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# Oxygen-sensing property of sol-gel-derived $SrTi_{1-x}Fe_xO_{3-\delta}$ thin films with different iron concentrations ($x = 0.2$–$0.8$)

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ABSTRACT

In this contribution, $SrTi_{1-x}Fe_xO_{3-\delta}$ thin film gas sensors with different iron concentrations ($x = 0.2$ to 0.8) were fabricated using a modified sol-gel spin-coating method and annealed at 650 °C for 1 h under synthetic air ambient. X-ray diffraction revealed the single phase polycrystalline structure of the thin films and their crystallinity decreased with iron concentrations. The films with high iron concentrations were not well crystallized and had large amount of amorphous-like structures, as indicated by transmission electron microscopy observation. The oxygen-sensing properties of the sensors were examined at different operating temperatures. The $SrTi_{1-x}Fe_xO_{3-\delta}$ thin film sensors with $x \leq 0.4$ showed a normal p-type-sensing response whereas sensors with $x \geq 0.5$ exhibited anomalous n-type-sensing response. This abnormal-sensing behavior can be explained by amorphous-like structures in the films with higher iron concentrations, which was caused by incomplete formation of cubic perovskite phase.



## 1. Introduction

Great interest has been shown in $ABO_3$ perovskite-type oxides owing to their attractive properties such as ferroelectricity, ferromagnetism, superconductivity, mixed ionic electronic conductivity, good thermal and chemical stability. In addition, perovskite oxides are susceptible to partial substitution in both A and B cation sites and able to accommodate large amount of dopants and defects, allowing for chemical tailoring to obtain unique electrical and electro-catalysis properties. This makes perovskite oxide an interesting material for applications such as electrodes of solid oxide fuel cell, oxygen separation membranes, components in electrochemical reactor, catalysts and gas sensors [1].

Gas sensor technology is one of the most important key technologies for future development with a constantly increasing number of applications in environmental monitoring, pollution control, healthcare, automobiles, hydrogen economy and technical processes control. Among all available sensor technologies, the semiconducting metal oxide gas sensors have received most attention due to their advantages of simple design, small size, high sensitivity, low cost and ease of fabrication. In addition to commonly used binary oxide, perovskite oxides appeared to be a potential candidate as gas-sensing materials. Specifically, strontium titanate ferrite materials (STFx in short) have been reported as a potential candidate as semiconductor type oxygen sensors [2,3]. STFx is a continuous solid-state solution between the two end members, $SrTiO_3$ and $SrFeO_3$. $SrTiO_3$ is a wide-bandgap semiconductor ($E_g = 3.2$ eV) with relatively low conductivity level, while $SrFeO_3$ is a mixed conductor with high level of electronic and ionic conductivities [4]. In the STFx system, the quadrivalent Ti ion ($Ti^{4+}$) is partially substituted by trivalent Fe ion ($Fe^{3+}$) without restoring the electroneutrality in the cation site. Hence, oxygen vacancy is formed to maintain charge balance in the system [4,5]. This inherent oxygen non-stoichiometry makes STFx highly sensitive to oxygen partial pressure ($pO_2$) and an excellent candidate for oxygen sensors. More important, the discovery of negligible resistance dependency at temperature between 700 and 900 °C for STF35 ($x = 0.35$) has provided a major motivation for its development as automotive oxygen sensors [6]. Consequently, a number of research works have been reported on the preparation methods, material properties, gas-sensing performance and defect chemistry of STFx materials [7–13].

In this study, we report the synthesis and fabrication of STFx thin film sensors using a modified sol-gel spin-coating method. In comparison to the conventional high-temperature solid-state reaction normally used to prepare STFx powder, sol-gel process has advantages of simple and low cost, easy control of composition, good homogeneity, thin film formability and low synthesis temperature. For our case where multi-component STFx has to be prepared, the hydrolysis rate of the multi-components alkoxide is very difficult to control. Hence, modified sol-gel process using metal salts such as nitrates and acetates was adopted instead of the conventional sol-gel method, which usually employs metal alkoxides. The physical properties of

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the thin films were studied using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The oxygen-sensing characterization results revealed that STFx sensors with $x \geq 0.5$ show an unusual n-type sensing while the typical p-type-sensing response is observed for the sensors with $x \geq 0.4$. The sensing behavior and mechanism are presented and discussed in detail.

## 2. Experimental details

The STFx thin films were deposited using a modified sol-gel method. Strontium acetate (Nacalai Tesque), titanium butoxide (97%, Aldrich) and iron nitrate (99%, Merck) were chosen as the starting materials for the sol-gel preparation. Using a magnetic stirrer, the titanium butoxide was first thoroughly mixed with acetylacetone (99%, Merck) at 60 °C with a mole ratio of 1:4. At the same time, iron nitrate was dissolved in 2-methoxyethanol (99.8%, Sigma-Aldrich) and acetylacetone at 60 °C with a mole ratio of 1:20:6. Next, the Ti and Fe precursors were mixed together and homogenized under continuous stirring for 30 min. In this process, acetylacetone played the role as chelating agent, which can stabilize the metal ions by forming metal complexes. On the other hand, the strontium acetate was dissolved in glacial acetic acid ($CH_3COOH$) and deionized water with a mole ratio of 1:15:90. Deionized water was added to help to dissolve the acetate powders, which normally have lower solubility in water and organic solvents than other metal salts. Finally, the dissolved Sr precursor solution was slowly dripped into the mixed Ti and Fe precursor under continuous stirring. The molarity of the final sol was adjusted using 2-methoxyethanol. The as-prepared solution was left overnight for 1 day to allow for sufficient hydrolysis before spin-coating deposition.

For sensor device fabrication, Au interdigitated microelectrodes with 25 μm line and spacing were deposited on $Si/SiO_2$ wafer substrate using the photolithography metal liftoff process. Ti (10 nm) followed by Au (100 nm) were deposited using E-beam evaporator. The STFx sol was spun on the wafer substrate with gold interdigitated electrodes using spin coater (Laurell Technologies) in a nitrogen chamber with 10% relative humidity. Each deposited sol layer was then soft-baked at 150 °C followed by 300 °C for 5 min each. Five spin-coated STFx layers thin films were obtained and patterned into gas-sensing devices. The final devices were annealed at 650 °C for 1 h under synthetic air ambient using Lindberg tube furnace.

The crystallography of the STFx sol-gel spin-coated thin films was studied using XRD measurements. The XRD patterns were recorded at room temperature using Siemens D5005 X-ray diffractometer with Cu K-alpha radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 40 mA. The 2-theta detector was scan from 20º to 80º with a scan rate of 1º per minute. A small glazing angle of 1° was used to ensure that the diffraction intensity came mostly from the measured samples. The surface morphologies of the thin films were observed using FESEM (Jeol-6340 F) at an operating voltage of 5 keV. The thin film TEM samples were prepared using focused ion beam technique (FEI Nova 600i), and the microstructure of the thin films was studied using a transmission electron microscope (JEOL 2010) with an acceleration voltage of 200 kV. Selected area electron diffraction (SAED) was also performed to obtain the crystallographic information of the thin films. The dc conductivity measurements of gas-sensing properties of the sensing devices were carried out with the Keithley 236 source measurement unit attached to a custom-designed gas-sensing characterization system programmed with the National Instruments' LABVIEW version 8.5. The sample mount test gas chamber was designed to strategically position the sensing device on the heater stage in the gas chamber with electrical feed through, under the direct influence of the test gas flow. The test gases (oxygen, carbon monoxide, ammonia) were supplied by SOXAL Gas Company.

## 3. Results and discussion

### 3.1. Material characterizations

Smooth and uniform sol-gel-derived STFx thin films with thickness of around 90 nm were deposited using spin-coating method. The FESEM images for the thin films with different iron concentrations are shown in Fig. 1. Different surface morphologies were observed for thin films with different iron concentrations. The STF20 thin film surface is made up of blisters with a few hundreds of nanometers size. The STF40 and STF60 films showed very similar morphology with the particles aligned along the circular pores on the surface. Finally, the surface of STF80 thin film showed very porous structure with large agglomerate of crystallites of around 40 nm.

A detailed XRD crystallography study was carried out on STFx films with different nominal compositions to study the phase formation. The XRD patterns are shown in Fig. 2. All the films were annealed at 650 °C for 1 h under synthetic air flow. It is evident that all the diffraction peaks could be indexed to the cubic perovskite structure of STFx (JCPDS 35-0734). No other miscellaneous peak was observed for all the patterns, indicating a continuous solid solution up to 80% Fe. However, the relative peak intensity of the perovskite peaks decreased as the Fe concentrations increased, suggesting lower crystallinity level of the films. The films with higher Fe concentrations were mainly in amorphous phase with very little crystallization. The average crystallite size for the STFx thin films were estimated using Scherrer's equation. The calculated average crystallite sizes for STF20, STF40, STF50, STF60 and STF80 thin films are 12.4 nm, 11.7 nm, 9.3 nm, 8.1 nm and 3.8 nm, respectively.

The microstructure of the STF40 and STF80 thin films was further characterized using TEM, and the bright-field TEM images are depicted in Fig. 3. The TEM images show a good coverage and adhesion between the thin film and the thermally grown amorphous $SiO_2$ substrate layer. For STF40 thin film, tiny STFx nanocrystals with a diameter of about 3 nm are clearly visible in the Fig. 3a. The electron diffraction pattern (see inset of Fig. 3a) further confirmed the polycrystalline structure of the thin film. Comparatively, with the same annealing temperature at 650 °C, STF80 thin film appeared to have much lesser STFx nanocrystals and majority of thin film remained in amorphous-like structure. This is further supported by the SAED pattern in inset of Fig. 3b. The TEM observations are in good agreement with the XRD results that the film crystallinity decreased with Fe concentrations.

### 3.2. Gas-sensing characterizations

Twenty percent oxygen gas diluted with dry nitrogen was injected onto the STFx thin film sensors at different operating temperatures of 150 °C–450 °C with an interval of 50 °C. The change in the electrical resistance of the sensors was measured and is depicted in Fig. 4a–c. The resistance change was caused by the formation of oxygen adsorbates species such as $O_2^-$, $O^-$ and $O^{2-}$ during the oxygen chemisorption on the grain surface of semiconductor metal oxide. Among these, $O_2^-$ is considered as the stable surface ion at temperature below 150 °C. On the other hand, $O^-$ is the most reactive species in the temperature range of 200 °C to 500 °C, in which most semiconductor gas sensors are operated [14]. The formation of oxygen adsorbates extracts electron from the metal oxide according to following equation:

$$O_2 + 2e^- \leftrightarrow 2O^-_{abs} \quad (1)$$

This builds an electron depletion region for n-type semiconductor and increases the resistance of the material. Similarly, for p-type semiconductor, the oxygen chemisorption generates an effective hole accumulation region, which gives a lower electrical resistance to the sensing material. In addition to surface absorption, the resistance change is also