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Magnetism and Faraday Rotation in Oxygen-Deficient Polycrystalline and Single-Crystal Iron-Substituted Strontium Titanate

Taichi Goto, Dong Hun Kim, Xueyin Sun, Mehmet C. Onbasli, Juan M. Florez, Shyue Ping Ong, Patricio Vargas, Karl Ackland, Plamen Stamenov, Nicolas M. Aimon, Mitsuteru Inoue, Harry L. Tuller, Gerald F. Dionne, J. Michael D. Coey, and Caroline A. Ross

1Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibari-Ga-Oka, Tempaku, Toyohashi 441-8580, Japan
2Department of Materials Science and Engineering, Myongji University, 116 Myongji-ro, Cheoin-gu, Yongin, Kyonggi-do 449-728, Korea
3School of Materials Science and Engineering, Harbin Institute of Technology, 92 West Dazhi Street, Nan Gang District, Harbin 150001, China
4Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA
5Departamento de Física, Universidad Técnica Federico Santa María, España 1680, Valparaíso, P.O. Box 110-V, Chile
6Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093, USA
7School of Physics, Trinity College Dublin, College Green, Dublin 2, Ireland

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Both polycrystalline and single-crystal films of iron-substituted strontium titanate, Sr(Ti0.65Fe0.35)O3−δ, prepared by pulsed laser deposition, show room-temperature magnetism and Faraday rotation, with the polycrystalline films exhibiting higher saturation magnetization and Faraday rotation. The magnetic properties vary with the oxygen pressure at which the films are grown, showing a maximum at pressures of approximately 4 μTorr at which the unit-cell volume is largest. The results are discussed in terms of the oxygen stoichiometry and corresponding Fe valence states, the structure and strain state, and the presence of small-volume fractions of metallic Fe in single-crystal films grown at the optimum deposition pressure. Integration of magneto-optical polycrystalline films on an optical-waveguide device demonstrates a nonreciprocal phase shift.

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I. INTRODUCTION

Complex oxides exhibit a wide range of useful properties such as high-temperature superconductivity, ferroelectricity, colossal magnetoresistance, magnetism, magnetoelectricity, magneto-optical activity, and multiiferroicity that have inspired spintronic, magnetoelectronic, and optical applications [1–6]. Transition-metal-substituted perovskites or perovskite-derived structures are particularly interesting because their properties can be tuned by cation substitution over extensive composition ranges, and because they can be epitaxially grown on a buffered Si substrate [7–10]. Beyond cation composition, the properties are also very sensitive to the growth conditions and substrate used, which affect the microstructure, film strain [7], oxygen deficiency, the cation valence states, and the ordering of cations within the A and B sites.

Iron-substituted strontium titanate or SrTi1−xFeO3−δ (STF) (here δ represents the oxygen deficiency with respect to a stoichiometric perovskite SrTi1−xFexO3, i.e., one in which the Fe is present as Fe4+) has been extensively characterized as a mixed electronic-ionic conductor [11–15] and for its magnetic, magneto-optical, ferroelectric, and catalytic properties [16–19]. Characterization of STF has included determining its oxygen content via thermogravimetric analysis and coulometric titration [20,21], and measurements of ionic and electronic conductivity and impedance [12,13,15,22–24]. The magnetic properties are believed to be related to oxygen vacancies [16,20,25], although the origin of the magnetism is not fully understood. We have previously found that epitaxial STF and Sr(Ti1−xCox)O3−δ (STCo) films on SrTiO3 (STO), LaAlO3, and CeO2/yttria-stabilized-zirconia-(YSZ) buffered (001) Si substrates grown in vacuum with x = 0.1 to 0.5, i.e., nondilute systems, exhibited room-temperature magnetism and anisotropy with an out-of-plane magnetic easy axis that was attributed to magnetoelastic effects [16,17,26–28]. However, films deposited in oxygen had no significant room-temperature magnetism. The magnetic moment of vacuum-deposited epitaxial STF films persisted to a temperature of >1000 °C
and the magnetization decreased slowly as a function of temperature [16,29,30]. Depending on the thickness and deposition conditions, STF could be grown as a single-crystal film on STO, or as a double-epitaxial film consisting of an (001)-oriented STF film with (011)-oriented crystals growing within it, both orientations being epitaxial with the substrate [31]. The single-crystal and double-epitaxial microstructures differed in their strain state, uniformity of the Fe distribution, and magnetic properties [19,31].

These experimental results led to the conclusion that strain and oxygen stoichiometry were key factors in determining the magnetic properties of the STF and STCo films (factors that are also important in many other oxide systems [29,32]), but there are few reports on the effect of oxygen pressure during growth [33,34], and polycrystalline films have not been investigated. We report on the correlations among the microstructure, valence, and distribution of the Fe ions as well as the room-temperature magnetic properties of STF films as a function of base pressure $P$, characterized by high-resolution x-ray diffraction (XRD), transmission electron microscopy (TEM), Faraday rotation (FR), magnetometry, and Mössbauer spectroscopy. The STF films on Si were polycrystalline but exhibited a magnetic moment and FR up to 65% higher than the single-crystal film deposited on an STO substrate. From the viewpoint of applications, the formation of polycrystalline magnetic perovskite films on silica or other nonepitaxial substrates allows the useful properties of STF to be easily introduced into complementary metal-oxide semiconductor devices and into optical devices such as isolators and magnetophotonic crystals [40–42], or magneto-optical holographic memories [43–46]. First-principles calculations demonstrate the importance of oxygen defects and exchange interactions in determining the magnetic properties.

II. FILM GROWTH AND CHARACTERIZATION

A. Film preparation

In this work, STF films are fabricated on silicon covered by a native oxide and on STO substrates under various $P$ using pulsed laser deposition (PLD). The SrTi$_{0.62}$Fe$_{0.38}$O$_{3-\delta}$ target is prepared using a conventional mixed oxide sintering method [47]. During film deposition, the KrF excimer laser (wavelength $\lambda = 248$ nm) is pulsed at a frequency of 10 Hz with a pulse duration of 25 ns. The spot size on the target is 0.5 mm $\times$ 2.0 mm, and the energy density at the target surface is approximately 1.3 J cm$^{-2}$ during the pulse. The deposition rate is 1.8–2.7 nm min$^{-1}$. STF films of thickness 70 $\pm$ 10 nm are deposited by PLD onto 0.38-mm-thick double-side-polished (001) Si substrates and onto 0.5-mm-thick double-side-polished (001) STO substrates. Films are grown simultaneously on both substrate types in each deposition run. The substrates are placed 80 mm from the target, and the substrate holder is heated to 650°C and is rotated for uniform growth. This temperature is chosen to minimize the formation of secondary phases such as iron oxides. Samples are prepared at a range of base pressures below 10 $\mu$Torr by pumping the chamber until a specific base pressure $P$ is reached. The substrate is then heated, which raises the total pressure of the chamber to about 30 $\mu$Torr due to chamber outgassing. The chamber pressure is then pumped back down to $P$ before deposition starts. Therefore, the pressure $P$ during deposition consists of residual gas which includes oxygen and water vapor. Predeposition ($5 \times 10^3$ laser pulses) is started with the shutter placed between the PLD target and the substrate, leading to an increase in the total chamber pressure by approximately 2 $\mu$Torr. After opening the shutter for film deposition ($2 \times 10^4$ pulses), the chamber pressure gradually decreases and returns to near $P$ at the end of the deposition. The substrate is cooled to room temperature at a rate of $-5^\circ$C min$^{-1}$ while pumping the chamber.

B. X-ray characterization

In-plane and out-of-plane lattice constants of single-crystal films on STO and polycrystalline films on Si are characterized by XRD (PANalytical, X’Pert) and two high-resolution XRD systems (HRXRD, Bruker-AXS D8 DISCOVER, and Rigaku Smartlab). XRD patterns are shown in Figs. 1(a) and 1(b) for STF/STO and STF/Si, taken using a Cu-K$\alpha$ radiation source at a wavelength of 0.15418 nm. Figure 1(a) is measured by XRD (PANalytical, X’Pert), in which K$\beta_1$ peaks from the Cu source are observed. Figure 1(b) is measured by HRXRD (Rigaku Smartlab). The STF/Si samples are tilted by 1° to eliminate the strong substrate peak. The out-of-plane lattice parameters of STF on STO and on Si, $c_{\text{STF on STO}}$ and $c_{\text{STF on Si}}$, vary with the deposition pressure, and exhibit a maximum at $P = 3–4 \mu$Torr, with the variation stronger for the STF/STO. This behavior is also confirmed with the (002) peak obtained from XRD (PANalytical X’Pert). The TiO$_2$ (202) peak in Fig. 1(a) originates from the substrate.

Reciprocal space mapping (RSM) is used to measure the in-plane lattice parameter $a_{\text{STF on STO}}$ for the STF/STO. Grazing-incidence diffraction was used to measure $a_{\text{STF on Si}}$ for the STF/Si samples grown at $P = 1$, 4, and 10 $\mu$Torr with the incident angle of the x rays $\omega$ fixed at 0.4°. Figure 1(c) shows the RSM data for the STF/STO samples for the asymmetric (310) peak. The intense upper peak arises from diffraction from the STO substrate, and the bottom peak corresponds to the STF films. Multiple peaks are attributed to twinning of the substrates. The film and substrate peaks align in $q_x$, indicating coherent cube-on-cube epitaxial growth of the STF films on the STO substrate, i.e., $a_{\text{STF on STO}} = a_{\text{STO}}$, whereas $q_z$ gives the out-of-plane lattice parameter $c$, which differs for the film and substrate. The RSM data gave a standard deviation of
<10^{-3} \text{ Å} for a_{\text{STF}/\text{STO}}. The difference in values for c from different diffractometers, given by (HRXRD value–XRD value)/HRXRD value, is less than 0.1%, and the value of c_{\text{STF}/\text{STO}} from RSM matches that measured by XRD. All the STF films on STO had out-of-plane lattice parameters greater than that of STO (a_{\text{STO}} = 3.905 Å) and are tetragonally distorted, with (c/a)_{\text{STF}/\text{STO}} = 1.013 to 1.030 indicating an in-plane compressive strain in the STF, similar to that found in prior work [16]. Figure 1(d) shows the variation of a_{\text{STF}/\text{STO}}, c_{\text{STF}/\text{STO}}, and unit-cell volume V_{\text{STF}/\text{STO}} with base pressure P.

For the samples of STF/Si, the in-plane and out-of-plane lattice parameters, a_{\text{STF}/\text{Si}} and c_{\text{STF}/\text{Si}}, and the unit-cell volume V_{\text{STF}/\text{Si}} are shown in Fig. 1(d). The data gave a standard deviation of approximately 6 \times 10^{-4} \text{ Å} for a, and 2 \times 10^{-3} \text{ Å} for c. The value of a_{\text{STF}/\text{Si}} is 3.955 \pm 0.003 \text{ Å} and shows little variation with P. Of the three STF/Si samples whose unit-cell volume is measured, the one grown at P = 4.0 \mu\text{Torr} shows the largest unit-cell volume, the same trend as for films on the STO substrate. The value of c_{\text{STF}/\text{Si}} is similar to or slightly smaller than a_{\text{STF}/\text{Si}}, i.e., (c/a)_{\text{STF}/\text{Si}} = 0.990 to 0.998, depending on P. Thermal mismatch on cooling would lead to a tensile strain in the STF/Si film (c/a < 1), since Si has a lower thermal expansion coefficient than STF. This differs from the films on STO where lattice mismatch governs the strain state and produces an in-plane compressive strain in the STF, with c/a > 1.

The larger unit-cell volume of the films compared to that estimated for bulk STF without oxygen vacancies [SrTi_{0.65}Fe_{0.35}O], V = \sim 60.13 \text{ Å}^3 interpolated linearly from the unit-cell volumes of STO (a = 3.9051 Å, V = \sim 59.55 \text{ Å}^3) [48] and SrFeO_3 (a = 3.9410 Å, V = \sim 61.21 \text{ Å}^3) [49] is a result of the greater oxygen vacancy content in the films compared to the bulk, which drives the Fe to lower valence states, expanding the lattice because of the larger ionic radii of the Fe. Other work on STO films [50] has shown changes in cation stoichiometry and hence lattice parameter at different laser focus conditions, but here we keep the deposition conditions nominally the same except for the base pressure, so we attribute changes in lattice volume to the oxygen vacancies and corresponding changes in Fe ionic radius. MacChesney...
et al. and Taguchi et al. showed that oxygen vacancies in SrFeO$_{3-\delta}$ and SrCoO$_{3-\delta}$, respectively, increased the unit-cell volume [51,52], and a sufficiently large oxygen deficiency ($\delta > 0.12$) promoted a cubic-to-tetragonal structural change in SrFeO$_{3-\delta}$ [42]. Perry et al. showed that the largest lattice parameter is obtained for STF annealed under the most reducing conditions, based on chemical expansion measurements [34]. Chakraverty et al. demonstrated that, for SrFeO$_{2.5}$ films on STO grown by PLD, the laser spot size, which affects the growth process, kinetics, and stoichiometry controlled the lattice parameter [53].

C. Film morphology.

Cross-sectional TEM images of STF/Si and STF/STO grown at $P = 1, 4$, and $10 \, \mu\text{Torr}$ are given in Fig. 2. All three STF/Si films have a polycrystalline columnar microstructure, and energy-dispersive x-ray spectroscopy (EDX) mapping of the 4-$\mu\text{Torr}$ sample, Fig. 3, indicates a spatial variation in the Fe content, with higher Fe content corresponding to a few of the columnar features. In agreement with the Mössbauer spectroscopy (described below), there is no clear evidence from high-resolution TEM that these columns are metallic Fe, and we presume they represent STF with a higher Fe content than neighboring grains. A similar inhomogeneity is found at $P = 1 \, \mu\text{Torr}$, but at $10 \, \mu\text{Torr}$ the Fe is uniformly distributed. The compound SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ is stable throughout the composition range [13,14], therefore, we assume that the inhomogeneity is different in origin from that seen in spinodal decomposition such as that of Cr-rich (Zn, Cr)Te [54], In-rich (Ga, In)N [55], or (Mn, Ga)As [56] systems. In comparison, the STF grown on STO is single crystal but shows contrast that indicates small-scale structural inhomogeneity, possibly representing layered vacancy ordering as seen in brownmillerite-structured SrFeO$_{2.5}$ [57] and in (La, Sr)CoO$_3$ [58,59].

At $P = 4 \, \mu\text{Torr}$, a few straight, vertical nanopillars are observed perpendicular to the substrate within the perovskite matrix. Lattice imaging reveals that the pillars are metallic $\alpha$-Fe. The pillars are sparsely distributed, with spacings of approximately 200 nm in the TEM image of a lamella approximately 20–50 nm thick. This suggests a density of 100–250 pillars per $\mu\text{m}^2$.

The pillar width is 3–5 nm, giving an estimate of the volume fraction of metallic Fe of 0.1%–0.4%. This volume fraction is small, but it could contribute a significant amount of the net magnetization because metallic Fe has...
a high saturation magnetization of 1700 emu cm\(^{-3}\). However, the majority of the Fe remains in the perovskite, e.g., the formation of even 0.5 vol\% metallic Fe would deplete Fe from approximately 8% of the STF volume. Films grown on STO at \(P = 1\) and 10 \(\mu\)Torr have no pillars, and the Fe is uniformly distributed.

### D. Fe valence state

Measurement of the atomic ratio of Ti and Fe is shown in Fig. 4(a) from energy-dispersive x-ray spectroscopy (EDS, FEI Philips XL 30), confirming that there is no systematic change in the ratio of Fe:Ti (=0.35:0.65) with \(P\).

The Fe valence state is characterized by conversion-electron Mössbauer spectrometry and by x-ray photoelectron spectroscopy (XPS). Conversion-electron Mössbauer spectrometry shows a difference between two films grown at \(P = 2\) \(\mu\)Torr on different substrates, as shown in Figs. 4(c) and 4(d). For the STF/Si, a weak paramagnetic signal of Fe\(^{3+}\) is detected (approximately 0.7% max emission). The signal may be fitted to a singlet (Gaussian) or, more justifiably (based on Fig. 4(d)), a doublet (2 pseudo-Voigt) as shown in Fig. 4(c), yielding an isomer shift relative to \(\alpha\)-Fe of 0.25 ± 0.04 mm s\(^{-1}\) and a quadrupole splitting of 0.89 ± 0.08 mm s\(^{-1}\). This signal may arise from Fe\(^{3+}\) associated with oxygen vacancies [60]. No other signals are resolved.

The STF/STO shows 0.5%–0.6% emission after optimization. Unlike the sample on Si, the STF/STO shows a metallic iron magnetic phase, identified not just because of the presence of a sextet but also because of the isomer shift of 0.00 ± 0.02 mm s\(^{-1}\), equal to that of \(\alpha\)-Fe [Fig. 4(d)]. The peak-intensity ratio of the sextet state indicates that the iron is not uniformly magnetized perpendicular to the substrate [61–63]. There is also a paramagnetic ferric doublet with an isomer shift of 0.35 ± 0.04 mm s\(^{-1}\) that accounts for 23% of the peak area. A measurement using Auger electrons sensitive to the top 20–30 nm of the film shows a lower peak-area fraction (15%) for the paramagnetic iron, suggesting a depth dependence of the iron valence state. These results indicate that metallic Fe is present in the STF/STO but not in the STF/Si grown at \(P = 2\) \(\mu\)Torr.

Figure 4(b) shows XPS results in which the Fe peaks are similar over the range of deposition pressures and the two substrate types. The peak positions are calibrated so that the Cu peak is present at 284.8 eV. There are no significant differences in the Sr, Ti, and O XPS peaks. The satellite peaks around the Fe \(2p_{3/2}\) and \(2p_{1/2}\) doublet indicate the presence of Fe\(^{3+}\) but not Fe\(^{2+}\), similar to epitaxial BiFeO\(_3\) [64] and iron oxides [65]. The lack of a metallic Fe peak in the 4-\(\mu\)Torr sample on STO differs from the TEM results and from the Mössbauer analysis of the \(P = 2\) \(\mu\)Torr sample. Since XPS is surface sensitive, we assume that the top parts of the Fe nanorods at the surface would be subject to oxidation, or their very small area coverage may have precluded the observation of a metallic Fe peak.

### E. Optical and magnetic characterization

Transmissivity of the films on the two substrates from visible to near-IR wavelengths is shown in Fig. 5. For energies below the band gap, the transmissivity of STF/Si is higher than that of bare silicon because of the antireflection effect that arises from introducing a lower refractive index film on a higher refractive index substrate. The transmissivity of STF/STO and bare STO are similar except for energies just below the band gap where the STF/STO became absorbent.

Atomic force microscope (AFM) images of the STF/Si and STF/STO grown at \(P = 4\) \(\mu\)Torr are shown as insets in Fig. 5. The films had a root-mean-square roughness of 1.8 and 2.2 nm, respectively, and have reflective film surfaces. The STF/Si grown at \(P = 1, 4,\) and 10 \(\mu\)Torr had similar surface topography, with in-plane feature sizes of 20–40 nm. In contrast, the STF/STO grown at \(P = 1\)
and 10 μTorr is much smoother than the film grown at 4 μTorr.

Figure 6 shows the room-temperature magnetic hysteresis loops from vibrating sample magnetometry (VSM) for films on both substrates as a function of $P$. Linear substrate signals are subtracted. Uncoated STO substrates subjected to thermal cycling in vacuum in the PLD chamber similar to the thermal cycling during film growth show a diamagnetic response with little change on annealing. For both substrates, the films grown at $P = 4.0 \mu$Torr show the largest saturation magnetization, while films grown at or above $P = 5 \mu$Torr do not exhibit a hysteresis loop. The magnetic easy axis is along the out-of-plane direction, with switching fields of 3–4 kOe and a high remanence. The hysteresis loop shape, switching field, and the anisotropy field are generally consistent with those seen in previous studies of STF/STO [16,27,28]. The STF/STO grown at $P = 4 \mu$Torr has $M_s = 17$ emu cm$^{-3}$, whereas—remarkably—the

FIG. 5. Optical properties of STF films. Transmission spectra of STF/Si, STF/STO, and their substrates; the insets show the AFM images of the surface topography.

FIG. 6. Magnetic properties of STF films measured by VSM. (a),(b) Magnetic properties of STF/Si specimens. (c),(d) Magnetic properties of STF/STO specimens, (a),(c) in plane and (b),(d) out of plane. Insets show the dependence of the magnetization on pressure at $H = 10$ kOe.
The oxygen content of the films and, therefore, $\delta$ is difficult to quantify because the sample volume is too small for thermogravimetric analysis, although other methods such as photoluminescence, direct imaging, or measurements of cation valence may be applicable [74,75]. However, Rothschild et al. [14] showed that Fe$^{3+}$ was the dominant valence state in STF over a range of pressures and temperatures including those corresponding to the growth conditions, i.e., the composition can be written $\text{SrTi}_{4-x}\text{Fe}_x\text{O}_{3-(s/2)-\gamma}$ with $\gamma$ representing the deviation from a state containing all Fe$^{3+}$. The presence of Fe$^{2+}$ became significant at extremely low oxygen pressures, e.g., below $10^{-9}$ Torr at 600 °C, whereas Fe$^{4+}$ was present at higher pressures, e.g., above 10 mTorr. Rodriguez et al. showed that a mixture of Fe$^{3+}$ and Fe$^{4+}$ was present in STF after synthesis at 1300 °C in oxygen [76], and Ferreira suggested that some Fe$^{4+}$ was present at room temperature [20]. It is not clear how well the PLD growth conditions correspond to these equilibrium conditions, but we expect that the oxygen content will be kinetically trapped after cooling the samples from the growth temperature, implying that the oxygen content and the average Fe valence state in the films will be lower for films grown at a lower base pressure.

The formation of sparsely distributed metallic Fe nanorods is inferred in the $P = 2$ and 4 μTorr STF/STO samples. This was not seen in our previous work on STF [16], but there have been several other observations of metallic transition metal nanorods forming in an oxide matrix, notably Fe in a (nonperovskite) LaSrFeO$_4$ matrix formed from the deposition of LaSr$_{0.4}$Fe$_{0.5}$O$_{1.5}$, and Co, Ni, or Fe in ceria or STO by codeposition of the matrix phase with a transition metal oxide [77–79]. In the $P = 4$ μTorr STF/STO, it is possible that the low base pressure combined with the large tetragonal distortion due to epitaxy promotes the precipitation of a fraction of the Fe as a strain relief mechanism that is not seen in the nonepitaxial films on Si. The precipitation of the small volume fraction of metallic Fe would lead to an excess of Sr in the perovskite matrix that could be accommodated through additional SrO layers as in Ruddlesden-Popper phases without disrupting the overall perovskite structure. In contrast, in the films on Si it appears that all the Fe is present within the perovskite lattice. The Fe distribution does, however, become less homogeneous at low base pressure. It is not clear why the STF unit-cell volumes decrease for $P < 4$ μTorr. This may indicate a different strain-relaxation mechanism becoming important, or a structural change due to the ordering of vacancies or the formation of Ti$^{3+}$.

In previous work, we have suggested that oxygen-deficient STF exhibits mixed valence Fe ions, leading to both ferromagnetic and antiferromagnetic interactions between nearest neighbors. A range of other Fe-based perovskites including Sr$_2$FeMoO$_6$ and Ba$_2$FeReO$_6$ also display room-temperature magnetism that originates on the...
Fe spins [80–82]. Moreover, the magnetic moment of Fe ions is dramatically affected by adjacent oxygen vacancies that break the symmetry of the oxygen coordination octahedron, as predicted theoretically in STCo [83]. Film strain leads to magnetoelastic anisotropy, which can orient the overall direction of magnetization in the film, accounting for the out-of-plane easy axis for STF/STO [16]. The resulting net magnetic moment of the STF and the hysteresis behavior is, therefore, highly dependent on the concentration and arrangement of the oxygen and Fe and the strain state, as well as the presence of Fe nanorods, and is expected to vary with all the film deposition conditions including $P$. In STCo, changes in $P$ are also found to affect the magnetic moment [22].

The most striking finding in the present work is the higher magnetization and FR in films made on Si compared to those on STO. The films differ in their microstructure and strain state, but may also have subtle differences in oxygen content, vacancy clustering, or Fe distribution despite being deposited simultaneously; this could result from different surface kinetics or surface chemistry during film nucleation, or differing substrate temperatures due to the differences in emissivity and thermal conductivity between the Si and STO substrates. The magnetic effects in STF/Si appear not to originate from metallic Fe, and are, therefore, intrinsic to the substituted perovskite. Metallic behavior has been calculated for STO surfaces [84], suggesting that the grain boundaries in the STF may play a role in its electronic properties. Unlike the STF/STO, which has a significant tetragonal distortion $(c/a > 1)$ leading to magnetoelastic anisotropy [27,85], the polycrystalline STF/Si has little strain, suggesting that the origin of its magnetism is microstructural [influenced by grain boundaries, oxygen content, vacancy clustering, or the inhomogeneous Fe distribution observed in Figs. 2(a)–2(c) and 3(b)] rather than magnetoelastic.

III. INTEGRATED MAGNETO-OPTICAL ISOLATOR

The polycrystalline STF/Si is suitable for magneto-optical devices because it is expected to grow on a variety of substrates and it has a large remanent Faraday rotation angle. As an illustration of the integration of polycrystalline STF into a magneto-optical device, a ring resonator is prepared from a silicon-on-insulator wafer consisting of a racetrack placed adjacent to a straight waveguide, similar to the devices shown in Refs. [4,5]. When light passing through the waveguide is resonant with the racetrack (i.e., when the racetrack circumference is an integral number of wavelengths), the light couples into the racetrack, and there is a drop in transmittance through the waveguide, as shown in Fig. 8. If the racetrack is clad on top with a magneto-optical material magnetized perpendicular to the waveguide, the transverse magnetic (TM) mode, but not the transverse electric (TE) mode, experiences a nonreciprocal phase shift (NRPS). This leads to a different resonant wavelength for clockwise and counterclockwise propagating TM light, which forms the basis of an isolator.

The waveguides have a thickness of 250 nm and a width of 450 nm. The racetrack is 290 $\mu$m long and 90 $\mu$m wide. A 200-$\mu$m-long, 20-$\mu$m-wide window is opened in the silica cladding of one of the sides of the racetrack and STF (at $P = 4 \mu$Torr) is deposited over the sample, so that the STF contacted the waveguide directly within the window. The transmittance of the waveguide or resonator is measured at a wavelength of around 1550 nm for a magnetic field of $\pm 2$ kOe applied in plane, perpendicular to the side of the racetrack. The resonant wavelength of both the TM and TE modes varies between successive measurements by up to 10 pm because of thermal drift or vibration, but the TM mode shows an NRPS of approximately 4 pm compared to the TE mode when the sign of the applied field is reversed.

Similar devices made with CeYIG cladding [5] (FR = $-1300^\circ$ cm$^{-1}$) with in-plane magnetization exhibit a NRPS of approximately 20 pm. The lower NRPS in the STF devices is a result of incomplete in-plane saturation, which requires a field $>5$ kOe. Based on the hysteresis loops, a 2-kOe in-plane field would lead to an in-plane magnetization of approximately 1/3 of the saturation magnetization. The FR scales with the magnetization, so we expect the STF to produce an NRPS of 1/3 of what would be produced at in-plane saturation. The NRPS of the STF devices is in reasonable agreement with the expected NRPS, considering the geometry of the resonator and the magnitude of the FR. The absorption of the STF at a wavelength of $\lambda = 1550$ nm is $31 \pm 2$ dB cm$^{-1}$, derived as shown in [70]. Hence, the figure of merit defined as the
ratio of saturation FR to absorption is 58° dB\(^{-1}\), which is good compared with other thin-film magneto-optical materials [17,33].

IV. ELECTRONIC STRUCTURE CALCULATIONS

We now present a brief discussion of the theoretical predictions for the electronic structure and the change of the lattice parameters as a function of the chemical pressure created by oxygen vacancies of STF based on hybrid density functional theory (DFT) [83], as described in the methods section. All possible vacancy and Fe configurations for STF with \(x = 0.125\) or 0.25 are evaluated.

From Fig. 9(a), we find that STF with \(\delta = 0.125\) and \(x = 0.125\) (one Fe atom and one vacancy in the \(2 \times 2 \times 2\) perovskite supercell) is a semiconductor with a band gap of approximately 1.1 eV. The \(e_g\) orbitals are partially occupied, which gives rise to the ferrimagnetism. From molecular orbital theory, we find that the high-low spin-gap energy is approximately 70 meV, which is actually larger than the approximately 40 meV required to take a spin to the \(e_g\) from the \(t_{2g}\) level [30]. A detailed analysis of the spin states in this system will be discussed in a subsequent publication.

We confirm the oxidation states are \(\text{Fe}^{2+}\) and \(\text{Ti}^{4+}\) rather than both ions being \(\text{Fe}^{3+}\), and the \(\text{Ti}^{4+}\) magnetic moment is negligible.

When \(x = 0.25\), the two Fe ions can be arranged along [001], [110], or [111]. In each case, the Fe-Fe distances are approximately 0.9 times the Ti-Ti distance in STO, and the final unit cell is distorted from cubic symmetry. In the \(\delta = 0\) case the Fe ions have an average moment of 3.7\(\mu_B\), with an antiferromagnetic ground state in the Fe-[001] arrangement. For the [110] and [111] arrangements where the Fe ions are further separated, the lowest energy ferromagnetic (FM) and AF states are almost degenerate within a small energy range <40 meV. The preponderance of [110] and [111] configurations in a crystal with random Fe-site distribution suggests an overall low moment due to dominant AF interactions.

An oxygen vacancy (\(\delta = 0.125\)) leads to a significant increase in the volume of the unit cell compared to \(\delta = 0\), in agreement with experiment. The volume increase is not due to the Fe-Fe interaction but to the chemical pressure created by the vacancy. When calculating the ground state for \(\delta = 0.125\), the spin and valence of the two Fe ions are initialized in all possible combinations (i.e., both \(\text{Fe}^{3+}\), one

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\[\text{FIG. 9. DFT calculations. (a) Total density of states for SrTi}_{0.875}\text{Fe}_{0.125}\text{O}_{2.875} (high spin Fe) obtained with HSE06. The supercell contains one Fe ion and one neighboring vacancy. (b) Spin density (HSE) projected onto the (100) plane for SrTi}_{0.75}\text{Fe}_{0.25}\text{O}_{3} in which the two nearest-neighbor Fe ions are aligned in the [001] direction, showing clearly their antiferromagnetic ordering. (c) Spin density (HSE) projected onto the (100) plane for SrTi}_{0.75}\text{Fe}_{0.25}\text{O}_{2.875} with an oxygen vacancy adjacent to one of the two Fe ions per unit cell. In both cases (b) and (c), the second-nearest Fe neighbors are also depicted and the color scale indicates the spin density normalized to the largest magnetic moment. The ferrimagnetic order in the O-deficient system is clear in (c). (d) Image showing the model in (c) in which the atomic positions are visible. The plane shown in (c) bisects the model passing through the Fe and Ti sites. Blue, Ti; brown, Fe; green, Sr; red, O.}\]
Fe$^{4+}$ and one Fe$^{2+}$, high and low spin, and FM and AF) and the lowest energy state after relaxation is defined as the ground state. The low-spin states tend to shift to high spin with approximately 4.1–4.2$\mu_B$, with the two Fe spins coupled AF in most but not all cases. However, even the AF-initialized cells have a net moment, i.e., they are ferrimagnetic, because the spin at each Fe location is not identical owing to their different locations with respect to the oxygen vacancy.

In the Fe-[001] case, the lowest energy configuration is one where the vacancy is between the two Fe ions, which eliminates the superexchange between the Fe ions that coordinate the vacancy. The magnetic moment is approximately 0.2$\mu_B$/Fe. In the Fe-[110] case, the two possible vacancy positions lead to similar energies, and the magnetization in the ground state is 0.3–0.4$\mu_B$/Fe. In the more symmetric case of Fe-[111], the FM and AF configurations are almost degenerate (i.e., <0.1 meV) because of the large separation between the Fe atoms. The final magnetic moment of the AF-initialized arrangement is once again 0.1–0.2$\mu_B$/Fe.

To better understand the effects of the vacancies on the magnetic behavior, we calculate the HSE spin density for a variety of nearest-neighbor configurations and resulting interactions to be present, including those addressed in the modeling. The crystal would then exhibit a relatively low net magnetic moment, dominated by AF coupling, analogous to a ferrimagnet but without long-range order.

In conclusion, STF (SrTi$_{0.95}$Fe$_{0.35}$O$_{3-\delta}$) films grown on Si or STO substrates by PLD show a strong dependence of microstructure and magnetic properties on the base pressure during deposition. At an optimum base pressure for deposition ($P = 4 \mu$Torr) the films show room-temperature magnetism of up to 0.53$\mu_B$/Fe with out-of-plane magnetic anisotropy, and a coercivity of 3 kOe as well as a FR of $-1900$ cm$^{-1}$ at a wavelength of 1550 nm. STF grown on STO at the optimum base pressure of $P = 4 \mu$Torr shows a low (<0.5%) volume fraction of metallic Fe nanorods not present at other pressures that contribute to the magnetic signal, but the polycrystalline STF films grown on Si show 65% greater magnetization and FR compared to the epitaxial films on STO. There is no evidence of metallic Fe in the STF/Si, indicating that the magnetic and magneto-optical properties are intrinsic to the substituted perovskite. Polycrystalline STF is grown onto a silicon ring resonator, and its FR produces a nonreciprocal phase shift. First-principles calculations show that oxygen vacancies increase both the unit-cell volume and the magnetic moment of the Fe ions. The dominant interactions are antiferromagnetic, leading to a material with a net magnetization below about 0.5$\mu_B$/Fe, which is reasonable compared with the experimental data. These results illustrate the important role of oxygen vacancies in determining the magnetic properties and structure of a Fe-substituted perovskite, and the integration of the perovskite in magneto-optical devices.

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APPENDIX A: TARGET PREPARATION

SrCO$_3$ (99.99%), TiO$_2$ (99.99%), and Fe$_2$O$_3$ (hematite, 99.945%) powders are stoichiometrically mixed, ball milled for 24 h, and calcined at 1200°C for 5 h, showing a single perovskite phase. The powder is pressed into a 1-inch-diameter pellet and sintered at 1300°C for 5 h.

APPENDIX B: SAMPLE PREPARATION FOR TEM

The samples are prepared using a focused ion beam (FEI-600), and then imaged on a JEOL 2010F field emission TEM at a 200-kV acceleration voltage. The element distribution in the sample is mapped by STEM EDX.

APPENDIX C: X-RAY DIFFRACTION

For STF/STO, the PANalytical X’pert is used. The wavelength is Cu-Kα ($\lambda = 1.540598$ Å), the source current is 40 mA, the voltage is 45 kV, and the scan step in $2\theta$ is 0.017°. There is no offset of $\omega$. For STF/STO reciprocal space maps, the Bruker-AXS D8 DISCOVER is used with Cu-Kα radiation. The x-ray beam is monochromated with the Ge(220) × 4, and the Gobel mirror slit is 0.8 mm. The first and second monochromator slits are 0.2 and 1 mm. For STF/Si, the Rigaku Smartlab is used because of its capability for in-plane grazing-incidence diffraction. The wavelength is Cu-Kα with a tube current of 200 mA and a voltage of 45 kV. The step of the $2\theta$ goniometer is 0.024°, and the incident angle of the x rays $\omega$ is fixed at 0.4°.

APPENDIX D: MÖSSBAUER SPECTROSCOPY

$^{57}$He Mössbauer spectroscopy with a $^{57}$Co/Rh source (of approximately 20 mCi of activity) is performed at 300 K in order to characterize the iron in the samples using the conversion-electron mode. The films are first metallized with a thin layer of aluminum (approximately 30–40 nm) to provide a good Ohmic contact and subsequently inserted into the cathode structure of a He-CH$_4$ filled (5% at 1.7 bar) gas-flow proportional counter, for measurements lasting approximately one week in each case. Energy-filtering-enabled Mössbauer spectra are acquired for the film (deep electrons and x-rays) and primarily from the surface (approximately 20–30 nm penetration depth, due to Auger electrons) for the sample on STO. No Mössbauer signal can be resolved for the lowest escape energies. The sample on Si has a weaker signal and no energy filtering is performed, so the data correspond to the full thickness. The spectra are fitted using the standard least-squares method, using a pure Fe metal foil for velocity calibration.

APPENDIX E: THEORETICAL METHOD

We perform spin-polarized DFT calculations with a Heyd-Scuseria-Ernzerhof (HSE) functional [86,87] as implemented in the Vienna $ab$ initio simulation package and within a projector-augmented-wave–Perdew-Burke-Ernzerhof framework [88]. Compared to semilocal DFT methods, HSE improves the accuracy of standard local magnetic moments as well as features of interest such as valence spin states, band gaps, and lattice parameters, as shown previously for SrCoO$_3$ and SrTiCoO$_3$ [83]. A $2 \times 2 \times 2$ perovskite supercell with 39 or 40 atoms for $\delta = 0$ or 0.125, respectively, is used. Monkhorst $k$-point meshes of $2 \times 2 \times 2$ and $4 \times 4 \times 4$ are used for relaxation and magneto-calculations, respectively. The energy cutoff used is 500 eV, and forces are converged to within $10^{-5}$ eV Å$^{-1}$.

We explore all possible FM and AFM initialized states in both high- and low-spin configurations for different combinations of valence states for Fe, i.e., $4\mu_B$ and $0\mu_B$ (high- and low-spin Fe$^{2+}$), $5\mu_B$ and $1\mu_B$ (high- and low-spin Fe$^{3+}$), and $4\mu_B$ and $2\mu_B$ (high- and low-spin Fe$^{4+}$). We also explore perturbations of $\pm 20\% \mu_B$ for every initialization. In total, a few hundred calculations are performed, and in all cases, the magnetic moments are allowed to fully relax to their final value. Some cases with $4 \times 4 \times 4$ supercells are also examined with $\epsilon = 0.25$ and $\delta = 0.125$, of which a few reach convergence within a reasonable time. These configurations show antiferromagnetic coupling between the Fe moments and agree with the $2 \times 2 \times 2$ supercell results.


[11] W. Jung and H. L. Tuller, Impedance study of SrTi_{1-x}FeO_{3−δ} (x = 0.05 to 0.80) mixed ionic-electronic conducting model cathode, Solid State Ionics 180, 843 (2009).


[71] T. Goto, M. C. Onbasli, and C. A. Ross, Magneto-optical properties of cerium substituted yttrium iron garnet films


[76] J. Rodriguez, J. A. Pereda, M. Vallet, J. G. Calbet, and J. Tejada, Mössbauer study of vacancy ordering in the system SrTi$_{1-x}$Fe$_x$O$_{3-y}$ (0.50 ≤ x ≤ 0.70), Mater. Res. Bull. 21, 255 (1986).


[85] P. Adler, Charge disproportionation in iron(IV) oxides: Electronic properties and magnetism in Sr$_3$Fe$_2-x$Ti$_x$O$_{7-y}$ annealed at high oxygen pressures, J. Mater. Chem. 9, 471 (1999).

