d core-level photoemission spectra, respectively.](image)
within the whole considered strain shows the vertical strain not only weaken (compression) but also strengthen (tension) the magnetic properties in contrast to the equilibrium state. The opposite effect may be associated with the anisotropy of the exchange interaction between Fe and O ions, but which has not often been considered in the previous studies.

3.5. Electronic reconstruction

However, compared with the above results from experiment, it should be noticed that two huge differences in the magnetic behavior based on the vertical strain effect. The first one is that the both measured $M_\text{S}$ are much lower than that in the calculation ($\sim 4 \mu B/\text{Fe}$); another displays an opposite trend in the changed $M_\text{S}$ with increasing in the vertical strain, which shows a comparison between the slight raised $M_\text{S}$ in the calculations and distinct reduced $M_\text{S}$ in the measurement. These investigations suggest that the consequence from other factors should exist in the experiment and need to be considered. Still back to the deposition process, the $V_\text{O}$ formed...
under low oxygen pressure may also have the influence on the magnetic behavior. Hence, despite the vertical strain effect, another set of calculations marked as Strained + vacancies were performed in the doped system. As shown in figure 4(b), the magnetic moment decreases to one fifth after the forming of oxygen vacancies, which confirmed there is a direct relationship between oxygen vacancy and magnetic behavior once again. Meanwhile, it is visible that the increased strain has a neglected impact on the magnetism when the STF films contain a certain amount of oxygen vacancies. These above results confirm that the VO effect dominate the tuning on the ferromagnetic behavior.

To determine the underlying mechanism of the VO effect on the magnetic properties, we need to focus on the difference of electronic structure before and after the addition of oxygen vacancy. The first influence is the change of the band gap as highlighted in figure 4(c), which illustrates the STF films transform from the half-metallicity to metallicity. After the addition, the distribution of TDOS near the EF is obvious and the Fermi level...
4. Conclusion

The strained STF films have been epitaxially fabricated on the STO (001) substrate via PLD and then postannealed in oxygen for the reduced VO and unstrained state. The induced VO during the deposition can enable not only the surface Sr enrichment to the elongated vertical lattice, but also the additional carriers to the upper Fermi level. More than this, the ferromagnetic behavior of the STF films can be eliminated by the VO effect. Our investigation can be extended to determine the dominated tuning effect between the strain and VO effect, and further enhance the ferroic in various perovskite oxide films.

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