Synthesis and gas sensing property of nanostructured strontium titanate ferrite

Chow, Chee Lap

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Synthesis and Gas Sensing Property of Nanostructured Strontium Titanate Ferrite

Chow Chee Lap

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Date

Chow Chee Lap

Summary

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. Strontium titanate ferrite ($\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ or STF x in short) appeared to be a promising sensing material due to its attractive properties such as excellent gas sensitivity, mixed ionic-electronic conductivity, excellent doping flexibility and able to accommodate large amount of dopants and defects. Oxygen vacancies generated by the Fe substitution make STF x highly sensitive to oxygen partial pressure and hence a potential candidate for oxygen sensor. In this thesis, semiconducting metal oxide oxygen sensors based on nanosized STF x materials have been successfully fabricated and characterized.

High-energy ball milling has been proven to be an effective method to prepare nanosized gas sensing materials. For the first part of the thesis, the STF x nanoparticles were synthesized using high-energy ball milling method for the first time. The phase formation and structural change at different stages of milling process were systematically studied. Single cubic perovskite STF x materials were successfully obtained for iron content up to 40% ($x = 0.4$). Miniaturized STF20 ($x =$

0.2) nanoparticles based gas sensors with gold interdigitated microelectrodes were designed and fabricated using standard silicon microfabrication techniques. Excellent gas sensitivity value of 2540 at 20 % oxygen gas in nitrogen was obtained for the sensor annealed at 550 °C for 1 hour. The optimum operating temperature was found to be around 250 to 300 °C. The improvement in the oxygen sensing performance was due to the smaller grain size and higher surface defects of the high-energy ball milled STF20 nanoparticles.

For the second part of the thesis, STFx sensing materials have been prepared using modified sol-gel spin-coating method which has advantages such as low synthesis temperature, simple, thin film formability, capable for large area coating and good homogeneity. Factors such as molarity, chelating agent and amount of deionized water were optimized to obtain stable and precipitation-free STFx sol-gel precursors. The crystallinity and surface morphology of the sol-gel derived STFx thin films with different annealing temperatures and iron contents were systematically characterized. For the first time, a change of sensing response type was observed for the STFx sol-gel thin film sensors. This sensing response transition was observed for a huge oxygen concentration range and also for reducing gases such as carbon monoxide and ammonia. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analysis revealed that the anomalous n-type sensing response of STFx thin films was caused by amorphous TiO_2 and Fe_2O_3 phases which existed for the film with low crystallinity, i.e. when the annealing temperature was insufficient or when the iron contents was too high.

The electrical transport property was studied and proposed to provide in-depth understanding on the sol-gel derived STFx materials. The oxygen sensitivity factor

(*m*) calculated from the oxygen partial pressure test was found to be smaller than the reported value, indicating that STF40 sol-gel thin film exhibited better gas sensing performance. Next, defect chemistry based on singly-charged oxygen vacancies was proposed to explain the electrical transport behavior of STF40 thin film sensors. The presence of singly-charged oxygen vacancies was further supported by the activation energy change estimated from the Arrhenius plot of STF40 thin film. Finally, ac impedance spectroscopy was successfully carried out on the STF40 sol-gel thin film sensors. An equivalent circuit model was then proposed based on the understanding of actual physical and chemical reactions that occurred at the gold electrode, grains and grain boundaries of the sensing material. Lastly, a schematic model was proposed to illustrate the electrical conduction and gas sensing behavior for n-type and p-type STF40 semiconductor metal oxide gas sensors.

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CHAPTER 1: INTRODUCTION

1.1 Motivations

With increasing world-wide awareness and concerns on the importance of the environmental protection and pollution control such as greenhouse effect, renewable energy, acid rain, ozone depletion and indoor air quality, research activities in the area of gas sensors have attracted intense attention in recent years. Gas sensors have been extensively used to detect and monitor low concentration of various toxic gases and vapors, such as carbon monoxide, ethanol, hydrogen sulfide, nitrogen oxide, sulfur dioxide, hydrogen, and flammable hydrocarbons [1]. In particular, oxygen sensors are playing an increasingly important role in a wide range of applications including automobile engine emission, industry processing, medical diagnostic, foods storage and foods processing, biological and chemical processing [2, 3].

In order to cater for the different applications, varieties of gas sensors have been developed and many of them are available commercially. Some commonly used gas sensors technologies are based on semiconducting metal oxide, catalytic combustion, solid electrolytes, aqueous electrochemical, thermal conductivity, fiber-optic and acoustic [4]. Among these, semiconducting metal oxide gas sensors, or so-called chemiresistors sensors, are probably the most investigated and commonly applied due to its relatively simple design, small size, low cost to cater for mass production, high sensitivity, and resistance to severe condition. However, they still pose the

challenging problems of poor selectivity, high operating temperature and lack of long term stability [5-7].

Although metal oxides have wide bandgaps typical of insulators, they possess conductivity in the range of semiconductors due to defects and doping in the crystal structure. Basically, semiconducting metal oxide gas sensors work on the principle of their electrical resistance change due to an interaction between the metal oxide materials and the oxidizing or reducing gas in the ambient. The use of semiconductor metal oxide for gas sensing applications was initiated by Sieyama et al. [8] based on zinc oxide (ZnO) in 1962 and the decisive step was taken when Taguchi [9] first brought tin oxide (SnO₂) based semiconductor gas sensors to an industry product at the same year. The other commonly used semiconductor metal oxides are indium oxide (In₂O₃), titanium oxide (TiO₂), iron oxide (Fe₂O₃) and tungsten oxide (WO₃). These are relatively simple binary metal oxides and are normally n-type semiconductors. Besides, there are the other promising new improved materials for gas sensing application, including ternary oxide and complex metal oxides, such as perovskite oxides with ABO₃ structure.

Perovskite type oxides are prominent catalysts used in modern chemical industry due to their attractive properties such as mixed ionic-electronic conductivity, ability to accommodate large amount of dopants and defects, high melting and/or decomposition temperatures [10, 11]. Perovskite structure has two cations with different sizes, which renders it amenable to a huge variety of dopant additions. This great doping flexibility allows for control of the electrical transport and catalytic properties of the materials to optimize their gas sensing performance [11-13]. Specifically, strontium titanate ferrite (SrTi_{1-x} Fe_xO_{3-δ} or STF_x in short) has been

reported as an excellent candidate for oxygen sensors. STFx is a continuous solid state solution between two end members namely strontium titanate (SrTiO_3) and strontium ferrite (SrFeO_3) [14]. Owing to the difference in the preferential oxidation states for Ti and Fe (+4 for Ti and +3 for Fe), oxygen vacancies are generated to maintain charge balance in the solid solution system. This inherent non-stoichiometry makes STFx highly sensitive to oxygen partial pressure ($p\text{O}_2$) [15, 16].

Up to now, most research work on STFx focuses on automotive oxygen sensing application due to the discovery of negligible resistance dependency of temperature between 700 to 900 °C for STF35 ($x = 0.35$) [17]. This observation has promoted STFx as a potential candidate to replace zirconia, titanate and strontium titanate as lean engine oxygen sensor. However, these STFx sensors were mainly synthesized using conventional high temperature solid-state reaction at 1200 °C and have very large grain size. Sensing material with large grain size is not favorable since gas sensing is a surface interaction which strongly depends on surface area. As reported by Yamazoe and co-workers [18, 19], grain size of the sensing material must be smaller than two times of the Debye length of the electron space charge layer (L) in order to enhance the sensitivity of a semiconductor gas sensor.

The thesis will therefore focuses on synthesis and preparation of nanosized STFx materials with various iron contents using high-energy ball milling technique and modified sol-gel method. The nanosized STFx materials based gas sensors with gold interdigitated microelectrode were fabricated using silicon manufacturing technology owing to the trend of miniaturization in electronic components. Their oxygen sensing properties were systematically characterized at lower temperature range (150 to 450 °C) and gas sensing mechanism was studied and discussed.

1.2 Objectives

This project focuses on fabricating the semiconducting metal oxide oxygen sensors based on nanosized STFx materials, and investigating their oxygen sensing properties and underlying gas sensing mechanisms that governing the performance of the sensors. The main objectives of the thesis are broadly classified as follows:

1. Synthesis of STFx nanoparticles and fabrication of nanoparticles based gas sensors

STFx nanoparticles were synthesized using high-energy ball milling and conventional high temperature solid-state reaction. The phase formation of the nanoparticles was studied using X-ray diffraction (XRD) in order to obtain single cubic perovskite phase materials. Next, the deposition of nanoparticles films was optimized to obtain uniform and crack-free nanoparticles coating. Their surface morphologies were observed using scanning electron microscope (SEM).

2. Preparation of STFx sol-gel precursors and deposition of sol-gel thin film sensors

Stable and precipitation-free STFx sol-gel precursors for different iron contents were prepared and optimized. Next, STFx thin films were deposited using spin-coating method and fabricated into sensing devices. The phase formation and surface morphologies of the films were characterized using XRD, field-emission scanning electron microscope (FESEM) and atomic force microscope (AFM).

3. Gas sensing characterization

Upon successful fabrication of both the STFx nanoparticles based and thin film based gas sensors, their sensing properties were characterized using a home-

designed gas sensing characterization system (GSCS). The effect of iron content, operating temperature, annealing temperature, oxygen concentration, relative humidity and long term stability were studied and evaluated systematically.

4. Gas sensing mechanism study

The electrical transport properties and gas sensing mechanisms for the sol-gel derived STFx thin film sensors were studied using X-ray photoelectron spectroscopy (XPS), oxygen partial pressure test, Arrhenius plot and ac impedance spectroscopy. Oxygen partial pressure test and Arrhenius plot were exploited to investigate the point defect system in the STFx materials, and defect chemistry reactions were proposed to understand the electrical transport property of the sensors. In addition, the equivalent circuit of the sensors was also modeled by referring to ac impedance spectra. A graphical representation of the sensor was proposed to extensively understand the gas sensing mechanism of the sensor.

1.3 Major contributions of the thesis

With reference to the four objectives outlined in the last section, few major research contributions have been achieved throughout this project. First of all, Fe-substituted SrTiO_3 or STFx solid solution with iron contents up to 40 % have been successfully synthesized using high-energy ball milling technique for the first time. The physical properties of the nanoparticles were extensively studied using various characterization tools such as XRD, DTA-TGA, XPS and zetasizer. XRD revealed that grain size of synthesized STF20 was reduced down to 10 nm by high kinetic energy during 120 hours of repeatedly milling. The synthesized STF20 was at a

metastable state and had a larger lattice constant compared to that of STF20 powder prepared by conventional high temperature solid state reaction.

Miniaturized STF20 nanoparticles based gas sensors with gold interdigitated microelectrodes were successfully designed and fabricated using standard silicon microfabrication techniques. The high-energy ball milled STF20 nanoparticles based sensors exhibited excellent oxygen sensing response. Optimal sensitivity value of 2540 at 20 % oxygen was achieved for sensor annealed at 550 °C at the operating temperature of 300 °C. In addition, the synthesized STF20 nanoparticles based sensors showed much promising oxygen sensing response compared to high-temperature sintered STF20 sensor and post-milled high-temperature sintered STF20 sensor. The improvement in the oxygen sensing performance was attributed to smaller grain size and higher surface defects of the high-energy ball milled STF20 nanoparticles.

For the second part of the thesis, modified sol-gel spin-coating technique was adopted as the thin film deposition process for STFx materials. Stable and precipitation-free sol-gel precursors were successfully synthesized using suitable sol molarity, amount of deionized water, and chelating agent. Uniform and crack-free thin films with thickness of around 90 nm were achieved for various iron contents. XRD study revealed that all the films were in STFx cubic perovskite phase without the presence of any impurity phase. An anomalous n-type gas sensing response was observed for thin films with iron content larger than 50 %. This n-type sensing response was also observed for STF40 thin films when the annealing temperature was decreased.

XPS characterization was systematically carried out to investigate the elements chemical binding energy shift in STF40 sol-gel thin films at different annealing temperatures. The XPS spectra showed that the formation of STFx cubic perovskite structure started at annealing temperature of 450 °C and completed at 650 °C. No lattice oxygen (O^{2-}) was observed for the film annealed at 400 °C. In addition, transmission electron microscope (TEM) observation also indicated that the STF40 thin film annealed at 450 °C had an amorphous-like structure with very little crystallization. Hence, the anomalous n-type sensing response of the STFx thin films was attributed to the presence of amorphous O-Ti-O and O-Fe-O phases which only existed in the thin films with low crystallinity at lower annealing temperature.

Another major achievement in this thesis was the proposal of defect chemistry for the sol-gel derived STF40 thin film sensors. The proposed defect chemistry was based on the existence of the singly-charged oxygen vacancies that occurred at the lower temperature regime (< 277 °C). It also explained the improved oxygen sensitivity factor (m) which was determined from the oxygen partial pressure test. In addition, the presence of singly-charged oxygen vacancies was also supported by the activation energy change estimated from the Arrhenius plot of STF40 thin film.

Then, ac impedance spectroscopy study was successfully carried out on the STF40 sol-gel thin film sensors under different oxygen concentrations. An equivalent circuit model was proposed to explain the physical properties for both n-type and p-type STF40 sensors. Different electronic components in the equivalent circuit model had been identified and the deviation of the parameters was explained based on the understanding of actual physical and chemical reactions that occurred at the gold electrode, grains and grain boundaries of the sensing material. Finally, a graphical

model was proposed to explain the gas sensing mechanisms of the sol-gel derived STF40 thin film sensors.

1.4 Organization of the thesis

The thesis is organized into seven chapters and the flow is structured as below:

Chapter 1 provides the introduction of the thesis, encompassing the motivation for this project, objectives, major contributions and the organization of the thesis.

Chapter 2 presents a comprehensive description of the background theory of semiconducting metal oxide gas sensors, including the basic gas sensing mechanisms, grain size effect and importance of nanostructured sensing materials. Next, a review on the physical properties, gas sensing properties and synthesis methods of STFx materials is also made.

In chapter 3, the experimental procedures used in this research work are outlined. The setup and equipment used for synthesis of STFx materials, gas sensor fabrication, material characterization, and gas sensing electrical characterization are discussed in detail.

Chapter 4 describes the synthesis of STFx nanoparticles with different iron contents using high-energy ball milling. The phase formation of the nanoparticles during milling process is discussed. Next, the optimization on nanoparticles coating and their oxygen sensing performance are also described.

Chapter 5 shows the preparation and optimization of STFx sol-gel solution. The crystal formation and surface morphology of the sol-gel derived STFx thin film are

also elaborated. The oxygen sensing properties of the thin film sensors, with emphasis on effect of iron contents and annealing temperatures, are discussed systematically.

Chapter 6 reports the gas sensing mechanism study of the STFx sol-gel thin film sensors. The anomalous n-type behavior of the sensing response for the thin film sensors are explained analytically using TEM and XPS. Next, the defect chemistry of the STFx thin film is proposed based on oxygen partial pressure dependency test and Arrhenius plot. The ac impedance response and the respective equivalent circuit model for the thin film sensors are also detailed in this chapter.

Finally, Chapter 7 concludes the thesis report and proposes recommendations for future direction of this research project.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to Semiconducting Metal Oxide Gas Sensors

In this section, an introduction of the resistive type semiconducting metal oxide gas sensors is presented. The general sensing principles which include surface oxygen adsorption and bulk lattice oxygen reaction are reviewed. The importance of nanosized and nanostructured sensing materials on gas sensing properties is also introduced. This serves to provide the fundamental background for the research on the STFx oxygen sensor.

2.1.1 Discovery of Semiconducting Metal Oxide Gas Sensors

A chemical gas sensor is a device that transforms chemical information of a specific gaseous compound into an analytically useful output signal [20]. It generally consists of two functions, which are namely the receptor function that recognizes or identifies a chemical substance, and the transducer function that transforms the chemical signal into a useful analytical output signal. Specifically for a semiconducting metal oxide gas sensor, the receptor function is provided by the surface of each semiconductor particle. The obtained chemical signal is then transduced through the microstructure of coagulating particles into the electrical signal of the polycrystalline element.

The basis for semiconductor gas sensing is that changes in stoichiometry due to redox reactions result in the isothermal generation of donor or acceptor states together with excess electrons or holes, respectively. Under such circumstances, the electrical resistance R is found to exhibit a power law dependence on the partial pressure of the relevant gas P [21], as shown in following equations:

$$R = aP^n \quad \text{or} \quad \log R = a' + n \log P \quad (2-1)$$

This effect was first observed by Brattein and Bardeen [22] on germanium (Ge) in 1957 and later metal oxide-gas reaction was also observed by Heiland [23], Beilanski et al. [24] and Seiyama et al. [8]. Since Taguchi first brought SnO₂ gas sensors as an industry product for the detection of inflammable gases in 1962 [9], many technological and research efforts have been made to improve their sensing performances for practical applications.

Meanwhile, extensive studies have been directed to the fundamental understanding of the gas sensing properties. The development of semiconductor metal oxide gas sensors was enhanced by the findings of Loh [25] and Shavor [26] that the sensitivity of gas sensing can be greatly improved by the addition of small amounts of noble metals such as platinum (Pt) and palladium (Pd). Since then various types of gas sensors for inflammable gases have been developed mainly using SnO₂ and ZnO. Grain size effect of SnO₂ on sensing performance was evaluated by Yamazoe and co-workers in early 1991 [18, 19]. Nanosized sensing materials with grain size below the Debye length of electron can greatly enhance the gas sensitivity. Next, various innovative material processing technologies were adopted to obtain nanocrystalline particles in order to improve the performance of the sensors. Besides, nanostructured metal oxides especially quasi-one dimensional nanostructures such

as nanowires, nanorods, and nanobelts were also extensively studied for gas sensing applications [27].

Since 1980's, Ogawa et al. [28], Clifford [29], Morrison [30] and Heiland [31] have reviewed the possible sensing principles and mechanisms of the semiconductor gas sensors by which the gas components in the surrounding atmosphere affect the changes in the electrical resistance or conductance of an n-type metal oxide semiconductor. Even though there are different models to explain the mechanisms of semiconductor gas sensors, the most commonly accepted model is the formation of surface charge depletion layer caused by oxygen adsorbates on the surface of metal oxide. However, for gas sensors working at high temperature range (700 to 1100 °C), gas sensing mechanism is usually described by bulk reaction which involves gas interaction and diffusion of oxygen defects in the lattice of metal oxide. These two sensing mechanisms will be discussed in detail next.

2.1.2 Surface Adsorption of Oxygen Species

Oxygen is a powerful electron acceptor and its interaction with metal oxides is very important in many catalytic applications. Several kinds of oxygen adsorbates species, such as O_2^- , O^- , and O^{2-} , are known to chemisorb on the surface of semiconductor metal oxides in air [32, 33]. The formation of such oxygen adsorbed species at the surface extracts electrons from the bulk of the metal oxide via several routes [34]:

Of these, O_2^- is considered as the stable surface ion at temperature below 150 °C, as shown in Figure 2-1. On the other hand, O^- is the most reactive with reducing gases in the temperature range of 200 to 500 °C, in which most semiconductor gas sensors are operated [35]. At temperatures above 550 °C, equilibration of lattice oxygen with the atmosphere occurs and the surface potential barrier collapses.

Figure 2-1 Adsorbed oxygen species detected on the surface of tin oxide at different temperatures with temperature programmed desorption (TPD), Fourier transformed infrared (FTIR) and electron paramagnetic resonance (EPR) analysis [35].

In the case of n-type semiconductor metal oxides, the formation of these oxygen adsorbates builds a space-charge region on the surfaces of the metal oxides grains, caused by electron transfer from the grain surfaces to the adsorbates [31, 36, 37]. The depth of this space-charge layer (L) solely depends on the surface coverage of oxygen adsorbates and intrinsic electron concentration in the semiconductor used. The resistance of n-type semiconductor gas sensors in air is therefore high, owing to the development of a potential barrier to electronic conduction at each grain boundary [37], as shown in Figure 2-2. The conduction electrons can move across

the potential barrier at each grain boundary to give the total conductivity of the sensing material.

Figure 2-2 Model for n-type gas sensor. (a) physical model illustrates depletion region at grain boundary and (b) band diagram model illustrates Schottky barrier at grain boundary [37].

When the n-type semiconductor sensors is exposed to an atmosphere containing reducing gases such as carbon monoxide, ammonia and hydrogen at elevated temperatures, the oxygen adsorbates are consumed by the reaction shown in equation (2-5). This establishes a lower steady-state surface coverage of the oxygen adsorbates on the grain surface.

During this process, the electrons trapped by the oxygen adsorbates are returned to the metal oxide grains, resulting to a reduction in the potential barrier height and a

drop in resistance. This resistance change is employed as the measurement parameter of a semiconductor gas sensor. The reactivity of the oxygen adsorbates is, of course, a function of the type of reducing gas present and operating temperature of the sensor. Since semiconductor gas sensors respond more or less to any reducing gas due to this mechanism, the sensors usually suffer from cross-sensitivity, that is, the lack of selectivity to a specific gas.

The response of n-type semiconductor gas sensors to oxidizing gases such as O_3 and NO_2 is relatively simple. The sensor resistance increases upon exposure to these gases as a result of their negatively charged chemisorptions on the grain surface as shown in equation (2-6). Therefore, the sensitivity is a function of the amount of chemisorption, provided that the surface coverage of oxygen adsorbates remains constant.

On the other hand, the resistance response for p-type semiconducting metal oxide sensors is totally opposite. Since the charge carriers in p-type metal oxides are positively charged holes, the formation of negatively charged oxygen adsorbates and the extraction of electrons from the bulk eventually increases the concentration of holes in the grain surface. Hence, the consumption of oxygen adsorbates by reaction with reducing gases leads to decrease in the charge-carrier concentration and hence to an increase in resistance, which is the reverse observation for the case of n-type metal oxides. On the other hand, the adsorption of oxidizing gases on p-type metal oxides results in a decrease in the resistance of the material.

2.1.3 Bulk Reaction through Diffusion of Oxygen Defects

This mechanism is normally used to explain oxygen sensing phenomena based on semiconducting metal oxides working at high temperature (700 to 1100 °C). Semiconducting metal oxides are non-stoichiometric oxides and their resistivity strongly depends on the oxygen partial pressure. The interstitial defects are decided by the space available and the electrostatic environment in the materials. Anion interstitial O_i can be dismissed due to the high enthalpy reaction for big radial oxygen anion in close-packed structure. Hence, oxygen defect in close-packed structure forms oxygen vacancy more easily than interstitial O_i [38].

The electrical conductivity of resistive-type sensors depends on oxygen partial pressure in the surrounding atmosphere, which is caused by the interactions of point defects in the metal oxides such as oxygen vacancies with oxygen gas from the ambient. Their sensing mechanism can be described by oxygen vacancies diffusing quickly from the interior of the grains to the surface or from the surface to the interior of the grains [3, 39-41]. The basic reaction between a regular oxygen site (O_O^x), oxygen molecules in the gas phase (O_2), and the oxygen vacancy with two fold-ionized positively ($V_O^{\bullet\bullet}$) in the bulk, can be expressed in the formalism of Kröger and Vink [42] as given in the equation:

The equilibrium constant given by the law of mass action is:

$$K = [V_O^{\bullet\bullet}][e']^2[p_{O_2}]^{1/2} \quad (2-8)$$

where $[e]$ is the concentration of electrons. Considering charge neutrality where $[V_O^{\bullet\bullet}] = 2[e]$, the equilibrium constant can be written as:

$$K = [2e][e]^2[p_{O_2}]^{1/2} \quad (2-9)$$

Hence, the relation between electron concentration and oxygen partial pressure is given as:

$$[e] \propto (p_{O_2})^{-1/6} \quad (2-10)$$

For n-type semiconductor where electron is the major charge carrier, the conductivity is hence proportional to oxygen partial pressure (p_{O_2}) with the oxygen sensitivity factor $m = -6$. However, the electrical conductivity (σ) is typically complicated by significant cross-sensitivity to temperature, as given by:

$$\sigma = A \exp\left(-\frac{E_a}{k_B T}\right) (p_{O_2})^{1/m} \quad (2-11)$$

where, k_B is the Boltzmann constant; E_a is the activation energy which represents the sensitivity of the electrical conductivity to temperature changes. The absolute value of $1/m$ represents the sensitivity of conductivity to oxygen partial pressure which is dependent on the dominating defects involved in the reaction between the oxygen gas and the sensor. The sign of $1/m$ depends on the conduction type, i.e. positive for p-type conduction and negative for n-type conduction.

Therefore, it is very important to select semiconducting metal oxide material with small activation energy and large $1/m$ value to obtain good oxygen sensitivity with minimum cross-sensitivity to temperature. In order to design temperature-independent devices (negligible E_a), an additional temperature compensating material can be added to eliminate temperature interference. Meanwhile, materials can also be synthesized to present an intrinsic temperature-independent characteristic through bandgap engineering [43]. Table 2-1 shows the value of

oxygen sensitivity factor and its respective defect type for some common semiconducting metal oxides used for high temperature oxygen sensors.

Table 2-1 Oxygen sensitivity factors for some common semiconductor metal oxides.

Semiconductor Metal Oxide	Conduction Type	Defect Type	Oxygen sensitivity factor, m	Reference
CeO ₂	n	$V_{\text{O}}^{\bullet\bullet}$	-5 to -7	[44]
Nb ₂ O ₅	n	$V_{\text{O}}^{\bullet\bullet}$	-4	[45]
Ga ₂ O ₃	n	$V_{\text{O}}^{\bullet\bullet}$	-4	[46]
TiO ₂	n	$V_{\text{O}}^{\bullet\bullet}, Ti_{\text{int}}^{\bullet}$	-4 and -6	[47]
SrTiO ₃	n, p	$V_{\text{O}}^{\bullet\bullet}, V_{\text{Sr}}^{\prime\prime}$	-4 to -6 and +4	[48]

2.1.4 Towards Nanosized and Nanostructured Gas Sensing Material

The semiconductor particles are coagulated together in the sensor element. The microstructure of these aggregates is considered to be very important for the transducer function. Each particle is connected with its neighbors either by grain-boundary contacts or by necks. Nanosized metal oxides are, in principle, expected to exhibit an improved sensitivity as well as a faster response and recovery time compared to microcrystalline materials due to the large surface-to-bulk ratio. The effect of microstructure of the polycrystalline element was first reported by Morrison [30]. Next, the grain size effect of SnO₂ on sensing performance was first reported by Yamazoe and co-workers in the early 1990s [18, 19] and further verified on other metal oxides by many other research activities [49-53].

A schematic model of the grain-size effect as shown in Figure 2-3 has been developed for better visualization of the grain size effect [19]. A gas element can be represented by a chain of crystallites.

Figure 2-3 Schematic model of grain size effect: D is the grain size and L is the depth of the space charge region [19].

When grain size is much greater than $2L$, grain boundary contacts are most resistant to electron conduction through the chain due to the low resistance in the core region. Hence, the grain boundary contacts will govern the electric resistance as well as the gas sensitivity of the chain. The gas sensitivity in this case is basically independent of grain size. When grain size is comparable to $2L$, necks become the most resistant among grain-boundary, core region and necks, thus it controls the gas sensitivity. As the grain size is less than $2L$, the whole crystallite is depleted of electrons. The assembly of crystallites is pictured as being connected by a large number of necks and a small number of grain-boundary. In this case, the electrical resistance of grains dominates the whole resistance of the chain and the sensitivity is controlled by the grains themselves. For the most investigated SnO_2 , L for sputtered thin film and sintered bulk elements were reported to be as small as 3 nm [54, 55].

Besides the particle size, microstructure technology also has great possibilities to improve sensing properties such as selectivity, sensitivity, operating temperature, response and recovery times [5, 6]. Important geometric parameters of metal oxides such as grain size, thickness, porosity, dominant orientation and faceting of crystallites can be controlled and deposited to enhance the sensing properties. Therefore, the use of nanosized and nanostructured materials (both in powder and thin-film form) in gas sensors is arousing interest rapidly in the scientific community. Various nanostructure engineering methods have been investigated such as chemical co-precipitation [56], electrospinning deposition [57], flame spray pyrolysis [58], metalorganic deposition (MOD) [59], plasma enhanced chemical vapor deposition (PECVD) [60], physical vapor deposition (PVD) [61], pulse laser deposition (PLD) [62], sol-gel process [63, 64] and high-energy ball milling [65-68].

In this project, STFx sensing materials are synthesized using two different techniques, namely high-energy ball milling and sol-gel process. These two methods have been proven to be a very effective route to prepare nanosized material for gas sensing applications.

2.2 Introduction to Strontium Titanate Ferrite

This section aims to provide a basic introduction on the STFx material. Their physical properties are reviewed and the reported preparation methods are summarized. This serves as the fundamental for the synthesis of nanosized STFx materials. Additionally, the current status of STFx gas sensors is also presented.

2.2.1 Physical Property of STFx

The ABO_3 perovskite materials display several interesting physical properties such as ferroelectricity ($BaTiO_3$), ferromagnetism ($SrRuO_3$), large thermal conductivity ($LaCoO_3$), insulator-to-metallic transitions of interest for thermistor applications ($LaCoO_3$), a fluorescence compatible with laser action ($LaAlO_3:Nd$), and transport properties of interest for high temperature thermoelectric power (La_2CuO_4) [10]. The ABO_3 perovskite structure can be best described as a cube with the B ion in the body-center, the A ion at the corners and the oxygen ions at the center of the faces, thus accounting for the octahedral symmetry of the B -atom [14]. Figure 2-4 shows the unit cell of the cubic perovskite. A is usually a rare earth cation and B is a transition metal cation.

Figure 2-4 Unit cell of the cubic perovskite structure.

Great interest has been shown in transition metal-containing ABO_3 perovskite-type oxides owing to their strong ability to stabilize higher oxidation states of 3d transition metal cations and to accommodate large amount of various dopants and oxygen vacancies. Perovskite oxides are able to maintain their basic structure even with very high defect concentrations, which exhibit unique electrical and electro-

catalytic properties. The partial substitution of A cation by foreign cations with different oxidation states gives rise to a change in the oxidation state of the B -site cations or structural defects such as anionic or cationic vacancies. On the other hand, the partial substitution of B cation can improve both the structure stability and the catalytic properties [69, 70]. Perovskite oxides are particularly attractive for high-temperature applications because of their high melting and/or decomposition temperature. This makes such materials interesting as mixed conductors for membranes for oxygen extraction, catalysts, components in electrochemical reactors, electrodes of solid oxide fuel cells (SOFCs) and gas sensors [11, 71-73].

Strontium Titanate Ferrite, STFx is a continuous solid state solution between the two end members, strontium titanate (SrTiO_3) and strontium ferrite (SrFeO_3). Strontium titanate is a wide-bandgap semiconductor ($E_g = 3.2$ eV) with rather low conductivity levels in pristine state, while strontium ferrite is a mixed conductor with high level of electronic and ionic conductivities [15]. In the STFx solid solution system, trivalent iron ion (Fe^{3+}) substitutes for the quadrivalent titanium ion (Ti^{4+}) without restoring electroneutrality in the cation site. Due to the difference in their preferential oxidation states, oxygen vacancies are formed to maintain charge balance in the system [14, 15] and its point defect reaction is given by:

Where according to Kröger and Vink notation, O_O^x is regular oxygen site, with effective zero charge; Sr_{Sr}^x is regular strontium site, with effective zero charge; V_{Sr}'' is doubly negative charge strontium vacancies; V_O'' is doubly positive charge oxygen vacancies and Fe_{Ti}' is iron-substituted Ti site, with effective singly negative charge.

STFx exists as a single phase cubic perovskite structure at low iron concentration, whereby the lattice parameter, a_o decreases with increasing Fe content. This may be associated with lower fraction of Fe^{4+} cations and/or a lower level of structural disorder when iron is introduced in the lattice [71, 72]. However, at higher iron concentrations ($x \geq 0.6$), a superstructure with lattice parameters $a' = 2a_o$, $b' = 2b_o$ and $c' = c_o$, where $a_o = b_o = c_o$ are the lattice parameters of ordinary perovskite; can be observed by TEM. These superstructures are formed during the cooling process owing to the diffusion and reordering of oxygen vacancies [71, 74]. The changes in some physical properties with various iron contents are shown in Table 2-2.

Table 2-2 Changes of lattice parameter (a_o), oxygen vacancy (y), bandgap (E_g) in STFx solid solution with different iron contents [71].

x	$a_o \pm 0.001 (\text{\AA})$	$y = 3 - (x/2)$	$E_g \pm 0.1 (\text{eV})$
0	3.907	3.0	3.2
0.1	3.907	2.95	2.8
0.2	3.906	2.9	2.6
0.4	3.900	2.8	2.2
0.5	3.896	2.75	2.1
0.6	3.890	2.7	2.2
0.8	3.878	2.6	2.1

The bandgap energy of STFx family varies systematically between the characteristic values of the two end members [16], as shown in Figure 2-5. By using the weighted least squares regression method, Rothschild et al. proposed that the variations in bandgap energy followed parabolic laws, $E_g(x) = 3.26 - 1.93x + 0.54x^2$ eV [15, 16]. SrTiO_3 has the maximum bandgap and the bandgap decreases with increasing iron content. In STFx system, the iron introduces discrete impurity levels within the bandgap of SrTiO_3 , which represents the separation between the O2p valence band

and the Ti3d conduction band. At higher iron concentration, the Fe orbitals overlap one another and form an impurity bands ($\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ acceptor levels) within the bandgap of the STFx system. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ acceptor level act as extra valance and conduction bands, in addition to the O2p and Ti3d bands. Hence, with increasing iron concentration, the acceptor levels broaden and the effective bandgap energy of STFx solid solutions decreases.

Figure 2-5 Bandgap of STFx as a function of iron content. (■ = measured data, solid line = fitting) [16].

2.2.2 Synthesis and Preparation of STFx Solid Solutions

From the vast amount of research done on STFx, many synthesis methods have been employed. As such, different forms of samples have been prepared to suit their own studies and applications. These methods will be reviewed under this section.

a) High temperature solid state reaction

Solid state reaction is the most widely used method for preparation of polycrystalline ceramic. In this conventional route, the powders of starting material are mixed together and homogenized, usually by ball-milling. The commonly used

starting materials are SrCO_3 , TiO_2 and Fe_2O_3 . After the mixing, a calcination process is needed to drive the solid-state-reaction at high temperatures, usually 1000 to 1200 °C. Single phase cubic perovskite STFx can be obtained consistently with this method and the produced macro-powders can be made into compacts, pellets, screen printed thick film and pulsed-laser-deposited thin film. STFx with various iron contents have been successfully fabricated by different research groups using this method [15, 62, 75, 76].

b) Liquid Mixed Technique

To ensure better homogeneity, a liquid medium, usually alcohol, water or acid, is used to dissolve the precursors and mix them evenly. This is then followed by high temperature calcination for solid-state-reaction. The reported liquid mixture is prepared using strontium carbonate, ammonium ferric citrate, and titanium citrate solutions. Powder obtained from this method has been pressed into tablet for defect structure and electrical conductivity studies [71, 77]. The advantage of this technique over conventional solid state reaction is an improved homogeneity of the final product. However, due to high temperature calcination, grain size of the synthesized powder usually in macro-scale.

c) Sol-precipitation or Wet Chemical Route

The conventional methods usually produce macro-powders due to the high temperature sintering. However, with a wet chemical route, nanosized powders can be obtained. A sol is prepared using strontium nitrate, iron (III) nitrate and titanium isopropoxide, dissolved in glacial acetic acid and water. The precursor sol is used for electrospinning and electrospraying to obtain nanostructured thin film. Besides,

the precipitation can be initiated by adding NaOH in the continuously stirred sol. The obtained nanopowders are then calcined and screen printed into thick film for sensing characterization [78, 79].

2.2.3 STFx as Potential Oxygen Sensors

Oxygen sensors also known as λ -sensors are widely used in automotive exhaust gas control systems to monitor the pO_2 in the exhaust gas and provide real-time feedback to optimize fuel combustion and conversion of hazardous combustion by-products such as CO, hydrocarbons, and NO_x to safer gases such as CO_2 , H_2O , and N_2 by the three way catalyst [16, 80]. Oxygen sensors are presently installed in nearly all automobiles worldwide and certainly represent the most successful commercial chemical sensor to date. The oxygen sensor market is dominated by electrochemical ZrO_2 -based potentiometric and amperometric sensors [43, 81]. However, potentiometric and amperometric sensors suffer from the shortcomings of small sensitivity to pO_2 in the exhaust gas and relatively complex design, respectively [80, 82]. Therefore, the resistive-type sensors based on semiconducting oxides such as TiO_2 [83] and $SrTiO_3$ [84] have been investigated due to their relatively simple design, high sensitivity to pO_2 and ease of fabrication with potential for reduced cost [43, 85]. Some commonly used semiconducting metal oxides and their oxygen sensitivity factors are listed in Table 2-1.

The solid solution system of STFx has gained a lot of interest in the field of lean engine oxygen sensor due to its advantages such as mixed ionic-electronic conductivity, ability to accommodate large amount of dopants and defects, tailorable electrical property, and high oxygen sensitivity [16, 17, 86, 87]. Figure 2-6 shows

the temperature coefficient of resistance for the system as a function of composition, pO_2 and temperature [15]. Generally, the conductivity curve is a typical bathtub curve and shows no evidence of a phase transition. The STFx system exhibits predominant n-type electronic conductivity at low pO_2 , ionic conductivity at intermediate pO_2 , and p-type electronic conductivity at high pO_2 . The $-1/4$ and $+1/4$ slopes for the electronic components of the conductivity in the n-type and p-type regimes, respectively, indicate that the oxygen vacancy concentration is independent of the pO_2 [15, 16].

Figure 2-6 Conductivity isotherms of STFx as a function of oxygen partial pressure at different (a) operating temperatures and (b) x values [15].

As illustrated in Figure 2-6, the total conductivity increases with iron content at all oxygen pressures, from an almost insulating characteristic for $x = 0.1$ to the semiconducting characteristic for $x = 1.0$. This is mainly due to the acceptor role of the iron, with decreased bandgap and the decreased activation energy for defects mobility, allowing for more carriers to be generated and ease of ionic flow [15, 71]. It is most noteworthy to observe the conductivity at $x = 0.35$; the conductivity coalesces to the same value at high pO_2 range, demonstrating a zero temperature coefficient of resistivity (TCR) [16, 17]. Material with this composition is sensitive to the oxygen partial pressure and independent to temperature fluctuation, making it a potential candidate to replace zirconia, titanate and strontium titanate as lean engine oxygen sensor.

However, the zero temperature coefficient of resistivity (TCR) was only observed in a very small pO_2 range (between 10^{-2} and 3×10^{-2} bar) and certain temperature range (700 to 900 °C). Therefore, bandgap engineering was used on STFx system to achieve negligible TCR at a specific range of pO_2 and operation temperature for automotive applications [43, 81, 88]. Moos et al. reported that the introduction of doping into STFx can tailor the pO_2 range of the negligible TCR property. Acceptor (Ga) doping shifts the negligible TCR to lower pO_2 range, while donor (La) doping results in a shift to higher pO_2 range as shown in Figure 2-7. Combined acceptor and donor doping were found to extend pO_2 range of negligible TCR [88].

One of the major drawbacks of the current reported STFx sensing materials is their large grain size which was caused by high temperature solid-state reaction synthesis process. Sensing material with large grain size is not favorable since gas sensing is a surface interaction which strongly depends on surface area.

Figure 2-7 Final resistance values of differently doped $(\text{Sr}_{1-a}\text{La}_a)(\text{Ti}_{0.7}\text{Fe}_{0.3})_{1-b}\text{Ga}_b\text{O}_{3-\delta}$ ceramic samples at 700, 800 and 900 °C [88].

In the actual application of STFx as real exhaust gas compatible thick-film sensor devices, upon annealing the STFx film at high temperature, STFx reacted with the sapphire substrate to form $\text{SrAl}_{12}\text{O}_{19}$. The STFx film was remarkably iron depleted, leading to an increase in bandgap and therefore the charge carrier density decreased and electrical resistance increased. In order to inhibit this undesirable reaction, MgO was suggested as replacement substrate for STFx due to greater stability with STFx film at elevated temperature [85]. Alternatively, an additional diffusion barrier layer (SrAl_2O_4) can be deposited between the substrate and sensor film to prevent reaction with substrate [75].

Another significant problem observed for actual application is sulfur oxide poisoning. This problem emerges in catalytically active perovskites and in mixed electronic ionic conductors which contain earth alkaline ions. Moos reported that resistance of STFx film increased and the temperature independence behavior disappeared after treating it in real exhaust gas for 8 hours. This sulfur poisoning is proposed to occur in two steps. In the first step, which can only be observed at low

temperature (600 to 700 °C), sulfur dioxide adsorbs at the surface of STFx grains and the resistance increased. The second step happens at high temperature (800 to 900 °C) where STFx decomposes into SrSO_4 , iron-depleted STFx and Fe_2TiO_5 . A porous sulfur absorber material (BaCO_3) on top of the sensitive film was proposed to overcome this problem [75, 89].

In this project, two effective synthesis routes were utilized to prepare nanosized STFx material which is helpful to promote gas sensitivity. Besides, Si/SiO₂ wafer substrate is chosen for fabrication of gas sensors to avoid reaction of STFx films with substrate. In addition, at the studied temperature range (150 to 450 °C) of this thesis, undesired interaction with other gas species was negligible.

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 Fabrication of STFx Nanoparticles Based Sensors

3.1.1 Synthesis of STFx Nanoparticles using High Energy Ball Milling

For the synthesis of STFx nanoparticles, starting materials of strontium oxide (SrO, Aldrich, 99.9 %), titanium oxide (TiO₂, Alfa Aesar, 99+% rutile) and iron oxide (α -Fe₂O₃, Alfa Aesar, 99.945 %) were mixed and homogenized with nominal compositions of different iron contents (x). The tungsten carbide vials (volume of 250 ml) and balls (inner diameters of 10 mm and 20 mm) with relatively high density of 14.75 g/cm³ were used for high energy ball-milling process to increase the impact energy [90]. The milling speed was set at 200 rpm and the balls-to-powder weight ratio was kept as 20:1.

The milling was carried out using the planetary ball mill (Fritsch Pulverisette 5) in 30-minute cycles with 25 minutes of milling followed by 5 minutes of pause to prevent overheating of the milling machine from prolonged milling. In order to study the milling time needed to form the cubic perovskite phase of STFx, the nanoparticles were prepared with different milling durations (2, 20, 60, 80, 120 hours) for crystallography study using XRD.

3.1.2 Synthesis of STFx Nanopowders using Solid State Reaction

For the synthesis of STFx powders using conventional high temperature sintering method, powders of strontium carbonate (SrCO_3 , Aldrich, 99.8 %), titanium oxide (TiO_2 , Alfa Aesar, 99+% rutile) and iron oxide ($\alpha\text{-Fe}_2\text{O}_3$, Alfa Aesar, 99.945 %) were used as starting materials. The starting materials with nominal compositions were mixed with ethanol and uniformly homogenized by using wet agate ball milling. The mixture was dried in oven at 100 °C and pressed into pellet form prior to high temperature sintering at 1200 °C for 12 hours under pure oxygen ambient.

3.1.3 Deposition and Fabrication of STFx Nanoparticles Based Sensors

The substrates used for the deposition and fabrication of STFx nanoparticles based sensors were Si/SiO₂ wafer. Gold interdigitated electrodes were deposited on the wafer using photolithography metal lift-off process. The wafer substrate was first coated with photoresist AZ5214 (Clariant). Next, the substrate was exposed to UV light and developed according to the electrode design. The design of the electrode (mask#1) is shown in Figure 3-1(a). The dimension for a single gas sensor is 7.5 mm x 6.5 mm, as shown in the enlarged image in Figure 3-1(b). Since the resistivity of STFx materials is relatively high, electrode design with width of 25 μm and spacing of 25 μm was used to fabricate gas sensors in order to obtain stable electrical measurement signal. 10 nm of titanium layer followed by 100 nm of gold layers were deposited using E-beam evaporator and finally, photoresist was washed away using acetone. Photo images of a Si/SiO₂ wafer substrate with patterned gold interdigitated microelectrode is pictured in Figure 3-2(a).

Figure 3-1 Photolithography mask design for fabrication of gas sensors: (a) mask #1 for interdigitated electrode patterning, (b) Enlarged mask design for one device, (c) mask#2 for device patterning.

Figure 3-2 Photo images of (a) Si/SiO₂ wafer with gold interdigitated microelectrode, (b) a ready STFx nanoparticles based sensor.

For the deposition of nanoparticles coating, the slurry of STFx nanoparticles has been prepared according to the process flow described in Figure 3-3. First, the nanoparticles were manually ground using agate mortar and pestle, and filtered using sieve to dislodge any agglomerated powders. Next, the nanoparticles were mixed and homogenized with 20 wt% of organic vehicle (3 wt% of ethyl cellulose (EC) in α -terpineol) using agate ball milling at 150 rpm for 6 hours. The organic vehicle act as temporary binder and helped to disperse the powders. Finally, the organic vehicle-coated nanoparticles were mixed with dispersion medium, 2-methoxyethanol (MOE), and further ball- milled for 12 hours to form well-dispersed slurry. The weight ratio of organic vehicle-coated nanoparticles to dispersion medium was set as 1:3.

The slurry was immediately spun onto the wafer substrate at 3000 rpm for 30 s by using spin coater (Laurell Technologies). The deposited film was then dried at 150 °C for 5 minutes and followed by heating at 300 °C for 5 minutes to burn off the organic compounds. Two layers of nanoparticle coatings were obtained. The final

film was annealed at different temperatures for one hour under air ambient with flow rate of one standard liter per minute (slm) using Lindberd tube furnace. The annealed films were then patterned into sensing devices using mask#2 (Figure 3-1(c)) using photolithography process followed by hydrofluoric acid (HF) etching. The final devices were attached on alumina substrate and Au wire was bonded to give electrical contact. Figure 3-2(b) shows the photo image for a ready STF_x nanoparticles based sensor.

Figure 3-3 Flow chart of STF_x slurry preparation.

3.2 Fabrication of STF_x Sol-Gel Thin Film Sensors

3.2.1 Preparation of STF_x Sol

Figure 3-4 illustrates the flow chart of detailed procedures for STF_x sol preparation.

Using a magnetic stirrer, the titanium butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$, Aldrich, 97%)

was first thoroughly mixed with acetylacetone (C_5H_7OOH , Merck, > 99%) with a mole ratio of 1:4. At the same time, iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck, > 99%) was dissolved in 2-methoxyethanol (MOE, $C_3H_8O_2$, Sigma-Aldrich, 99.8%) and acetylacetone with a mole ratio of 1:20:6. Next, the Ti and Fe precursors were mixed together and homogenized under continuous stirring. At the same time, the strontium acetate ($Sr(CH_3COO)_2 \cdot 1/2H_2O$, nacalai tesque) was dissolved in glacial acetic acid (CH_3COOH) with a mole ratio of 1:15. Suitable amount of deionized water was also added to help dissolve the acetate powders. Finally, the dissolved Sr precursor solution was slowly dripped into the mixture of Ti and Fe precursor under continuous stirring using a magnetic stirrer. The viscosity and the molarity of the final sol were adjusted using MOE. The as-prepared solution was left overnight for one day to allow sufficient hydrolysis before spin-coating deposition.

Figure 3-4 Flow chart of STF_x sol preparation.

3.2.2 Deposition and Fabrication of STF_x Sol-Gel Thin Film Sensors

The stable and precipitation-free STF_x sol was spun onto the Si/SiO₂ wafer substrate with gold interdigitated electrodes at 3000 rpm for 30 seconds. The interdigitated electrodes pattern was same as the one shown in Figure 3-1. The soft bake temperatures were set as 150 °C and 300 °C for 5 minutes each. Then, the spin-coating cycle was repeated for five times to obtain multiple-layer thin films sensors. The final film was annealed at different temperatures for one hour under air ambient with flow rate of 1 slm using Lindberd tube furnace. The annealing temperatures required to crystallize the films were confirmed by X-ray diffraction and thermal analysis. The annealed films were then patterned into sensing devices using photolithography process followed by HF etching. The final devices were attached on alumina substrate and Au wire was bonded to give electrical contact,

3.3 Material Characterizations

Various characterization techniques were utilized to investigate the properties of interest such as surface morphology, crystalline structure, grain size, surface chemical state of the STF_x materials. A brief description for each characterization is given in the following section.

a) X-ray diffraction (XRD)

XRD technique is a non-destructive and simple tool in characterizing crystalline materials. It determines the preferred crystal orientation or crystal planes of a sample corresponding to its characteristic diffracted angles. In this project, the XRD patterns were recorded at room temperature using Siemens D5005 X-ray

diffractometer with Cu K-alpha radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The 2-theta detector was scan from 20 to 80° with a scan rate of 1° per minute. For thin film samples, small glazing angle of 1° was used to ensure that the diffraction intensity came mostly from the measured samples. Scherrer's equation was employed to estimate the average grain size, D , along the surface normal direction:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3-1)$$

where K is Scherrer constant, an arbitrary value that falls in the range 0.70 - 1.70, usually taken as 0.9, λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) of the diffraction peak (radians) located at 2θ and θ is the diffraction angle.

b) Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

TGA measures the amount and the rate of change in the weight of a sample as a function of temperature in a controlled atmosphere. Measurements are used to determine the change in composition of a sample and to predict its thermal stability up to temperatures as high as 1000 °C. On the other hand, DTA measures the endothermic and exothermic transitions as a function of temperature. It can determine transitions such as glass transition temperature, melting, crystallization, curing, onset of oxidation and heat capacity. Thus, putting the TGA and DTA plots together as a function of temperature provides useful information on the kinetics and composition change of the sample with increasing temperature. In the analysis, the thermal properties of a sample are compared with that of a standard reference material which is thermally stable and undergoes no transition in the temperature

range of interest. The most commonly used standard reference used is powdered alumina. The TGA and DTA analysis was performed on the Perkin-Elmer 7 series with nitrogen as the purging gas at 30 ml/min. The heating rate was 1 °C/min and heating range was from 30 °C to 1000 °C.

c) Scanning electron microscope (SEM)

SEM is a versatile and most commonly used technique in coating characterization work to investigate the surface morphology and composition (if equipped with energy-dispersive x-ray). SEM is capable of producing a plan view that shows the grain size, uniformity, coverage, film voids and micro-cracks. In addition, SEM is also used to obtain cross-sectional views of multilayer structure that show the interfacial information between the substrate and the film. A JSM-5600LV scanning electron microscope was used to study the surface morphology of nanoparticles coatings. However, a Jeol JSM-6340F field-emission scanning electron microscope (FESEM) was used for thin films since FESEM is capable of producing brighter and finer electron beam, thus giving higher resolution as compared to conventional SEM.

d) Atomic force microscope (AFM)

AFM is one of the foremost characterization tools for imaging, measuring, and manipulating surface morphology at nanoscale using a mechanical probe, which is usually made using silicon nitride. Unlike electron microscope which is more suitable for imaging conducting or semiconducting surfaces, AFM can be used to observe almost any type of surface, which is very suitable for highly resistive STFx materials. A Nanoscope IIIA AFM (Dimension 3100, Digital Instruments) in tapping mode was used to characterize the surface roughness of the STFx thin films.

e) Transmission electron microscope (TEM)

TEM is an important analysis tool in nanotechnology research as it is capable in imaging and analyzing the microstructure of materials down to atomic scale resolution. The bright and dark field imaging modes of TEM, together with electron diffraction are invaluable in providing information about the crystal phases, morphology and defects in a material. The microstructures of the sol-gel derived thin films were studied using a JEOL 2010 TEM with acceleration voltage of 200 kV. Selected area electron diffraction (SAED) was also performed to obtain the crystallographic information of the nanostructured films.

f) X-ray photoelectron spectroscopy (XPS)

XPS is a very useful technique that measures the surface chemistry of a material. This analysis technique is used to determine the chemical and electronic state of the surface of a material, usually 3 to 10 nm deep. In this project, the XPS characterization was carried out using a Kratos AXIS spectrometer with monochromatic Al K_{α} (1486.6 eV) X-ray radiation powered at 150 W. The base pressure in the sample analysis chamber was set to less than 1×10^{-8} mbar. To minimize the charging effects, a low energy electron flood gun was used as charge neutralizer. The survey spectra (pass energy of 160 eV) in the range of 0-1200 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra (pass energy of 40 eV) over different element peaks in 0.1 eV steps.

After Shirley background subtraction, the XPS peaks fitting were performed by a combination of 30 % Gaussian and 70 % Lorentzian method (LG (30)). The atomic concentration was calculated according to the following equation [91]:

$$\%n_i = 100 \left[\frac{\frac{I_{ij}}{\sigma_{ij} E^{0.7}}}{\sum \frac{I_{ij}}{\sigma_{ij} E^{0.7}}} \right] \quad (3-2)$$

$$\text{where, } I_{ij} = K \cdot T(E) \cdot L_{ij}(\gamma) \cdot \sigma_{ij} \cdot n_i \cdot \lambda(E) \cdot \cos(\theta) \quad (3-3)$$

and:

- n : atomic quantity;
- I_{ij} : area peak j from element i ;
- K : instrumental constant;
- $T(E)$: transmission function of analyzer;
- $L_{ij}(\lambda)$: angular asymmetric factor of orbital j of element i ;
- σ_{ij} : photoionization cross-section of peak j from element i ;
- E : kinetic energy of the emitted electron;
- $\lambda(E)$: inelastic mean free path;
- θ : take-off angle of the photoelectrons measured with respect to surface normal.

3.4 Gas Sensing Characterization

Gas sensing characterization based on dc electrical measurement was carried out using a home-designed gas sensor characterization system (GSCS). GSCS is a computer-based system capable of measuring conductive types of gas sensors fabricated using both thick and thin film technology. In this system, a personal computer was used to control the overall data measurement operation through a software system, developed using National Instruments Labview 9.5 package. It

adopts the virtual instrumentation (VI) technique commonly used in the field of data acquisition application. The sample mount test gas chamber was designed to strategically position the gas sensing device, on the heater stage in the gas chamber with electrical feedthroughs, under the direct influence of the test gas flow. The complete block diagram of the GSCS is given in Figure 3-5.

Figure 3-5 Block diagram of the home-designed gas sensor characterization system.

The gas type, flow rate, humidity and concentration of the test gas are regulated using four MKS1179A mass flow controllers (MFC), which are electronically controlled via the MKS247C four-channel-readout and the MKS232 interface unit. The overall gas flow of 500 sccm was chosen for all measurements. Compressed dry air or pure nitrogen were the diluting gases, while test gases used in this project were oxygen, carbon monoxide and ammonia, all supplied by SOXAL. The HFS heater stage was controlled from room temperature (24 °C) to 500 °C by the Linkam

TMS93 temperature controller. The temperature controller heated up or cooled down the heater stage, according to the specified ramp rate, to desired set temperature and maintained the temperature for the defined hold time duration. The actual temperature at the sample surface was measured by two k-type thermocouples. The direct current-voltage (I-V) measurement was measured using the Keithley 236 source measurement unit. Constant voltage was supplied continuously to the sample and the measured resistance was used to study the gas sensing response. In this project, fabricated gas sensors were first stabilized in the test chamber by heating from room temperature to 450 °C under constant flow of diluting gas (either dry N₂ or dry air, depending on test gas) and voltage source. Gas sensing characterization was carried out using different test gases, in order to investigate the gas sensitivity of the gas sensors. Effects of operating temperature, gas selectivity, gas concentration and humidity on gas sensing properties of STFx sensors were studied systematically.

Besides, ac impedance spectroscopy measurement was used to investigate the equivalent electrical circuits in STFx sensors and to study the underlying gas sensing mechanism. The measurement was carried out using a Solatron impedance analyzer (SI 1260) which was connected to GSCS in place of the Keithley 236 source measurement unit. An ac amplitude of 50 mV was used to measure the impedance spectroscopy in the frequency range from 0.1 Hz to 1 MHz. This frequency range was enough to demonstrate the ac conduction behavior of the sensors and no significant difference was observed for measurement at lower frequency range (down to 0.1 mHz), as proven in an individual experiment. A series of ac impedance measurement was carried out on the sensors under different oxygen concentration at

optimal operating temperature of 300 °C. The impedance spectra were fitted using Zview software (Scribner Associates Inc.) and a gas sensing mechanisms model was proposed with reference to the equivalent electrical circuits of the STFx sensors.

CHAPTER 4: SYNTHESIS AND OXYGEN SENSING

PROPERTY OF STFx NANOPARTICLES BASED

SENSORS

4.1 Synthesis and Characterization of STFx Nanoparticles

The high-energy ball milling technique, which is also known as mechanical alloying, was originated by John Benjamin [92-95] around 1972. This technique is most commonly used in metal alloying and able to synthesize non-equilibrium alloys from the elemental powder blends. Besides, it also has been researched and utilized in different areas of material processing and applied to many different material systems such as the preparation of nanostructured pure elements, intermetallic compounds, non-equilibrium materials and ceramic compounds. In high-energy ball milling, the milling times are longer, in terms of days. The materials for the bowls and balls have higher density, such as tungsten carbide, to increase the impact energy [90, 96, 97].

High-energy ball milling is a complex process whereby optimization of various factors is necessary to achieve the desired product phase and microstructure. Some of the critical parameters that have an effect on the final constitution of the powder can be summarized as follows [97]:

- a) milling container and grinding medium

The density of the milling container and grinding medium (balls) should be high enough so that the high impact energy can be created on the powder. Some commonly used materials for high-energy ball milling are hardened steel, hardened chromium steel, tempered steel, stainless steel, and tungsten carbide. In addition, the size of the grinding medium also has an influence on the milling efficiency. In general, a large size (and high density) balls is useful to create more impact energy to the powder. However, balls with smaller size give better homogenization.

b) milling speed

It is understandable that faster milling speed would produce higher energy input into the powder. However, there is a critical maximum speed where the balls will be pinned to the inner walls of the vial and hence do not fall down to exert any impact force. Another limitation to the maximum speed is the generation of large amount that causes uncertainties in the final product of the milling.

c) milling time

The milling time is the most important parameter. Normally the time is so chosen as to achieve a steady state between the fracturing and cold welding of the powder particles. Prolonged milling duration may cause large amount of contamination and formation of undesirable phases.

d) balls-to-powder weight ratio

The weight ratio of the balls to the powder, also known as charge ratio, is an important variable in the milling process. The weight proportion of the balls will

influence the number of collisions per unit time, and hence the amount of impact energy. It has been commonly varied from 10:1 to 50:1.

e) extent of filling the vial

In mechanical alloying, it is necessary to have enough space for the balls and the powders to move around freely in the milling container. If the filling of the balls and the powder is very small, then the production rate is very low. In contrast, if the quantity is large, then there is not enough space for the balls to move around and hence reduce the impact energy. Generally, about 50% filling of the vial space is appropriate.

All these process variables are not completely independent. Hence, careful optimization is necessary for each different desired material system.

Jiang [98, 99] was the first to report the use of this technique for the preparation of nanosized powder particles of $\alpha\text{-Fe}_2\text{O}_3$ for gas sensing applications. Since then, it inspired more research interest and has been proven to be a very effective route to prepare nanosized solid solution with grain size down to nano-scale for gas sensing applications [65-67, 100-102]. In the first part of the research, the high-energy ball milling was employed to synthesize the nanosized STFx sensing materials. By referring to previous work from our group [65, 66], tungsten carbide vials and balls were chosen to carry out the milling process. The milling speed was set at 200 rpm and the balls-to-powder weight ratio was kept as 20:1. As a comparison, STFx material was also prepared using conventional high temperature solid state reaction. In this section, the synthesis process of STFx materials will be studied

systematically. Physical properties such as crystal phase, grain size and surface element composition will be presented.

4.1.1 Milling Time Study on STF20 Nanoparticles

The XRD pattern is a conventional and effective technique to identify the crystalline structure of the milled powder particles. At the first place, a detailed milling time study was carried out using XRD in order to investigate the crystalline phase change during the high-energy ball milling process at 200 rpm. This is to determine the milling time needed to obtain single cubic perovskite phase STF_x materials. In this study, STF_x with 20 % iron content (STF20) was chosen for this study. Figure 4-1 illustrates the XRD patterns for ball-milled STF20 (STF20BM) with different milling hours, i.e. 2, 20, 60, 80 and 120 hours. As-mixed starting materials (SrO, TiO₂ rutile and α -Fe₂O₃) were also inserted as reference sample at 0 hour. As a comparison, STF20 powders were also synthesized using conventional high-temperature solid state reaction (STF20HT) by sintering at 1200 °C for 12 hours. The XRD pattern for STF20HT with single cubic perovskite structure is also inserted in Figure 4.1 for comparison.

During the high-energy ball milling process, the powders go through four different stages of the mechanical alloying process, namely initial, intermediate, final, and completion stage [90, 97, 103]. Phases observed from as-mixed starting materials (0 hour) are SrCO₃, rutile-TiO₂ and α -Fe₂O₃. These results are in accordance with the expectation that SrO strongly chemisorbs carbon dioxide from its environment to form SrCO₃. After 2 hours of milling, broadening of XRD peaks for the starting materials was observed, indicating the grain sizes of the starting materials were

decreased by repeatedly milling with high kinetic energy at the initial stage. However, no significant phase change was detected at this stage of milling.

Figure 4-1 XRD patterns for synthesized STFHT and STF20BM at different milling times.

From the XRD profiles, the cubic perovskite phase formation could be first observed after 20 hours of milling time. The starting materials and perovskite phase of STF20 co-existed until 60 hours of milling. This is the intermediate stage where breaking down of the chemical bonds of the starting materials and formation of new chemical bonds of the synthesized STF20 occurred concurrently. At 80 hours of milling, no starting material phase was observed and the XRD peaks for the cubic perovskite phase of the STF20 structure appeared distinctively. This phase was maintained up to 120 hours of milling time. The final and completion stage were observed to be at around 80 to 120 hours of milling and the synthesized STF20 nanoparticles possessed an extremely deformed metastable structure. High-energy ball milling

process at 200 rpm with 120 milling hours was successfully used to synthesize STF_x nanoparticles and subsequently used in this project.

The average grain size of the STF20 synthesized at 120 milling hours (STF20BM) was quantitatively calculated using the Scherrer's equation and was estimated to be 10.5 nm. On the other hand, average grain size for STF20HT was determined to be 27.8 nm, which was much larger than high-energy ball milled nanoparticles. The large average grain size of STF20HT was caused by high temperature induced grain growth. The lattice constants for the STF20BM and STF20HT were found to be 3.9086 Å and 3.8911 Å, respectively. Due to high impact energy during high-energy ball milling, the synthesized STF20BM remained at a high energy metastable state with high density of defect vacancies, and its lattice constant was larger than STF20HT [66, 103, 104].

4.1.2 Synthesis of STF_x Nanoparticles with Various Iron Contents

By referring to the milling time study for synthesized STF20BM, STF_x nanoparticles with various iron content ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) were synthesized using 120 hours of high-energy ball milling and their XRD patterns were illustrated in Figure 4-2. The cubic perovskite peaks (JCPDS No. 35-0734) were observed for all the synthesized STF_x nanoparticles but single phase nanoparticles were only successfully obtained for STF_x with lower iron contents (STO, STF20 and STF40). Diffraction pattern for iron oxide (α -Fe₂O₃) was detected for STF_x with $x \geq 0.6$ (STF60, STF80 and SFO) and the relative intensity of the iron oxide phase was found to be increased with iron content. This indicated that iron

oxide was not fully diffused and reacted in the STFx solid solution during the high-energy ball milling process. Instead, it existed as impurity phase in the materials.

Figure 4-2 XRD patterns for synthesized STFx nanoparticles with different iron contents at 120 hours of milling time.

Normally, it is expected that the single perovskite phase $(A_{1-y}A_y^I)BO_3$ or $A(B_{1-x}B_x^I)O_3$ can be fully formed over a wide composition range when the A or B cations are substituted by other A^I or B^I cations with the same charge and similar ionic radius. This has been proven by successful synthesis of a continuous solid solutions of $SrTi_{1-x}Ru_xO_3$ [105, 106]. However, the solid solubility limit of cation substitution in perovskite solid solutions was also reported, e.g. $(Sr_{1-x}Mg_x)TiO_3$ [107], $Sr(Fe_{1-x}Mo_x)O_3$ [108] and $Sr_{0.7}Ce_{0.3}Mn_{1-x}Al_xO_{3-\delta}$ [109].

The achievable solid solubility is strongly dependent on synthesis method, as well as other parameters such as oxygen contents, ambient pressure and temperature. In our case where high-energy ball milling at 200 rpm was employed, the maximum

complete solid solution of iron cation in the perovskite lattice of STF_x was approximately 40%. Besides, our group also reported the synthesis of full continuous solid solution of STF_x up to $x = 1.0$ using conventional high-temperature solid state reaction at 1200 °C for 48 hours, as shown in Figure 4-3 [110].

The extension of solid solution of iron in STF_x solid solution for higher x value was investigated and achieved by increasing the ball milling speed and will be presented in the section on Future Recommendations. In the following section, the oxygen sensing characterization was focused on STF_x with 20% iron content (STF20BM).

Figure 4-3 XRD patterns of STF_x at different x synthesized using high temperature solid state reaction [110].

4.1.3 Thermal Stability

Figure 4-4 shows the DTA-TGA plots for the synthesized STF20BM and STF20HT particles. For both plots, a small gradual weight loss was observed throughout the whole analyzed temperature range (30 to 1000 °C). Since the thermal analysis was carried out under pure N₂ flow, the gradual weight loss was due to oxygen loss from the materials during the heating [111, 112]. At the lower temperature range (< 400 °C), the weight loss was due to desorption of chemisorbed oxygen species on the grain surface of the material. While at higher temperature range, where the kinetic energy was high enough, the internal oxygen diffusion from the lattice oxygen (O²⁻) to the grain surface was possible. Therefore, lattice oxygen was expected to be lost from the bulk material and the oxygen stoichiometry decreased, causing gradual weight loss of the nanoparticles.

Figure 4-4 DTA-TGA plots for (a) STF20BM and (b) STF20HT powders in nitrogen with heating rate of 1 °C/min.

Quantitatively, one can see the percentage of weight loss for STF20BM nanoparticles was 3.3 times larger than the weight loss for STF20HT. This was due to larger amount of surface defects generated during repeatedly high-energy milling,

which served as adsorption sites for oxygen gas. In general, both STF20BM and STF20HT particles were thermally stable with no change in its crystal structure, except the lattice oxygen content.

4.1.4 Surface Chemical Study of High-Energy Ball Milled STFx

Nanoparticles

The surface element chemical state and composition of the high-energy ball milled STFx nanoparticles with varied iron contents was identified using XPS measurements. The survey spectra in the range of 0 to 1200 eV were recorded in 1 eV step for each nanoparticle sample and the spectra are shown in Figure 4-5. Only Sr, Ti, Fe, O and C elements were detected within the binding energy range. These five element peaks were chosen and characterized in high resolution XPS scan with 0.1 eV step.

Figure 4-5 XPS spectra in the wide-scan binding energy range of 0 to 1200 eV for (a) STO, (b) STF20, (c) STF40, (d) STF60, (e) STF80 and (f) SFO.

The deconvolution of XPS spectra for the C1s, Sr3d, Ti2p, Fe2p, and O1s of STF_x nanoparticles are depicted in Figure 4-6 to Figure 4-8. The calibration of the binding energy scale was performed with the C1s peak (BE = 285 eV) from the ubiquitous carbon contamination. Table 4-1 summarizes the atomic concentration for each element at its respective chemical state.

Table 4-1 Summary of surface atomic concentration for each element in the synthesis STF_x nanoparticles with different iron contents (*x*).

Element	Label	Binding Energy (eV)	Assignment	Atomic concentration (%) for STF _x					
				x = 0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1.0
C1s	C1s A	285.0	C-H	16.98	36.42	32.34	36.11	48.02	43.02
	C1s B	286.0	C-O	8.32	6.28	7.17	7.78	7.15	7.44
	C1s C	289.5	CO ₃	3.75	4.98	8.86	7.96	5.17	7.55
Sr3d	Sr3d 5/2A	133.0	Sr ²⁺ (STF)	8.15	4.41	3.87	3.73	2.32	1.84
	Sr3d 3/2A	134.8	Orbital Splitting	5.43	2.93	2.57	2.48	1.55	1.22
	Sr3d 5/2B	133.8	Sr ²⁺ (Carbonate)	1.92	2.27	3.51	3.49	2.56	4.29
	Sr3d 3/2B	135.6	Orbital Splitting	1.28	1.51	2.34	2.32	1.71	2.86
Ti2p	Ti2p 3/2A	458.0	Ti ⁴⁺ (STF)	7.07	3.98	1.99	1.24	0.31	—
	Ti2p 1/2A	463.7	Orbital Splitting	3.27	1.94	0.99	0.62	0.15	—
Fe2p	Fe2p 3/2A	712.0	Fe ³⁺ (STF)	—	0.69	0.90	1.31	1.12	1.05
	Fe2p 1/2A	725.3	Orbital Splitting	—	0.46	0.58	0.88	0.56	0.70
	Fe2p 3/2sat	719.3	Satellite	—	0.18	0.22	0.32	0.17	0.45
	Fe2p 1/2sat	733.9	Orbital Splitting	—	0.08	0.15	0.20	0.14	—
O1s	O1s A	529.3	O ²⁻ lattice oxygen	27.75	17.77	11.56	8.94	2.87	4.17
	O1s B	531.4	Surface carbonate	12.90	12.89	20.32	19.08	21.60	20.60
	O1s C	532.8	Adsorbed O species	3.18	3.21	2.64	3.53	4.59	4.81

Figure 4-6 XPS high resolution (a) C1s and (b) Sr3d spectra for high-energy ball milled STFx nanoparticles with different iron contents.

Figure 4-7 XPS high resolution (a) Ti2p and (b) Fe2p spectra for high-energy ball milled STFx nanoparticles with different iron contents.

Three C1s peaks were observed for all the synthesized STFx nanoparticles as shown in Figure 4-6(a), namely C1s A (285.0 eV), C1s B (~286.0 eV) and C1s C (~289.5 eV). The lowest binding energy peak at 285 eV with strong intensity was assigned to the adventitious carbon (C-H) from atmospheric hydrocarbon contamination which present in almost all the solid surfaces. Adventitious carbon is generally comprised of a variety of (relatively short chain, perhaps polymeric) hydrocarbons species with small amounts of both singly and doubly bound oxygen functionality [113]. Hence, the position for this peak was used as the calibration reference. The C1s B at higher binding energy was possibly due to the C-O like species on the surface. The peak at around 289.5 eV was caused by the presence of surface strontium carbonate species (CO₃ bond). Huge amount of surface carbonate species was expected for STFx materials due to high reactivity of Sr element in the structure to carbon dioxide from the ambient. Carbonate formation phenomenon was also reported for other perovskite-type materials containing alkaline-earth cations such as SrTiO₃ [114-117], BaSrTiO₃ [118], and BaTiO₃ [115]. The reported C1s peaks positions of carbonate species were very close to our results.

As illustrated in Figure 4-6(b), two pairs of Sr3d doublet peaks were fitted. The doublet peaks are corresponding to the spin-orbit splitting phenomenon which was only observed for p, d and f orbitals. The doublet peaks Sr3d A located at higher binding energies (133.8 and 135.6 eV) were located at the same binding energy with the Sr peaks of SrCO₃, and hence were assigned as Sr²⁺ for carbonate. Another doublet peaks B at lower binding energies (133.0 and 134.8 eV) were attributed to Sr²⁺ ions in STFx cubic perovskite structure.

The XPS spectra of Ti2p was deconvoluted into a single doublet peaks around 458 eV and 463.7 eV labeled as Ti2p 3/2A and Ti2p 1/2A respectively. This doublet peaks were sharp and intense, indicating that the only Ti^{4+} species that existed in the synthesized nanoparticles [117, 119, 120].

For Fe2p spectra shown in Figure 4-7(b), a pair of asymmetric doublet peaks with satellite peak located at around 719 eV was observed. Mills et al. reported that the broadening of the Fe2p peaks was due to unresolved multiplet splitting phenomenon, which caused a FWHM of 3.8 to 4.4 eV for the Fe2p peak. The phenomenon of multiplet splitting associated with photoelectron peaks was due to the presence of unpaired valence electrons, resulting in an exchange interaction which affected differently the remaining spin-up or spin-down core electrons [121]. Hence, the asymmetric peaks could not be deconvoluted using Gaussian-Lorentzian fitting. However, the binding energy of the Fe2p satellite peak could be used for the identification of chemical state of Fe element. Satellite peak of Fe2p at around 719 eV indicated that the chemical state of Fe in the STFx materials was at oxidation state of 3+. From the literature, satellite peaks for Fe_2O_3 (Fe^{3+}) was reported to be located at approximately 8 eV higher than Fe 2p_{3/2} peak, while satellite peak for FeO (Fe^{2+}) was approximately 6 eV higher than Fe 2p_{3/2} peak. There is no satellite peak observed for Fe_3O_4 (Fe^{4+}) [122, 123]. In our case, the satellite peak which located at around 719 eV corresponded to the Fe with oxidation state of 3+ (Fe^{3+}).

The high resolution XPS spectra of O1s are plotted in Figure 4-8. The deconvolution of the spectra revealed the occurrence of three species, namely O1s A (529.3 eV), O1s B (531.4 eV), and O1s C (532.8 eV). The O1s A peak with lowest binding energy was assigned as the double-charged lattice oxygen (O^{2-}) in the cubic

perovskite structure [124-127]. The O1s lateral oxygen peaks at the higher binding energy range corresponded to the ionizations of weakly adsorbed species or excess oxygen on the material surface, as compared to the reported binding energy scale of O1s [124]. In our case, O1s B and O1s C were assigned as surface carbonate species and adsorbed oxygen molecule species, respectively. The atomic concentration of the O1s B peak was tallied with the carbonate peak Sr3d B and C1s C.

Figure 4-8 XPS high resolution O1s spectra for high-energy ball milled STFx nanoparticles with different iron contents.

The surface composition for the STFx nanoparticles was estimated and listed in Table 4-2. In this semi-quantitative analysis, the atomic ratio of Sr and O was calculated with respect to that of elements Ti and Fe, by assuming the sum of Ti and Fe as 1.00. One can observe that the compositions of Ti and Fe were very close to the ideal stoichiometric value. Quantitative analysis has shown that with increasing of the iron content in STFx nanoparticles, the composition of lattice oxygen (O1s A)

decreased. This observation was caused by the partial substitution of quadrivalent Ti ions (Ti^{4+}) with trivalent Fe ions (Fe^{3+}) without restoring electroneutrality in the cation site of the perovskite structure. Hence, oxygen vacancies were formed to maintain charge balance in the system and led to the reduction of the lattice oxygen [15]. Lastly, the composition of Sr was higher than the stoichiometric value of 1, indicating that Sr was segregated toward the surface of the nanoparticles samples [128, 129].

Table 4-2 Estimated surface composition for high-energy ball milled STF_x nanoparticles based on XPS analysis.

STF _x	Atomic Ratio			
	Sr	Ti	Fe	O
STO	1.31	1.00	0.00	2.68
STF20	1.00	0.81	0.19	2.42
STF40	1.33	0.62	0.38	2.39
STF60	1.36	0.41	0.59	1.96
STF80	1.56	0.19	0.81	1.17
SFO	1.39	0.00	1.00	1.90

4.2 Deposition and Optimization of STF20 Nanoparticles

Coating

In order to obtain uniform and crack-free nanoparticles coating for fabrication of gas sensors, a stable and well-homogenized slurry or colloidal dispersion was necessary. The stability of colloidal dispersions depends highly on the interaction forces

between colloidal particles and the confining geometries. This is especially obvious for concentrated colloidal dispersion where particles are more easily to come in close contact with one another and become more ordered in the confined environment. Dispersion of nanoparticles is affected by several important factors, such as solid loading, particles size, dispersion medium, pH value of the dispersion medium and addition of organic binder [130, 131]. These factors have been considered and studied in this project in order to obtain a stable colloidal dispersion for STF20BM nanoparticles.

4.2.1 Particle Size Distribution of STF20BM Nanoparticles

Nano-sized particles are more susceptible to agglomeration than the micron-sized counterparts due to extremely high specific surface area. Undesired agglomerates can be created during powder synthesis, drying, or even during storage. In addition, the synthesized STF20BM nanoparticles are in metal-stable state and full of surface defect, and hence more prompt to agglomerations. Hence, an effective dispersion preparation is needed to break the agglomerations, reduce the particle size and separate the nanoparticles to produce stable and well-homogenized slurry. In this section, the STF20BM nanoparticles at different stages during slurry preparation were taken out and then dispersed in ethanol for particle size distribution study.

The procedures of slurry preparation were already described in Chapter 3. For each preparation steps, small portion of powders were taken out and ultrasonically homogenized with ethanol. The particle size of the dispersions was then measured using a zetasizer (Nano ZS). Table 4-3 shows the average particle size of STF20BM nanoparticles at different stages of slurry preparation. Without any prior processing,

the stored synthesized STF20BM nanoparticles showed a large average particle size of around 730 nm, which was caused by the high surface energy of the meta-stable nanoparticles. The nanoparticles were then thoroughly ground using agate mortar and pestle, followed by filtering using sieve with mesh size of 325 (44 μm). This step was aimed to break and remove any large agglomeration of nanoparticles. The average particle size was effectively reduced down to 336 nm.

Besides, additives also play another important role in improving the stability of the colloidal dispersion. In this project, the organic binder ethyl-cellulose (EC) dissolved in α -terpineol was used. Another additive studied was polyvinylpyrrolidone (PVP), which act as stress-reducer to suppress crack-formation during annealing process for coatings. The effect of these additives on the stability of the colloidal dispersion was evaluated. The ground and sieved nanoparticles were mixed with organic binder using two different methods, namely ultrasonication and agate ball milling. From Table 4-3, the average particle size after addition of organic binder and ultrasonication did not improve significantly. This showed that ultrasonication was not effective to homogenize the nanoparticles with organic binder. On the other hand, agate ball milling appeared to be a more suitable method to homogenize the nanoparticles with the organic binder and further break down the agglomerated nanoparticles. The average particle size was further reduced down to around 230 nm.

Figure 4-9 shows the photo image of the STF20BM nanoparticle dispersions at different preparation stage after settling for 24 hours. It was observed that most of the particles settled down in the first three dispersions (a), (b) and (c). After the addition of organic binder and agate ball milling, very stable and homogenized

dispersions were obtained even after letting them settle for 24 hours, as illustrated in dispersions (e) and (f). In conclusion, stable and well-dispersed slurry was successfully obtained in this project using the described preparation procedures.

Table 4-3 Average particle size of synthesized STF20BM nanoparticles at different dispersion steps.

Dispersion steps of STF20BM nanoparticles	Average particle size (nm)
(a) Stored nanoparticles	729
(b) Grinding and sieving	337
(c) Grinding and sieving + ultrasonication with EC	325
(d) Grinding and sieving + ball milling with PVP	229
(e) Grinding and sieving + ball milling with EC	228
(f) Grinding and sieving + ball milling with EC and PVP	244

Figure 4-9 Photo image of STF20BM nanoparticles dispersions at different preparation stages after settling for 24 hours: (a) stored nanoparticles, (b) ground and sieved, (c) ground and sieved, then EC added with ultrasonication, (d) ground and sieved, then PVP added with ball-milling, (e) ground and sieved, then EC added with ball-milling, (f) ground and sieved, then PVP and EC added with ball-milling.

4.2.2 Surface Morphology

After optimization of the nanoparticle dispersion, the slurry was spin-coated on the wafer substrate with gold interdigitated electrode and annealed at different temperatures. The STF20 particles were prepared using three different routes and fabricated into nanoparticles coating for oxygen sensing characterization:

- a) high-energy ball milling process for 120 hours (STF20BM)
- b) high-temperature solid state reaction (STF20HT)
- c) STF20HT with 20 hours of post high-energy ball milling (STFHTBM)

The surface morphology and cross-sectional view of three different nanoparticle coatings are shown in Figures 4-10 to 4-12. All the coatings were annealed at 550 °C for 1 hour under synthetic air flow. It can be seen that all the coatings showed uniform crack-free microstructures. However, agglomerates of nanoparticles with the size of around 1 μm could be observed. For STF20HT and STF20HTBM, coating with individual particles and pores could be clearly observed from the images in Figures 4-11 and 4-12. On the other hand, STF20BM coating showed a very dense morphology owing to the high surface energy state of the high-energy ball milled nanosized particles.

From the cross sectional view images, the thicknesses of three particle coatings were estimated to be around 0.9 μm to 1.1 μm . The thickness of the coatings prepared using the spin-coating method was in between those of screen printed thick film (> 10 μm) and thin film (< 100 nm). This coating technique was possible to achieve using standard microfabrication processes and hence avoided traditional screen printing process commonly used for gas sensors fabrication. This can realize the miniaturization of particle based gas sensor using microfabrication technology.

Figure 4-10 SEM micrographs for STF20BM nanoparticles based sensor annealed at 550 °C for 1 hour (a) planar view, (b) cross-sectional view.

Figure 4-11 SEM micrographs for STF20HT nanoparticles based sensor annealed at 550 °C for 1 hour (a) planar view, (b) cross-sectional view.

Figure 4-12 SEM micrographs for STF20HTBM nanoparticles based sensor annealed at 550 °C for 1 hour (a) planar view, (b) cross-sectional view.

4.3 Oxygen Sensing Properties of STF20 Nanoparticles Based Sensors

Uniform and crack-free STF20 nanoparticles coatings were successfully deposited and fabricated into gas sensors using standard microfabrication processes. Gas sensing characterization was carried out to study their oxygen sensing performance. The oxygen gas sensitivity S is defined as the resistance ratio $R_{\text{nitrogen}}/R_{\text{oxygen}}$, where R_{nitrogen} and R_{oxygen} are the electrical resistance of the sensors in background nitrogen ambient and in oxygen ambient, respectively. The effect of annealing temperature, synthesis method and long term stability will be investigated and discussed.

4.3.1 Effect of Annealing Temperature

After deposition and patterning, the sensors were annealed at different temperatures (550 to 850 °C) for 1 hour under synthetic air flow. Annealing temperatures higher than 500 °C were chosen to fully burn off the organic binder (ethyl cellulose) in the coatings. 20% oxygen with nitrogen as diluting gas was injected into the testing chamber at different operating temperature (150 to 450 °C) and the electrical resistance of the sensors was measured. The resistance change of the sensors during oxygen gas injection at different operating temperatures is illustrated in Figure 4-13.

In the tested operating temperature range, resistance drop was observed upon oxygen gas exposure. This indicates that the STF20BM material exhibit a predominantly p-type electronic conductivity, which is in good agreement with reported works [62, 76, 132, 133]. This sensing response occurs through the following reactions:

Surface chemisorption:

Bulk reaction:

According to a notation proposed by Kröger and Vink, O_O^x denotes regular oxygen sites, $V_O^{\bullet\bullet}$ are doubly ionized oxygen vacancies and e^- represents electron in the conduction band.

Figure 4-13 Gas sensing response to 20% oxygen gas at different operating temperatures for STF20BM nanoparticles based sensors annealed at (a) 550 °C, (b) 650 °C, (c) 750 °C and (d) 850 °C for 1 hour (pink region = oxygen gas injection).

Oxygen gas is adsorbed on the surface of the sensing material (equation (4-1)), and diffused into the lattice to replace any available oxygen vacancy (equation (4-2)). Both chemisorption and bulk reactions consume electrons, or in other words, generate holes into the semiconductor material. This causes a drop in the electrical resistance of STF_x material, which is a p-type semiconductor.

The corresponding oxygen gas sensitivity was calculated and plotted in Figure 4-14. The optimum operating temperature was found to be around 250 to 300 °C. It can be clearly observed that the STF20BM nanoparticles based sensor annealed at 550 °C showed the best oxygen sensing responses with optimal sensitivity value of 2540 at operating temperature of 300 °C. To the best of our knowledge, this value is much higher than the values reported for STF_x oxygen sensors with operating temperature of 700 to 900 °C.

One can observe that the sensitivity degraded as the annealing temperature increased. For sensor annealed at 850 °C, no significant sensing property was observed (Figure 4-13(d)). This degraded gas sensing performance was due to grain growth and defects relaxation during high temperature annealing process. Figure 4-15 shows the XRD patterns for STF20BM nanoparticles coatings with different annealing temperatures and their corresponding calculated lattice constant and grain size.

As observed, the grain size of the STF20BM nanoparticles increased with increasing annealing temperature. When the grain size of the metal oxide is small enough ($D < 2L$, where D is the actual grain size and L is the depth of the depletion layer), the whole crystallite is depleted of electrons or, for p-type semiconductor, accumulated

of holes (see Figure 2-3) [19]. Hence the influence of oxygen adsorption is more significant and the change in resistance is greatly enhanced.

Figure 4-14 Gas sensitivity at 20% oxygen concentration at different operating temperatures for STF20BM nanoparticles based sensors annealed at different temperatures.

On the other hand, it is observed that the lattice constant of the STF20BM nanoparticles decreased with annealing temperature. Due to high impact energy during high-energy ball milling, the synthesized nanoparticles were full of defects such as surface defects and excess oxygen vacancies. The nanoparticles were at a high energy metastable state and had a larger lattice constant. During high temperature annealing process, the lattice constant was decreased down to a more stable value. This suggested that the structural defects in the nanoparticles were fairly relaxed [134, 135]. Since the surface defects and excess oxygen vacancies play an important role in oxygen sensing through the reactions described in equations (4-1) and (4-2), relaxation of these defects has inevitably degraded the gas sensitivity of the sensing material.

Figure 4-15 (a) XRD patterns and (b) calculated lattice constant and grain size for STF20BM nanoparticles coatings annealed at different temperatures.

4.3.2 Effect of Synthesis Method

In the previous section, STF20BM showed excellent oxygen sensing response with optimal annealing temperature of 550 °C. In comparison, STF20 were also prepared using two more methods, i.e.:

- high-temperature solid state reaction at 1200 °C for 12 hours (STF20HT)
- STF20HT with 20 hours of post high-energy ball milling (STF20HTBM)

All three different sensors were annealed at 550 °C for 1 hour and the gas sensitivity at 20 % oxygen at different operating temperatures is plotted in Figure 4-16 (note the sensitivity is plotted in logarithmic scale for better illustration). One can observe that STF20HT sensor has the lowest oxygen sensitivity at all the operating temperatures. Majority of the reported STF_x oxygen sensors were also prepared using high temperature solid state reaction and our sensitivity values prepared using this method were consistent with those reported works. After post-treatment with 20 hours high-energy ball milling, a significant improvement on oxygen sensitivity was

observed for STF20HTBM sensor. However, its sensitivity was still much poorer compared to that of the synthesized STF20BM sensor.

Figure 4-16 Gas sensitivity to 20% oxygen concentration at different operating temperatures for different sensors annealed at 550 °C for 1 hour.

Figure 4-17 shows the XRD patterns for different STF20 particle coatings annealed at 550 °C for 1 hour and their corresponding lattice constant and grain size. With 20 hours of high-energy milling, the grain size of STF20HTBM was smaller and comparable to that of the synthesized STF20BM. Besides, the lattice constant of STF20HTBM was also found to be slightly larger than that of the STF20HT. Through this experiment, high-energy ball milling was proven to be an effective route to prepare material of very small grain size which is advantageous for gas sensing applications.

Figure 4-17 (a) XRD patterns and (b) calculated lattice constant and grain size for different STF20 coatings annealed at 550 °C for 1 hour.

4.3.3 Long Term Stability

One of the major setbacks for the semiconducting metal oxide gas sensors is that they suffer long term stability. The long term stability behavior for the STF20 sensing material synthesized using high-energy ball milling technique was hence investigated. The STF20BM nanoparticles based sensor annealed at 550 °C for 1 hour was chosen for the test and its sensing response to 20 % oxygen at operating temperature of 300 °C was tested after few months. The long term oxygen sensing response is plotted in Figure 4-18. The measurements show a significant drop in the resistance change of the sensor after 160 days. This was most probably because of the relaxation of highly reactive surface defects which generated during the high-energy ball milling process. Hence, there is always a trade-off between gas sensitivity and stability of a metal oxide sensing material.

Figure 4-18 Long term sensing responses to 20% oxygen gas for STF20BM nanoparticles based sensors annealed at 550 °C for 1 hour at operating temperature of 300 °C.

CHAPTER 5: DEPOSITION AND OXYGEN SENSING

PROPERTY OF STFx SOL-GEL THIN FILM

SENSORS

5.1 Preparation and Deposition of STFx Sol-Gel Thin Films

Sol-gel process is an attractive alternative to other method of synthesis of ceramic owing to its advantages such as low temperature synthesis, simple equipment to be used, thin film formability, capable for large area coating, easy control of composition and good homogeneity. Usually, metal alkoxides have been employed in sol-gel process because they can undergo catalyzed hydrolysis and condensation to form nanoscale oxide particles. However, many of the alkoxides are very difficult to be obtained and dealt with because of their high sensitivity to the atmospheric moisture. In addition, for our case where multi-component metal oxide has to be prepared, the hydrolysis rate of the alkoxide is very difficult to control [136].

Therefore, modified sol-gel process using metal salts such as nitrates, acetates, chlorides, and sulfides has been introduced and developed to overcome the limitation of metal alkoxides sol-gel process. Metal salts are relatively cheaper and easier to handle. More importantly, they can be dissolved in proper chelating agent to form metal complexes in the solution which later can be converted to oxides by thermal decomposition.

In this chapter, the modified sol-gel spin-coated technique was utilized to deposit STFx thin films for oxygen sensing characterization. The preparation of STFx sol-gel with various iron contents was studied and optimized in order to obtain stable and precipitation-free sol-gel. Material characterizations of the STFx thin films such as XRD, FESEM and AFM were carried out and are presented in this section.

5.1.1 Preparation and Optimization of STFx Sol Solution

A sol-gel is a colloidal solution of metalorganic ($M(OR)_n$) or metalorganic-oxygen-metalorganic $[(OR)_{n-1}M-O-M(OR)_{n-1}]$ molecules which are linked into a O-M-O polymeric network. The solution is formed by controlled hydrolysis and condensation reactions of metal complexes. If the hydrolysis and condensation reactions go unchecked, macro-molecules containing M-O-M segments (precipitations) will form. These reactions can take time from less than a second to weeks. The speed of the reactions depends on the concentration of the initial compounds (sol molarity) and can be altered by other reactants which inhibit the gelation process [136, 137]. For example, by varying the amount of water, it is possible to control the speed of hydrolysis. In addition, chelating compounds include β -diketones such as acetylacetone and carboxylic acids such as acetic acid can also modify the gelation process. Hence, in order to obtain a stable and precipitation-free STFx sol-gel, various factors such as selection of starting materials, choice of chelating agents, sol molarity (concentration) and water contents have been considered and investigated in this project.

The detailed procedures for sol-gel preparation have already been described in Chapter 3. The starting materials chosen were strontium acetate, titanium butoxide,

and iron (III) nitrate, which are some common metal alkoxides and metal salts used in sol-gel processes. Suitable chelating agents were added to stabilize the metal ions by forming metal complexes. However, the challenge is to simultaneously control the hydrolysis and condensation reaction for all three different metal complexes in the solution, while maintaining the homogeneity of the solution. Study was first focused on STF20 sol-gel where the effect of sol molarity and water content was investigated.

In the sol preparation, the water content was calculated as the mole ratio of water to strontium. Acetates normally have lower solubility in water and organic solvents than other metal salts. Acetates are prone to re-crystallization if they were dissolved in improper amount of solvent or without enough chelating reaction [136]. From a separate experiment, minimum water content ratio to fully dissolve all the strontium acetate was determined as 36:1. However, besides assisting to dissolve strontium acetate, the water also plays a role to provide enough hydrolysis reaction for titanium butoxide.

Table 5-1 shows the observations on the stability of STF20 sol with different molarities and water amounts. It was found that white powder-like precipitation appeared when water content was insufficient at lower sol molarity. The white precipitation could be dissolved in excess water and from the EDX study it mainly consisted of strontium, carbon and oxygen. Hence, it is believed that the formation of precipitation was due to recrystallization of strontium acetate when the water content was insufficient.

Table 5-1 Stability of STF20 sol with different molarities and water contents.

Water Content (H ₂ O:Sr)	STF20 Molarity				
	0.2 M	0.15 M	0.1 M	0.05 M	0.02 M
36	Clear	Clear	Precipitation	Precipitation	Precipitation
54	Clear	Clear	Clear	Precipitation	Precipitation
72	Clear	Clear	Clear	Precipitation	Precipitation
90	Clear	Clear	Clear	Clear	Precipitation
108	Clear	Clear	Clear	Clear	Precipitation

By setting the mole ratio of water to strontium as 90:1, stability of STF_x sol with varied iron contents and molarities was investigated and the observations are shown in Table 5-2. White powder-like precipitation was no longer found in the sol solutions with 90 parts water for $x > 0.2$. However, crystal-like precipitation was found in the solution with high iron content and high molarity. The crystal-like precipitation could not be dissolved in excess water. It was formed due to uncontrolled hydrolysis of titanium butoxide when relative water content was too high i.e. when molarity was high and when amount titanium butoxide was low ($x > 0.2$). Hence, water amount in the sol set the upper and lower limit of the molarity and iron content of the STF_x sol and must be carefully control to obtain stable sol solution. In the subsequent experiments, all STF_x sol were prepared using 90 parts of water with molarity of 0.1M.

Table 5-2 Stability of STF_x sol with 90 parts water and different molarities.

STF _x	Molarity				
	0.2 M	0.15 M	0.1 M	0.05 M	0.02 M
STF10	Clear	Clear	Clear	Precipitation	Precipitation
STF20	Clear	Clear	Clear	Clear	Precipitation
STF30	Crystal	Clear	Clear	Clear	Clear
STF40	Crystal	Crystal	Clear	Clear	Clear
STF60	Crystal	Crystal	Clear	Clear	Clear
STF80	Crystal	Crystal	Clear	Clear	Clear

5.1.2 Crystallography Study of STF_x Thin Films

5.1.2.1 Effect of Annealing Temperature on STF40 Thin Films

After stable and precipitation-free STF_x sols were successfully prepared, sol-gel thin films were then deposited onto Si/SiO₂ wafer substrate using spin-coating method. The spin-coated sol-gel thin films (5 layers thick) were annealed at different temperatures for 1 hour under synthetic air ambient using Lindberd furnace. In this project, STF40 was selected for a detailed annealing temperature study. The structural development in the thin films was studied and characterized using an X-ray diffractometer. The small glazing angle of 1° was used to ensure that the diffraction intensity came mostly from the measured thin film samples.

Figure 5-1 illustrates the XRD patterns for as-deposited STF40 thin film and thin films annealed at different temperatures of 400, 450, 550, 650 and 750 °C for one hour. No significant phase existed for as-deposited film and film annealed at 400 °C. For films annealed at 450 °C and above, the main peaks observed coincided with the

standard pattern of STF_x materials with cubic perovskite structures. There was no miscellaneous peak observed in all the profiles indicating that no other intermediate phase existed. In the sol solution, all three metal complexes were well stabilized by appropriate chelating agent and did not crystalized out as individual oxide. This resulted in homogenous thin film with no impurity phase.

Figure 5-1 XRD patterns of the STF40 sol-gel thin films annealed at different temperatures for 1 hour.

From the XRD profiles, the intensity of the peaks of STF40 thin films annealed at 450 °C was relatively low, indicating initial formation of the cubic perovskite phase of STF40. At higher annealing temperatures, the cubic perovskite peaks appeared more distinctively and the cubic perovskite phase had been developed more completely. Therefore, STF40 sol-gel thin films with better crystallinity could be obtained at higher annealing temperatures. In subsequent study, the annealing

temperature was fixed at 650 °C to investigate the phase formation in thin film with different iron contents.

5.1.2.2 STFx Thin Films with Different Iron Contents

By referring to the structural development study of STF40 thin films, the cubic perovskite phase formation in STFx thin films with different iron contents ($x = 0.2, 0.4, 0.5, 0.6$ and 0.8) was characterized. All the films were annealed at 650 °C for 1 hour under synthetic air flow. The X-ray diffraction patterns of the STFx sol-gel thin films with different iron contents are shown in Figure 5-2. It was clearly observed that the STFx cubic perovskite phase existed in all the films. However, the relative peak intensity of the perovskite peaks decreased as the iron contents increased, indicating lower crystallinity level of the films. The films with higher iron contents were mainly in amorphous phase with very little crystallization.

Figure 5-2 XRD patterns of the STFx sol-gel thin films with different iron contents annealed at 650 °C for 1 hour.

5.1.3 Surface Morphology Observation of STF_x Sol-Gel Thin Films

5.1.3.1 Film Thickness and Contact with Gold Interdigitated Electrode

In this project, gold interdigitated electrode was patterned and deposited on Si/SiO₂ wafer using E-beam evaporation. 10 nm Ti were deposited as the adhesion layer between the Au electrode and the SiO₂/Si substrate. For the fabrication of resistive type gas sensors, the STF_x sol-gel thin films were spin-coated on the wafer substrate with gold interdigitated electrode and annealed at different temperatures. The quality and contact between the thin film and the gold electrode was examined using FESEM. The cross-sectional view and planer view of a typical five layers thick STF40 thin film annealed at 650 °C are illustrated in Figure 5-3(a) and (b), respectively. From Figure 5-3(a), the thickness of the five layers thin film was measured and estimated to be around 90 nm. The images showed smooth and good film coverage at the interface between the thin film and gold electrode. This ensured a stable electrical measurement signal during gas sensing characterization.

Figure 5-3 FESEM micrographs for STF40 sol-gel thin film deposited on the interdigitated gold electrode (a) cross-sectional view, (b) planar view.

5.1.3.2 FESEM Observation of STF40 Thin Films with Different Annealing Temperatures

The structural development of STF40 thin films has been discussed in previous section. Here, the surface morphologies for STF40 thin films with different annealing temperatures were studied using FESEM and the images are shown in Figure 5-4. The films annealed at 450 °C and 550 °C were very dense with small grains. Some pores could be observed on the surface of the thin film, which were caused by the decomposition of organic compounds in the sol-gel thin films during the sintering. At higher annealing temperature of 650 and 750 °C, significant grain growth induced by the high temperature annealing process was observed. The surface morphology of the films appeared to be denser with uniform grains of around 30 to 50 nm in size.

5.1.3.3 AFM of STF40 Thin Films with Different Annealing Temperatures

AFM was used to study the surface roughness of sol-gel thin film samples. Figure 5-5 shows the AFM images for the STF40 thin films annealed at different temperatures with the scanning area of 2 x 2 μm . The corresponding root mean square surface roughness (R_q) was also indicated in the figures. It was found that the surfaces of thin film annealed at 450, 550 and 650 °C have large amount of pores and non-uniformity structure, which was caused by decomposition of organic compounds from the thin film during annealing process. Hence, the R_q values are relatively larger. Dense and uniform polycrystalline grains were observed for the film annealed at 750 °C. Significant grain growth at high annealing temperature partially filled up the pores and contributed to a smaller surface roughness.

Generally, AFM observations were very similar to the FESEM observation. However, for STF_x materials which are highly resistive at room temperature, AFM characterization appeared to be more convenient tool for surface morphology characterization. It can avoid surface charging effect which normally occurred during FESEM characterization, especially for highly resistive materials.

Figure 5-4 FESEM micrographs for STF₄₀ sol-gel thin films annealed at (a) 450 °C, (b) 550 °C, (c) 650 °C and (d) 750 °C for 1 hour.

Figure 5-5 AFM surface morphology and 3D-topology for STF40 thin films annealed at (a) 450 °C, (b) 550 °C, (c) 650 °C, and (d) 750 °C for 1 hour.

5.1.3.4 FESEM Observation of STF_x Thin Films with Different Iron Contents

Figure 5-6 shows the FESEM images for STF_x sol-gel thin films with varied iron contents. All the films were annealed at 650 °C for 1 hour under synthetic air flow. It was observed that the thin films with varied iron contents had different surface morphologies. The STF20 thin film surface was made up of blisters with a few hundreds of nanometers size. The STF40 and STF60 films showed very alike morphology with grains aligned along the circular pores on the surface. The surface of STF80 thin film showed large grain of around 50 nm with very porous structure.

Figure 5-6 FESEM micrographs for (a) STF20, (b) STF40, (c) STF60, and (d) STF80 sol-gel thin film annealed at 650 °C for 1 hour.

5.2 Oxygen Sensing Properties of STFx Sol-Gel Thin Film

Sensors

Single cubic perovskite phase STFx sol-gel thin film sensors were successfully fabricated with appropriate annealing temperature. Gas sensing characterization was carried out to study their oxygen sensing properties. The effect of iron contents and annealing temperatures on the oxygen sensing response was investigated systematically. Next, effect of oxygen concentrations, sensing response to reducing gases and humidity effect were also characterized.

5.2.1 Effect of Iron Content

In order to investigate the effect of iron content, all STFx thin film sensors were annealed at temperature of 650 °C for 1 hour. 20% oxygen gas diluted with dry nitrogen was injected onto the STFx thin film sensors at different operating temperatures of 150 to 450 °C with interval of 50 °C, and the electrical resistance of the sensors was measured. The oxygen sensing responses of the sensors with different iron contents are shown in Figure 5-7.

For the STF20 and STF40 film sensors, resistance drop was observed during oxygen gas exposure, indicating a predominantly p-type sensing response, which is in good agreement with reported works of STFx sensors [76, 132, 133]. According to equations (4-1) and (4-2), adsorption and bulk reaction of oxygen gas with semiconductor metal oxide consume electron or generate holes, which causes a resistance drop for a p-type semiconductor. On the other hand, for the sensors with iron content $\geq 50\%$, it is worth to note that the resistance of the sensors increased

during exposure to oxygen gas, which indicated a predominantly n-type electrical conductivity. This anomalous n-type oxygen sensing response for the STF x thin film sensors with $x \geq 0.5$ is very interesting and has never been reported.

Figure 5-7 Gas sensing responses to 20% oxygen gas at different operating temperatures for STF x sol-gel thin film sensors annealed 650 $^{\circ}\text{C}$ for 1 hour (pink region = oxygen gas injection).

To further investigate this anomalous phenomenon, STF40 and STF80 film sensors annealed at 650 °C were selected for an in-depth study. Sensors with these two iron contents have lower resistivity compared to STF20 (p-type) and STF60 (n-type), hence a more stable measurement signal was attainable. Figure 5-8 illustrates the effect of the oxygen concentration (1 to 100 %) on the sensing response of STF40 and STF80 film sensors at operating temperature of 300 °C. It is observed that STF40 sensor showed a consistent p-type response to whole concentration range of oxygen gas, while STF80 sensor showed the reverse sensing response type. All the sensing responses were repeatable and reversible.

Figure 5-8 Gas sensing responses to oxygen gas with different concentrations at operating temperature of 300 °C for STF40 and STF80 sol-gel thin film sensors annealed at 650 °C for 1 hour (pink region = oxygen gas injection).

Effect of Fe substitution on the electrical properties of STFx materials was widely investigated. Indeed, Fe was regarded as an impurity with an acceptor-like character in STFx material which contributes to p-type conductivity [17]. Hence, in our case,

the n-type conductivity was not triggered by Fe substitution. Instead, it was suspected that the anomalous n-type oxygen sensing response was caused by the low crystallinity of the sol-gel thin films with high iron contents.

5.2.2 Effect of Annealing Temperature

Thin film with iron contents of 40, 50 and 60% were chosen for a detailed study since the switch in the sensing response type was observed at iron content around 50%. The first phase of the experiment was to increase the annealing temperature of STF50 and STF60 film sensors, from 650 °C to 750 and 850 °C, all for 1 hour. This was intended to increase the crystallinity of the thin film and to completely form the STF_x cubic perovskite structure. Figure 5-9 illustrates the resistance change of the STF50 and STF60 sensors to 20% oxygen gas at different operating temperatures. All the sensors with different annealing temperatures show consistently n-type oxygen sensing response manifested by an increase in resistance during oxygen gas exposure.

Figure 5-9 (a)

Figure 5-9 (continue)

Figure 5-9 Gas sensing responses to 20% oxygen gas at different operating temperatures for (a) STF50 and (b) STF60 sol-gel thin film sensors annealed at different temperatures for 1 hour (pink region = oxygen gas injection).

Next, the second phase of the experiment was to vary the annealing temperature of STF40 sensors from 400 to 750 °C. The XRD characterization of the STF40 thin films with different annealing temperatures was already discussed in Chapter 5.1.2. The sensing responses of the STF40 films sensors annealed at different temperatures to 20% oxygen gas are shown in Figure 5-10. For the sensors annealed at 500 °C and higher, the resistance drop with the 20% oxygen gas pumped in, indicating a normal p-type sensing response (Figure 5-10(b)). However, opposite oxygen sensing response type was observed for the sensors annealed at 450 °C and lower, as shown in Figure 5-10(a). Once again, the n-type sensing response was observed for STF40 film sensors with lower crystallinity, which is very similar to the case of STF80 sensor. The underlying reason for this anomalous n-type gas sensing response has been further investigated and will be presented in next chapter.

Figure 5-10 Gas sensing responses to 20% oxygen gas at different operating temperatures for STF40 sol-gel thin film sensors annealed at different temperatures for 1 hour: (a) n-type response, (b) p-type response (pink region = oxygen gas injection).

5.2.3 Effect of Oxygen Gas Concentration

The effect of the oxygen concentration (1 to 100%) on the sensing response at operating temperature of 300 °C was studied. The resistance change for STF40 film sensors annealed at 450 and 650 °C are illustrated in Figure 5-11. As shown in the figure, the STF40 film sensor annealed at 450 °C showed a consistent n-type response to 1 to 100% oxygen gas. For the STF40 film sensor annealed at 650 °C, the sensors showed consistent p-type response to whole concentration range of oxygen gas. All the sensing responses are repeatable and reversible.

Figure 5-11 Gas sensing response to oxygen gas with different concentrations at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 450 and 650 °C for 1 hour (pink region = oxygen gas injection).

The gas sensitivity for the sensors at different oxygen gas concentration were calculated and plotted in Figure 5-12. The curve shows a typical trend of the gas sensitivity versus gas concentration curve for the semiconductor metal oxide gas sensor. The increase in the gas sensitivity values became more and more gradual at

higher oxygen concentration. With a fixed surface area for the sensing material, the adsorption of gas molecules on the metal oxide surface was lower at a lower gas concentration. An increase in the gas concentration would raise the surface reactions due to a higher surface adsorption. When the gas adsorption on the fixed surface area is saturated, further increase in surface reactions would be gradual and hence a slow increase in gas sensitivity.

Figure 5-12 Gas sensitivities to oxygen gas with different concentrations at operating temperature of 300 °C for STF40 thin film sensors annealed at (a) 450 and (b) 650 °C for 1 hour.

5.2.4 Reducing Gas Sensing Response

In order to ascertain the abnormal n-type sensing response of the devices is not only applicable for oxygen gas sensing, 100 ppm of CO and NH₃ in dry air were chosen for reducing gas sensing characterization for STF40 film sensors annealed at 450 and 650 °C. The reactions between the reducing gases and surface adsorbed oxygen species are as follow:

During reducing gas exposure, the electrons trapped by the surface adsorbed oxygen are returned to the sensing material and causes a change in electrical resistance.

Figure 5-13 shows the reducing gas sensing response of the STF40 film sensors. Similar to the oxygen sensing response type, STF40 film sensor annealed at 450 °C exhibited n-type sensing response to 100 ppm of CO and NH₃ gases and the electrical resistance decreased with the reducing gas pumped in. Likewise, the STF40 film sensor annealed at 650 °C showed p-type sensing response, the resistance increase with 100 ppm of CO and NH₃ gases pumped in. These reducing gas sensing results once again confirm the n- and p-type of the STF40 film sensors annealed at 450 and 650 °C, respectively. In addition, the sensors showed relatively low sensing response to these reducing gases. Hence, cross-sensitivity to other gas will not be an issue.

Figure 5-13 Sensing response to reducing gases at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 450 and 650 °C for 1 hour.

5.2.5 Effect of Humidity

For semiconductor gas sensors operated at temperatures between 100 and 500 °C, the interaction with water vapor leads to molecular water and hydroxyl group adsorption [138, 139]. In all the reported works, interaction with water vapor resulted in the increase of surface conductance. There are generally three types of mechanism explaining the increase of surface conductivity of the metal oxide in the presence of water vapor. Two are direct mechanisms, which were proposed by Heiland and Kohl [140]. The third one is an indirect mechanism, suggested by Morrison and by Henrich and Cox [141]. However, the actual reaction remains a matter of debate.

In this section, effect of humidity on oxygen sensing response for STF40 sol-gel thin film sensor annealed at 650 °C was evaluated. Figure 5-14 shows the sensing response to 20% oxygen gas under ambient with different relative humidity levels (0, 10, 20, 30, 50 and 80 % RH) at operating temperature of 300 °C. As expected, the electrical resistance decreased with increasing relative humidity. The significant drift in the base resistance (R_{N_2}) caused a drop in the calculated sensitivity values, as shown in the inset of Figure 5-28. The humidity effect remained as one of the challenges of semiconducting metal oxide sensors, and further improvement is needed to overcome this problem.

Figure 5-14 Gas sensing response to 20 % oxygen gas with different % RH at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 650 °C for 1 hour.

CHAPTER 6: GAS SENSING MECHANISM AND ELECTRICAL TRANSPORT PROPERTY OF STF_x SOL-GEL THIN FILM SENSORS

6.1 Investigation on N-Type Sensing Response for STF40 Sol- Gel Thin Film Sensors

In this section, the underlying reason of the anomalous n-type gas sensing response for the STF40 thin films sensors was investigated in detail. Firstly, reported works on transition of gas sensing type are reviewed and presented. Next, the STF40 film sensors were systematically examined using XPS and TEM characterization to explain the origin of the n-type sensing response. XPS is a powerful analysis method to study the surface element chemical state and its atomic concentration. Chemical shift in the binding energy of the elements in the STF40 thin films with different annealing temperatures was determined to understand the changes in the chemical state of the thin film surface. In addition, the crystallinity of the thin films was also observed using HRTEM images and selective area electron diffraction (SAED).

6.1.1 Overview of Gas Sensing Response Transition

Semiconducting metal oxide sensors are usually classified according to the direction of the resistance change when exposing to reducing gases, which are “n-type”

sensors and “p-type” sensors. The sensing response depends on the surface conductivity type of the metal oxides, which is determined by the dominant electronic carriers at the surface, for example electrons or holes. However, dual sensing response or transition of the sensing response of the oxides (from p to n or vice versa) have also been observed and reported. The explanation of the switching of sensing response type is still a matter of debate. Various mechanisms have been adopted to explain the transition of gas sensing response. Basically, there are two main categories of explanations proposed:

- i) sensing response type changes when the sensors are operated at different ambient, gas concentrations, relative humidity and temperature ranges [142-146],
- ii) sensing response type changes when the sensors are pretreated under different conditions such as annealing, high-energy ion beam, doping and substitution [147-153].

For example, Huang et al. reported that the n-p-n transition of ZnO-modified SnO₂ nanorod H₂ sensor was caused by the formation of the n-ZnO/p-Zn-O-Sn/n-SnO₂ heterojunction structures [147]. Siciliano et al. proposed two different interactions between TeO₂ nanowires sensors and ethanol gas, causing transition of sensing response at different ethanol concentration and working temperature [142]. Gurlo et al. attributed the n-p transition of n-type α -Fe₂O₃ and In₂O₃-Fe₂O₃ sensors to the formation of inversion layer caused by large amount of oxygen adsorption [143, 144]. However, since our oxygen responses are consistent for huge range of oxygen concentration, the transition of oxygen sensing response cannot be explained by the proposed formation of inversion layer.

In our case, the anomalous n-type sensing response was obviously caused by low annealing temperature of the STF40 film sensor and we believed that the different phase structure of the films resulted in the different sensing response types in our sensors. Similar phenomenon was also reported on p-type sol-gel dip-coated TiO₂ thin films with low annealing temperature [148]. Sánchez et al. reported that the sol-gel dip-coated TiO₂ film with annealing temperature of 400 °C shows unusual p-type ammonia sensing response which could be related to the abundance of hydroxyl groups or Ti³⁺ sites in the films annealed at low temperature.

Lower annealing temperature (≤ 450 °C) was insufficient to completely form the p-type cubic perovskite phase of STF40. As elucidated by XRD study (Figure 5-1), the STF40 thin films annealed at 450 °C or lower were not crystallized well to form cubic perovskite structure. Hence, the films mainly contained the amorphous phases such as O-Ti-O and O-Fe-O which were formed by the decomposition of the sol-gel precursor. The observed n-type sensing response was plausibly resulted from these n-type amorphous phases. At higher annealing temperatures (500 °C and higher), the STF40 film crystallized well into p-type STF40 phase and showed normal p-type response to both oxygen and CO/NH₃ reducing gases. The presence of amorphous phase and chemical state of the elements in the sol-gel thin film were characterized using TEM and XPS. The findings will be presented next.

6.1.2 TEM Observation for STF40 Thin Films

The microstructure of the STF40 thin films was characterized using a HRTEM operated at 200 kV. The thin film TEM samples were prepared using focused ion beam (FIB) technique. Figure 6-1 shows the FESEM image for a ready TEM sample

taken in the FIB system. On the top surface of thin film, a thin layer of Pt was deposited in the FIB system in order to prevent the thin film from damage during TEM sample preparation. The sample was further fine-milled down to thickness of around 60 nm.

Figure 6-1 FESEM micrograph for TEM sample prepared using FIB technique.

Figure 6-2 shows the low magnification bright field TEM image for STF40 thin films annealed at 450 °C. A high resolution TEM image from the area marked as a square in Figure 6-2 was taken and is shown in Figure 6-3(a). The microstructure of thin film annealed at 450 °C had an amorphous-like morphology with initial crystallization, as verified by the electron diffraction pattern (see inset). This indicated that the thin film was still in amorphous phase and starting to form STF40 cubic perovskite phase. On the other hand, the film annealed at 650 °C had polycrystalline phase and tiny STF40 nanocrystals with diameter about 3 nm were clearly visible in Figure 6-3(b). This was further confirmed by electron diffraction pattern shown in the inset. The TEM observations were certainly in good agreement with the XRD measurements which was reported in Chapter 5.1.2.1. In our case, this

particular amorphous phase had given rise to the anomalous n-type gas sensing response for the film sensor annealed at 450 °C. In next section, we shall investigate the chemical state of this amorphous phase using XPS.

Figure 6-2 Low magnification TEM images for STF40 sol-gel thin films annealed 450 °C for 1h.

Figure 6-3 HRTEM images and SAED patterns for STF40 sol-gel thin films annealed at (a) 450 °C and (b) 650 °C for 1h.

6.1.3 XPS Analysis of STF40 Sol-Gel Thin Films

In this section, the XPS analysis was systematically carried out for the STF40 sol-gel thin films annealed at 400, 450, 550, 650 and 750 °C for 1 hour under 1 slm synthetic air flow. The chemical state of all the elements in STF40 thin films with different annealing temperatures were studied to elucidate the existence of amorphous n-type TiO_2 and Fe_2O_3 in the film annealed below lower temperatures. Figure 6-4 shows that only Sr, Ti, Fe, O and C elements were found from the XPS survey spectra for all the STF40 sol-gel thin films. The high resolution XPS spectra for the $\text{C}1s$, $\text{Sr}3d$, $\text{Ti}2p$, $\text{Fe}2p$, and $\text{O}1s$ are plotted in Figures 6-5 to 6-7. Table 6-1 summarizes the atomic concentration for each element at its respective chemical state.

Figure 6-4 XPS spectra in the wide-scan binding energy range of 0 to 1200 eV for STF40 sol-gel thin films annealed at different temperatures.

Table 6-1 Summary of surface atomic concentration for each element in the STF40 sol-gel thin films annealed at different temperatures.

Element	Label	Binding Energy (eV)	Assignment	Annealing Temperatures				
				400 °C	450 °C	550 °C	650 °C	750 °C
C1s	C1s A	285.0	C-H	7.68	16.24	14.24	11.96	13.93
	C1s B	285.7	C-O	5.41	4.04	2.45	3.25	2.14
	C1s C	289.4	CO ₃	15.95	2.44	2.72	2.38	2.95
Sr3d	Sr3d 5/2A	132.9	Sr ²⁺ (STF)	—	6.83	6.73	7.85	6.46
	Sr3d 3/2A	134.7	Orbital Splitting	—	4.55	4.48	5.23	4.3
	Sr3d 5/2B	133.7	Sr ²⁺ (Carbonate)	8.5	1.68	1.85	1.1	1.84
	Sr3d 3/2B	135.5	Orbital Splitting	7.66	1.34	1.02	0.9	1.23
Ti2p	Ti2p 3/2A	458.0	Ti ⁴⁺ (STF)	—	3.66	4.34	5.25	5.07
	Ti2p 1/2A	463.7	Orbital Splitting	—	1.69	1.93	2.56	2.37
	Ti2p 3/2B	459.2	Ti ⁴⁺ (TiO ₂)	0.63	1.34	0.85	—	—
	Ti2p 1/2B	464.8	Orbital Splitting	0.31	0.56	0.47	—	—
Fe2p	Fe2p 3/2A	712.0	Fe ³⁺ (STF)	0.49	2.58	3.17	3.06	2.99
	Fe2p 1/2A	725.3	Orbital Splitting	0.26	1.51	1.99	1.60	1.74
	Fe2p sat	719.3	Satellite	—	0.72	0.66	0.93	0.76
O1s	O1s A	529.3	O ²⁻ lattice oxygen	—	24.56	30.36	31.7	32.4
	O1s B	531.4	Surface carbonate	39.38	21.28	18.58	16.98	19.32
	O1s C	532.8	Adsorbed O species	13.73	4.98	4.17	5.26	2.49

Figure 6-5 XPS high resolution (a) C1s and (b) Sr3d spectra for STF40 sol-gel thin films annealed at different temperatures.

Figure 6-6 XPS high resolution (a) Ti2p and (b) Fe2p spectra for STF40 sol-gel thin films annealed at different temperatures.

Three C1s peaks were fitted for all the thin film samples, as shown in Figure 6-5(a). The calibration of the binding energy scale was performed with the C1s A peak (285 eV) from the ubiquitous carbon contamination which exist at the surface of almost all solid materials. Next, C1s B (285.7 eV) was assigned to C-O bonds from contaminations. Generally, peaks A and B were observed for all the samples. The C1s C (289.4 eV) peak represented carbonate species in the samples. Large amount of carbonate species existed in the STF40 film annealed at 400 °C because the annealing temperature was insufficient to fully burn-off all the carbonate species in the sol-gel film.

As illustrated in Figure 6-5(b), two pairs of Sr3d doublet peaks were fitted. The doublet peaks Sr3d B located at higher binding energy (133.7 eV) were located at the same binding energy with the Sr peaks of SrCO₃, and hence were assigned as Sr²⁺ for carbonate. Another doublet peaks Sr3d A positioned at lower binding energy (132.9 eV) were assigned as Sr²⁺ in cubic perovskite structure. STF40 film annealed at 400 °C only consisted of strontium carbonate species. The formation of STF_x perovskite structure reflected by the doublet peak A peaks only appeared for films annealed at 450 °C and higher.

It is remarkable to observe two different pairs of Ti2p peaks from the XPS spectra, labeled as doublet peaks Ti2p A and Ti2p B, as depicted in Figure 6-6(a). The doublet peaks B at higher binding energy (459.2 eV) is similar to the Ti⁴⁺ peaks of the commercial rutile TiO₂ which was detected in another independent XPS experiment. On the other hand, the doublet peaks A with slightly lower binding energy was assigned as the Ti⁴⁺ in the cubic perovskite structure. The lowering of binding energy of Ti2p XPS peaks was also reported when comparing STO with

TiO₂ [117, 120]. Only Ti2p B was detected in the film annealed at 400 °C, showing that the element Ti was in the TiO₂-like bonding (O-Ti-O). Since no TiO₂ crystal structure peaks were observed from the XRD pattern, we can assume that the TiO₂ was in amorphous phase. At annealing temperatures of 450 and 550 °C, this peak B co-existed with peak A, indicating that the Ti was bonded in two different types of bonding i.e. Ti-O bond in TiO₂ structure and Ti-O bond in perovskite structure. For films annealed at higher annealing temperatures (650 and 750 °C), only doublet peaks Ti2p A existed. This showed that STF40 perovskite phase formation was completed at annealing temperatures higher than 650 °C.

Figure 6-6(b) shows asymmetric Fe2p spectra with satellite peak located at 719 eV. The location for Fe2p satellite peak indicated that the Fe was at oxidation state of 3+ (Fe³⁺) [122, 123]. However, due to the asymmetry and broadening of the Fe2p peaks, there was no any significant information obtained about structure change from the XPS patterns as annealing temperature increased.

As illustrated in Figure 6-7, O1s XPS spectra mainly consisted of three peaks: O1s A (529.3 eV), O1s B (~531.3 eV), and O1s C (~532.6 eV). The O1s A peak with lowest binding energy was assigned as the double-charged lattice oxygen (O²⁻) in the cubic perovskite structure. It was observed that the lattice oxygen only existed for films annealed at 450 °C and higher. For film annealed at 400 °C, no lattice oxygen existed and the film was still in amorphous phase. The O1s lateral oxygen peaks at the higher binding energy range corresponded to the ionizations of weakly adsorbed species or excess oxygen on the surface. Specifically, O1s B and O1s C were assigned to surface carbonate species and adsorbed oxygen molecule species (O_{ads}⁻), respectively.

Figure 6-7 XPS high resolution O1s spectra for STF40 sol-gel thin films annealed at different temperatures.

As a summary, all the results evidenced that the formation of STF_x perovskite structure only started at annealing temperature of 450 °C. The film annealed at 400 °C was still in amorphous phase and no O²⁻ lattice oxygen was observed. This was in good agreement with the XRD and TEM observations which were presented in previous sections. Therefore, it can be concluded that the n-type sensing response observed in the STF40 film sensor annealed at lower temperatures was resulted by the presence of n-type amorphous phases.

6.2 Electrical Transport Property and Defect Chemistry of STF40 Sol-Gel Thin Film Sensors

Next, the electrical transport property of the STF40 sol-gel thin film sensors was studied through the dependency of electrical resistance to pO₂ and temperature. The

oxygen sensitivity factor (m) and activation energy (E_a) were determined, which can give information about the corresponding ionic defects that contribute to the electrical transport property of the sol-gel derived STF40 thin films. From there, the defect chemistry that contributed to the oxygen sensing behavior of STF40 material was proposed and discussed.

6.2.1 Oxygen Partial Pressure Dependency and Oxygen Sensitivity Factor

When a semiconductor metal oxide is exposed to an atmosphere with oxygen gas, it is found that the electrical conductivity (σ) is proportional to a power of oxygen pressure when the sample is operated at a constant temperature, as shown in the following equation:

$$\sigma \propto (p_{O_2})^{1/m} \quad (6-1)$$

where m is the oxygen sensitivity factor. It has been known that this proportionality is a consequence of the theory of defect equilibrium [42, 154, 155]. The absolute value of $1/m$ represents the sensitivity of conductivity to p_{O_2} which is dependent on the dominating defects involved in the reaction between the oxygen gas and the sensor. The sign of $1/m$ depends on the conduction type, i.e. positive for p-type conduction and negative for n-type conduction. By taking temperature into consideration, the relation between the electrical conductivity (σ), temperature (T) and p_{O_2} can then be written as:

$$\sigma = A \exp\left(-\frac{E_a}{k_B T}\right) (p_{O_2})^{1/m} \quad (6-2)$$

where k_B is the Boltzmann constant, E_a is the activation energy which represents the sensitivity of the electrical conductivity to temperature change.

Detailed oxygen sensing test with different oxygen concentration at operating temperature of 300 °C was carried out on STF40 thin film sensors annealed at 450 °C and 650 °C and the results were already presented in Chapter 5.2.3 (Figure 5-11). The logarithms of relative conductance values were calculated and plotted against $\log pO_2$, as shown in Figure 6-8.

Figure 6-8 pO_2 dependences of the electrical conductance at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 450 and 650 °C.

Converting Equation (6-2) into logarithms form gives:

$$\log \sigma = \log \left[A \exp \left(-\frac{E_a}{k_B T} \right) \right] + \frac{1}{m} \log(p_{O_2}) \quad (6-3)$$

Hence, the value of oxygen sensitivity factor can be estimated from the slope in the Figure 6-8. STF40 sensor annealed at 450 °C showed a negative slope with $m = -2$. This indicated that the sensor exhibited an n-type electrical conductivity, which is similar with the observation from dc sensing characterization. On the other hand, STF40 sensor annealed at 650 °C showed a positive slope with $m = +2.53$, indicating a p-type conductivity behavior.

This absolute values of m were smaller than the value of 4 from both theoretical defects chemistry and reported literatures [15, 88], indicating that the STF40 sol-gel thin films exhibited better oxygen sensitivity. The deviation of the observed pO_2 dependence of the conductivity for the sensors can be explained by the presence of additional ionic defects [11]. The detailed defect chemistry for the STF40 sol-gel thin film sensors will be discussed in next section.

6.2.2 The Defect chemistry of STF40 Sol-Gel Thin Films

Reported works showed that pO_2 dependence of conductance for STFx materials $-1/4$ at low pO_2 range while $+1/4$ at high pO_2 ranges. The point defect which contributed to this phenomenon was the double-charged oxygen vacancy ($V_O^{\bullet\bullet}$) and the reaction with oxygen gas and lattice oxygen is given by:

However, the defect chemistry using double-charged oxygen vacancy was reported mainly at high temperature regime (> 700 °C). At lower temperature regime (< 277 °C or 550K), the oxygen species vacancies were reported to be singly-charged ($V_O^{\bullet}$) [156-159]. Since our operating temperature is near to this temperature regime, singly-charged oxygen vacancies was used in the defect chemistry of the sol-gel derived STF40 thin film.

The understanding of defect chemistry of STFx material was mainly based on STO, with extra oxygen vacancies introduced by Fe substituting Ti sites. The intrinsic ionic point defects in STO were strontium and oxygen vacancies (i.e. Schottky defects) [160]. However, for Fe substitution in STO, additional oxygen vacancies

were formed during the substitution, as shown in the following equation:

At lower temperature regime ($< 277^\circ\text{C}$), the doubly-charged oxygen vacancies were replaced by the singly-charged vacancies according to equation:

where according to *Kröger* and *Vink* notation, O_O^x is regular oxygen site, with effective zero charge; Sr_{Sr}^x is regular strontium site, with effective zero charge; V_{Sr}'' is doubly negative charge strontium vacancies; V_O'' is doubly positive charged oxygen vacancies, V_O' is singly positive charged oxygen vacancies and Fe_{Ti}' is iron-substituted Ti site, with effective singly negative charge. It is assumed that the electroneutrality condition is approximated by:

$$[V_O'] = 2[V_O''] = [Fe_{Ti}'] \quad (6-7)$$

This means that for every Fe substituted Ti site, one singly-charged oxygen vacancy was created. These additional oxygen vacancies introduced in STF_x rendered this material with improved sensitivity to pO_2 , as compared to STO.

For n-type STF40 sensor annealed at 450°C , the predominant point defects were oxygen vacancies and electrons and the oxygen sensing reaction happened according to the following equation:

The equilibrium given by law of mass action is:

$$K_I = \frac{(p_{O_2})^{1/2}(n)[V_O']}{[O_O^x]} \quad (6-9)$$

where K_I is the mass action constant for equation (6-8). For unit activity of oxygen ions on oxygen sites ($O_O^x = 1$), this implies that:

$$n = (K_I)[V_O]^{-1}(p_{O_2})^{-1/2} \quad (6-10)$$

Substituting equation (6-7) gives:

$$n = (K_I)[Fe'_{Ti}]^{-1}(p_{O_2})^{-1/2} \quad (6-11)$$

This illustrates the electron concentration, and hence the n-type electrical conductivity is proportional to $(p_{O_2})^{-1/2}$.

On the other hand, for p-type STF40 sensor annealed at 650 °C, the predominant point defects were strontium vacancies and holes which can be formed by oxygen occupying a vacant SrO unit on the surface according to reaction below:

The equilibrium given by law of mass action is:

$$K_{II} = \frac{p[O_O^x]}{(p_{O_2})^{1/2}[V_O]} \quad (6-13)$$

where K_{II} is the mass action constant for equation (6-12). For unit activity of oxygen ions on oxygen sites ($O_O^x = 1$), the dependency of hole concentration on the oxygen partial pressure is given by:

$$p = (K_{II})[V_O](p_{O_2})^{1/2} \quad (6-14)$$

Substituting equation (6-7) gives:

$$p = (K_{II})[Fe'_{Ti}](p_{O_2})^{1/2} \quad (6-15)$$

This illustrates that the hole concentration and hence the p-type electrical

conductivity of the sensor is proportional to $(pO_2)^{+1/2}$.

In conclusion, for both n-type and p-type STF40 film sensors, the theoretical dependencies of electrical conductivity on pO_2 estimated using defect chemistry were very close to the experimental values obtained from Figure 6-8. This confirmed that singly-charge oxygen vacancies played an important role in the electrical transport and sensing properties of our STF40 sol-gel thin film at the tested pO_2 and operating temperature range.

6.2.3 Arrhenius Plot and Activation Energy

Many properties of solids, in particular their electrical conductivity, are found to obey the Arrhenius equation, as shown in Equation (6-15)

$$Z = Z_0 \exp \left(-\frac{E_a}{k_B T} \right) \quad (6-16)$$

Where Z is the property of interest, E_a is the activation energy, Z_0 is the value of Z at absolute zero, k_B is boltzmann constant (8.6173324×10^{-5} eV/K) and T is the temperature [155]. A plot of $\ln Z$ against $1/T$ (or $1000/T$) is called an Arrhenius plot and a straight line is obtained with a slope of $-(E_a/k_B)$.

Taking the natural logarithm ($\ln$) of equation (6-2), the dependence of conductivity of a metal oxide with temperature can be written as:

$$\ln \sigma = \ln \left[A(p_{O_2})^{1/m} \right] - \left[\left(\frac{E_a}{k_B} \right) \left(\frac{1}{T} \right) \right] \quad (6-17)$$

Figure 6-9 illustrates the Arrhenius plot of $\ln$ conductivity vs. $1000/T$ for both n-type and p-type STF40 sensors under 20 % O_2 ambient. The operating temperature was

varied from 30 to 450 °C. The activation energy E_a was estimated from the gradient of the plot. Both sensors showed positive slope with the change of activation energy (gradient) at temperature around 500 K (227 °C). This temperature was very close to the optimal operating temperature of our STF40 sensors.

Figure 6-9 Arrhenius plot under 20% O₂ ambient for STF40 sol-gel thin film sensors annealed at 450 and 650 °C for 1 hour.

For STF40 sensor annealed at 450 °C (n-type), the activation energy at 20 % O₂ ambient decreases from 0.673 eV to 0.420 eV as temperature increased. This activation energy change of 0.253 eV was very close to the reported energy needed for conversion of $V_{\dot{O}}$ to $V_{\ddot{O}}$. At higher temperature regime (> 277 °C or 550 K), the singly-charged oxygen vacancies converted to doubly-charged vacancy according to equation:

Applying the law of mass action gives:

$$\frac{[V_{\dot{O}}]n}{[V_{\ddot{O}}]} = K_{V_{\dot{O}}^{1 \rightarrow 2}} \exp\left(-\frac{E_{V_{\dot{O}}^{1 \rightarrow 2}}}{k_B T}\right) \quad (6-19)$$

where $E_{V_{\dot{O}}^{1 \rightarrow 2}}$ is the ionization energy needed to convert $V_{\dot{O}}$ to $V_{\ddot{O}}$ and $K_{V_{\dot{O}}^{1 \rightarrow 2}}$ is the equilibrium constant for the respective reaction. The ionization energy $E_{V_{\dot{O}}^{1 \rightarrow 2}}$ was reported to be around 0.2 to 0.3 eV [157, 159]. Ionization of $V_{\dot{O}}$ to $V_{\ddot{O}}$ introduced more electron carriers, and increased the conductivity of the n-type STF40 sensor. Therefore, the activation energy of conduction was reduced by an amount equal to $E_{V_{\dot{O}}^{1 \rightarrow 2}}$.

On the other, for STF40 sensor annealed at 650 °C (p-type), the activation energy under 20 % O₂ ambient increased from 0.320 eV to 0.628 eV. The difference of 0.308 eV was also caused by the conversion of $V_{\dot{O}}$ to $V_{\ddot{O}}$. Ionization of $V_{\dot{O}}$ to $V_{\ddot{O}}$ will consumed hole carriers according to equation:

Lower concentration of hole carrier reduced the conductivity of the p-type STF40 sensor (annealed at 650 °C). Therefore, the activation energy of conduction was increased by an amount equal to $E_{V_{\dot{O}}^{1 \rightarrow 2}}$.

These findings further confirmed the presence of singly-charged oxygen vacancies in STF40 sol-gel thin film sensors at operating temperature of around 300 °C, which contributed to the enhanced oxygen sensing performance.

6.3 Equivalent Circuit Modeling and Gas Sensing Mechanism

Electrochemical impedance spectroscopy is a powerful tool in the mechanistic study of corrosion, semiconductors, batteries, electroplating and electro-organic synthesis. For gas sensing applications, it can be used to study the gas adsorption on gas sensing semiconductor structures [161-164]. The measured electrical impedance is defined as the ratio of incremental change in voltage to the resulting change in current, and calculated as the ratio between the system voltage phasor, $U(j\omega)$, and the current phasor, $I(j\omega)$, generated by a frequency response analyzer, as shown in equation (6-21). The complex impedance is normally presented as the sum of the real, $Z_{re}(\omega)$ and imaginary, $Z_{im}(\omega)$ components originated mainly from the resistance and capacitance of the cell, respectively.

$$Z(j\omega) = \frac{U(j\omega)}{I(j\omega)} = Z_{re}(\omega) + jZ_{im}(\omega) \quad (6-21)$$

where $\omega = 2\pi f$ and $j = \sqrt{-1}$.

The main advantage of impedance spectroscopy is that a purely electronic model can be used to represent a physical device. Any electrochemical reaction is typically analogous to a change in the electronic circuit consisting of a specific combination of resistors and capacitors. In practical, an impedance plot obtained can be correlated with one or more equivalent circuits. There is no unique equivalent circuit model to fit the measurement data, or the best models might not perfectly fit the data. However, it is very important to setup the equivalent circuit according to the actual physical or chemical process of the device [165].

In this section, the STF40 thin film sensors were characterized using a Solatron impedance analyzer (SI 1260) and the data were fitted using the Zview software.

The equivalent circuit model was proposed according to the considerations of actual physical and chemical reactions that occurred at the gold electrode, grains and grains boundary of the sensing material. This could provide insights into the electrical charge transport across the grains and grain boundaries which help to understand the gas sensing response of our sensors. Finally, a schematic model was proposed to explain the gas sensing mechanisms of our STF40 thin film sensor.

6.3.1 Ac Impedance Spectra and Equivalent Circuit Modeling

A series of ac impedance measurement under different oxygen concentration (0 to 100%) at operating temperatures of 300 °C was carried out on the STF40 sol-gel thin film sensors annealed at 450 and 650 °C. Figures 6-10 and 6-11 show the variation of $|Z|$ and theta with respect to the frequency for the sensors annealed at 450 and 650 °C, respectively.

Figure 6-10 The variation of (a) $|Z|$ and (b) theta with frequency under different oxygen concentration at operating temperature of 300 °C for the STF40 sol-gel thin film sensors annealed at 450 °C for 1 hour.

Figure 6-11 The variation of (a) $|Z|$ and (b) theta with frequency under different oxygen concentration at operating temperature of 300 °C for the STF40 sol-gel thin film sensors annealed at 650 °C for 1 hour.

The respective ac complex impedance spectra (Nyquist plot) for both sensors are illustrated in Figure 6-12. The plots show a semicircle within the frequency range, which is a common feature observed in most polycrystalline ceramic and films. One can clearly observe that the size of the semicircle was greatly affected by the oxygen concentration. The semicircle is generally fitted as an equivalent circuit consisting of a resistor R_c in series with a Randle loop (parallel combination of a resistor R_l and a constant phase element), as shown in Figure 6-13. Due to slight depression of the semicircle, a constant phase element (CPE) was used in the fitting instead of an ideal capacitor. The impedance of the CPE is defined as:

$$Z_{CPE} = \frac{1}{C(j\omega)^n} \quad (6-22)$$

in which C is a capacitance value which corresponds to an ideal capacitor, ω and j are the angular frequency and the imaginary unit, respectively. The depression parameter n is less than one depending on the depression of the arc. If $n = 1$, the equation is identical to that of a capacitor and the behavior of CPE is identical to an

ideal capacitor. For a chemical gas sensor, some common underlying physical reasons that contributed to the non-ideality of the capacitor are surface roughness of the electrode, inhomogeneous oxygen adsorption rate, varying film thickness or composition and non-uniform current distribution along the film [166-170].

Figure 6-12 Impedance spectra under different oxygen concentrations at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed of (a) 450 and (b) 650 °C.

Figure 6-13 The ac equivalent circuit model for STF40 sol-gel thin film sensor.

The impedance spectra were then fitted using the proposed equivalent circuit model and the values of parameters R_c , R_1 , C and n for both sensors under varied oxygen concentrations are plotted in Figure 6-14. In the following section, the physical meaning and deviation of each electronic component are discussed in details.

Figure 6-14 Fitted parameters of equivalent circuit elements under different oxygen concentration at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 450 and 650 °C: a) R_c and R_1 , b) C and n .

a) Resistor R_c

From Figure 6-14(a), one can clearly observe that variation of resistance R_c is insignificant under different oxygen concentrations. For a metal oxide gas sensor, R_c could be attributed to the contact resistance for the sensor during electrical measurement, which was mainly contributed by the contact between the gold electrode and STF40 sensing material. The work function of gold (5.1 eV) is normally higher than the work function of semiconducting material. When the gold interdigitated electrodes are brought in contact with a p-type semiconducting sensitive material, the equilibrium of free charge carriers is established to level out their Fermi-energies, as shown in Figure 6-15. This builds a band bending in the semiconductor ($q\Delta V_s$) and its value is equal to the initial deference of their Fermi-energies ($\phi_{gold} - \phi_{STFx}$). The resistance associated with the gold-semiconductor contact R_c is directly correlated to the band bending as shown below [138, 171]:

$$R_c \sim \exp\left(\frac{q\Delta V_s}{k_B T}\right) = \exp\left(\frac{\phi_{gold} - \phi_{STFx}}{k_B T}\right) \quad (6-23)$$

According to the reported modeling by Barsan et al. [138], for “normal” contact areas in the order of nanometers, the influence of gas ambient on the contact resistance will be negligible during the measurement. The value of the R_c is primarily dependent on the preparation and fabrication of the sensors itself. Hence, the value for R_c is independent of oxygen concentrations. However, a slight increase in the R_c at higher oxygen concentration was due to a larger surface band bending induced by oxygen chemisorption.

Figure 6-15 Schematic representation of work function change before (left) and after (right) contact between the gold electrode and the p-type semiconductor sensing material.

b) Resistor R_I

In contrast to R_c , resistance R_I showed a great dependency on oxygen concentration, as illustrated in Figure 6-14(a). For STF40 sensor annealed at 450 °C, R_I increased with oxygen concentration, from $1.1 \times 10^6 \Omega$ at pure N_2 to $1.2 \times 10^8 \Omega$ at pure O_2 ambient. On the other hand, STF40 sensor annealed at 650 °C responded in the opposite direction, R_I decreased from $2.6 \times 10^6 \Omega$ at pure N_2 to $2 \times 10^4 \Omega$ at pure O_2 ambient. This observed variation direction in the R_I value was exactly the same as the observations for dc oxygen sensing characterization.

The relative conductivity value was obtained from fitted R_I value, and the pO_2 dependence of the conductivity is plotted in Figure 6-16. The dc sensing results from

Figure 6-8 were also inserted for comparison. The oxygen sensitivity factor ($1/m$) was estimated from the slope of the plots and listed in Table 6-2. It is observed that the values of $1/m$ for both STF40 sensors were very similar to the values obtained from dc oxygen sensing results. Therefore, R_I was assigned as the total resistance of the STF40 sensing material which is very sensitive to oxygen concentration.

Figure 6-16 pO_2 dependence of the ac conductivity and dc conductivity at operating temperature of 300 °C for STF40 sol-gel thin film sensors annealed at 450 and 650 °C.

Table 6-2 Oxygen sensitivity factor ($1/m$) value obtained from ac impedance spectroscopy and dc oxygen sensing characterization.

	Oxygen sensitivity factor ($1/m$)	
	dc measurement	ac measurement
STF40 Sensor Ann: 450 °C	-1/2.00	-1/2.28
STF40 Sensor Ann: 650 °C	+1/2.53	+1/2.21

c) Constant phase element (C and n)

Figure 6-14(b) shows the deviation of parameters C and n for both STF40 sensors under different oxygen concentrations. Some common capacitance values due to specific processes are summarized in Table 6-3 [172]. Our observed range of capacitance values suggested that the CPE corresponded to the capacitance effect caused by the grain boundaries and the space charge region at the surface of the grains [148, 173]. One can observe that the capacitance C for STF40 sensor annealed at 650 °C did not change significantly with oxygen concentration. However, capacitance C for STF40 sensor annealed at 450 °C dropped drastically when exposed to 1% of oxygen, and then gradually decreased at higher oxygen concentration.

Table 6-3 Typical capacitance values for some processes [172].

Process	Capacitance (F)
Bulk	10^{-12}
Minor, second phase	10^{-11}
Grain boundary	10^{-11} to 10^{-8}
Sample-electrode interface	10^{-7} to 10^{-5}
Electrochemical reactions	10^{-4}

This variation in the capacitance C could be explained using a schematic representation of electrical conduction path for both p- and n-type STF40 sensing materials, as shown in Figure 6-17. When the semiconductor materials were exposed to pure N_2 ambient, there was no chemisorption of oxygen gas and hence no electron depletion region or hole accumulation region was formed. In this case, the conduction path for both p- and n-type STF40 sensors were same and the capacitance effect was mainly contributed by the grain boundary. When the sensors were exposed to oxygen ambient and chemisorption of oxygen gas occurred, and electron depletion region (for n-type semiconductor) or hole accumulation region (for p-type semiconductor) was evolved. For p-type STF40 sensor, the electrical current mainly flows through the accumulation region, and the capacitance effect was still contributed by the grain boundary (C_{GB}). Hence, the value for C did not vary significantly. In contrast, current in n-type STF40 sensor flow through the grains, electron depletion region and grain boundaries. Hence, the capacitance effect was contributed by both the high resistive electron depletion region (C_d) and grain boundary (C_{GB}), which gave a smaller value of C . By using the model of a spherical capacitor of two concentric spheres with radii a and b ($b > a$), as shown in Figure 6-17, the capacitance value of the material can be estimated from equation (6-24):

$$C = \frac{4\pi\epsilon}{\left(\frac{1}{a} - \frac{1}{b}\right)} \quad (6-24)$$

Where $2b$ is the average grain size of the material, and $2a$ can be seen as the diameter of the grain bulk after chemisorption of oxygen (which is approximately equal to the grain diameter $2b$ minus two times of the depth of depletion region). The size $2a$ decreased with the formation of electron depletion region, which gave a lower capacitance C value at higher oxygen concentration.

Figure 6-17 Schematic representation of electrical conduction path under oxygen ambient for STF40 sol-gel thin film sensors annealed at 450 and 650 C for 1 hour.

6.3.2 Gas Sensing Mechanism Modeling

By combining all the physical explanations on the R_c , R_l , and CPE, the n-type and p-type STF40 semiconductor metal oxide gas sensor could be modeled using schematic representations illustrated in Figure 6-18. Our STF40 sol-gel thin film gas sensor could be modeled as a series combination of gold electrode and large amount of sensing material grains connected through grain boundaries. The gas insensitive resistor R_c corresponded to the contact resistance between electrode and sensing material, as discussed in the previous section. Oxygen as a powerful electron acceptor chemisorbed on the surface of the STF40 materials to form O⁻ adsorbates at operating temperature of 200 to 500 °C. The formation of the oxygen adsorbates built a space-charge region on the grains surfaces.

Figure 6-18 Schematic representation for STF40 sol-gel thin film sensors annealed at (a) 450 °C and (b) 650 °C for 1 hour.

For n-type STF40 sensor (electron as main charge carrier), the electron depletion region is highly resistive compared to grain region. Therefore, the current mainly flow through the depletion regions, grains, and the grain boundaries. The effective resistance $R_{I(n-type)}$ of the sensor is given as:

$$R_{I(n-type)} = R_{depletion} + R_{grain} + R_{grain\ boundary} \quad (6-25)$$

When the sensor is exposed to higher oxygen concentration, the depth of the space-charge layer is larger and $R_{depletion}$ increases. This increases the $R_{I(n-type)}$ and effectively an increment in the electrical resistance of the device will be observed.

For p-type STF40 sensor (hole as main charge carrier), space charge region serves as a hole accumulation region, which is less resistive compared to other resistance component. As a consequence, the current does not flow over the grain region, but mainly flows around the accumulation regions and grain boundaries. Hence, the total resistance $R_{I(p-type)}$ of the sensor is given as:

$$R_{I(p-type)} = R_{accumulation} + R_{grain\ boundary} \quad (6-26)$$

When the sensor is exposed to higher oxygen concentration, the depth of the accumulation region is larger and $R_{accumulation}$ decreases. This will effectively decrease the $R_{I(p-type)}$.

From here, one can see that if both n- and p-type STF40 sensors were operated under pure N_2 ambient, the resistance values (R_I) of both sensors were very close to each other ($1 \sim 2 \times 10^6 \Omega$), as shown in Figure 6-14. There was no space charge region formed under N_2 ambient and the electrical conduction path for both n- and p-type sensor were identical, i.e. flow through grains and grain boundaries. With the exposure to O_2 , even with concentration as low as 1%, space charge region was built up, and the $R_{I(n-type)}$ increased by one order ($10^7 \Omega$), while $R_{I(p-type)}$ decreased by one order ($10^5 \Omega$).

CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

The fabrication and investigation of semiconducting metal oxide gas sensor based on STFx materials have been reported in this thesis. Through gas sensing characterization and electrical property study, we have demonstrated the potential of using STFx material with ABO_3 structure for oxygen sensing applications. With the advantages such as great doping flexibility and ability to accommodate large amount of defects, perovskite oxides could serve as an alternative for binary oxides in gas sensing technology.

In the first part of the thesis, nanosized STFx sensing materials with iron content up to 40 % were successfully synthesized using high-energy ball milling technique. With milling at 200 rpm for 120 hours, the grain size of STF20 nanoparticles was decreased down to 10.5 nm resulted from the high-energy impacts during the collision. The synthesized STF20 was at a metastable state and full of surface defects. Quantitative XPS analysis demonstrated that the atomic percentage of lattice oxygen (O^{2-}) decreased as iron content increased. This reflected the formation of oxygen vacancies due to partial substitution of quadrivalent Ti ions (Ti^{4+}) with trivalent Fe ions (Fe^{3+}) without restoring electroneutrality in the cation site of the

perovskite structure. This inherent non-stoichiometry rendered STF_x materials highly sensitive to pO₂.

With optimized slurry preparation procedures, uniform and crack-free STF20 nanoparticles coating with thickness of around 1 μm were deposited using spin-coating method. The nanoparticles coating was next fabricated into miniaturized gas sensor with gold interdigitated microelectrodes using standard microfabrication techniques. Excellent oxygen sensitivity value of 2540 at 20 % oxygen was obtained for the synthesized STF20 nanoparticles based sensor annealed at 550 °C for 1 hour in air and operating at a temperature of 300 °C. In addition, the high-energy ball milled STF20 nanoparticles based sensors showed much better oxygen sensing response compared to high-temperature sintered STF20 sensor and post-milled high-temperature sintered STF20 sensor. This improvement was due to smaller grain size and higher surface defects of the high-energy ball milled STF20 nanoparticles.

In the second part of the thesis, STF_x thin films with different iron contents were successfully deposited using modified sol-gel spin-coating method. Instead of conventional sol-gel method which usually employs metal alkoxides, modified sol-gel process using metal salts such as nitrates and acetates was adopted in this project since the hydrolysis rate of the multi-components alkoxide is very difficult to be controlled. Factors such as selection of starting materials, molarity, choice of chelating agents and amount of deionized water were thoroughly studied in order to prepare stable sol-gel precursors with various iron contents. According to the XRD study, STF_x thin films with better crystallinity could be obtained at higher annealing temperature or lower iron content. Oxygen sensing results of STF_x thin film sensors showed an anomalous n- type gas sensing response when iron contents increased.

Additionally, the n-type sensing response was also observed for STF40 thin films when annealing temperature decreased. This change of sensing response type was observed for a large range of oxygen concentrations and also applicable to reducing gases such as carbon monoxide and ammonia.

The n-type sensing response of STF40 thin films has not been reported before and it is worth for in-depth study. In our case, the n-type sensing response was triggered by the low crystallinity of the thin films. We believed that the phase structure of the thin films resulted in this n-type response. TEM observation revealed that the STF40 thin film annealed at 450 °C was still in amorphous phase with poor crystallization while the film annealed at 650 °C shows polycrystalline structure. The surface chemistry of the thin films with different annealing temperatures was analytically investigated using XPS. XPS spectra showed that the formation of cubic perovskite structure started at annealing temperature of 450 °C and completed at 650 °C. No lattice oxygen (O^{2-}) was observed for the film annealed at 400 °C. The existence of amorphous TiO_2 in the thin film annealed at lower temperatures was evidenced by an extra doublet peaks in the $Ti2p$ spectra. Hence, we can conclude that the anomalous n-type sensing response of the STF x thin films was attributed to the amorphous O-Ti-O and O-Fe-O phases in the thin films with low crystallinity.

Next, the electrical transport property of the STF40 sol-gel thin film sensors was studied through the dependency of electrical resistance to pO_2 . For both n-type and p-type STF40 thin film sensors, smaller absolute value for oxygen sensitivity factor (m) was obtained indicating the improved oxygen sensing performance. A defect chemistry based on singly-charged oxygen vacancies was proposed to explain the improved oxygen sensitivity factor for the thin film sensors. This presence of singly-

charged oxygen vacancies was supported by the activation energy change (0.2 to 0.3 eV) estimated from Arrhenius plot of STF40 thin film. Finally, ac impedance spectroscopy was carried out and a graphical model was proposed to explain the electrical conduction path and gas sensing mechanisms of the sol-gel derived STF40 thin film sensors. Every component in the equivalent circuit model was explained based on the understanding of actual physical and chemical reactions occurred in the sensors.

7.2 Future Recommendations

This thesis works have demonstrated the fabrication and development of semiconducting metal oxide oxygen sensor based on nanosized STFx materials. Potentially, there are still several areas which can be considered for future research.

a) Extension of high Fe content in the synthesized high-energy ball milled STFx materials.

In this project, high-energy ball milled STF20BM nanoparticles based sensor has shown excellent oxygen sensing response. Theoretically, higher Fe substitution into STFx solid solution system can generate more oxygen vacancies. Hence, it will be very interesting to study the sensing performance and electrical transport property of STFx materials with higher iron contents. Preliminary experiment to extend the solid solubility Fe on high-energy ball milled STF80 was carried out where the milling speed was increased from 200 rpm to 230 rpm. Figure 7-1 shows the XRD patterns of STF80 nanoparticles with different milling parameters. One can observe that the α -Fe₂O₃ impurity phase vanished after milling speed was increased to 230 rpm.

Hence, it is worth to further improve the synthesis of STF_x nanoparticles with high iron contents and investigate the possibility in oxygen sensing applications.

Figure 7-1 XRD patterns for high-energy ball milled STF80 nanoparticles with different milling parameters.

b) Oxygen sensing characterization at higher temperature range for automobile applications.

Automobile oxygen sensors represent to most successful commercial chemical sensor owing to its important role in fuel combustion optimization and pollution control. Up to now, the oxygen sensor market is dominated by electrochemical ZrO₂-based sensors [80]. However, both potentiometric and amperometric electrochemical based sensors still possess their own limitations for optimum sensing performance.

Semiconducting metal oxide sensors appeared to be a possible alternative to ZrO₂-based sensors due to its advantages such as simple design and high sensitivity to pO₂.

Hence, it would be very valuable and meaningful to investigate the oxygen sensing performance of STFx sensors at higher operating temperature regime (700 to 900 °C) which could not be carried out using our current GSCS setup. Integration of a high temperature furnace into current GSCS was recommended for gas sensing test at higher temperature. The cooling system and the sample mount chamber must be carefully redesigned to accommodate operation at such high temperature range. In addition, the annealing temperature of the STFx sensors must also be higher than the desired operating temperature to ensure a stable sensing behavior.

c) Stability improvement for STFx materials

One of the important problems limiting the applicability of the perovskite-type materials containing significant amounts of alkaline-earth cations is their reactivity with some gases such as carbon dioxide [72]. For STFx materials, significant amount of strontium carbonate was detected from both XRD and XPS analysis as a result of the high reactivity of Sr element in the structure to carbon dioxide from the ambient. Presence of surface carbonate species reduces the surface area for the sensing material and resulted in degradation of sensing performance. This problem can be partially suppressed by the creation of moderate A-site deficiency [174]. Besides, formation of carbonate species may also be decreased by substituting strontium with other elements such as lanthanum (La).

d) Growth of one-dimensional STFx nanostructures

The stability of the gas sensing materials has been a challenging issue to address since the relatively high operating temperature of metal oxide sensors for surface

reactions to take place induces grain growth by coalescence, resulting in the drift of the sensor output [175]. More recently, the successful preparation of stable single crystal one-dimensional (1-D) and quasi 1-D semiconducting oxides nanostructures such as nanorods, nanowires, nanobelts, nanotubes, or nanoribbons) [176, 177] has inspired new approaches to improve the stability of metal oxide gas sensors. The 1-D nanostructures are very promising for gas sensors owing to their advantages such as single crystalline structure, high surface-to-volume ratio and nanosized for complete depletion of conduction carriers [178].

Gas sensors based on one-dimensional nanostructures with some common metal oxide such as SnO_2 , ZnO and TiO_2 have been prepared using various synthesis methods such as evaporation-condensation method, chemical vapor deposition, pulsed laser deposition, hydrothermal synthesis, thermal evaporation, and spray pyrolysis. However, syntheses of complex ternary oxide materials have only been emerging rapidly over the last 5 years [179]. There are numerous challenges associated with the synthesis of perovskite nanostructures such as well-controlled size, phase purity, crystallinity and chemical composition. Hence, the preparation of STFx nanostructures for gas sensing applications remains a topic of interest and worth for further research.

e) Work towards real life gas detection

In this project, nanosized semiconducting STFx oxygen sensors were successfully fabricated using standard microfabrication processes. This type of gas sensor possesses advantages of small size, portability, high sensitivity and low cost due to batch processing. Hence, it appears to be a potential candidate to replace current

dominating electrochemical-based oxygen sensors. However, there are still various aspects that need to be taken care of for developing the STFx oxygen sensors for real life applications.

First of all, repeatability and reliability test should be carried out with different batches of devices. The synthesis and deposition process must be further optimized in order to produce consistent and high quality gas sensors during large-scale manufacturing.

Next, a platinum (Pt) microheater is suggested to be integrated into our gas sensor to replace the external heating source. This can be achieved by depositing a patterned Ti/Pt thin film followed by an electrical insulating layer prior to the deposition of the gold electrodes and STFx sensing materials. In this case, only simple external data readout circuitry and power source are needed to carry out the real-life gas detection, making the sensor small size and portable. Moreover, the addition of Pt microheater requires lower power consumption compared to external heating source.

Finally, the oxygen sensors must be able to operate under open and harsh environment during real life gas detection. The influence of other unwanted factors such as temperature, humidity and other reactive gases should be minimal. Interaction with humidity or reactive gases may causes a change in the electrical resistance of the sensor and hence give a false signal. On the other hand, fluctuation in the ambient temperature may induce drift in the base resistance of the gas sensor. One of the possible solutions is to add surface additives or filter on top of our sensing materials to minimize interference to humidity and other reactive gases.

Besides, an additional temperature compensating material can be added to eliminate temperature interference.

Author's Publications

Journal Papers

- 1) C. L. Chow, P. Y. Tan, O. K. Tan, M. S. Tse, and Y. S. Phuan, "Oxygen sensing properties of strontium titanate ferrite composite films at low temperature," *Sensor Lett.*, vol. 9, pp. 343-347, 2011.
- 2) C. L. Chow, H. Huang, W. C. Ang, H. Liu, Y. Huang, M. S. Tse and O. K. Tan, "Effect of Annealing Temperature on the Crystallization and Oxygen Sensing Property of Strontium Titanate Ferrite Sol-Gel Thin Films," *Sensors and Actuators B: Chemical*, 2012 (In press).
- 3) C. L. Chow, W. C. Ang, M. S. Tse and O. K. Tan, "Oxygen sensing property of sol-gel derived $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ thin films with different iron concentrations ($x = 0.2$ to 0.8)," *Thin Solid Films*, 2012 (Minor revision).

International Conference

- 1) C. L. Chow, O. K. Tan and M. S. Tse, "N-P Transition Sensing Response of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ Sol-Gel Thin Films", 14th International Meeting on Chemical Sensors, Nuremberg, Germany, 20-23 May 2012. [Poster]
- 2) C. L. Chow, O. K. Tan and M. S. Tse, "Oxygen Sensing Response Transition of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ Sol-Gel Thin Films", 5th MRS-S Conference on Advanced Materials, Singapore, 20-22 March 2012. [Poster]

- 3) C. L. Chow, H. Huang, W. C. Ang, H. Liu, Y. Huang, M. S. Tse and O. K. Tan , "Oxygen Sensing Properties of Strontium Titanate Ferrite Thin Films Prepared by Modified Sol-Gel Spin Coating Method," 9th Asian Conference on Chemical Sensors, Taipei, Taiwan, 14-17 November, 2011. [Oral]
- 4) C. L. Chow, P. Y. Tan, O. K. Tan, M. S. Tse, and Y. S. Phuan, "Oxygen Sensing Properties of Strontium Titanate Ferrite Composite Films," 8th Asian Conference on Chemical Sensors, Daegu, Korea, 11-14 November, 2009. [Oral]

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