Room-temperature ferromagnetism and oxygen pressure-dependent optical, ferromagnetic properties in SrSn$_{0.5}$Co$_{0.5}$O$_3$ thin films

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ABSTRACT
Room-temperature ferromagnetism was obtained in SrSn$_{0.5}$Co$_{0.5}$O$_3$ (SSCO) epitaxial film on SrTiO$_3$ substrate by pulsed laser deposition, and the effects of oxygen pressure (P$_{O_2}$) on the microstructure, optical and magnetic properties were examined. An interesting hybrid epitaxial film embedded with polycrystalline SSCO and SrCoO$_x$ nanoparticles was observed. The increase of P$_{O_2}$ relaxed the film/substrate compressive strain, promoted the growth of crystallites and reduced the optical band gap (from 2.43 to 1.68 eV). The SSCO film deposited at 0.1 Pa exhibited good ferromagnetism at 100–300 K, while the ferromagnetism in the film with higher and lower oxygen pressure (1 Pa and 10$^{-4}$ Pa) was weak.

IMPACT STATEMENT
Room-temperature ferromagnetism and tunable optical band gap (2.34–1.68 eV) were demonstrated in Co-doped SrSnO$_3$ thin film grown on SrTiO$_3$ single-crystal substrate by pulsed laser deposition with varying oxygen pressure.

Introduction
Perovskite oxide semiconductors in ABO$_3$ structure are the long-lasting hot spots among functional oxides due to their excellent optical, electronic and magnetic properties [1], and vast applications in superconductors [2], piezoelectric/ferroelectric/thermolectric devices [3–5], etc. Recently, the rapid rise of the room-temperature transparent ferromagnetism in Co-doped La$_{0.5}$Sr$_{0.5}$TiO$_3$–δ [6] and Mn-doped BaSnO$_3$ [7] has spurred interest on visible-light absorption perovskites and diluted magnetic perovskites [8,9]. The combination of tunable transparency and ferromagnetism will provide more optical/electrical dimensions to the spintronic devices, thus more suitable for the function integration. However, it is not easy to precisely modulate the band gap and magnetic properties of perovskite oxides. In ABO$_3$-type perovskites, slight buckling and distortion of chemical bonds can reduce the coordination number of ‘A’ cations and/or ‘B’ cations, producing lower-symmetry distortions, and accordingly resulting in significant variations in the electronic and magnetic properties [10]. Compared with the preparation techniques of bulk materials, the thin film epitaxy is more favorable for the optical and magnetic modulation of perovskites. The substrate can induce film lattice distortions, which greatly affect the electronic/magnetic behaviors [11,12]. Moreover, the films via vacuum-based deposition can generate oxygen vacancies easily, which play important roles in tuning the electric and magnetic behaviors [13].

Strontium stannate (SrSnO$_3$) is a typical wide band gap (4.27 eV) and diamagnetic perovskite [14]. For the thin films of SrSnO$_3$, previous studies mainly focused on
the doping technique used in the transparent conductive films, photocatalysis and afterglow phosphors [15,16]. The efforts on the band gap modulation and ferromagnetism are very limited. Shein et al. [17] predicted that the band gap of SrSnO$_3$ could be as low as 0.7 eV by doping Fe and Co. The optical band gap of 2.36 eV was realized in epitaxial SrSn$_{1-x}$Fe$_x$O$_3$ films on MgO [18] and 2.44 eV in epitaxial SrSn$_{1-x}$Co$_x$O$_3$ films on SrTiO$_3$ (STO) [19]. There is no report on the ferromagnetism of thin films up to now, though weak ferromagnetism was reported in bulk SrSnO$_3$ doped by Fe or Cr [20,21].

Herein, we took SrSnO$_3$ as an example and demonstrated the potential of the thin film epitaxial in tuning the microstructure, optical and magnetic properties of the perovskite materials. By simply varying the oxygen pressure, we obtained distinctive nanoparticles embedded in epitaxial thin films and achieved tunable band gap down to 1.68 eV and the room-temperature ferromagnetism with the saturated magnetization of 12 emu cm$^{-3}$.

**Methods**

Ceramic targets of SrSnO$_3$ and SrSn$_{0.5}$Co$_{0.5}$O$_3$ (SSCO) were prepared via high-temperature solid-state reaction from SrCO$_3$, SnO$_2$ and Co$_2$O$_3$ powders (Aladdin, 99.8%). Corresponding thin films were grown via the pulsed laser deposition on STO single-crystal substrates, which were ultrasonically rinsed in water, alcohol and acetone successively. The laser source was a 248-nm KrF excimer laser (Lambda physik Compex 201, Germany) with the repetition rate of 5 Hz and the energy density of 200 mJ per pulse. The substrate temperature was fixed at 650°C. The deposition lasted for 1.5 h. The oxygen pressure (P$_{O_2}$) ranged from $10^{-4}$ to 1 Pa for SSCO films and was fixed at 0.1 Pa for SrSnO$_3$ film.

The crystallinity was characterized by a two-circle Bruker D8 diffractometer with the Cu-K$_{α1}$ radiation. The microstructures were measured by atomic force microscopy (AFM, SH SPI-3800I, Japan) and FEI Tecnai G2 F20 field emission transmission electron microscope (TEM). The film composition was analyzed on ESCALAB 250 X-ray photoelectron spectrometer (XPS). The optical transmittance spectra were measured with a spectrophotometer (Hitachi, U-4100, Japan). The ferromagnetic properties were measured by Quantum Design MPMS XL5 electrical magnetic measurement system at temperatures of 100, 200, 300 and 400 K.

**Results and discussion**

Figure 1(a) presented X-ray diffraction (XRD) patterns of SSCO films with P$_{O_2}$ of $10^{-4}$–1 Pa. Only the reflections from the (00l) planes of SSCO and STO (00l) planes were observed, and no other phase or randomly oriented grains were detected. Figure 1(a) inset showed the shifting trend of the (001) peak towards higher 2θ direction with the P$_{O_2}$ increasing, approaching to the (001) peak of STO, indicating the decrease of the lattice constant and the relaxation of the compressive strain at the film/substrate interface. With the increase of P$_{O_2}$, the concentration of oxygen vacancies in the film decreased, and the coulombic repulsion between cationic Sr and Sn decreased correspondingly [22], which resulted in the reduced lattice constant.

The ω-scan rocking curves and the φ scans were also measured and given in Figure S1. The small full width at half maximum (FWHM) values in the (001) peak of the SSCO films (P$_{O_2}$: 0.1 Pa) (film: 0.04°, substrate: 0.02°) further confirmed the high crystallinity of the film. The appearance of four distinct peaks at an interval of 90° in the φ scans indicated the cubic epitaxial structure of the SSCO films on STO(001) substrates.

The AFM images (Figure 1(b)) showed that the crystallite size and the overall roughness of the SSCO film...
increased significantly with $P_{O_2}$. The film deposited at $10^{-4}$ Pa was much smoother (root mean square (RMS) roughness: 0.199 nm) than that deposited at 1 Pa (RMS roughness: 1.590 nm), in which large particles with the average size of 100–200 nm were observed. The $P_{O_2}$ of 0.1 Pa seemed to be a turning point where the crystallites started to grow (5–10 nm) and the film still exhibited smooth morphology (RMS roughness: 0.541 nm). This behavior was related to the film growth mode and the mobility of atoms on the SSCO film surface during pulsed laser deposition process [23]. When $P_{O_2}$ was low, the film was grown in a layer to layer mode and the atoms deposited on the surface of film preserved a suitable mobility. In contrast, the higher $P_{O_2}$ hindered the atoms’ mobility effectively, and correspondingly the island growth mode was preferred [24].

The TEM image in Figure 2(a) showed that the SSCO film was dense and uniform, free from any detectable pores or defects, with the thickness of $\sim 261$ nm. The typical energy-dispersive spectrum (Figure 2(c)) showed that the film was composed of four elements with the atomic ratio of Sr:Sn:Co = 1:0.426:0.361. The Sn and Co content were slightly lower than the stoichiometric ratio of SSCO, possibly due to their different partial volatilization in the plasma plume during the deposition process. The selective area electron diffraction pattern (Figure 2(b)) indicated three sets of diffraction patterns, the single-crystal SSCO spot array, the poly-crystalline diffraction rings of SSCO and SrCoO$_x$. The ‘x’ value in SrCoO$_x$ was deduced between 2.5 and 3.0 based on the detailed examination on the diffraction features of SrCoO$_x$ with ‘x’ values of 2.52, 2.61, 2.80 and 3.
The high-resolution TEM image in Figure 2(d) showed that discontinuous polycrystalline SrCoO$_x$ nanoparticles existed in the bulk epitaxial film. The high-resolution TEM image of the film/substrate interface (Figure 2(e)) showed the high epitaxial quality around the film/substrate interface. The detailed microstructure of an embedded SrCoO$_x$ particle (Figure 2(f)) showed an obviously polycrystalline feature in both particle and transitional region between particle and bulk film. Furthermore, we carried out the electron dispersive spectrum line-scanning analysis to the film, and the result is shown in Figure S2. The element distribution of Sr, Co and O both along the perpendicular and parallel scanning lines generally maintained a stable level, ~60% for Sr, ~25% for O and ~15% for Co. However, the distribution of element Sn along two lines was discontinuous, and some ‘zero Sn content’ zones were detected, which further proved that the polycrystalline particles embedded in the film were SrCoO$_x$. The formation mechanism of embedded SrCoO$_x$ nanoparticles may be explained by the limited solid solubility of Co atom in SrSnO$_3$ lattice. Previous studies on SrSn$_{1-x}$Co$_x$O$_3$ ($x = 0, 0.16, 0.33, 0.5$) ceramics proved that the SrCoO$_{2.52}$ (JCPDS No. 40-1018) phase could be formed in a high Co-substituting SSCO sample [25], which indicated the low solubility of Co atom in the lattice of SrSnO$_3$.

Figure 3(a) displayed the XPS spectrum of Co 2p electron of the SSCO film grown at 0.1 Pa. Two distinct peaks located at 780.80 and 796.02 eV with a separation of 15.22 eV were recorded, corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ core peaks. Two satellite shoulders located at 787.2 and 803.2 eV were also the characteristic of Co$^{2+}$, which originated from the charge-transfer band structure of the 3d transition metal monoxides [26]. There was no signal at 778.3 eV, indicating the nonexistence of free Co clusters in the film. The O1s spectra of SrSnO$_3$ and SSCO films (Figure 3(b)) exhibited an obviously asymmetric shape, indicating that the oxygen on grain surfaces was in different chemical conditions, and the right peak at 529.85 eV originated from the lattice oxygen and the left one at 531.7 eV originated from the defective oxygen ions on the grain surface [27]. The peak intensity related to the oxygen vacancies in the SSCO film was higher than that in the pure SrSnO$_3$ film, implying that more oxygen vacancies were introduced by Co doping.

The magnetization of the SSCO film grown at 0.1 Pa measured as a function of magnetic field ($M$ vs. $H$) at 100–400 K are presented in Figure 4(a). The hysteresis loops were observed at all four investigated temperatures and testified the room-temperature ferromagnetism of the SSCO film. Especially, the magnetic properties of the film at room temperature were fairly good compared with previous reports [7,20–22], and exhibited the saturated magnetization ($M_s$) of 12 emu cm$^{-3}$, the remnant magnetization ($M_r$) of 4.3 emu cm$^{-3}$, the coercive field ($H_c$) of 316 Oe and saturated field ($H_s$) of 5000 Oe. In view of the relatively high $M_r/M_s$ ratio (300 K: 0.358; 100 K: 0.57) and $H_c/H_s$ ratio (300 K: 0.12; 100 K: 0.40), the film was more close to the hard magnetic material. The oxygen pressure had significant effects on the magnetic properties of the SSCO film; the film deposited at 1 Pa and 10$^{-4}$ Pa showed very weak magnetic properties (Figure 4(b)).

The magnetic moments in the film originated from the cobalt–oxygen vacancy complexes with Co in the +2 valence state [28]. The ferromagnetism of the SSCO could be interpreted using the ‘bound magnetic polaron’ model [29,30], in which the Co ions were spin polarized through the mediation of adjacent oxygen vacancies, resulting in the formation of a bound magnetic polaron.
Figure 4. Magnetic hysteresis loops of SSCO film deposited at oxygen temperature of (a) 0.1 Pa and (b) 1 Pa on STO (001) substrate. The diamagnetic signals from the STO substrate were subtracted.

Based on this mode, the ferromagnetism of the SSCO film was affected greatly by two underlying factors: the antiferromagnetic coupling of Co pairs and the concentration of oxygen vacancies (Ov) [31,32]. The antiferromagnetic coupling of Co pairs was suppressed at low temperature and became manifest at high temperature [33], which resulted in the hard to soft magnetic transition with the temperature increase. The concentration of Ov was mainly affected by the P\text{O}_2. The higher the P\text{O}_2 was in the deposition atmosphere, the lower the concentration of Ov was in the film. For the film deposited at 1 Pa, weak ferromagnetism was ascribed to the much decreased concentration of Ov and the much lower magnetic moment than that in films with lower P\text{O}_2. At moderate P\text{O}_2, the concentration of Ov in the film maintained a good balance with that of Co\textsuperscript{2+} ions, forming the bound magnetic polaron [34] and improving the magnetic moment [35]. So good ferromagnetism was observed in the film grown at moderate P\text{O}_2 of 0.1 Pa. At low P\text{O}_2, though the concentration of Co–Ov complexes was high due to the high concentration of Ov, the ferromagnetism was weakened by the large film–substrate stains in these films. It has been reported that the strain could induce the ferromagnetic to antiferromagnetic phase transition in SrCoO\textsubscript{x} films [36,37] and that the large interfacial strain at the SrCoO\textsubscript{x} film/substrates could deteriorate the film ferromagnetism [38]. Thus, very weak ferromagnetism in the film with P\text{O}_2 of 10\textsuperscript{-4} Pa was observed in our work.

We further carried out the sheet resistivity at room temperature of SSCO film (Table S2). All films showed a high sheet resistance of > 10\textsuperscript{8}Ω/square, indicating that the SrSn\textsubscript{1−x}Co\textsubscript{x}O\textsubscript{3} films were intrinsically insulating.

The optical transmittance spectra of four SSCO films grown on STO substrate are given in Figure 5(a). In the visible band, the transmittance was affected significantly by the oxygen pressure. For the film with P\text{O}_2 of

Figure 5. (a) Optical transmittance and (b) (\text{α}h\nu)^2 ∼ h\nu curves of SSCO film on STO (001) substrate deposited at different oxygen temperatures.
10^{-4} \text{ Pa}, the absorption edge started from \sim 500 \text{ nm} and the transmittance of 44\% was maintained at \sim 400 \text{ nm}. The absorption edge of other three films with higher P_{O2} started from 640 \text{ nm}, and the visible transmittance decreased with the increase of P_{O2}. The film with the P_{O2} of 1 \text{ Pa} exhibited the lowest transmittance, lower than 20\% at 400 \text{ nm}. The optical direct allowed band gap of the SSCO films was calculated from the \((\alpha h\nu)^2 \sim \text{photon energy} h\nu\) curves (Figure 5(b)) according to the established protocol, where \(\alpha\) is the absorption coefficient. With the increase of P_{O2} from 10^{-4} to 1 \text{ Pa}, the band gap of the SSCO film decreased from 2.43 to 2.07 \text{ eV}, 1.90 \text{ eV} and finally 1.68 \text{ eV}, which was much lower than previous reports (2.36 and 2.44 \text{ eV}) [21,22]. The band gap of ABO_{3} perovskites was determined by the 3d orbit of B cation(s) (conduction band) and the 2p orbit of oxygen (valence band) [39]. The decrease of the oxygen vacancies concentration with P_{O2} increasing might slightly raise the energy level of O 2p orbit or pull down the level of Co^{2+} by partially changing its oxidation status, thus reducing the optical band gap. Similar results were also reported in other perovskite materials [40].

In summary, we prepared room temperature ferromagnetism SSCO film on STO substrate via pulsed laser deposition. By simply changing the oxygen pressure, we realized the optical band modulation from 2.43 to 1.68 \text{ eV}, room temperature ferromagnetism with the saturated magnetization of 12 \text{emu cm}^{-3}. The concentration of oxygen vacancies, the embedded polycrystalline nanoparticles and the interfacial strain at the film/substrate were responsible for the film optical band gap changes and ferromagnetism properties. The work demonstrated a novel film with hybrid microstructure and introduced a general and effective route to tune the optical and magnetic properties of perovskite materials, which would be a benefit to the development of various perovskite-based photovoltaic/photo catalysis/ferromagnetic devices.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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