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**Nano-sized Strontium Titanate
Metal Oxide Semiconductor
Oxygen Gas Sensors**

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

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Summary

SUMMARY

The metal oxide semiconducting oxygen gas sensors have received the most attention because of their advantages of low cost, small size, simple structure, convenient integration and no reference electrode. However, the relative high operating temperature and lack of long-term stability have restricted their application in the medical, environmental and domestic fields. Reducing the grain sizes of the metal oxides semiconducting materials and synthesizing new materials are the available techniques to decrease the operating temperature. The metal oxide semiconducting materials in nano-sized range are surface conducting type (that is, grain surface control, when the actual grain size is smaller than two times the space-charge depth) and their carriers can move along the surface of the materials with minimum energy. Hence the nano-sized material can function well at low temperature.

The project focuses on strontium titanate (SrTiO_3) material, a very important material for oxygen sensors. The advantages of the material are low cost and stability in thermal and chemical atmospheres. However they have high operating temperatures ($> 700\text{ }^\circ\text{C}$) because they are mainly produced by the conventional high temperatures solid-state reaction method and it is very difficult to obtain nano-sized materials. Using the high-energy ball milling technique, a new form of nano-sized (27 nm) SrTiO_3 material with unique presence of the singly charged “O” ions in the lattice oxygen sites has been synthesized. The derived SrTiO_3 -based sensors were found to have better oxygen sensing properties and humidity-resistant property at $40\text{ }^\circ\text{C}$ (the lowest temperature ever reported for SrTiO_3 -based sensor). It has significantly extended the application areas of the conventional metal oxide semiconducting oxygen gas sensors ($> 300\text{ }^\circ\text{C}$) to the low temperature application areas such as in medical,

Summary

environmental and domestic fields etc. The special low temperature oxygen sensing mechanisms for the sensors have also been studied.

In the first part, nano-sized (27 nm) SrTiO_3 materials obtained from synthesized and commercial SrTiO_3 materials respectively using high-energy ball milling technique were used to fabricate thick film sensor devices. The gas sensing properties of the samples were characterized systematically. The synthesized nano-sized SrTiO_3 materials and sensors exhibit good thermal stability, oxygen sensing properties and independence of the relative humidity at near human-body temperature by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), and gas sensor characterization system.

For the second part of the thesis, the sensing mechanisms for the nano-sized SrTiO_3 materials were investigated systematically. The unique presence of the single-charged "O⁻" ions in the lattice sites (with the new forms of Form II: $\text{Sr}^{2+}\text{Ti}^{3+}\text{O}^{2-}_2\text{O}^-$ and Form III: $\text{Sr}^{2+}\text{Ti}^{3+}\text{O}^{2-}_2\text{O}^-$) confirmed by X-ray photoelectron spectroscopy (XPS) explains the better oxygen sensing properties for synthesized nano-sized SrTiO_3 materials. The different forms of the chemisorption oxygen for superoxide ion $\frac{1}{2}(\text{O}_{2\text{ ads}})^-$ below 40 °C and oxide ion O_{ads}^- above 40 °C, respectively, reveal the mechanism of 40 °C optimal operating temperature. A detailed defect chemistry analysis explains the transition from p-type to n-type for the nano-sized SrTiO_3 materials at 1 atm oxygen partial pressure (Po_2) and 40 °C operating temperature.

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CHAPTER ONE

INTRODUCTION

1.1 Motivation

Near room- and moderate-temperature oxygen sensor materials attract a lot of attention owing to their wide prospective applications in medical, environment and domestic fields [1-3], especially in life support: area monitoring, hospital oxygen, breathing gases, physiological testing, etc; and process control: chemical production, pharmaceuticals production, industrial gas production (O_2 , N_2 , H_2 ...), fruit storage, etc. In the market, the oxygen sensors available in this temperature range are the electrochemical cell [4], which have the shortcoming of high cost, periodic maintenance, and a liquid electrolyte.

The semiconductor metal oxide materials have always received the most attention with the advantages of low cost, small size, simple structure, and the ease of integration [5]. They do not require any reference electrode. However, they still pose the problems of relative high operating temperature and no long-term in stability. These not only limit their applications but also reduce their reliability. In order to enhance the sensitivity and decrease the operating temperature, decreasing the grain

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sizes of the materials is one possible way [6]. It has been well understood that when the grain size is small enough, the surface-to-bulk ratio of materials is much greater than that of coarse materials and a large fraction of the atoms are present at the surface. Hence, the surface properties become paramount. When the actual grain size D is less than two times the space-charge depth L , the depletion layer takes over the bulk. It becomes difficult to distinguish surface from bulk conduction and the whole grain is almost the surface conduction. The material resistivity is determined mainly by grain surface control (although there is also some grain-boundary component in the material) or surface conduction type (figure 1-1 [6]). The carriers in the material are surface diffusion and can operate at low temperature. On the other hand, for the coarse semiconductor metal oxide materials ($D \gg 2L$), the material resistivity is determined mainly by grain-boundary control or bulk conduction type (figure 1-1 [6]). The carriers in the material need enough energy to overcome the Schottky barriers, and hence must operate at high temperature ($> 700\text{ }^{\circ}\text{C}$). For the surface conduction semiconductors oxygen gas sensors (such as SnO_2 , ZnO , TiO_2 , CeO_2 , Nb_2O_5 , WO_3 , Ga_2O_3 , and $x\text{-Fe}_2\text{O}_3\text{-(1-x)ZrO}_2$ etc [5, 7]), the operating temperature is between 300 and 500 $^{\circ}\text{C}$.

Figure 1-1 Schematic models for grain-size effects [6]. D --the actual grain size, L --the space-charge depth.

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Strontium titanate (SrTiO_3) is a very important semiconductor metal oxide material for oxygen gas sensors. The low cost and the stability of the perovskite structure in thermal (up to 1200 °C) and chemical atmospheres [8] allow for possible adjustment of the electronic properties by dopants and maintenance of stable property as the grain size decreases to nano-scale. Up to now, most research work in SrTiO_3 focuses on bulk conduction type [8-22], or grain-boundary control, with high operating temperatures (700-1000 °C) [5]. In order to decrease the operating temperature of SrTiO_3 oxygen sensors, the nano-sized materials for the surface conduction type must be obtained. The high-energy ball milling or mechanical alloying has been proved to be a very effective route to prepare nano-sized solid solution for gas sensor application recently [23-26]. The thesis will therefore focus on strontium titanate material, using high-energy ball milling technique to obtain the nano-sized powders as the sensing materials, and thick film technology to fabricate the device. We will investigate their oxygen sensing properties and mechanism specifically at low operating temperatures.

1.2 Objectives

In this thesis, the main objectives are:

1. SrTiO_3 nano-sized powders are produced from both synthesized and commercial SrTiO_3 at room temperature using the high-energy ball milling technique. The microstructure and hydroxyl (OH^-) property of the materials are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM) and Fourier transform infrared (FTIR).
2. The conventional thick film technology is adopted to fabricate the sensor devices. The sensing properties at low temperature for the different SrTiO_3 sensors (nano-sized synthesized and commercial) in different ambient (annealing temperature,

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operating temperature, oxygen partial pressure and relative humidity) are characterized.

3. The sensing mechanisms for the different SrTiO₃ materials (nano-sized synthesized and commercial) in the different ambient (annealing temperature, operating temperature, oxygen partial pressure) are studied using DTA / TGA, XPS and ac impedance. The models are established and formulated to explain these sensing properties.

1.3 Major Contribution of the Thesis

The major contributions achieved in this research work are summarized as follows:

- 1 The new forms (Form II: Sr²⁺Ti³⁺O²⁻₂O⁻ and Form III: Sr²⁺Ti³⁺O²⁻₂O⁻) of nano-sized SrTiO₃ materials has been successfully synthesized for the first time using the high-energy ball milling technique [27]. The unique presence of the singly charged “O⁻” ions in the lattice oxygen sites of the nano-range crystal grain material has been observed using the X-ray photoelectron spectroscopy (XPS). The derived SrTiO₃ oxygen gas sensors were found to operate at 40 °C, the lowest temperature ever reported for SrTiO₃-based sensor. This is much lower than that of the conventional metal oxide semiconducting oxygen gas sensors (300-500 °C) [5, 28-30] and SrTiO₃ oxygen gas sensors (> 700 °C) [8]. This has significantly extended the application areas of the conventional metal oxide semiconducting oxygen gas sensors (> 300 °C) to the low temperature application areas such as in medical, environmental and domestic fields.
- 2 The synthesized nano-sized SrTiO₃ materials have exhibited excellent thermal stability and humidity-resistant property [31-32]. The particle sizes (27 nm), micro-structural and hydroxyl properties with different milled times and annealing

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temperatures of the material were characterized using XRD, TEM, DTA/TGA and FTIR. The thermal stability of the perovskite structure for the nano-sized SrTiO_3 material is confirmed across a wide temperature range up to 800 °C.

- 3 The synthesized nano-sized SrTiO_3 -based screen-printed oxygen sensors exhibit good oxygen sensing properties at low temperature [31-33]. The optimal relative resistance ($R_{\text{nitrogen}}/R_{20\% \text{ oxygen}}$) value of 6.35 is obtained at annealing temperature of 400 °C and operating temperature of 40 °C, which is comparable to the relative resistance of the conventional doped SrTiO_3 oxygen gas sensors at operating temperature above 700 °C [34-36], which is 3 times better than that of the nano-sized commercial SrTiO_3 sample in the same ambient. They show good repeatability with 1.6 minutes response time and 5 minutes recovery time. The detection range is 1-20 % oxygen. The oxygen sensing properties of the synthesized nano-sized SrTiO_3 -based sensors are found to be independent of the relative humidity. The sensors with annealing at 400 °C and operating at 40 °C exhibit no change in the impedance in 20% oxygen ambient with different relative humidity (RH) (dry, 20% RH, 80% RH, near 100% RH) from 1 mHz to 10 MHz. The effect of different annealing temperatures on the gas sensing properties of the synthesized SrTiO_3 sensor from nitrogen to 20% oxygen was characterized [37]. The sensing property of the synthesized nano-sized SrTiO_3 with annealing temperature of 400 °C is better than that of other annealing temperatures. The reason is that the material average grain size at 400 °C annealing temperature is the smallest in the annealing temperature range of 400-800 °C, and the thick-film devices must be annealed above 400 °C so that the organic constituents in the material paste can be evaporated.

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- 4 XPS characterization has been systematically carried out to investigate the different low-temperature oxygen sensing mechanisms for the nano-sized synthesized SrTiO₃ and commercial SrTiO₃ materials, respectively [27]. The unique presence of the single-charged “O[•]” ions in the lattice oxygen has rendered the nano-sized synthesized SrTiO₃ to exhibit better oxygen sensing properties than that of the nano-sized commercial SrTiO₃ at near human body temperature operation. The near ½ slope obtained in the logarithmic relationship plot of the electrical conductivity with respect to the oxygen partial pressure (Po₂) for the nano-sized synthesized SrTiO₃ is the highest value ever reported [8, 16, 38-39] for the Type II: $\frac{1}{2}\text{O}_2^{(g)} + \text{V}_{\text{O}}^{\bullet} \rightleftharpoons \text{O}_{\text{O}}^{\times} + \text{h}^{\bullet}$ sensing mechanism and ¼ slope achieved for the commercial nano-sized SrTiO₃ with Type I: $\frac{1}{2}\text{O}_2^{(g)} + \text{V}_{\text{O}}^{\bullet\bullet} \rightleftharpoons \text{O}_{\text{O}}^{\times} + 2\text{h}^{\bullet}$ mechanism. These experimental results have also been substantiated by XPS characterization. The XPS results of the synthesized nano-sized SrTiO₃ materials with the different annealing temperatures further provide the quantitative analysis of the mole ratio value of the single-charged “O[•]” ions in the lattice oxygen to the total oxygen in the materials that in terms affects and correlates with the low-temperature oxygen sensing property of the materials directly.
- 5 The anomalous positive slopes in the Arrhenius plots against temperature have been observed for the first time in the low-temperature oxygen ambient for the new forms of the synthesized nano-sized SrTiO₃ within the operating temperature 25-70 °C range [40]. The Arrhenius plots were obtained from the ac impedance spectroscopy characterization of the synthesized nano-sized SrTiO₃ material with different operating temperatures in 20% O₂ in background N₂. The two distinct positive slopes at the 40 °C boundary corresponding to two different activation energies in the Arrhenius plots are due to the different forms of the chemisorption

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oxygen, namely oxygen superoxide ion ($\frac{1}{2}(\text{O}_{2\text{ ads}})^{\cdot -}$) below 40 °C and oxide ion ($\text{O}_{\text{ads}}^{\cdot -}$) above 40 °C temperature regimes [40]. The 40 °C transition temperature matches the optimal operating temperature of the oxygen gas sensor. The detail thermodynamic analysis from the defect chemistry for the $\text{V}_{\text{O}}^{\cdot}$ defect in the p-type material further reveals the mechanism of the anomalous positive slopes in the Arrhenius plots for the synthesized nano-sized SrTiO_3 in oxygen ambient below 70 °C range.

- 6 An anomalous transition from p-type to n-type has been discovered for the first time for the nano-sized SrTiO_3 materials at 1 atm oxygen partial pressure (Po_2), 400 °C annealing temperature and 40 °C operating temperature. A detailed defect chemistry analysis was carried out to explain this anomaly. There are different low-temperature oxygen sensing mechanisms that occur in the ranges of Po_2 0.03-1 atm and 1-5 atm for the synthesized nano-sized SrTiO_3 material, respectively. The p-type mechanisms in the 0.03-1 atm range with the slope gradient of near 1/2 in the logarithmic relationship of the electrical conductivity (σ) with Po_2 for the synthesized nano-sized SrTiO_3 material is mainly due to the presence of the single-charged " $\text{O}^{\cdot -}$ " ions in the lattice oxygen. In the range of Po_2 1-5 atm, the synthesized nano-sized SrTiO_3 material has an n-type mechanism with a near -1/4 slope gradient in the logarithmic relationship of σ with Po_2 due to the different oxygen sensing mechanism.
- 7 A total of 5 papers have been published/in press in the international journals, 5 papers have been presented in international conferences, and a chapter of a book "Encyclopedia of Sensors" has been in press.

Chapter 1 Introduction

1.4 Organization of the Thesis

This thesis emphasizes on the new forms of the nano-sized SrTiO_3 (27 nm) material with the singly charged “O⁻” ions in the lattice oxygen sites for the special oxygen sensing application areas at the near human-body temperature. It is organized into six chapters.

In chapter 1, the motivation, objectives, main contributions, and organization of the report are presented.

Chapter 2 presents the background theory on semiconducting metal oxide sensors, including oxygen gas sensors and SrTiO_3 oxygen gas sensors, the preparation and analysis of nano-sized powders, and the current status and problems of semiconductor gas sensors. The aim of this chapter is to provide the foundation and basis for the work on nano-structured metal oxide semiconductor gas sensors.

In chapter 3, the experimental procedures used in this research work are presented. The preparation of the nano-sized powder using high energy ball milling technique, the fabrication of the thick film gas sensors, the characterization of the physical microstructure and the hydroxyl (OH⁻) property of the powders, the characterization of sensing properties, and the annealing temperature and humidity effects of thick film gas sensors, XPS property and the ac and dc electrical conduction of the material discs are described in detail.

Chapter 4 details the synthesized and commercial nano-sized SrTiO_3 oxygen gas sensors. The mechanical synthesis, the thermal stability and the hydroxyl (OH⁻) property of the nano-sized SrTiO_3 powders are presented first. The effect of the annealing temperature and humidity on the sensing properties of the sensors are

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investigated. The optimal material, annealing temperature, operating temperature and oxygen partial pressure for the oxygen sensing properties are obtained.

In Chapter 5, the oxygen sensing mechanisms for the different materials with different operating temperatures and oxygen partial pressures are analyzed using XPS, dc I-V, ac impedance spectroscopy and the defect chemistry.

Finally, the conclusions and recommendation for the SrTiO_3 oxygen gas sensors are listed in chapter 6.

CHAPTER TWO

BACKGROUND ON SEMICONDUCTING OXIDE GAS SENSORS

In this chapter, an introduction is given to semiconducting metal oxide gas sensors. The general principles of semiconducting metal oxide gas sensors, in particular, oxygen sensors and the basic oxygen sensing mechanism of SrTiO_3 oxygen gas sensors with high operating temperature are presented. With the emerging research on the advantageous gas sensing application of nano-crystalline powders and gas-sensing materials, the preparation and analysis of nano-sized powders are also discussed in this chapter. These serve to provide the background for the work on the nano-structured synthesized and commercial SrTiO_3 thick film gas sensors.

2.1 Semiconducting Metal Oxide Sensors and Sensing Mechanisms

Oxide ceramics exhibit a number of special characteristics that make them particularly attractive for sensor applications. These include marked sensitivity to oxidizing and reducing gases or to temperature excursions. Additionally, high ionic

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conductivities render some oxides unique choices in electrochemical-based sensors [41].

Each type of sensor must satisfy certain criteria. Semiconducting gas sensors, while responding readily to modulations in gas composition, should be insensitive to temperature. Thermistors, on the other hand, rely on their sensitivity to temperature excursions but must do so while exhibiting little or no sensitivity to the ambient atmosphere. Sensors operating on electrochemical principles cannot tolerate electronic conduction but must exhibit exceptionally high ionic conduction and is often insufficient to predict sensor response because of only bulk electrical characteristics. At present, two basic approaches for detecting the composition of gases with electrical ceramics exist. The first relies on the atmospheric dependence of electrical conductivity exhibited by some ceramic semiconductors. The second utilizes ionic conductors as solid electrolyte membranes in electrochemical concentration cells. The following sections will introduce the principal characteristics of semiconducting gas sensors.

The basis for semiconducting gas sensors 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 conductivity is found to follow a power law dependence on the partial pressure of the relevant gas.

In 1962, it was understood that the electrical properties of some semiconducting metal oxides were sensitive to the gas composition of a surrounding atmosphere, especially at elevated temperatures. By utilizing this phenomenon, thin-film ZnO [42]

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and porous SnO_2 [43] ceramics were first demonstrated as gas-sensing devices that year. Later, the addition of small amounts of noble metals (such as Pt and Pd) to these oxides was found to be effective in improving their sensing properties [44]. After these first demonstrations, major efforts allowed semiconductor gas sensors based on the variation in the resistance (or conductance) of semiconducting metal oxides to reach the market as leakage monitors for town gas and liquefied petroleum gas (LPG) in 1968 [45].

In addition, subsequent research and development to expand the practical applications of semiconductor gas sensors, and extensive studies have been directed to the fundamental understanding of their sensing properties. Some of the key factors are found to affect the sensing properties of these materials, such as the effects of grain size and the geometry of grain connection, the promoting of noble metals, and the effects of sensor configuration, etc. [46-50].

2.1.1 Basic Gas Sensing Mechanisms

Semiconductor sensors detect gases via variations in their resistances (or conductances). The most widely accepted explanation for this is that negatively charged oxygen adsorbates play an important role in detecting reducing gases such as H_2 and CO . Actually, several kinds of oxygen adsorbate species, such as O_2^- , O^- , and O^{2-} , are known to cover the surface of semiconductive metal oxides in air [51]. Of these, O^- is the most reactive with reducing gases in the temperature range of 300-500 $^\circ\text{C}$, in which most semiconductor gas sensors are operated, and eventually the variation in surface coverage of O^- dominates the sensor resistance. In the case of n-type semiconductive metal oxides, the formation of these oxygen adsorbates builds a

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spaces-charge region on the surfaces of the metal-oxide grains, resulting in an electron transfer from the grain surfaces to the adsorbates as follows:

The depth of this space-charge layer (L) is a function of the surface coverage of oxygen adsorbates and intrinsic electron concentration in the bulk. The resistance of an n-type semiconductor gas sensor in air is therefore high, due to the development of a potential barrier to electronic conduction at each grain boundary, as shown in figure 2-1 [52]. When the sensor is exposed to an atmosphere containing reducing gases at elevated temperatures, the oxygen adsorbates are consumed by the subsequent reactions, so that a lower steady-state surface coverage of the adsorbates is established. During this process, the electrons trapped by the oxygen adsorbates are returned to the oxide grains, leading to a decrease in the potential barrier height and a drop in resistance. This resistance change is used as the measurement parameter of a semiconductor gas sensor, with relative resistance (S) defined as the ratio of the resistance in air to that in a sample gas containing a reducing component. The reactivity of the oxygen adsorbates is, of course, a function of both the type of reducing gas present and the sensor operating temperature. Therefore, the temperature T_M at which the maximum relative resistance S_M is observed is dependent upon the particular reducing gas present. 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.

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Figure 2-1 Model for adsorbate-dominated n-type semiconducting powder in gas sensing: (a) Physical Model: three contacting powder grains are shown to illustrate how depletion region dominates the inter-granular contact and (b) Band Model: corresponding to (a) indicating the Schottky barrier at the inter-granular contact [52].

Occasionally, the reducing gases interact directly with the sensor materials; for example, hydrogen is chemisorbed negatively on SnO_2 under certain conditions [53-54]. Such phenomena are usually observed at lower temperatures, at which the

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reaction with the oxygen adsorbates, the electrical interactions with intermediate products of the reducing gases lead to more complicated sensor responses [55-56].

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

Since the charge carriers in p-type semiconducting metal oxides are positive holes, the resistance in air is low because of the formation of negatively charged oxygen adsorbates, and the extraction of electrons from the bulk eventually enhances the concentration of holes in the grain surface. The consumption of oxygen adsorbates by reaction with reducing gases leads to an increase in resistance, which is the reverse for the case of n-type metal oxides. Conversely, the adsorption of oxidizing gases on p-type metal oxides results in a decrease in the resistance.

In general, the measurement of a higher resistance in the presence of a sample gas than that in air is accompanied by some problems associated with signal handling (the higher the resistance, the worse the signal-to-noise ratio), which is why n-type semiconducting metal oxides are usually employed as sensor materials for reducing gas detection due to their lower resistance in reducing gas.

2.1.2 Semiconductor Oxygen Sensors and Sensing Mechanisms

Nowadays, the most widely used gas sensor versions are oxygen sensors, most of which directly indicate the presence, concentration, and quantity of oxygen in their environment. All of which are currently used in numerous fields, including

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environmental control, modified atmospheres (e.g. greenhouses, gas industries, respiratory gases), safety in industrial environments, emission control and combustion optimization [57-60]. No single material or method can be employed over such a wide variety of oxygen sensing environments, which range from the interior of living tissues to liquid steel melts. Hence the role of oxygen and the measurement of its concentration have always been the research focus worldwide. There is also an increasing demand for small-scale solid-state sensors, allowing rapid, easy, precise and cheap measurement under a wide range of conditions [61].

The semiconducting metal oxide oxygen gas sensors have always received the most attention with the advantages of low cost, small size, simple structure, and ease of integration with no reference electrode compared to concentration and electrochemical pumping types of oxygen sensors [4]. Semiconductor oxygen gas sensors fall into two types: one is based on bulk conducting semiconductors and another is based on surface conducting semiconductors [5].

Oxygen sensors based on bulk conducting semiconductors work at high temperatures (700-1100 °C); they are a non-stoichiometric oxide and their resistivities strongly depend on the air-to-fuel (A/F) ratio. The interstitial defects are decided by the space available and the electrostatic environment in the materials [62, 63]. Anion interstitial O_i can be dismissed due to the high enthalpy reaction for big radial oxygen anion in closed-packed structure. Hence, oxygen defect in closed-packed structure easily forms oxygen vacancies rather than interstitial O_i [62, 63].

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

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grains. The basic reactions between a regular oxygen site (Oo^x), oxygen molecules in the gas phase ($\text{O}_2^{(g)}$), and the oxygen vacancy with twofold-ionized positively (Vo'') in the bulk, can be expressed in the formalism of Kröger and Vink [64] as follows:

The well-known relation between the electrical conductivity (σ) and the oxygen partial pressure (P_{O_2}) can be obtained:

$$\sigma = A \exp(-E_a/KT) \text{P}_{\text{O}_2}^{1/m} \quad (2.3)$$

Here, E_a is the activation energy which represents the sensitivity of the electrical conductivity to temperature changes. The absolute values of $1/m$ depend 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; for the p-type conduction, the value of $1/m$ is positive, and for the n-type conduction it is negative. $|1/m|$ represents the sensitivity of σ to change in the oxygen partial pressure. Therefore, it is very important to select oxygen sensitive materials with small E_a and large $|1/m|$ to obtain oxygen sensors with good sensitivity to changes in the oxygen pressure. Normally, oxygen sensors based on bulk conducting semiconductors are TiO_2 , Nb_2O_5 , $(\text{TiO}_2)_x(\text{NbO}_{2.5})_{1-x}$, CeO_2 , Ga_2O_3 , SrTiO_3 , LaNiO_3 and ZnO [5, 65-78].

The other type of oxygen sensors based on surface conducting semiconductors mainly operates at low and medium temperatures (about 300-500 °C). Some surface conduction materials are SnO_2 , ZnO , TiO_2 , CeO_2 , Nb_2O_5 , WO_3 , Ga_2O_3 and $x\alpha\text{-Fe}_2\text{O}_3-(1-x)\text{ZrO}_2$ [28, 79-81].

The basic oxygen sensing mechanism of oxygen sensors based on semiconducting oxide [5] is their strong dependencies of electrical conductivity on oxygen partial

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pressures. At low and medium temperatures (about 300-500 °C), for the surface conduction mechanism of semiconducting oxide sensors, chemisorption of oxygen at the surface of the oxide grains and at the grain boundaries lead to the formations of surface oxygen ions and Schottky barriers between the grains. The density of surface oxygen ions and the height and width of the Schottky barriers depend on the oxygen partial pressure in the surrounding atmosphere.

The oxygen gas sensors working at low temperature have the advantage of good properties such as: avoiding instabilities that occur during cooling and heating; the long-term stability and energy saving during operating period [82]. Hence, selecting good surface conducting semiconductor material is the key to good low temperature oxygen gas sensors.

In the various semiconducting materials, the perovskite oxides (ABO_3) has attracted much attention because of their low cost and high stability in thermal and chemical atmospheres. Out of which, strontium titanate (SrTiO_3) shows unique electronic and structure properties [34, 83] that are presented in the following section.

2.1.3 SrTiO_3 Oxygen Gas Sensors and Sensitive Mechanisms

2.1.3.1 Current Status of the SrTiO_3

Strontium titanate (SrTiO_3) is an important ternary oxide, which has a cubic perovskite structure with a lattice parameter of 0.3905 nm at 27 °C. It has been extensively studied because of its electronic properties and structure. The important electronic properties include ferroelectricity [84-86], semiconductivity and superconductivity. The SrTiO_3 perovskite structure is shown in figure 2-2. The strontium ions are located at the corners of the unit cell. SrTiO_3 is light colored,

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insulating material at room temperature in air. By analogy with BaTiO_3 , one would expect SrTiO_3 to be an oxygen-excess composition with p-type conduction, since n-type material is normally dark colored and semiconducting.

Figure 2-2 Perovskite structure of SrTiO_3 [41]. (a) Perovskite crystal unit cell; (b) Ion positions in perovskite structure.

The theoretical examination of the electronic energy bands of strontium titanate has been carried out by Kahn and Leyendecker [87]. Their calculations indicate filled valence bands derived primarily from the oxygen 2p orbitals and empty conduction bands derived predominantly from the titanium 3d orbitals. From the optical transmission studies on single-crystal SrTiO_3 which was heated in vacuum, H.W. Gandy [88] determined an energy gap of 3.15 eV. The conductivity and the Hall and Seebeck coefficients of the reduced and doped strontium titanate have been measured

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over the temperature range 4.2-300 K by Frederikse et al. [89], who found a band-type conduction process with an electron effective mass much greater than the free-electron mass and low-temperature mobility greater than $1000 \text{ cm}^2/\text{V}\cdot\text{sec}$.

SrTiO_3 is a promising material for resistive high temperature ($T > 700^\circ\text{C}$) oxygen sensors [9, 34-36]. All of the reported studies on SrTiO_3 indicate that for both the polycrystalline and single-crystal state SrTiO_3 , in the P_{O_2} range near 1 atm, when the oxygen partial pressure changes from low to high, there is a transition from n-type conduction at low P_{O_2} to p-type conduction at high P_{O_2} in SrTiO_3 [38]. The ternary metal oxide for SrTiO_3 is able to tolerate large levels of dopants without phase transformations [17, 90], and the perovskite crystal structure is stable in a large temperature range ($T < 1200^\circ\text{C}$). This enables adjustment of the electronic properties by doping the parent structure oxide with alternative metal ions rendering some interesting combinations of sensor properties.

Since 1980's, there are four directions in the SrTiO_3 research areas:

1. Selecting different donor doped SrTiO_3 to expand the n-type ranges to higher oxygen partial pressures and achieve a fast oxygen sensor (10^{-15} - 10^4 Pa) (n-type ranges) (figure 2-3) [8-12, 91].
2. Selecting different donor or acceptor doped SrTiO_3 to achieve temperature independent oxygen sensors over a certain range of oxygen partial pressures, and shift the zero-TCR (temperature coefficient of resistance) point (to higher or lower oxygen partial pressures), and extend the zero-TCR region [12-16, 92]. Up to now, a family of the temperature independent semiconducting oxides including $\text{Co}_{1-x}\text{Mg}_x\text{O}$, $\text{SrMg}_{0.4}\text{Ti}_{0.6}\text{O}_3$, $\text{BaFe}_{0.8}\text{Ta}_{0.2}\text{O}_3$ and

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- $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_3$ (about 10 ms response time) etc. have been studied [14-15, 93].
- Investigating the high temperature behaviour of undoped and acceptor doped SrTiO_3 materials and studying the bulk behaviour in the p-type ranges [17, 21, 93-100].
 - Investigating the electrical behaviour and humidity effects for the SrTiO_3 -based materials [21, 22, 101-103].

Figure 2-3 Characteristic curves, $\sigma \propto P_{\text{O}_2}^{1/m}$, of donor doped ($1/m = -1/4$) and acceptor doped ($1/m = \mp 1/4$) strontium titanate. Doping content 0.5 at.%. For $\text{Sr}_{0.995}\text{La}_{0.005}\text{TiO}_3$ (donor doped) and for $\text{SrTi}_{0.995}\text{Fe}_{0.005}\text{O}_3$ (acceptor doped) [8].

The theory of the sensing mechanism for the SrTiO_3 -based sensors above 700 °C operating temperature has been well-established [8, 16, 22, 38, 39, 101]. The

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electrical conductivity (σ) dependence of Po_2 for the SrTiO_3 -based sensors obeys equation (2.3) for the normal metal oxide semiconducting oxygen gas sensors [5].

The defect chemistry of strontium titanate has been treated in detail in the literature [8, 39]. In this section, the most important defect reactions as shown in the formalism of Kröger and Vink [64] are discussed. Except for the definition made earlier in section 2.1.2, the following notations and their representation are: $\text{Sr}_{\text{Sr}}^{\times}$: the regular strontium site; V_{Sr}'' : the strontium vacancy with twofold-ionized negatively; $[\text{A}']$: the negatively charged acceptor concentration, $[\text{D}']$: positively charged donor concentration; $p \equiv [\text{h}']$; $n \equiv [\text{e}']$; “[]” denotes the concentration of the defects.

(I) The formation of oxygen vacancies that is thermally activated by the reduction enthalpy ΔH_{Red} is described by:

(II) The generation / recombination of electronic defects over the band-gap E_g is:

$$n\text{il} = \text{e}' + \text{h}' \quad (2.4)$$

(III) The formation of doubly negative charged strontium vacancies (metal vacancy) V_{Sr}'' in the cation sublattice, is described by the Schottky reaction with the Schottky energy E_s :

(IV) The charge balance of the different charged defect concentrations is governed by:

$$n + 2[\text{V}_{\text{Sr}}''] + [\text{A}'] = p + 2[\text{Vo}'] + [\text{D}'] \quad (2.6)$$

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Depending on the oxygen partial pressure and the amount of dopant, the charge balance equation (2.6) can be simplified. In the case of donor doping and a characteristic value for $m = -1/4$ (figure 2-3), equation (2.6) simplifies to

$$2[V_{Sr}'] \approx [D'] \quad (2.7)$$

That is the positively doping charge is compensated mainly by the negatively charged strontium vacancies. Applying the mass-action law to equations (2.2) and (2.5) obtains the equations (2.8) and (2.9),

$$[V_{O}']n^2Po_2^{1/2} = K_{Red}(T) = K_{Red}^\circ \exp(-\Delta H_{Red}/(kT)) \quad (2.8)$$

$$[V_{Sr}'] [V_{O}'] = K_s(T) = K_s^\circ \exp(-E_s/kT) \quad (2.9)$$

where $K_{Red}(T)$, $K_s(T)$ the equilibrium constants for the reactions at the temperature T respectively. Combining with equations (2.7) to (2.9), we get,

$$n = (1/2 [D'] (K_{Red}^\circ / K_s^\circ))^{1/2} \exp(-(\Delta H_{Red} - E_s)/2)/(kT)) Po_2^{-1/4} \quad (2.10)$$

Comparing to equation (2.3), the activation energy for electrical conduction is given by:

$$E_a = (\Delta H_{Red} - E_s) / 2 \quad (2.11)$$

that has a very high temperature dependence. For lanthanum doped strontium titanate [8, 39] with ΔH_{Red} : 6.1 eV and E_s : 2.5 eV, E_a is around 1.8 eV.

In the case of acceptor doping and for high oxygen partial pressure, $m = +1/4$ (figure 2-3), equation (2.6) is simplified to

$$[A'] \approx 2[V_{O}'] \quad (2.12)$$

Here, the negatively doping charge is compensated mainly by positively charged oxygen vacancies. Similarly, applying the mass-action law to equations (2.4), we get,

$$np = K_i(T) = K_i^\circ \exp(-E_g/(kT)) \quad (2.13)$$

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where $K_i(T)$ represents the equilibrium constants for the reactions at the temperature T . Combining with equations (2.8), (2.12) and (2.13), we get,

$$p = (1/2 [A'] K_i^{\circ 2} / K_{\text{Red}}^{\circ})^{1/2} \text{Po}_2^{1/4} \exp(-((2E_g - \Delta H_{\text{Red}}) / 2) / (kT)) \quad (2.14)$$

Combining to equation (2.3), the activation energy for electrical conduction is given by:

$$E_a = (2E_g - \Delta H_{\text{Red}}) / 2 \quad (2.15)$$

The band-gap of undoped strontium titanate is 3.2 eV, decreasing with an increasing iron content to 2.1 eV [17]. Consequently, it is possible to adjust E_a to near zero by an appropriate iron acceptor content.

2.1.3.2 Problems Faced in SrTiO₃ Research

Most research work focuses on bulk conduction type in SrTiO₃ with high operating temperatures (700-1000 °C) [5, 8-22]. The sensing material is produced by the conventional high temperature solid-state reaction method because of its high melting point (2080 °C) [16, 34-35, 39, 101, 104]. This method has several problems [98] relating to grain growth, change in stoichiometry, and ease of second phase formation [105, 106]. Hence nano-sized SrTiO₃ is difficult to be produced by this method. For SrTiO₃ oxygen sensors that operate at low temperatures, the surface conduction type in SrTiO₃ must be obtained. Hence, the key factor is in synthesizing nano-sized material for good low-temperature oxygen gas sensors.

2.2 Nano-sized Materials: Preparation and Analysis

In materials science, the emphasis is currently being given to work on structures at the nanometer scale in order to study the unique physical properties that can be derived from the size reduction to these dimensions [107]. In nano-sized materials,

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because the surface-to-bulk ratio is much greater than that for coarse materials, surface properties become paramount. Another important effect, in relation to the particle size, is associated with the depth of the surface space charge region affected by gas adsorption. When the particle size gets into the nano-range, the depletion layer takes over the bulk, and it becomes difficult to distinguish surface from bulk conduction. These characteristics of nano-sized particle make the materials particularly appealing in applications of gas sensors [6]. Thus the use of nano-structured materials (both in powder and thin-film) in gas sensors is arousing interest rapidly in the scientific community [6, 23-24, 90, 108-121].

2.2.1 Preparation of Nano-sized Materials

Nano-sized powders have been prepared using various methods, including: (a) Chemical co-precipitation [122]; (b) Sol-gel process [123]; (c) Metalorganic deposition (MOD) [124]; (d) Plasma enhanced chemical vapor deposition (PECVD) [125]; (e) Atmospheric-pressure chemical vapor deposition (APCVD) [126]; (f) Physical vapor deposition (PVD) [127, 128]; (g) Low-pressure flame deposition (LPFD) [109]; (h) Laser ablation [129]; and (i) High-energy ball milling or mechanical alloying [23-26, 37, 40, 110, 128-134].

Methods (a) through (e) are basically chemical processing techniques aiming to obtain homogeneous structure on an extremely fine scale of a few nanometers at the molecular level. The others are physical processing techniques. Most of SrTiO_3 sensing materials are produced by the conventional high temperatures solid-state reactions method [8, 16, 34-35, 101, 104]. Even for SrTiO_3 thin films fabricated with methods such as CSD (chemical solution deposition) [42], sol-gel process [41, 135]

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and sputtering technique [136, 137], they all undergo a high temperature (1100 °C) process to form ceramic devices. Hence nano-sized SrTiO_3 is difficult to be produced by these methods. The high-energy ball milling or mechanical alloying has proved to be a very effective route to prepare nano-sized solid solution for gas sensor application [23-27, 33, 120, 138, 139]. Specifically, W. Cao, and O. K. Tan used high-energy ball milling technique and thick-film screen-printing technique to obtain ZrO_2 based oxygen gas sensor at low operating temperature of 320 °C [110]. The high-energy ball milling has the advantages of high product yield, simple technology, low cost, mass production, and can achieve high melting metal or alloy. The thick-film screen-printing technique has the advantage of low cost, high reliability, good heat dissipation, and a wide range of component values. The combination of these two technologies enables the advantage of high product yield, high reliability, simple technology, low cost, and mass production.

In our work, nano-sized SrTiO_3 powders made from synthesized and commercial SrTiO_3 with grain size of down to 27 nm were successfully prepared using this technique.

2.2.2 The Mechanical Alloying Process

Mechanical alloying, the innovation of Benjamin [140] thirty years ago, has changed the traditional method in which production of materials is carried out by high temperature synthesis. It is a ball milling process where a powder mixture placed in the ball mill is subjected to high-energy collision from the balls. It has attracted much attention and inspired numerous research interests because of its promising results, wide possible applications and potential scientific values. Mechanical alloying has

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now been recognized as a unique technique. It has been utilized in different areas of material processing and applied to many different material systems such as the preparation of nano-structured pure elements, metallic alloys, intermetallic compounds, and ceramic compounds. The achievement is not possible by means of traditional techniques.

The alloying process can be carried out using different apparatus, namely, attritor, planetary mill or a horizontal ball mill. However, the principles of operation are the same to all the techniques. Since the powders are cold welded and fractured during mechanical alloying, it is critical to establish a balance between the two processes in order to alloy successfully. Planetary ball mill is a very often used system for mechanical alloying. Only a very small amount of powder is required, hence the system is suitable for research purposes in the laboratory. The ball mill system consists of one turn disc (turn table) and two or four bowls. The turn disc rotates in one direction while the bowls rotate in the opposite direction. The centrifugal forces, created by the rotation of the bowl around its own axis together with the rotation of the turn disc, are applied to the powder mixture and milling balls in the bowl. The powder mixture is fractured and cold welded under high-energy impact.

Figure 2-4 shows the motions of the balls and the powder. Since the directions of rotation of the bowl and turn disc are opposing, the centrifugal forces are alternately synchronized. Thus friction resulted from the hard milling balls and the powder mixture being ground alternately rolling on the inner wall of the bowl and striking the opposite wall. The impact energy of the milling balls in the normal direction attains a value of up to 40 times higher than that due to gravitational acceleration. The powder

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particles are subjected to high energetic impact. Microstructurally, the mechanical alloying process can be divided into four stages: (a) initial stage, (b) intermediate stage, (c) final stage, and (d) completion stage [140].

Figure 2-4 Schematic view of motion of the ball and powder mixture [140].

At the initial stage of ball milling, the powder particles are flattened by the compressive forces due to the collision of the balls. Micro-forging leads to changes in the shapes of individual particles, or cluster of particles being impacted repeatedly by the milling balls with high kinetic energy. However, such deformation of the powders shows no net change in mass.

At the intermediate stage of the mechanical alloying process, significant changes occur in comparison with those in the initial stage. Cold welding is now significant.

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The intimate mixture of the powder constituents decreases the diffusion distance to the micrometer range. Fracturing and cold welding are the dominant milling processes at this stage. Although some dissolution may take place, the chemical composition of the alloyed powder is still not homogeneous.

At the final stage of the mechanical alloying process, considerable refinement and reduction in particle size is evident. The microstructure of the particle also appears to be more homogenous in microscopic scale than those at the initial and intermediate stages. True alloys may have already been formed.

At the completion stage of the mechanical alloying process, the powder particles possess an extremely deformed metastable structure. At this stage, the lamellae are no longer resolvable by optical microscopy. Further mechanical alloying beyond this stage cannot physically improve the dispersoid distribution. Real alloy with composition similar to the starting constituents is thus formed.

In our research, planetary ball milling has been used to prepare nano-sized non-equilibrium powder. For a gas sensor material, the number of available reactive sites per unit volume of a solid depends on the specific surface area of the sample. This property influences the reactivity of the oxide. In addition, both surface area and porosity are crucial factors in determining the activity of oxide catalysts.

2.2.3 Characterization of Nano-sized Materials

Various methods can be employed to identify and characterize nano-sized powders. These methods involve diffractometry, spectroscopy, thermal analysis, microscopy, and electrical measurements [141, 142].

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The basic and effective methods are in the field of diffractometry and involve interaction of X-rays (X-ray diffraction, XRD), electrons (electron diffraction, ED) or neutrons (neutron diffraction) with the atoms of a solid. Among these methods, X-ray diffraction is the most widely used, it was selected to analysis the structure of our materials.

The second group of methods is the spectroscopic methods. They produce spectra that are caused by the interaction of electromagnetic radiation with the materials. The type of interaction (electronic or nuclear transition, molecular vibration or electron loss) depends on the wavelength of the radiation. The most widely applied techniques are infrared (IR), X-ray photoelectron (XPS), Mössbauer, and ultraviolet-visible (UV-Vis) spectroscopy. Fourier-transform-infrared-spectroscopy (FTIR) measurements represent a very important tool for characterizing gas sensing materials because they provide information on both the electronic properties of the powders and the surface species formed in the presence of various testing gases [117]. Less widely used techniques at present are Raman, secondary ion imaging mass spectroscopy (SIMS), Auger electron spectroscopy, electron spin resonance (ESR), nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS).

X-ray Photoelectron Spectroscopy (XPS) was developed in mid-1960s by Kai Siegbahn and his research group at the University of Uppsala, Sweden. Surface analysis by XPS involves irradiating a solid in vacuum with monoenergetic soft x-rays and analyzing the emitted electrons by energy [143]. The spectrum is obtained as a plot of the number of detected electrons per energy interval versus their kinetic energy. Each element has a unique spectrum. The spectrum from a mixture of

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elements is approximately the sum of the peaks of the individual constituents. Because the mean free path of electrons in solids is very small, the detected electrons originate from only the top few atomic layers, making XPS a unique surface-sensitive technique for chemical analysis. Quantitative data can be obtained from peak heights or peak areas, and identification of chemical states often can be made from exact measurement of peak positions and separations, as well as from certain spectral features [143]. It was selected to analysis the valence shift of the elements in our materials. FTIR was analysis the surface species formed in air.

A third group of techniques concerns methods of thermal analysis, i.e. the specific reactions of a solid upon application of heat. The most common of these techniques are differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) together with differential scanning calorimetry (DSC).

DTA measures the temperature difference between a sample and a thermally inert reference as the temperature is raised. The plot of this differential provides information on exothermic and endothermic reactions taking place in the sample. Temperatures for phase transitions, melting points, crystallization can all be determined using the computer controlled graphics package. TGA measures changes in weight of a sample with increasing temperature. Moisture content and volatile species presence can be determined with this technique. The computer controlled graphics is used to calculate the weight percent losses. DTA/TGA were performed the thermal analysis for our materials.

Microscopy is a common way to observe the microstructure of nano-sized powders, such as transmission electron microscopy (TEM) and atomic force microscopy

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(AFM). In addition to all these methods, electrical characterizations including dc or impedance, thermally stimulated current (TSC) are essential to analyze and understand the sensing mechanism of nano-sized materials. TEM served as the observing tool for the microstructure of our materials.

All the above techniques provide information on the structure, electronic characteristics or extent of metal substitution and, in many cases, have been used to monitor chemical reactions and interactions [142].

CHAPTER THREE

EXPERIMENTAL PROCEDURES

In this chapter, we describe the detailed experimental procedures for

- (a) Synthesis of nano-sized SrTiO_3 materials from synthesized and commercial materials respectively via the high-energy ball milling technique.
- (b) Fabrication of thick film devices using the screen-printing technology.
- (c) Microstructure, thermal stability and hydroxyl (OH^{-1}) characterization of the nano-sized sensing material including X-ray diffraction (XRD), transmission electron microscope (TEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR).
- (d) Characterization of sensing properties.
- (e) X-ray photoelectron spectroscopy (XPS) characterization.
- (f) Electrical conductivity measurement including ac impedance characterization and dc I-V property.

3.1 High-energy Ball Milling of Synthesized and Commercial SrTiO_3 Powders

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The starting materials for the synthesized SrTiO_3 were powder of strontium oxide (SrO , 99.9% purity, density 4.700 g/cm^3 , Aldrich Chemical) and titanium (IV) oxide (TiO_2 , 99+% purity, rutile, Johnson Matthey); and that for the commercial SrTiO_3 was strontium titanium oxide (SrTiO_3 , 99+% purity, Johnson Matthey). The mixing was carried out using the planetary ball mill (Fritsch Pulverisette 5). An open container with tungsten carbide (93 wt% WC and 6 wt% Co) vials and balls were chosen. The tungsten carbide vials and balls with relatively high density of 14.75 g/cm^3 were used to increase the impact energy [125]. The vial has a volume of 250 ml with an inner diameter of 75 mm and the balls have diameter of 10 mm and 20 mm. The milling speed was set at 200 rpm and the ball-to-power weight ratio was 20:1[24].

During milling, air was constantly available to the oxide powder. The milling was carried out in 30 minute cycles with 25 minutes of milling followed by 5 minutes of pause to prevent overheating of the milling system from prolonged milling. At selected intervals, some amount of the milled powder was taken out from the vial for analysis and preparation of the thick film paste. The right number of balls were also taken out so as to roughly maintain the 20:1 ball-to-powder weight ratio. The intervals were fixed at 2, 20, 40, 80 and 120 hours of milling.

3.2 Fabrication of Thick Film Devices

The fabrication of the thick film devices comprises (a) processing of the sensing materials powders for: synthesized SrTiO_3 (120h milling) and commercial SrTiO_3 (120h milling) using the high energy ball milling technique and un-milled

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commercial SrTiO_3 powders, (b) preparation of the paste, and (c) fabrication of the thick film device using the conventional screen printing technology. The whole process flowchart is depicted in figure 3-1.

Figure 3-1 Thick film fabrication flow chart.

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3.2.1 Preparation of Thick Film Paste

Each sample of the milled powders had to be formed into paste to allow for screen printing into thick film. This was manually done using agate mortar and pestle. The commercial organic vehicle ESL-400 from ESL inc. was added to the mixed powder with a weight ratio of 20 to 30 percent. Different percents of the organic vehicle were used for different samples to allow a fixed viscosity of the prepared paste as required for the thick film screen-printing. The mixture was then thoroughly ground in the agate mortar for around two hours until a very smooth paste was formed.

3.2.2 Screen printing of Gas Sensors

The 2×2 square inches, 0.001-inch thick alumina substrates were used for the screen printing of the gas sensors. First the substrates were cleaned with acetone in ultrasonic bath. After drying in the oven at 150 °C for 15 minutes, the interdigital gold electrodes were screen printed with the Dupont gold paste (5715) using the Presco 465 screen printer from AMI. The printed gold paste was leveled for 15 minutes at room temperature and dried in the oven at 110 °C for 15 minutes. Finally, the printed gold electrodes were fired at 850 °C in the BTU belt furnace with a belt speed of 1.8 inch per minute. The sensing thick film layer was then printed on top of the electrodes. To ensure that there were no cracks on the film, 2 layers were printed consecutively. Each layer was allowed to settle for 15 minutes and dry in the oven at 110 °C for another 15 minutes. The final film was dried at 350 °C in the BTU belt furnace with a belt speed of 2 inch per minutes. Figure 3-2 shows the layout of a 3 × 3 device array on the 2 × 2 square inches substrate with inter-digital Au electrodes (each with length of 0.25 mm and separation of 0.5 mm). The device was then diced

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out individually and annealed at 400, 500, 600, 700, and 800 °C for synthesized SrTiO_3 (120h milling) respectively, 400 °C for the commercial SrTiO_3 (120h milling) and un-milled commercial SrTiO_3 for one hour in air at 1 standard liter per minute (slm) flow rate.

Figure 3-2 Layout of the thick film devices on a 2x2 square inches ceramic substrate.

3.3 Fabrication of Disc Samples

The disc samples were produced from the synthesized SrTiO_3 (120h milling) powders with annealing in air at 400 °C for 1 hour, which were pressed into discs in sandwiched structure with aluminium foil electrodes. The thickness is 1 mm and diameter is 15 mm.

3.4 Characterization

3.4.1 Characterization of Powders

3.4.1.1 Physical and Microstructure Properties

The X-ray diffraction pattern is a conventional and effective technique to identify the crystalline structure of the milled powders. The different composition powder samples, at different milling times and different annealing temperatures were characterized at room temperature using a SHIMADZU XRD-6000 X-ray diffractometer with Cu K α radiation (1.54056 Å) at 40 kV 30 mA in the range of $20^\circ \leq 2\theta \leq 60^\circ$ with a sweep rate of 2° per minute.

The microstructure of the milled powders and heat-treated powders were studied using a Jeol JEM2010 Transmission Electron Microscope (TEM). The TEM specimens were prepared by dispersing the fine powders in ethanol solution using ultrasonic vibration and then sprayed on-to holey carbon films, and dried in air. It was found that the specimen was stable under the 200 keV electron beam.

3.4.1.2 Thermal Stability

DTA/TGA were performed using the Perkin Elmer differential thermal analyzer (DTA-7) and thermogravimetric Analysis (TGA-7) for the milled 120 hours synthesized SrTiO₃ powder. The temperature range was selected from room temperature (25 °C) to 900 °C with the raising rate of 4 °C per minute.

3.4.1.3 Hydroxyl (OH⁻) Property

The hydroxyl (OH⁻) in the powders of synthesized SrTiO₃ (120h milling), commercial SrTiO₃ (120h milling) and un-milled commercial SrTiO₃ at room temperature were detected by Fourier transform infrared (FTIR) (FT-IR Spectrometer

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Spectrum 2000, PERKIN ELMER) from wave number $2000\text{--}4000\text{ cm}^{-1}$. The samples were obtained by first grinding the sample in anhydrous KBr at a ratio of approximately 1 part sample to 100 parts KBr, and then pressing into a disc.

3.4.2 Characterization of the Sensing Properties for Sensors

The final sensing film for the synthesized SrTiO_3 (120h milling) with $400\text{ }^\circ\text{C}$ annealing temperature was observed to have a $45\text{-}\mu\text{m}$ thickness at room temperature using the JEOL 5410 scanning electron microscope (SEM) at 20 kV and shown in figure 3-3.

Figure 3-3 The cross-section of SEM image for the synthesized SrTiO_3 sensing film (120h milling) with annealing at $400\text{ }^\circ\text{C}$.

3.4.2.1 Sensing Properties

The direct current (dc) resistance and relative resistance for synthesized SrTiO_3 (120h milling) with $400\text{--}800\text{ }^\circ\text{C}$ annealing temperatures, commercial SrTiO_3 (120h milling) and un-milled commercial SrTiO_3 with $400\text{ }^\circ\text{C}$ annealing temperature thick film devices were respectively characterized with a 5-V applied voltage in different gas environments. The test gas was oxygen diluted by nitrogen and the carrier gas was

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nitrogen. All these gases were calibrated and supplied by SOXAL Gas Company. The electrical properties of the gas sensors were performed using a Keithley 236 source measurement unit. The gas sensing properties based on ac and dc electrical measurement were characterized using a home-designed gas sensor characterization system, as shown in figure 3-4. In this system, a personal computer (PC) was used to control the overall data measurement operation. The flow rate and concentration of test gas were controlled using four MKS1179A Mass Flow Controllers (MFC) that were electronically controlled via a MKS247C four channel-readout and a MKS232 interface unit. The overall gas flow of 500 sccm was chosen for the measurement. The sample mount test gas chamber is shown in figure 3-5. The temperature of the tested sensors was controlled by a Linkam TMS93 temperature controller from room temperature (25 °C) to 500 °C. Temperature scans were performed using a closed cycle water cooler and a resistor heater. The temperature at the sample surface was measured by two thermocouples. The software programs for gas sensing measurements and GPIB interface to the various equipment were designed using the National Instruments Labview 6.1 package.

The Arrhenius plots against temperature (dc electrical property) for the synthesized nano-sized SrTiO₃ sensor in 20 % O₂ in background N₂ were characterized using the same characterization system.

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Figure 3-4 Block diagram of gas sensor characterization system

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Figure 3-5. Schematic representation of the sample mount test gas chamber. TC1, TC2 are thermocouples of type K.

3.4.2.2 Humidity Effect

The ac impedance property for the synthesized nano-sized SrTiO_3 sensor with 400 °C annealing temperature in 20 % O_2 ambient were characterized at 40 °C operating temperature in different relative humidity (RH) of dry, 20% RH, 80% RH and near 100% RH, respectively. The experiment was carried out in the frequency range of 1 mHz to 10 MHz with the ac level of 50 mV. The impedance spectroscopy measurement system is a Solartron SI1260 impedance/gain-phase analyzer in conjunction with SI1296 (Solartron Group Ltd, Farnborough England) that allows the measurement of very high impedance range up to $10^{14} \Omega$. The relative humidity (RH) measurement is done with a NIST Traceable Digital Hygrometer/Thermometer, VWR Scientific 35519-043.

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3.4.3 Analysis of the Sensing Mechanisms

3.4.3.1 X-ray Photoelectron Spectroscopy (XPS) Characterization

X-ray Photoelectron Spectroscopy (XPS) characterization was employed to analyze and confirm the oxygen sensing mechanism of commercial SrTiO₃ and synthesized SrTiO₃. The XPS experiments were performed using a VG ESCALAB 220i-XL instrument with a monochromatic Al K α x-ray source (1486.6 eV photons) operated at a power of 300 W. All XPS measurements were done at a take-off angle of 90° with respect to the sample surface plane. The analyzer was set at a constant pass energy of 20 eV for high-resolution spectrum acquisition and 150 eV for survey spectrum acquisition. The base pressure in the analysis chamber was set to less than 1×10^{-10} mbar. To minimize the charging effects, a low energy electron flood gun in conjunction with a transmitting fine mesh proximity screen was used. The quantification was carried out using the relative sensitivity factors (RSFs) taking into consideration both the photoionization cross-sections and the transmission function of the spectrometer. The reference of the binding energy scale was performed with the O 1s line (531.0 eV) in the materials [144]. The XPS spectra were analyzed using a peak synthesis program whereby a Shirley background was chosen and the fitting peaks of the experimental data were defined by a combination of 50% Gaussian and 50% Lorentzian after the optimization.

3.4.3.2 Electrical Conduction Measurements

The ac impedance properties for the synthesized nano-sized SrTiO₃ disc sample with 400 °C annealing temperature were studied in N₂ and 20% O₂ in background N₂ respectively. The spectroscopy measurements were carried out using the same

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impedance spectroscopy system in the frequency range of 1 mHz to 10 MHz with an ac level of 50 mV from 25-70 °C operating temperature. The Zplot software (Scribner Associates) was used for the measurement control and data recording.

The dc I-V characterizations in N₂ and 20% O₂ in background N₂ respectively for the synthesized nano-sized SrTiO₃ disc sample were also measured with the applied dc voltage from -10 V to +10 V using gas sensor characterization system.

CHAPTER FOUR

CHARACTERIZATION OF LOW-TEMPERATURE NANO-SIZED SrTiO₃ OXYGEN GAS SENSORS

In this chapter, by utilizing the high-energy ball milling technique and taking advantage of the low cost and thermal stability for SrTiO₃ materials, we have successfully synthesized nano-structured SrTiO₃ material and decreased the operating temperature to near human-body temperature. This is a first reported work on the possibility for the semiconducting metal oxide oxygen sensing materials application into the areas of the medical, environmental and domestic fields at such low temperatures.

Firstly, we study the material properties during the mechanical alloying and thermal process for the nano-sized SrTiO₃ from synthesized and commercial materials respectively using high-energy ball milling technique. The microstructure, thermal stability and hydroxyl (OH⁻¹) characterization of the nano-sized SrTiO₃ are characterized using XRD, TEM, DTA/TGA and FTIR, respectively. Next, the gas sensing properties of the fabricated sensor devices are systematically characterized. The effect of the different annealing temperature and humidity are also investigated. Finally, the sensing properties of the different material sensors (nanosized synthesized,

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nanosized commercial and un-milled commercial SrTiO₃-based sensors) annealed at 400 °C are characterized and compared. The different sensing mechanism models for the nanosized synthesized and commercial SrTiO₃ sensors are established according to their different Po₂ dependence of the electrical conductance.

4.1 Characterization of Materials

4.1.1 Mechanical Alloying Process

In our research, the high-energy ball milling was employed to obtain the nano-sized sensing materials. Tungsten carbide bowls and balls with higher density were used to increase the impact energy. The milling time was also longer in terms of days.

4.1.1.1 XRD Patterns of Milled Powders

Figure 4-1 shows the XRD patterns for the synthesized SrTiO₃ samples with different milling times. For the synthesized SrTiO₃ material, the perovskite phase formation could be observed after 2 hours of milling time. At 20 hours of milling, the XRD peaks for the cubic perovskite phase of the SrTiO₃ structure appeared distinctively. This phase was maintained up to 120 hours of milling time. The changes can be explained by the fact that during the milling process, the powders go through four different stages of the mechanical alloying process, namely (a) initial, (b) intermediate, (c) final, and (d) completion stages [140]. These involved the breaking down of the chemical bonds of the starting materials, SrO and TiO₂, followed by the forming of the new chemical bonds of the synthesized SrTiO₃. The completion stage for this material was observed to be at around 20 hours of milling. In contrast, for the commercial SrTiO₃ material, the perovskite structure was maintained throughout the 120 hours of milling as shown in figure 4-2.

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Figure 4-1 XRD patterns for synthesized SrTiO_3 after different milling times.

Figure 4-2 XRD patterns for commercial SrTiO_3 after different milling times.

From the XRD peaks, the average crystal grain sizes and the lattice constants for the materials can be obtained. The average grain sizes were calculated using the Scherrer equation [140]:

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$$B = \lambda \zeta / (d_c \cos \theta) \quad (4.1)$$

Where B in radians is the broadening of the diffraction peak due to crystalline size measured at half of its maximum intensity; λ , wavelength of radiation; θ , Bragg angle; d_c , diameter of crystalline size; and ζ , a constant. The constant ζ depends mainly on the crystalline shape and indices. It has a value of about 0.9 [140].

Besides the broadening of the peak due to the decrease in crystalline size, the instrument and non-uniform strain will also affect the broadening of X-ray diffraction peaks. Considering the size effect, strain effect and instrument effect, equation (4.1) can be modified as [140]:

$$(B_M^2 - B_I^2)^{1/2} \cos \theta = C \sin \theta + \lambda \zeta / d_c \quad (4.2)$$

$$C = -2\Delta d / d \quad (4.3)$$

Where B_M is breadth of the measured peak at half-maximum intensity, B_I is the broadening due to the X-ray spectrometer (B_I is measured under similar geometrical conditions using a material with a crystallite size well in excess of 100 nm.), d is the lattice spacing and Δd is the change in lattice spacing due to residual strain [140].

Based on this principle, the average crystal grain sizes and the lattice constants were computed and plotted for both the synthesized SrTiO₃ and commercial SrTiO₃ with different milling times as shown in figures 4-3 and 4-4, respectively. For the synthesized SrTiO₃ material, these calculations were made only after the full formation of the perovskite structure at the beginning of 20 hours. SrTiO₃ is a ternary oxide that has a cubic perovskite structure and hence it only has one lattice constant a . Before 20 hours, the average grain size of the commercial SrTiO₃ rapidly decreased to a minimum at 20 hours; at the same time the lattice constant increased rapidly and peaked at 20 hours. It is possible that the material bonds were broken due to the great impact energy derived during high-energy ball milling, and the material is at the

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highest energy state. Between 20 and 120 hours, the average grain sizes of the synthesized and commercial SrTiO₃ materials increased slightly to a stable value of 27 nm. At the same time, the lattice constants of the synthesized SrTiO₃ and commercial SrTiO₃ materials decreased gradually down to a stable value of after 120 hours of ball milling. This is consistent with lattice contraction for nanosized materials. It is due to the grain-size effect on the nano-material induced by surface bond contraction [145]. Hence, the lattice constant of the material at 120 h milling with meta-stable energy is smaller than that at 20 h milling time with un-stable state energy and bigger than that of the un-milled material with stable state energy.

Figure 4-3 Average grain size of synthesized and commercial SrTiO₃ samples for different milling times computed from their XRD patterns.

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Figure 4-4 Lattice constant a of synthesized and commercial SrTiO_3 samples for different milling times computed from their XRD patterns.

4.1.1.2 TEM Observation of Milled Powders

The TEM results for the synthesized SrTiO_3 material (120h milling) are shown in figures 4-5 to 4-7. The bright-field images in figures 4-5 and 4-6 show a cluster of grains pattern of around 27 nm estimated from XRD peaks. Specifically, figure 4-6 shows the lattice structure of the synthesized SrTiO_3 material. The Selected Area Diffraction (SAD) pattern in figure 4-7 shows that the powder of the synthesized SrTiO_3 material is a mixture of nano-polycrystalline and amorphous states. The TEM results for the un-milled commercial SrTiO_3 material (in figures 4-8 and 4-9) and commercial SrTiO_3 material (120h milling) (in figures 4-10 and 4-11) are also shown respectively for comparison.

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(a)

(b)

Figure 4-5 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling) (a) and (b).

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Figure 4-6 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling) lattice structure.

Figure 4-7 TEM SAD pattern for synthesized nano-sized SrTiO_3 (120h milling).

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(a)

(b)

Figure 4-8 TEM bright-field images for un-milled commercial SrTiO_3 (a) and (b).

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The TEM image in figure 4-8 for the un-milled commercial SrTiO_3 material shows the grain size of about $0.3\ \mu\text{m}$, which is consistent with the estimated from XRD peaks. Figure 4-9 displays the TEM SAD pattern for the un-milled commercial SrTiO_3 material. It shows only the diffraction of a single crystal grain due to the fact that the grain size is bigger than the beam spot.

Similarly, the TEM image of figure 4-10 (a) shows the grain size of the commercial SrTiO_3 material (120h milling) material in the nano-size range and figure 4-10 (b) also clearly shows the lattice structure after 120 hours ball milling. The corresponding diffraction pattern in figure 4-11 shows that the powder is also a mixture of polycrystalline and amorphous states.

Figure 4-9 TEM SAD pattern for un-milled commercial SrTiO_3 .

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(a)

(b)

Figure 4-10 TEM bright-field images for commercial nano-sized SrTiO_3 (120h milling) (a) and (b).

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Figure 4-11 TEM SAD pattern for commercial nano-sized SrTiO_3 (120h milling).

4.1.2 Thermal stability

4.1.2.1 DTA-TGA Analysis

Figure 4-12 shows an endothermic peak at about 100 °C in the DTA curve. It is possible that water evaporated as the TGA curve also shows some weight lost. An exothermic peak at near 550 °C is possibly due to some chemical absorption oxygen being desorbed from the powders and the growth of the grains [5, 108, 146]. Similar weight lost is observed in the TGA curve around 550 °C. In the whole temperature range (25-900 °C), the synthesized SrTiO_3 material maintained the thermal stability with no change in its structure. This is further confirmed by the XRD and TEM experiments.

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Figure 4-12 Thermal analysis results of synthesized nano-sized SrTiO_3 (120h milling) powders at a heating rate of $4^\circ\text{C}/\text{min}$.

4.1.2.2 XRD Analysis

The XRD patterns of the synthesized SrTiO_3 powders with 120 hours milling and different annealing temperatures were shown in figure 4-13. Their average grain sizes for different annealing temperatures were shown in figure 4-14.

As seen in figure 4-13, the perovskite crystal structure of SrTiO_3 remained stable for the synthesized SrTiO_3 with the different annealing temperatures from 400 to 800 $^\circ\text{C}$. It confirms the thermal stability of the synthesized SrTiO_3 crystal structure. In figure 4-14, the average grain size of the synthesized SrTiO_3 powders increased with increasing annealing temperature from the initial value of 27 nm for the as-milled samples to 70.5 nm at 800 $^\circ\text{C}$. Below 600 $^\circ\text{C}$, the average grain size increased gradually possibly due to the grain growth [147]. It was also observed in the TEM experiments as shown in figures 4-16, 4-17 and figures 4-19, 4-20, respectively. Beyond 600 $^\circ\text{C}$, it increased rapidly, possibly due to the grains combining with one another. Grain growth is the process by which the average grain size of strain-free or

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nearly strain-free material increases continuously during heat treatment without change in the grain-size distribution [147].

Figure 4-13 X-ray diffraction patterns of the synthesized nano-sized SrTiO_3 powders milled for 120 hours and heat-treated at different temperatures.

Figure 4-14 Variation of the average grain sizes of the synthesized nano-sized SrTiO_3 powders (120h milling) with annealing temperature.

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In order to clarify the effect of different annealing temperatures on the crystal structure, the lattice constant **a** for the synthesized SrTiO₃ powders with different annealing temperatures was computed and showed in figure 4-15. The lattice constants of the un-milled and 120h milled commercial SrTiO₃ were also compared. In figure 4-15, the lattice constant **a** of the synthesized SrTiO₃ (120h milling, no annealing) was almost the same as that of commercial SrTiO₃ (120h milling, no annealing). The lattice constant **a** of synthesized SrTiO₃ (120h milling) decreased slightly at annealing temperature at 400 °C and after that, it decreased rapidly and down to almost a constant value between 500 to 800 °C. At annealing temperature 800 °C, the lattice constant **a** of synthesized SrTiO₃ (120h milling) was comparable to that of commercial SrTiO₃ (no milling and no annealing). Due to the high impact energy during high energy ball milling, the synthesized SrTiO₃ (120h milling, no annealing) is at a high energy meta-stable state [140] and its lattice constant is bigger than that of the un-milled commercial SrTiO₃. During the annealing process up to 800 °C, it is possible that synthesized SrTiO₃ (120h milling) derived enough energy to overcome the meta-stable energy barrier of synthesized SrTiO₃ (120h milling) up to 400 °C, and shifted down to the low energy stable state between 400-800 °C. As a result its lattice constant is also reduced to the stable value at 800 °C, which is similar to that of the stable state of the commercial SrTiO₃ (no milling and no annealing). In fact, we discovered that the annealing process of synthesized SrTiO₃ is equivalent to the reverse process of the material during the ball milling process in figure 4-4. Through the annealing process, the lattice constant for the material recovered from the metal-state after ball milling process to the stable state before ball milling process.

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Figure 4-15 Lattice constant *a* for the synthesized nano-sized SrTiO₃ powders versus annealing temperature.

4.1.2.3 The TEM Observation

TEM bright-field images and SAD patterns for synthesized SrTiO₃ powders annealed at 400 °C, 600 °C and 800 °C are shown in figures 4-16 to 4-24, respectively. These figures show the increase in grain size of synthesized SrTiO₃ powders with annealing temperatures. TEM bright-field images in figures 4-17, 4-20 and 4-23 also show the lattice structures clearly. It confirms the thermal stability of the lattice structure of synthesized SrTiO₃ from 400 to 800 °C. The diffraction patterns in figures 4-18, 4-21 and 4-24 show that the powder is a mixture of poly-crystalline and amorphous states. With increasing annealing temperature, the SAD pattern density decreases due to the grain size increasing. This is consistent with the XRD results.

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(a)

(b)

Figure 4-16 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 400 °C) (a) and (b).

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Figure 4-17 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 400 °C) lattice structure.

Figure 4-18 TEM SAD pattern for synthesized nano-sized SrTiO_3 (120h milling, annealing 400 °C).

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(a)

(b)

Figure 4-19 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 600 °C) (a) and (b).

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Figure 4-20 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 600 °C) lattice structure.

Figure 4-21 TEM SAD pattern for synthesized nano-sized SrTiO_3 (120h milling, annealing at 600 °C).

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(a)

(b)

Figure 4-22 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 800 °C) (a) and (b).

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Figure 4-23 TEM bright-field images for synthesized nano-sized SrTiO_3 (120h milling, annealing 800 °C) lattice structure.

Figure 4-24 TEM SAD pattern for synthesized nano-sized SrTiO_3 (120h milling, annealing 800 °C).

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4.1.3 FTIR Analysis

For the synthesized SrTiO_3 (120h milling), commercial SrTiO_3 (120h milling) and un-milled commercial SrTiO_3 , figure 4-25 shows the O-H absorption peak [148] at 3415 cm^{-1} , the C=O group absorption peaks [148] at 1633 cm^{-1} and 1462 cm^{-1} , the SrTiO_3 group absorption peaks [149] at 860 cm^{-1} and 617 cm^{-1} . The amount of OH^{-1} ions in synthesized SrTiO_3 (120h milling) material is less than that in commercial SrTiO_3 (120h milling). The following section will present the oxygen sensing properties of the synthesized SrTiO_3 -based sensor (120h milling) that is better than that of the commercial SrTiO_3 -based sensors (120h milling) at low temperature. Hence it is concluded that the OH^{-1} ions are not a key factor during the oxygen sensing reaction process.

Figure 4-25 FT infrared spectra for synthesized nano-sized SrTiO_3 (120h milling), commercial nano-sized SrTiO_3 (120h milling) and un-milled commercial SrTiO_3 .

4.2 Characterization of Sensors

4.2.1 The Synthesized SrTiO₃ Sensors

4.2.1.1 Effect of Annealing Temperature

The effect of different annealing temperatures on the gas sensing properties for the synthesized SrTiO₃ sensors to 20% of oxygen in nitrogen was characterized. The thick film devices were annealed for one hour in air at 400, 500, 600, 700 and 800 °C respectively. The device of the synthesized SrTiO₃ (120h milling and annealing at 800 °C) is insulating and has no sensing property. The relative resistances for the other devices with different annealing temperatures and operating at different temperatures are plotted in figure 4-26.

Figure 4-26 Relative resistance of synthesized nano-sized SrTiO₃-based for different annealing temperatures.

The optimal relative resistance ($R_{\text{nitrogen}} / R_{20\% \text{ oxygen}}$) value of 6.35 is obtained for the synthesized SrTiO₃ sample annealed at 400 °C and operating at 40 °C. This value is

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comparable to the reported relative resistance of doped SrTiO₃ series oxygen gas sensors with operating temperature at 700-800 °C [30-32]. The figure also shows that most of the samples annealed at different temperatures have the same optimal operating temperature of 40 °C. This optimum operating temperature is much lower than that of the conventional metal oxide semiconducting oxygen gas sensors (300-500 °C) [5, 28-30] and SrTiO₃ oxygen gas sensors (> 700 °C) [5, 8].

At the operating temperature of 40 °C, the relationship between relative resistance ($R_{\text{nitrogen}}/R_{20\% \text{ oxygen}}$) and grain size for different annealing temperatures of the synthesized SrTiO₃ devices is depicted in figure 4-27. The grain sizes of the synthesized SrTiO₃ increased with increasing annealing temperature, especially above 600 °C. At the same time, the device relative resistance decreased with increasing annealing temperature. When the grain size of the material is small enough ($D < 2L$, D : the actual grain size, L : the depth of the depletion layer), the material resistivity of the device is determined by the grain surface control and the material conduction type is surface conduction dominant (figure 1-1) [6, 108]. The grain sizes of synthesized SrTiO₃ with annealing 400 °C is around 30 nm; this dimension is compared to the reported range of L for the semiconducting oxide materials chemisorbed oxygen of 10^{-6} - 10^{-5} cm [47], hence it is surface conduction dominant and the surface-to-bulk ratio for the material is much greater than that for coarse material [107]. The grain size of the material is therefore one of the factors to control the gas sensing properties of the material [107]. Between 400 and 600 °C, the grain size of material increased gradually while the relative resistance of the device decreased rapidly. Above 600 °C, the grain size of material increased rapidly while relative resistance of the device decreased gradually. There should be other factors that affect the gas sensing properties of the material besides the grain size factor in the surface conduction dominant range. We

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will further discuss the factor of the single-charged “O⁻” ions of the lattice oxygen in the synthesized SrTiO₃ that affect the sensing property of sensors in the next chapter. As annealing temperature further increased to above 800 °C, the material resistivity of the device becomes an insulator and the material changes to neck control type ($D \geq 2L$, high resistance, figure 1-1) [6, 108]. Below 700 °C annealing, our sensors have the low-temperature oxygen sensing due to the materials being grain surface control ($D < 2L$, low resistance, figure 1-1) [6, 108].”

Figure 4-27 Relationship between gas relative resistance and grain size for different annealing temperatures of synthesized nano-sized SrTiO₃-based devices.

4.2.1.2 Effect of Gas Concentration

The relative resistance of the device in different oxygen concentrations was measured. The device is the 120-hours milled synthesized SrTiO₃ thick film sample annealed at 400 °C for 1 hour in air and operating at 40 °C. The detecting oxygen concentrations are from 10⁴ ppm to 2 x 10⁵ ppm (air composition). Figure 4-28 shows the variation of relative resistance of the device with different ppm oxygen in background nitrogen. The relative resistance of the device increased from 2.3 at 10⁴ ppm oxygen to 6.35 at 2

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x 10⁵ ppm oxygen (air composition). This provides a wide concentration range for our oxygen sensor devices at near room operating temperature. At low oxygen concentrations, the relative resistance of the synthesized SrTiO₃ device increased rapidly with increasing oxygen concentration, however, at higher concentrations, the increase became more gradual. For a sample with a fixed surface area, the gas relative resistance will also reach a saturation value when the surface reactions are saturated.

Figure 4-28 The relative resistance of the synthesized nano-sized SrTiO₃-based device vs. oxygen concentration in nitrogen (a) in linear scale and (b) in logarithmic scale.

4.2.1.3 Effect of Humidity

The humidity effect for the gas sensors normally was tested by impedance measurement as it would reveal the mechanism present readily than that in dc measurement [22]. Figure 4-29 shows that there are no effect of different relative humidity (dry, 20% RH, 80% RH, near 100% RH) on the impedance of the synthesized SrTiO₃ sensor with annealing at 400 °C and operating at 40 °C in 20% oxygen ambient. This is consistent with the reported fact that the relative effects of

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humidity tends to decrease with decreasing temperature within operating temperature 200–400 °C for SrTiO₃-based material [22]. The FTIR result in Figure 4-25 also shows the synthesized SrTiO₃ material lacks the capability of the adsorbing OH⁻¹. Hence it is safe to ignore humidity effect for our samples operating at a very low temperature of 40 °C.

Figure 4-29 Impedances of the synthesized nano-sized SrTiO₃-based sensor with annealing at 400 °C, operating at 40 °C, in 20% oxygen ambient with different relative humidity.

4.2.1.4 Response Time

When an input signal goes through a well defined change, the output response is defined by the time interval between 10% and 90% of the stationary value [150]. To investigate the response time and sensing reversibility, the sensor of the synthesized SrTiO₃ annealed at 400 °C in air for 1 hour was characterized for its transient response cycle. Figure 4-30 shows the response property of the sensor resistance undergoing from N₂ to 20% O₂ (N₂ as the carrier gas) ambient, and repeating for three cycles.

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Figure 4-30 Response times of synthesized nano-sized SrTiO₃-based sample with annealing at 400 °C and operating at 40 °C. (a) for several cycles, (b) for detail one cycle.

The figure indicates that this oxygen gas sensor exhibits good repeatability as the relative change of resistance value is consistent in each cycle. The response time is 1.6 minutes and the recovery time is 5 minutes. We believe there are no reported metal

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oxide semiconducting oxygen gas sensors that operate at such a low temperature. Only the practical Calvanic cell-type operates at room temperature, but it has high ionic conduction and is often difficult to predict the sensor response [4].

4.2.2 The different SrTiO₃ Sensors

The sensing properties of the different material sensors (synthesized nano-sized, commercial nano-sized and un-milled commercial SrTiO₃-based sensors) annealed at 400 °C were characterized. The un-milled commercial SrTiO₃-based sensor annealed at 400 °C exhibited no sensing property as it is still an insulating material. The changes of the relative resistance ($R_{\text{nitrogen}}/R_{\text{oxygen}}$) of the devices to 20% oxygen gas in nitrogen were characterized and depicted in figure 4-31. Compared to the commercial SrTiO₃-based sensors (120h milling), the optimal relative resistance change 6.35 for the synthesized SrTiO₃-based sensor (120h milling) was observed to be more than 3 times better at 40 °C operating temperature.

Figure 4-31 The relative resistance of the synthesized and commercial nano-sized SrTiO₃-based sensors (120h milling) annealed at 400 °C to 20% O₂ in background N₂ at different operating temperatures.

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Figure 4-32 P_{O_2} dependences of the electrical conductance of the synthesized nano-sized SrTiO₃ (120h milling) and the commercial nano-sized SrTiO₃ (120h milling)-based sensors operating at 40 °C.

Figure 4-32 shows the P_{O_2} dependence of the conductance of the synthesized SrTiO₃-based (120h milling) and the commercial SrTiO₃-based (120h milling) sensors operating at 40 °C. Both the positive slopes for the two material sensors in the curves of the $\log \sigma$ to $\log P_{O_2}$ indicate that the two materials are p-type [5]. The detection range of 0.03 to 1 atm P_{O_2} in figure belongs to the high P_{O_2} region ($P_{O_2} > 10^{-4}$ atm), there are possibly two types of sensing mechanisms present in the oxygen sensors. In addition to the definition in the formalism of Kröger and Vink in chapter 2 [64], the following notations and their representation are: $V_O^{\bullet}$: the oxygen vacancy with single-ionized positively; K_1 and K_2 are the equilibrium constants for the respective reactions.

$$p = K_1 [V_O^{\bullet}]^{1/2} P_{O_2}^{1/4} \quad (4.5)$$

$$\log \sigma \propto 1/4 \log P_{O_2} \quad (4.6)$$

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$$p = K_2 [\text{V}_{\text{O}}^{\cdot}] P_{\text{O}_2}^{1/2} \quad (4.8)$$

$$\log \sigma \propto 1/2 \log P_{\text{O}_2} \quad (4.9)$$

The slope of 1/3.85 for the commercial SrTiO₃-based (120h milling) sensor shown in figure 4-32 is close to ¼, mainly Type I mechanism [8, 16]. Interestingly, the slope of 1/2.18 for the synthesized SrTiO₃-based (120h milling) sensor shown in figure 4-32 is close to ½, hence it predominantly has Type II mechanism. We believe this slope that is near ½ is the best value ever achieved; all other reported work are in the ¼ value range and hence exhibit Type I sensing mechanism [5, 8, 16]. These sensing mechanisms have been further investigated and confirmed by the XPS experiments as discussed in the next chapter.

CHAPTER FIVE

MECHANISM OF LOW-TEMPERATURE NANO-SIZED SrTiO₃ OXYGEN GAS SENSORS

The theory of the oxygen sensing mechanisms for the conventional SrTiO₃ operating above 700 °C temperature range have been well-established [8, 16, 22, 38-39, 101]. However, the oxygen sensing mechanisms for the SrTiO₃ materials at low operating temperature are relatively unknown. In this chapter, the sensing mechanisms for the nano-sized SrTiO₃ materials were investigated systematically. The XPS characterization are systematically carried out to investigate the different low-temperature oxygen sensing mechanisms for the synthesized nano-sized SrTiO₃ and commercial nano-sized SrTiO₃ material respectively obtained by using the high-energy ball milling technique. The ac impedance characterization is investigated to elucidate the mechanism of the 40 °C optimal operating temperature and the anomalous positive slopes in the Arrhenius plot of electrical conductance below the 70 °C regime for the nano-sized synthesized SrTiO₃ in oxygen ambient at different operating temperatures. A detailed defect chemistry analysis is also carried out to explain for an anomalous transition from p-type to n-type phenomenon on the

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synthesized nano-sized SrTiO₃ materials at 1 atm oxygen partial pressure (P_{O₂}), 400 °C annealing temperature and 40 °C operating temperature.

5.1 XPS Characterization

In this section, the XPS characterizations are systematically carried out for the synthesized nano-sized and commercial nano-sized SrTiO₃ materials and un-milled commercial SrTiO₃ material. The new forms of the nano-sized SrTiO₃ (27 nm) material with the singly charged “O⁻” ions in the lattice oxygen sites are revealed by the XPS study. The sensing mechanisms established in the last chapter for the synthesized nano-sized and commercial nano-sized SrTiO₃ materials are further confirmed.

5.1.1 The reference of the Binding Energy Scale

In the XPS experiments, the reference of the binding energy scale was carried out with the O 1s (531.0 eV) in the wide-scan XPS spectra of the materials. The normal reference of the binding energy scale with C 1s is not possible as the C 1s peak is near the Sr 3p peaks in SrTiO₃ and hence is seriously affected by the Sr 3p peaks as shown in figure 5-1 (b). The use of O 1s (531.0 eV) for the reference of the binding energy scale in SrTiO₃ has also been reported [144]. With reference to this O 1s (531.0 eV), all the binding energy positions of Sr, Ti, O, and C for the synthesized SrTiO₃ (120h milling) in the wide-scan range of 0-1100 eV XPS spectra correlate well with their respective standard binding energy positions in figure 5-1 (a) [143].

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(a) The binding energy scale of Sr, Ti, O, and C.

(b) An enlarged part of XPS spectra of Fig 4-1 (a).

Figure 5-1 Analysis of the XPS spectra of the synthesized nano-sized SrTiO_3 (120h milling) in the wide-scan binding energy range of 0-1100 eV.

The comparison of the XPS spectra in the wide-scan range for the un-milled commercial SrTiO_3 , commercial SrTiO_3 (120h milling) and synthesized SrTiO_3 (120h milling) are shown in figure 5-2 (a), (b) and (c), respectively. These three materials are almost with the same positions for their respective standard binding energy positions [143].

Chapter 5 Mechanism of Low-temperature Nano-sized SrTiO_3 Oxygen Gas Sensors (a) The un-milled commercial SrTiO_3 . (b) The commercial nano-sized SrTiO_3 (120h milling). (c) The synthesized nano-sized SrTiO_3 (120h milling).

Figure 5-2 XPS spectra of the materials in the wide-scan binding energy range of 0-1100 eV.

5.1.2 XPS Results for Different Materials

The high-resolution XPS spectra for the O 1s, Sr 3d, Ti 2p, and C 1s regions of the three materials were scanned at room temperature. Figure 5-3 shows the XPS spectra

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for the un-milled commercial SrTiO₃. The O 1s spectrum labeled as Peak B at 530.99 eV corresponds to the range of 528.0-531.0 eV for the double-charged “O²⁻” ions of the lattice oxygen (O²⁻_{latt}) [143]. The Sr 3d spectrum labeled as Peak D at 138.76 eV for Sr 3d_{3/2} and Peak E at 137.07 eV for Sr 3d_{5/2} also fits well with the reported 1.79 to 2 eV difference between Sr 3d_{3/2} and Sr 3d_{5/2} [143]. The Ti 2p_{3/2} Peak G (460.64 eV, corresponding to the peak of Ti⁴⁺) and the C 1s Peak J (288.41 eV) were shown in figure 5-3. The Sr 3d and Ti 2p_{3/2} spectra all fit well with the binding energy standard scale for the elements, respectively [143]. The C 1s Peak J (288.41 eV) is a little higher relative to the binding energy scale of C 1s [143], which maybe affected by the Sr 3p peaks that is close by.

For the commercial SrTiO₃ material after 120h of high-energy ball milling process, in addition to the peaks found in the un-milled commercial SrTiO₃ material, that is, the O 1s Peak B (529.81 eV, O²⁻_{latt}); the Sr 3d Peak D (137.10 eV, Sr 3d_{3/2}) and Peak E (135.18 eV, Sr 3d_{5/2}); the Ti 2p_{3/2} Peak G (458.16 eV); and the C 1s Peak J (284.22 eV)), there are new O 1s Peak A (531.61 eV) and the Ti 2p_{3/2} Peak H (456.82 eV, corresponding to the peak of “Ti³⁺”) as seen in figure 5-4.

The Peak A in the range of 531.0-532.0 denotes O1s lateral structure. This lateral peak corresponds to the ionizations of weakly adsorbed species on the material surface and normally can be described as “O⁻_{ads}” species or excess oxygen [7, 144, 151]. The presence of the Peak A (O⁻_{ads}) in the commercial nano-sized (27 nm) SrTiO₃ (120h milling) indicates that the milled material has absorbed oxygen that gives rise to the oxygen sensing at near human-body temperature (figure 4-31). This is because the average grain size of the milled material has decreased down to the nano-size range as compared to the un-milled material. The “Ti³⁺” peak in the commercial SrTiO₃ (120h

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milling) material also leads to the increase in defect density of the material and hence improves on the oxygen sensing property.

Figure 5-3 XPS spectra for the O 1s, Sr 3d, Ti 2p and C 1s obtained from un-milled commercial SrTiO₃ at room temperature.

Compared to the commercial SrTiO₃ (120h milling), besides Peak A (530.52 eV, O⁻_{ads}) and Peak B (528.52 eV, O²⁻_{latt}), an extra new Peak C (526.50 eV) in O 1s exists in the synthesized SrTiO₃ (120h milling) material as depicted in figure 5-5. The Peak C binding energy position tallies to that of the O⁻_{latt} (the single-charged “O⁻” ions of the lattice oxygen) of commercial SrO₂ at 525.72 eV derived in an independent XPS experiment for the un-milled commercial SrO₂ in table 5-1.

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Figure 5-4 XPS spectra for the O 1s, Sr 3d, and Ti 2p and C 1s obtained from commercial nano-sized SrTiO₃ (120h milling) at room temperature.

Figure 5-5 XPS spectra for the O 1s, Sr 3d, and Ti 2p and C 1s obtained from synthesized nano-sized SrTiO₃ (120h milling) at room temperature.

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The three possible forms of SrTiO₃ structure are postulated:

where the single-charged lattice oxygen ion O⁻ is also present in the Forms II or III besides the double-charged lattice oxygen ion O²⁻ in Form I. The O⁻_{latt} presence, as indicated by Peak C in the O 1s XPS spectrum for the synthesized SrTiO₃ (120h milling) has provided strong evidence to this postulation.

The XPS spectra of Sr and Ti were further investigated to reconfirm the existence of Forms II or III in the synthesized SrTiO₃ material. Compared with the commercial SrTiO₃ (120h milling), the Sr 3d spectrum of the synthesized SrTiO₃ (120h milling) has an additional new Peak F (134.84 eV) as observed in figure 5-5 besides Peak D (140.32 eV, Sr 3d_{3/2}) and Peak E (138.21 eV, Sr 3d_{5/2}). This Peak F is attributed to the Sr 3d_{5/2} ions that bind with the lattice “O⁻” ions in the synthesized SrTiO₃ that is analogous to the form in SrO₂. Hence, Peak F is closely associated to Peak C (O⁻_{latt}) in figure 5-5. Quantitative analysis of these two peaks would be carried out later. The Ti 2p_{3/2} spectrum of the synthesized SrTiO₃ (120h milling) can also be resolved into three peaks: Peak G (458.47 eV, the peak of “Ti⁴⁺”), Peak H (457.25 eV, the peak of “Ti³⁺”) and Peak I (454.99 eV, the peak of “Ti²⁺”). Compared with the un-milled commercial SrTiO₃, the peaks of “Ti³⁺” and “Ti²⁺” in the synthesized SrTiO₃ (120h milling) are the new peaks, which consistently point to the Forms II and III presence in the synthesized SrTiO₃ material respectively. Peak H (“Ti³⁺”) and Peak I (“Ti²⁺”) are also related to Peak C (the “O⁻” ions of the lattice oxygen) in figure 5-5. All the Ti 2p_{3/2} peak positions of the synthesized SrTiO₃ (120h milling) also fit the scale well [143]. The quantitative analysis of these peaks would be similarly carried out later. The C 1s

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peak of the synthesized SrTiO₃ (120h milling) labeled as Peak J (284.28 eV) in figure 5-5 fits the standard scale well [143].

Table 5-1 summaries the detail information of the average core level binding energies (BEs) and average atomic concentrations (At %) of the O 1s, Sr 3d, Ti 2p_{3/2} and C 1s in the XPS spectra of the three different materials and un-milled SrO₂ for comparison. The quantitative relation of Ti and O for the synthesized SrTiO₃ (120h milling) can be derived from the mole ratio (At %) of Ti 2p_{3/2} and O 1s in Table 5-1. If the synthesized SrTiO₃ (120 milling) contains:

then:

$$[\text{O}^-]_{\text{latt}} = [\text{O}^-]_{\text{latt II}} + [\text{O}^-]_{\text{latt III}} = [\text{Ti}^{3+}] + 2 [\text{Ti}^{2+}] \quad (5.6)$$

where $[\text{O}^-]_{\text{latt II}}$ and $[\text{O}^-]_{\text{latt III}}$ denote the concentration of the “O[•]” ions of the lattice oxygen in Form II and Form III of SrTiO₃, respectively.

In Table 5-1 the sum of 2 $[\text{Ti}^{2+}]$ and $[\text{Ti}^{3+}]$ is 11.22% (At%, Average atomic concentrations) which is very close to the $[\text{O}^-]_{\text{latt}}$ 10.67% (At%). This verifies equation (5.6) and confirms that the synthesized SrTiO₃ (120 milling) contains both Form II and Form III.

The mole ratio (At %) of O 1s and Sr 3d_{5/2} of the synthesized SrTiO₃ (120h milling) is also shown in Table 5-1. If the lattice “O[•]” ions was assumed in the form of SrO₂, then,

$$[\text{O}^-]_{\text{latt}} = 2 [\text{Sr } 3\text{d}_{5/2}]_{\text{Peak F}} \quad (5.7)$$

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Table 5-1 Average core level binding energies (BEs) and average atomic concentrations (At %) of O 1s, Sr 3d, Ti 2p_{3/2} and C 1s for synthesized nano-sized SrTiO₃ (120 h milling), commercial nano-sized SrTiO₃ (120h milling), un-milled commercial SrTiO₃, and un-milled commercial SrO₂.

Element	Synthesized nano-sized SrTiO ₃ (120 h milling)			Commercial nano-sized SrTiO ₃ (120 h milling)			Commercial SrTiO ₃ (un-milled)			Commercial SrO ₂ (un-milled)		
	Main peak (eV)	At (%)		Main peak (eV)	At (%)		Main peak (eV)	At (%)		Main peak (eV)	At (%)	
O 1s	O ⁻ _{ads}	A: 530.52	4.62		A: 531.61	13.19						
	O ²⁻ _{latt}	B: 528.52	20.48		B: 529.81	34.68		B: 530.99	41.45			
	O ⁻ _{latt}	C: 526.50	<u>10.67</u>							C: 525.72	<u>52.58</u>	
Sr 3d	Sr 3d _{3/2}	D: 140.32	12.34		D: 137.10	10.08		D: 138.76	13.23	D: 137.93	16.33	
	Sr 3d _{5/2}	E: 138.21	18.47		E: 135.18	<u>19.01</u>		E: 137.07	<u>18.13</u>			
		F: 134.84	<u>5.51</u>	<u>23.98</u>						F: 135.45	<u>28.84</u>	
Ti 2p _{3/2}	Ti ⁴⁺	G: 458.47	13.09		G: 458.16	16.15		G: 460.64	<u>17.75</u>			
	Ti ³⁺	H: 457.25	<u>8.58</u>	<u>22.99</u>	H: 456.82	3.2	<u>19.35</u>					
	Ti ²⁺	I: 454.99	<u>1.32</u>									
C 1s	J: 284.28	4.94		J: 284.22	3.68		J: 288.41	9.44		J: 284.64	2.25	

Note: O⁻_{ads}: the adsorbed "O" ions on surface; O²⁻_{latt}: the lattice "O²⁻" ions; O⁻_{latt}: the lattice "O" ions.

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From table 5-1, two times $[\text{Sr } 3d_{5/2}]_{\text{Peak F}}$ is 11.02% (At%) and is also very close to $[\text{O}^-]_{\text{latt}}$ 10.67% (At%). This again confirms that the lattice “O⁻” ions in the synthesized SrTiO₃ (120h milling) is in the form of SrO₂. As an analogous comparison, the same quantitative result is also achieved for the un-milled commercial SrO₂ in Table 5-1, where the ratio of $[\text{O}^-]_{\text{latt}}$ to $[\text{Sr } 3d_{5/2}]_{\text{Peak F}}$ (52.58 / 28.84) is 1.82 which is close to the value 2.

Besides the relations of Sr and O, Ti and O, Table 5-1 also shows the mole ratio of Sr to Ti for the three different materials. The quantities of Sr and Ti are calculated from the average atomic concentrations (At %) of Sr 3d_{5/2} and Ti 2p_{3/2}.

For the synthesized SrTiO₃:

$$[\text{Sr } 3d_{5/2}] = [\text{Sr } 3d_{5/2}]_{\text{Peak E}} + [\text{Sr } 3d_{5/2}]_{\text{Peak F}} = 23.98 \quad (5.8)$$

$$[\text{Ti } 2p_{3/2}] = [\text{Ti}^{4+}] + [\text{Ti}^{3+}] + [\text{Ti}^{2+}] = 22.99 \quad (5.9)$$

The mole ratios of Sr to Ti are 19.01 / 19.35 and 18.31 / 17.75 for the commercial SrTiO₃ (120h milling) and un-milled commercial SrTiO₃, respectively. Hence, the mole ratio of Sr to Ti of nearly 1 is consistent for all the three different materials.

The XPS analysis shows that the synthesized SrTiO₃ (120h milling) has the combination of the all three possible forms of SrTiO₃ (Form I, Form II and Form III).

It is the presence of these three different forms that provides for better sensitivity of the synthesized SrTiO₃-based sensor (120h milling) than that of the commercial SrTiO₃-based sensor (120h milling) for oxygen sensing at near human body temperature as illustrated earlier in figure 4-31.

The difference of the single-charged O⁻ ions and the double-charged O²⁻ ions in the lattice oxygen present in the different materials has also expounded the new oxygen sensing mechanisms for the near ½ slope and the near ¼ slope respectively as described in the last chapter and reproduced here for clarity.

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The slope of 1/3.85 for the commercial SrTiO₃-based (120h milling) sensor is very near ¼, hence it has mainly the mechanism of Type I [8, 16] for equations 4.4-4.6.

It is now clear from the XPS results that the commercial SrTiO₃-based (120h milling) material is mainly in Form I of SrTiO₃ with the double-charged lattice oxygen ion O²⁻, which is easily associated with the V_O^{••} defect in the Type I mechanism.

The slope of 1/2.18 for the synthesized nano-sized SrTiO₃-based (120h milling) sensor is very near ½, hence it has mainly the mechanism of Type II for equations 4.7-4.9.

From the XPS results, the synthesized nano-sized SrTiO₃ (120h milling) material is mainly in the new Forms II or III of SrTiO₃ with the single-charged lattice oxygen ion O⁻, which again can be easily associated with the V_O[•] defect in the Type II mechanism.

5.1.3 XPS Characterization for Synthesized SrTiO₃ Material with different Annealing Temperatures

The effect of the single-charged “O⁻” ions in the lattice oxygen on the low-temperature oxygen sensing property of the synthesized nano-sized SrTiO₃ materials is further analyzed quantitatively. This is carried out using the XPS characterizations for the synthesized nano-sized SrTiO₃ materials with different annealing temperatures. Figure 5-6 shows the XPS spectra scanned at room temperature for the O1s regions of synthesized SrTiO₃ (120h milling) with different annealing temperatures (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

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Figure 5-6 XPS spectra for the O1s regions of synthesized nano-sized SrTiO₃ (120h milling) at room temperature with different annealing temperatures (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

Table 5-2 provides the detail quantitative information of figure 5-6 for the average core level binding energies (BEs) and the average atomic concentrations (At %) of O 1s of synthesized SrTiO₃ (120 h milling) with the different annealing temperatures. The mole ratio value of the single-charged “O⁻” ions in the lattice oxygen to the total oxygen for the synthesized nano-sized SrTiO₃ material ($[O^-_{latt}]/[O]_{total}$, where $[O]_{total}$ includes $[O^-_{ads}]$, $[O^{2-}_{latt}]$ and $[O^-_{latt}]$), is computed and included in table 5-2. The ratio basically decreased with increasing annealing temperature except 700 °C. $[O^-_{latt}]/[O]_{total}$ 5.9 % in annealed 700 °C material is close to and slight higher than that of 5.4% in annealed 600 °C material. This is maybe due to the experimental deviation in the ratio because the relative resistances ($R_{N_2}/R_{20\% O_2}$) in annealed 700 °C material is also close to that in annealed 600 °C material in figure 4-27. Figure 5-7 shows that the

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curve of $[O^-_{latt}]/[O]_{total}$ with different annealing temperatures correlates remarkably with the curve of the relative resistance ($R_{N_2}/R_{20\% O_2}$) with different annealing temperatures for the synthesized nano-sized SrTiO₃ (120h milling) materials. It gives yet another strong evidence that the single-charged “O⁻” ions in the lattice oxygen of the synthesized nano-sized SrTiO₃ material directly affect the low-temperature oxygen sensing property for the synthesized nano-sized SrTiO₃ material.

Figure 5-7 The relation of the relative resistance ($R_{N_2}/R_{20\% O_2}$) and $[O^-_{latt}]/[O]_{total}$ for the synthesized nano-sized SrTiO₃ (120h milling)-based sensors with different annealing temperatures.

Table 5-2 Average core level binding energies (BEs) and average atomic concentrations (At %) of O 1s of synthesized nano-sized SrTiO₃ (120 h milling) with different annealing temperatures.

Synthesized nano-sized SrTiO ₃ (120h milling) with different annealing temperatures									
400 °C			500 °C			600 °C		700 °C	
Element	Main peak (eV)	At (%)	Main peak (eV)	At (%)	Main peak (eV)	At (%)	Main peak (eV)	At (%)	
O 1s	O ⁻ _{ads}	A: 530.40	12.54	A: 531.15	5.60	A: 530.3	8.85	A: 533.87	0.70
	O ²⁻ _{latt}	B: 528.11	24.63	B: 529.04	38.36	B: 528.49	35.81	B: 529.53	48.97
	O ⁻ _{latt}	C: 525.09	8.53	C: 525.82	4.17	C: 525.71	2.55	C: 525.14	3.11
[O ⁻ _{latt}]/[O] _{total} (%)		18.7		8.7		5.4		5.9	

Note: O⁻_{ads}: the adsorbed “O⁻” ions on surface; O²⁻_{latt}: the lattice “O²⁻” ions; O⁻_{latt}: the lattice “O⁻” ions.

5.2 The Conduction Properties for Synthesized SrTiO₃

Material

The ac impedance characterization of the synthesized nano-sized SrTiO₃ has been investigated to elucidate the mechanism of the anomalous positive slope in Arrhenius plot. The two anomalous positive slopes are: (a) below 70 °C regime that is near zero positive slope; and (b) below the 40 °C regime that is positive slope. These are measured for the synthesized nano-sized SrTiO₃ in nitrogen and 20% oxygen in background nitrogen at different operating temperatures.

Normally, the slope has a negative value for the semiconductor characteristics in the Arrhenius plots against temperature as given in equation (2.3) ($\sigma = A \exp(-E_a / KT) P_{O_2}^{1/m}$) [5]. However, the anomalous positive slopes in the Arrhenius plots against temperature in oxygen ambient have been reported in SnO₂ around 160 °C, ZnO around 220 °C as well as other materials around 150-250 °C [152, 153]. The anomalous conductance changes induced by the oxygen in these reported materials are due to the conversion of chemisorbed oxygen from superoxide ion ($\frac{1}{2}(O_{2\text{ ads}})^{\cdot -}$) to oxide ion (O_{ads}^-) as the operating temperature changing from below to above a certain temperature. It is confirmed by EPR measurements [152]. For the dc electrical property of our synthesized nano-sized SrTiO₃ material in figure 5-8, there are three slopes in Arrhenius plots against temperature in oxygen ambient. Above 70 °C region, the slope is normally negative; between 40-70 °C region, the slope is near to zero; and below 40 °C, the anomalous positive slope occurs. This is the first time to report the anomalous positive slope phenomenon in SrTiO₃ materials. In order to further reveal the mechanisms of the anomalous positive slope and 40 °C optimal operating

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temperature for the synthesized nano-sized SrTiO₃ material, the ac impedance and dc I-V characterizations of the material were investigated.

Figure 5-8 Arrhenius plot of the electrical conductance vs 1000/T for the synthesized nano-sized SrTiO₃-based sensor with 400 °C annealing temperature in 20% O₂ in background N₂.

5.2.1 The ac Electrical Conductivity Properties

Figures 5-9 and 5-10 show the variations of $|Z|$ and theta with respect to the frequency for the synthesized SrTiO₃ (120h milling) with annealing temperature at 400 °C and operating temperature at 40 °C in N₂ and 20% O₂ in background N₂, respectively.

Figure 5-11 shows the impedance spectra of synthesized SrTiO₃ samples with annealing at 400 °C and operating at 40 °C in N₂ and 20% O₂ in background N₂ respectively. Using the Zplot software (Scribner Associates) analysis, the equivalent circuit of the synthesized SrTiO₃ material derived from the impedance spectra can be represented by two parallel RC network as shown in figure 5-12. The fitting

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parameters R_{Gb} , C_{Gb} , R_{GS} , and C_{GS} represent the resistance and capacitance of the grain boundary and grain surface for the synthesized SrTiO₃ material, respectively.

Figure 5-9 The variation of $|Z|$ with frequency for the synthesized nano-sized SrTiO₃ (120h milling) with annealing temperature at 400 °C and operating at 40 °C in N₂ and 20% O₂ in background N₂.

Figure 5-10 The variation of theta with frequency for the synthesized nano-sized SrTiO₃ (120h milling) with annealing temperature at 400 °C and operating at 40 °C in N₂ and 20% O₂ in background N₂.

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Figure 5-11 Impedance spectra of synthesized nano-sized SrTiO₃ samples with annealing at 400 °C and operating at 40 °C in N₂ and 20% O₂ in background N₂.

Figure 5-12 The ac equivalent circuit model.

When the grain size is small enough ($D < 2L$), the material resistivity is determined mainly by grain surface control or surface conduction type (figure 1-1 [6]). The depletion layer affected by gas adsorption almost takes over the whole grain. Although there is also some grain-boundary component in the material (figure 1-1 [6]), the resistance and the capacitance of the grain surface constitute the main part in the material. Hence, the time constant $R_{GS}C_{GS} > R_{Gb}C_{Gb}$, and the second semicircle at low frequency represents the grain surface effect. It is different from the conventional coarse semiconductor

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metal oxide materials ($D \gg 2L$), where the material resistivity is determined mainly by grain-boundary control or bulk conduction type (figure 1-1 [6]). The resistance and the capacitance of the grain boundary constitute the main part in the material. Hence, the time constant $R_{Gb}C_{Gb} > R_G C_G$ (R_G , C_G represent the resistance and capacitance of the grain bulk for the material respectively), and the second semicircle at low frequency represents the grain boundary effect.

Our sample for the ac impedance experiment is a discs with simple electrode geometry in sandwiched structure. Hence, the current distribution is relative uniform and there is almost no frequency dispersion arising from the electrodes [154]. Due to the lower operating temperature, the time constant of the material will often increase [154]. Hence, a bigger semicircle for the grain surface is observed within the lower frequency in our material as shown in figures 5-11 and 5-12.

The corresponding material conductivity of the grain boundary and grain surface, σ_{Gb} and σ_{GS} , can be approximate calculated according to the formula:

$$\sigma = t / (\pi r^2 R) \quad (5.10)$$

where t is the thickness of the pressed disc; r , the radius; and R , fitted resistance value for the grain boundary or grain surface. For the same sample, t and r are constants.

Figures 5-13 and 5-14 show the Arrhenius plot of $\ln \sigma$ (including grain, grain boundary parts) vs. $1000/T$ in the operating temperature range of 25-70 °C for the synthesized nano-sized SrTiO₃ with annealing at 400 °C in 20% O₂ in background N₂, and in N₂, respectively. Above 70 °C range, the measured data range has gone beyond the resolution of the characterization system and hence the experimental results were meaningless and hence not collected. This is alright for us since we are mainly interested on the non-negative slope mechanisms and the 40 °C optimal operating temperature for the synthesized nano-sized SrTiO₃ material that our research mainly

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focuses on. There are two positive slopes at the 40 °C boundary in Arrhenius plot for the synthesized nano-sized SrTiO₃ in 20% oxygen in background nitrogen below 70 °C regime in figure 5-13. This is consistent with the dc characterization of Arrhenius plots against temperature in oxygen ambient for the synthesized nano-sized SrTiO₃-based sensor in figure 5-8. where it has a near zero positive slope in the 70-40 °C regime. The slopes in the Arrhenius plots change from negative value above 70 °C to positive value below 40 °C as the operating temperature decreases. This anomalous phenomena for the two distinct positive slopes in our synthesized nano-sized SrTiO₃ material should not be only due to the reported conversion of chemisorbed oxygen from $\frac{1}{2}(\text{O}_{2\text{ ads}})^-$ to O_{ads}^- as the operating temperature changing from below to above a certain temperature [152] but also the presence other mechanisms which will be discussed next.

Figure 5-13 Arrhenius plot of $\ln \sigma$ vs. $1000/T$ for synthesized nano-sized SrTiO₃ with annealing at 400 °C characterized in 20% O₂ in background N₂ at different operating temperatures.

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In section 5.1.2, the Type II sensing mechanism (equation (4.7)) established by the Po₂ dependence of the conductance was confirmed by XPS results. That means the singly ionized (V_O[•]) is the main defect in the synthesized nano-sized SrTiO₃ material. In the following part, we will discuss Type II sensing mechanism (equation (4.7)) based on thermodynamic analysis.

$p = K_2 [\text{V}_{\text{O}}^{\bullet}] \text{P}_{\text{O}_2}^{1/2}$ (4.8)

In addition to the definition in the formalism of Kröger and Vink earlier [64], the following notations and their representation are: (O_{2 ads})' and (O_{ads})' represent the chemisorption of superoxide ion O₂⁻ and oxide ion O⁻, respectively.

Figure 5-14 Arrhenius plot of $\ln \sigma$ vs. $1000/T$ for synthesized nano-sized SrTiO₃ with annealing at 400 °C characterized in N₂ at different operating temperatures.

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For the thermodynamic analysis of the activation energies of the synthesized nano-sized SrTiO₃, we can refer to the thermodynamic analysis of the conventional SrTiO₃ oxygen gas sensors at the 1000-1400 °C operating temperature first [39].

The equation (4.7) can be expressed in a series of reactions:

At lower temperatures (about 550 K) the oxygen vacancies become singly ionized $\text{V}_\text{O}^{\cdot}$ (equation (5.11)) [155]. Equation (2.4) describes the generation-recombination of electronic defects [17, 39].

The mass-action law for equations (2.2), (2.4) and (5.11) can be formulated as:

$$[\text{V}_\text{O}^{\cdot\cdot}] n^2 \text{Po}_2^{1/2} = K_{\text{Red}}(T) = K_{\text{Red}}^{\circ} \exp(-\Delta H_{\text{Red}} / (kT)) \quad (2.8)$$

$$np = K_i(T) = K_i^{\circ} \exp(-E_g / (kT)) \quad (2.13)$$

$$[\text{V}_\text{O}^{\cdot\cdot}] n / [\text{V}_\text{O}^{\cdot}] = K_{\text{V}_{\text{O}1 \rightarrow 2}}(T) = K_{\text{V}_{\text{O}1 \rightarrow 2}}^{\circ} \exp(-E_{\text{V}_{\text{O}1 \rightarrow 2}} / (kT)) \quad (5.12)$$

Besides $K_{\text{Red}}(T)$, $K_i(T)$, ΔH_{Red} (6.1 eV) and E_g (3.2 eV) for SrTiO₃ material in chapter 2 [39], $K_{\text{V}_{\text{O}1 \rightarrow 2}}(T)$ and $E_{\text{V}_{\text{O}1 \rightarrow 2}}$ (0.3 eV) represent the equilibrium constant and endoenergetic respectively for the reaction from $\text{V}_\text{O}^{\cdot}$ to $\text{V}_\text{O}^{\cdot\cdot}$ at the temperature T [39].

Combining with equations (2.8), (2.13) and (5.12):

$$p = (K_i^{\circ} (K_{\text{Red}}^{\circ})^{-1} (K_{\text{V}_{\text{O}1 \rightarrow 2}}^{\circ})) \exp((\Delta H_{\text{Red}} - E_{\text{V}_{\text{O}1 \rightarrow 2}} - E_g) / (kT)) [\text{V}_\text{O}^{\cdot}] \text{Po}_2^{1/2} \quad (5.13)$$

Equation (5.13) should be corrected with the intrinsic threshold voltage V_T for the very low temperature ambient condition due to $\text{V}_\text{O}^{\cdot}$ being in “frozen-in” condition at this temperature [156, 157].

$$p = (K_i^{\circ} (K_{\text{Red}}^{\circ})^{-1} (K_{\text{V}_{\text{O}1 \rightarrow 2}}^{\circ})) \exp((\Delta H_{\text{Red}} - E_{\text{V}_{\text{O}1 \rightarrow 2}} - E_g - V_T) / (kT)) [\text{V}_\text{O}^{\cdot}] \text{Po}_2^{1/2} \quad (5.14)$$

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For the synthesized nano-sized SrTiO₃ disc sample, a V_T value of 2.37 eV was obtained from the I-V characterization in figure 5-16. The equation (5.14) is consistent with the equation (4.8).

The activation energy E_a 0.23 eV calculated from the equation (5.14) ($\Delta H_{\text{Red}} - E_{V_{O1} \rightarrow 2} - E_g - V_T$) is consistent with the experimental value of 0.17 eV obtained for the grain type of conductivity for the synthesized nano-sized SrTiO₃ material operating between 40-70 °C range as shown in figure 5-13. In all the thermodynamic analysis, there is always a certain error that is hard to avoid, for example the ΔH_{Red} in equation (5-14) is 6.1 ± 0.2 eV [39]. Comparing to this ± 0.2 eV error; our 0.06 eV error between the calculated and experimental values is considered very small and is reasonable. From the calculation for all the activation energies for Type I and Type II in n-type and p-type, only Type II in p-type material can give rise to a positive slope in the Arrhenius plot against temperature. This explains the mechanism of the positive slopes below the 70 °C regime for the synthesized nano-sized SrTiO₃ material in oxygen ambient in figure 5-13 that is due to the main $V_{O'}$ defect in p-type material.

From figure 5-13, it can be observed that the activation energy of the grain boundary and grain surface for the 40-70 °C range is about 1.13-1.3 eV lower than that for below 40 °C range. Again it fits with the reported process of the chemisorbed $\frac{1}{2}(\text{O}_{2\text{ ads}})^-$ corresponding to the exothermic energy of 1.45 eV [47, 152]. As reported for solid state oxygen gas sensor, oxygen is mainly chemisorbed as $\frac{1}{2}(\text{O}_{2\text{ ads}})'$ at 27 °C and above 50 °C the $(\text{O}_{\text{ads}})'$ ions become the dominant chemisorbed ions [157]. It shows that the phenomenon for the chemisorption $\frac{1}{2}(\text{O}_{2\text{ ads}})'$ below 40 °C operating temperature and $(\text{O}_{\text{ads}})'$ above 40 °C operating temperature for our material is consistent. This is also the reason for the positive slopes of the Arrhenius plot for other materials [152, 153]. The transition temperature at 40 °C is also consistent with the 40

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°C optimal operating temperature for our synthesized nano-sized SrTiO₃-based oxygen gas sensor in figure 4-26.

Another evidence of the chemisorption $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ for below 40 °C and $\text{O}_{\text{ads}}^{-}$ for above 40 °C on the synthesized nano-sized SrTiO₃ material surface can also be verified through the analysis for the capacitances of the grain surface and grain boundary parts of the material. The capacitances of the grain surface and grain boundary parts of the synthesized nano-sized SrTiO₃ material originate from the depletion layer due to the chemisorption oxygen on the material surface. In table 5-3, the capacitances of the grain surface and grain boundary parts of the synthesized nano-sized SrTiO₃ material were derived from the impedance spectra of the material with different operating temperatures in 20% O₂ in background N₂.

Using the model of a spherical capacitor of two concentric spheres with radii a and b ($b > a$) as shown in figure 5-15, one grain capacitance of the material can be approximately obtained from equation (5.15) [158].

$$C = 4\pi\epsilon / (1/a - 1/b) \tag{5.15}$$

where $2b$ is considered the average grain size of the material. It is a constant for one material. $2a$ can be seen as the core diameter of the grain material, which is approximately equal to the grain diameter $2b$ minus two times the width of the depletion layer of the material. The larger the $2a$ value of the material, the larger the capacitance value of the material as in equation (5.15).

Figure 5-15 Spherical capacitor.

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Table 5-3. The capacitance of grain surface and grain boundary parts of the synthesized nano-sized SrTiO₃ in 20% O₂ in background N₂, respectively. (C_{Gb}: the capacitance of grain boundary; C_{GS}: the capacitance of grain surface.)

Operating temperate	20% O ₂ in N ₂	
	C _{Gb} (F)	C _{GS} (F)
Below 40 °C	1E-10	2.5E-6
Above 40 °C	8E-11	2.27E-6

If the main chemisorption oxygen on the synthesized nanosized SrTiO₃ material surface would change from $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ to $\text{O}_{\text{ads}}^{-}$ as the operating temperature increased from the below 40 °C to the above 40 °C range, it should lead to the electrical charge distribution density increasing on the surface of the material and result in values of C_{Gb} and C_{GS} of the material decreasing for the p-type property of the synthesized nano-sized SrTiO₃ material in the range of P_{O₂} 0.03-1 atm. The results obtained in table 5-3 showed that the values of C_{Gb} and C_{GS} for the material in 20% O₂ in background N₂ for the above 40 °C range are lower than those of the below 40 °C range. Hence, the chemisorption $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ below 40 °C and $\text{O}_{\text{ads}}^{-}$ above 40 °C on the synthesized nano-sized SrTiO₃ material respectively hold true here.

Comparing figures 5-14 to 5-13, there is almost no change in the grain boundary activation energy in the below and above 40 °C operating temperature ranges, respectively. This is due to the fact that grains for the synthesized SrTiO₃ material are in the nano-sized range exhibiting grain surface control or surface conduction type [6, 108].

The change of the material electrical conductance in different ambient is mainly determined by the depth change of the space-charge layer of the material, or grain

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surface control [6, 108]. The difference of 0.9 eV between the grain surface activation energies in 20% O₂ in background N₂ and in N₂ for the below 40 °C operating temperature also serves to verify that this big difference in the activation energies (compared to the difference value of 0.06 eV for the above 40 °C) actually originate from the exothermic energy of 1.45 eV for the chemisorbed $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ on the material surface below 40 °C [47, 153].

The dc I-V relation of the synthesized nano-sized SrTiO₃ material will further confirm the presence of chemisorption $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ below 40 °C on material surface.

5.2.2 The dc I-V Relation

Figure 5-16 shows the I-V relation of the synthesized nano-sized SrTiO₃ material with annealing at 400 °C and operating at 40 °C in the ambient of 20% O₂ in background N₂ and N₂, respectively.

Figure 5-16 I-V relation of the synthesized nano-sized SrTiO₃ material with 400 °C annealing temperature and operating at 40 °C.

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In this figure, the slope of 0.18 for the I-V relation of the synthesized SrTiO₃ material in N₂ or 20% O₂ in background N₂ is almost the same; only the threshold voltages (V_T) of the material are different and they are 2.37 V in 20% O₂ in background N₂ and 3.79 V in N₂. Their I-V expression can be expressed as:

$$I_{20\% O_2} = 0.18 (V - V_{T 20\% O_2}) = 0.18 (V - 2.37) \quad (5.16)$$

$$I_{N_2} = 0.18 (V - V_{T N_2}) = 0.18 (V - 3.79) \quad (5.17)$$

The V_{T 20% O₂} is lower than the V_{T N₂} by 1.42 V for the synthesized nano-sized SrTiO₃ material. This 1.42 eV difference in energy for the synthesized nano-sized SrTiO₃ material (with operating at 40 °C in 20% O₂ in background N₂) is required to compensate the exothermic energy of 1.45 eV (or 140 kJ/mole [47]) for the chemisorption process on the material surface from 1/2O₂^(g) to 1/2(O_{2 ads})⁻, this again points towards the fact that the chemisorption oxygen type on the synthesized nano-sized SrTiO₃ surface below 40 °C is mainly 1/2(O_{2 ads})⁻.

With the different chemisorption 1/2(O_{2 ads})⁻ below 40 °C and O_{ads}⁻ above 40 °C for the synthesized nano-sized SrTiO₃ material, equation (4.7) could further be resolved as:

a). Below 40 °C operating temperature, $1 \times 10^4 \leq P_{O_2} \leq 2 \times 10^5$ ppm:

b). Above 40 °C operating temperature, $1 \times 10^4 \leq P_{O_2} \leq 2 \times 10^5$ ppm:

5.3 The Electrical Transport Properties for Synthesized SrTiO₃ Material with different Po₂

Among the metal oxide semiconducting oxygen gas sensing materials, SrTiO₃ materials have been most studied. Their electrical conduction mechanisms in oxygen ambient are also well-established in the relative high operating temperature range (> 700 °C) [[8, 16, 22, 38-39, 101]. However, their conduction behaviours in oxygen ambient at the low temperature regime are relatively unknown. In order to investigate their low temperature oxygen sensing conduction mechanisms, their electrical transport property analysis in the different oxygen partial pressures (Po₂) and the different operating temperatures for the materials were carried out.

Figure 5-17 Po₂ dependences of the conductance of the nano-sized synthesized and commercial SrTiO₃ sensors respectively with annealing at 400 °C operating at 40 °C.

Figure 5-17 shows the Po₂ dependences of the electrical conductance for the nano-sized synthesized and commercial SrTiO₃ sensors with annealing at 400 °C and

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operating at 40 °C temperature. For the synthesized nano-sized SrTiO₃ sensor the slopes of the $\log \sigma$ to $\log P_{O_2}$ are 1/2.18 (p-type) in the P_{O_2} range of 0.03-1 atm and -1/3.9 (n-type) in the P_{O_2} range of 1-5 atm. While those for the commercial nano-sized SrTiO₃ sensor are 1/3.85 (p-type) and -1/3.8 (n-type), respectively. This anomalous p- to n-type conduction transition with respect to increasing P_{O_2} is the first reported work for SrTiO₃ materials and totally different from the reported works on the conventional SrTiO₃ materials that exhibit the property of n-type conduction in the low P_{O_2} range and p-type conduction in the high P_{O_2} range above 700 °C operating temperature [8, 16, 38-39]. The difference can be explained from the relationship of the resistance with the operating temperature for the synthesized nano-sized SrTiO₃ sensor in 20% O₂ in N₂ as shown in figure 5-18.

Figure 5-18 The relationship of the resistance with operating temperature in 20% O₂ in N₂ for the synthesized nano-sized SrTiO₃ material with a rate of 2 °C/minute.

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For temperature range below 40 °C the synthesized SrTiO₃ material displays the positive temperature coefficient of resistance (PTCR) behaviour. This is consistent with the PTCR behaviour for the conventional SrTiO₃-based materials reported below certain temperature [159, 160]. The conventional SrTiO₃-based materials normally operate above 700 °C and away from PTCR range in the NTCR (the negative temperature coefficient of resistance) range [159, 160]. Hence the p-type property is observed for the synthesized nano-sized SrTiO₃ initially in the low Po₂ range when the operating temperature is at 40 °C or below.

The electrical transport property analysis from the defect chemistry aspect for the materials is further carried out. According to the formalism of Kröger and Vink [64], the following notations represent: $\text{Sr}_{\text{Sr}}^{\times}$: the regular strontium site; $\text{V}_{\text{Sr}}^{\times}$: the strontium vacancy; $\text{V}_{\text{Sr}}^{\prime\prime}$: the strontium vacancy with twofold-ionized negatively; $\text{V}_{\text{Sr}}^{\prime}$: the strontium vacancy with single-ionized negatively; $\text{O}(\text{II})_{\text{O}(\text{II})}^{\times}$: the regular oxygen site with the double-charged “O²⁻” ions in the lattice oxygen; $\text{V}_{\text{O}(\text{II})}^{\times}$: the oxygen (the double-charged “O²⁻” ions in the lattice oxygen) vacancy; $\text{V}_{\text{O}(\text{II})}^{\prime\prime}$: the oxygen (the double-charged “O²⁻” ions in the lattice oxygen) vacancy with twofold-ionized positively; $\text{V}_{\text{O}(\text{II})}^{\prime}$: the oxygen (the double-charged “O²⁻” ions in the lattice oxygen) vacancy with single-ionized positively; $\text{O}(\text{I})_{\text{O}(\text{I})}^{\times}$: the regular oxygen site with the single-charged “O⁻” ions in the lattice oxygen; $\text{V}_{\text{O}(\text{I})}^{\times}$: the oxygen (the single-charged “O⁻” ions in the lattice oxygen) vacancy; $\text{V}_{\text{O}(\text{I})}^{\prime}$: the oxygen (the single-charged “O⁻” ions in the lattice oxygen) vacancy with single-ionized positively; $\text{O}(\text{II})_{\text{O}(\text{I})}^{\prime}$: the oxygen (the double-charged “O²⁻” ions) in the regular oxygen site (the single-charged “O⁻” ions) with single-ionized negatively; K_3 to K_{14} , are the equilibrium constants for the reactions respectively.

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In the Po₂ range of 0.1-1 atm, the 1/3.85 slope gradient of the log σ to log Po₂ detected for the commercial nano-sized SrTiO₃ sensor is very near 1/4, hence it has dominantly the defect of the double-charged oxygen vacancy ($V_{O(II)}''$) and the p-type mechanism of Type I [8, 16, 38-39]:

However, at lower temperatures (about 550 K) the oxygen vacancies become singly ionized, $V_O^{\cdot}$ [155]. Hence in the low-temperature regime around room temperature, all oxygen vacancies reported are of the singly ionized ($V_O^{\cdot}$) [39, 155, 156]. The mechanisms for the commercial nano-sized SrTiO₃ should therefore include the following equations:

The mass-action law of equations (5.22)-(5.24) can be formulated as:

$$p^2 = K_3 [V_{O(II)}''] Po_2^{1/2} \quad (5.25)$$

$$[V_{O(II)}^{\cdot}] / ([V_{O(II)}''] n) = K_4 \quad (5.26)$$

$$[V_{O(II)}^{\cdot}] n / [V_{O(II)}^x] = K_5 \quad (5.27)$$

Combining with equations (5.25)-(5.27), we obtained:

$$p = (K_3 (K_4 K_5)^{-1})^{1/2} ([V_{O(II)}^{\cdot}] [V_{O(II)}^x]^{-1/2}) Po_2^{1/4} \quad (5.28)$$

The singly ionized oxygen vacancy ($V_{O(II)}^{\cdot}$) concentration in Form I of the conventional SrTiO₃ structure is controlled by a strong thermal-activated diffusion mechanism; and at temperatures below 400 K, these $V_{O(II)}^{\cdot}$ can be regarded as “frozen-in” [155, 156]. $[V_{O(II)}^x]$ in the high Po₂ (Po₂ > 10⁻⁴ atm) is very small and its change can be omitted [62]. Hence,

$$\log \sigma \propto 1/4 \log Po_2 \quad (4.6)$$

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In the Po₂ range of 1-5 atm, the commercial nano-sized SrTiO₃ material shifts to the n-type and has -1/3.8 (near -1/4) slope gradient in curve of the log σ to log Po₂ (figure 5-17). In this higher Po₂ range, the *intrinsic acceptors* strontium vacancies are created in oxygen-rich atmospheres [39].

In the low-temperature regime, oxygen vacancies and strontium vacancies reported are of the singly ionized ($\text{V}_{\text{O}}^{\cdot}$) and ($\text{V}_{\text{Sr}}^{\cdot}$) [39, 155, 156]. Therefore, equation (5.29) should be combined with the following equations:

This is consistent with the conventional undoped-SrTiO₃ material where strontium vacancies have been found to be the dominant intrinsic acceptors in oxygen-rich atmospheres [39, 90, 161, 162]. The shear structures (Ruddlesden–Popper phases, SrO_{R/P} [163, 164]) have also been proposed acting as a sink or source for the strontium.

The created $\text{V}_{\text{Sr}}^{\cdot}$ in the material will neutralize and consume the $\text{h}^{\cdot}$ in the material, while the $\text{V}_{\text{O}_{(\text{II})}}^{\cdot}$ in the material will introduce $\text{e}^{\cdot}$ in order to maintain the electroneutrality in the material. Hence,

The mass-action law of equations (5.29)-(5.33) can be formulated as:

$$[\text{V}_{\text{Sr}}''] [\text{V}_{\text{O}_{(\text{II})}}''] = K_6 \quad (5.34)$$

$$[\text{V}_{\text{Sr}}^{\cdot}] / ([\text{V}_{\text{Sr}}''] p) = K_7 \quad (5.35)$$

$$[\text{V}_{\text{O}_{(\text{II})}}^{\cdot}] p / [\text{V}_{\text{O}_{(\text{II})}}''] = K_8 \quad (5.36)$$

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$$[V_{Sr}^x]/([V_{Sr}']p) = K_9 \quad (5.37)$$

$$[V_{O(II)}^x]/([V_{O(II)}']n) = K_{10} \quad (5.38)$$

Combined equation (5.28) with equations (5.34)-(5.38) we obtained:

$$n = ((K_3)^{-1/2}(K_4K_5)^{1/2}(K_6 K_7 K_8 K_9 K_{10})^{-1}) \cdot ([V_{O(II)}']^{-1} ([V_{Sr}^x] [V_{O(II)}^x]) [V_{O(II)}^x]^{1/2}) P_{O_2}^{-1/4} \quad (5.39)$$

In addition to the reason for $[V_{O(II)}']$ and $[V_{O(II)}^x]$ being constant which have been presented earlier, $[V_{Sr}^x] [V_{O(II)}^x]$ is constant at a certain temperature [39]. Hence,

$$\log \sigma \propto -1/4 \log P_{O_2} \quad (5.40)$$

For the synthesized nano-sized SrTiO₃ sensor, the 1/2.18 slope gradient of the $\log \sigma$ to $\log P_{O_2}$ in the P_{O_2} range of 0.03-1 atm is very near $1/2$, hence it has dominantly the defects of the single-charge oxygen vacancy ($V_{O(I)}'$) originating from the single-charge “O⁻” ions in the lattice oxygen as confirmed by XPS experiment and the p-type mechanism of Type II:

$$p = K_{11} [V_{O(I)}'] P_{O_2}^{1/2} \quad (5.42)$$

In comparison with the high P_{O_2} region for the convention SrTiO₃ material (above 700 °C), equation (4.4) exists.

At such a high temperature, the Schottky equilibrium is of importance when considering the strontium vacancies V_{Sr}'' . However, at the temperatures of interest here, the Schottky equilibrium is frozen. That is, the Sr vacancies are immobile giving rise to a constant V_{Sr}'' concentration that also fixes the V_O'' concentration under the electro-neutrality condition in very pure material. Here, the conductivity is determined only by the minority carriers, namely the electronic carriers, holes at high P_{O_2} and

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conduction electrons at low P_{O_2} . As a consequence, the $\log \sigma$ vs $\log P_{O_2}$ isotherms of pure SrTiO₃ usually reflect $\pm 1/4$ power laws [165].

For conventional SrTiO₃ material operating in the high-temperature regime (above 300 °C), even at very low P_{O_2} , the doubly ionized oxygen vacancies ($V_{O''}$) are the majority defect and its concentration depends on both the temperature and the oxygen partial pressure P_{O_2} of an ambient gas atmosphere [155, 156]. However, in the low-temperature regime around room temperature, all oxygen vacancies reported are of the singly ionized ($V_{O'}$) that is similar in our synthesized SrTiO₃ [39, 155, 156]. Similarly, the Sr vacancies $V_{Sr'}$ are immobile at low temperature and this constant $V_{Sr'}$ concentration [39] also gives rise to a constant $V_{O'}$ concentration under the electro-neutrality condition in very pure material. The $\log \sigma$ vs $\log P_{O_2}$ isotherms of pure SrTiO₃ reflect 1/2 power laws in equation (4.9). It is consistent with P_{O_2} dependence of the conductance for our material as shown in figure 5-17. Hence,

$$\log \sigma \propto 1/2 \log P_{O_2} \quad (4.9)$$

In the P_{O_2} range of 1-5 atm, the synthesized nano-sized SrTiO₃ material shifts to the n-type that has -1/3.9 (near -1/4) slope in $\log \sigma$ vs. $\log P_{O_2}$ (figure 5-17). Although this slope is similar to that for the commercial nano-sized SrTiO₃, the creation of the *intrinsic acceptors* strontium vacancies with increasing P_{O_2} in the range of 1-5 atm also occur mainly due to the oxygen-rich atmospheres [39].

In the low-temperature regime, strontium vacancies are the same as the singly ionized ($V_{Sr'}$) [39, 155, 156]. Hence, equation (5.30) is also added:

At the same time, with sufficient energy, the O(II) in the lattice of the material also fill the $V_{O(I)}^x$.

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The created V_{Sr}' in the material will also neutralize and consume the h' in the material, while the $\text{V}_{\text{O(I)}}^{\times}$ in the material will also introduce e' in order to maintain the electroneutrality in the material. Hence,

The mass-action law of equations (5.43)-(5.45) can be formulated as:

$$[\text{V}_{\text{Sr}}']^{1/2} [\text{V}_{\text{O(I)}}^{\cdot}] = K_{12} \quad (5.46)$$

$$[\text{O(II)}_{\text{O(I)}}'] [\text{V}_{\text{O(II)}}^{\times}] / ([\text{V}_{\text{O(I)}}^{\times}] n) = K_{13} \quad (5.47)$$

$$[\text{V}_{\text{O(I)}}^{\times}] / ([\text{V}_{\text{O(I)}}^{\cdot}] n) = K_{14} \quad (5.48)$$

For electroneutrality condition:

$$n + [\text{O(II)}_{\text{O(I)}}'] = [\text{V}_{\text{O(I)}}^{\cdot}] + p \quad (5.49)$$

Equation (5.49) can be simplified due to the low concentration of *intrinsic* ionization (n and p) [39]:

$$[\text{O(II)}_{\text{O(I)}}'] \approx [\text{V}_{\text{O(I)}}^{\cdot}] \quad (5.50)$$

Combined equation (5.42) with equations (5.35), (5.37), (5.46)-(5.48) and (5.50), we obtained:

$$n = (K_7 K_9)^{-1/4} (K_{11} K_{12} K_{13} K_{14})^{-1/2} (([\text{V}_{\text{Sr}}^{\times}] [\text{V}_{\text{O(II)}}^{\times}]) [\text{V}_{\text{O(II)}}^{\cdot}])^{1/4} P_{\text{O}_2}^{-1/4} \quad (5.51)$$

For the same reason presented earlier, $(([\text{V}_{\text{Sr}}^{\times}] [\text{V}_{\text{O(II)}}^{\times}]) [\text{V}_{\text{O(II)}}^{\cdot}])$ are constant. Hence,

$$\log \sigma \propto -1/4 \log P_{\text{O}_2} \quad (5.40)$$

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATION

In this thesis, the preparation of the nano-sized metal oxide semiconducting SrTiO_3 materials, characterization of the materials and the gas sensing properties of the devices have been systematically investigated. The sensing mechanisms for the different nano-sized SrTiO_3 materials have been analyzed in detail. The main conclusions and recommendation are presented in this chapter.

6.1 Conclusions

6.1.1 The Preparation of Nano-sized SrTiO_3 Materials

In this study on the nano-structured SrTiO_3 -based metal oxide semiconductor gas sensors, the high-energy ball milling technique was employed to prepare the nano-sized powders. The nano-sized SrTiO_3 powders with perovskite structure obtained from synthesized SrTiO_3 and commercial SrTiO_3 materials respectively during high-energy ball milling time at room temperature were studied by XRD and TEM. The change of the average grain sizes and lattice constants for the two materials during the whole high-energy ball milling process were investigated. Nano-sized powders with an average grain size of 27 nm for the two materials were obtained at 120h milling time. The DTA/TGA and FTIR results of the synthesized SrTiO_3 powders

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demonstrated that the high-energy ball milling is an effective route to synthesize the nano-sized SrTiO_3 material at room temperature for gas sensing applications. They also confirmed the thermal stability and humidity-resistant property of the synthesized material.

6.1.2 Sensing Properties of the Nano-sized SrTiO_3 Oxygen Gas Sensors

The thick film oxygen gas sensors were fabricated using the screen-printing process. The gas sensing properties for the nano-sized SrTiO_3 oxygen gas sensors were investigated systematically. The sensing properties of the synthesized nano-sized SrTiO_3 are found to be better than that of the commercial nano-sized and un-milled SrTiO_3 . The sensing properties of the synthesized nano-sized SrTiO_3 sensor device affected by the annealing temperature were studied in the range of 400-800 °C. The 400 °C annealing temperature is optimal due to the change of the grain size of the material (the smaller grain size of the material, the bigger its ratio of surface to bulk). The optimal relative resistance ($R_{\text{nitrogen}}/R_{20\% \text{ oxygen}}$) value of 6.35 is obtained for the pure synthesized nano-sized SrTiO_3 sample annealed at 400 °C and operating at 40 °C. This is comparable to the reported relative resistance of doped SrTiO_3 series oxygen gas sensors with operating temperature at 700-800 °C. The 40 °C operating temperature is much lower than that of conventional metal oxide semiconducting oxygen gas sensors (300-500 °C) and SrTiO_3 oxygen gas sensors (> 700 °C). The response and recovery times are 1.6 minutes and 5 minutes respectively. The detected range of 1-20 % oxygen is possible for our sensor material operating at near human-body temperature. The humidity has been confirmed to have no effect on the impedance property of the synthesized SrTiO_3 sensor.

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6.1.3 Sensing Mechanisms of the Nano-sized SrTiO₃ Materials

The sensing mechanisms for the nano-sized SrTiO₃ materials were investigated systematically. The XPS results reveal the different low-temperature oxygen sensing mechanisms for the synthesized (120h milling) and commercial SrTiO₃ (120h milling) respectively obtained by high-energy ball milling technique. The single-charged “O⁻” ions of the lattice oxygen in the synthesized SrTiO₃ (120h milling) material leads to the oxygen sensing mechanism of near ½ slope (the highest value ever reported) for the logarithmic relationship of the electrical conductivity to the oxygen partial pressure at near human body temperature. This is better than that of ¼ slope for the commercial SrTiO₃ (120h milling) at the same ambient. It allows these two nano-sized SrTiO₃ materials to be used for near human body temperature oxygen sensing especially in medical fields. The XPS results obtained from the synthesized nano-sized SrTiO₃ materials with the different annealing temperatures further manifest that the quantity of the mole ratio value of the single-charged “O⁻” ions in the lattice oxygen to the total oxygen directly affects the low-temperature oxygen sensing property for the synthesized nano-sized SrTiO₃ materials.

The ac impedance characterization has been investigated to enunciate the mechanism of the positive slopes in Arrhenius plot below 70 °C regime and 40 °C optimal operating temperature for the synthesized nano-sized SrTiO₃ in nitrogen and 20% oxygen in background nitrogen. The thermodynamic analysis for the V_O[•] defect in the p-type material reveals the mechanism of the positive slopes below the 70 °C regime. A transition point at the 40 °C boundary occurs below 70 °C range corresponding to two different activation energies in the Arrhenius plots against temperature for the synthesized nano-sized SrTiO₃. This is found to be due to the different forms of the chemisorption oxygen in the higher and lower than 40 °C temperature regimes. The

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chemisorption of superoxide ion $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$ below 40 °C and oxide ion $\text{O}_{\text{ads}}^{-}$ above 40 °C respectively, explained that the activation energies below 40 °C for the grain surface of the material are about 1.3 eV higher than that above the 40 °C range. This corresponds to the exothermic energy 1.45 eV for the process of the chemisorbed superoxide ion $\frac{1}{2}(\text{O}_{2\text{ ads}})^{-}$. The 40 °C transition temperature matches the dc optimal operating temperature of the gas sensor obtained.

The electrical transport property analysis of the synthesized nano-sized SrTiO_3 and the commercial nano-sized SrTiO_3 materials reveals the different low-temperature electrical conduction mechanisms in the range of Po_2 0.03-5 atm that fit the conductance plots of $\log \sigma$ vs $\log \text{Po}_2$. The anomalous transition from p-type to n-type at Po_2 of 1 atm and operating temperature 40 °C for these two materials were also explained. A detailed defect chemistry analysis was carried out to explain the p-type mechanism in the 0.03-1 atm Po_2 range with a slope of near 1/2 (the best value ever reported) for the synthesized nano-sized SrTiO_3 material was due to the presence of the singly charged “O⁻” ions in the lattice oxygen; and the near 1/4 for commercial nano-sized SrTiO_3 material respectively in the logarithmic relationship of the electrical conductance with Po_2 . In the range of Po_2 1-5 atm, the n-type synthesized nano-sized SrTiO_3 and commercial nano-sized SrTiO_3 materials have the same near - 1/4 slope gradient in the logarithmic relationship of σ with Po_2 but exhibit different oxygen conduction mechanisms.

6.2 Recommendations for Further Research

The select properties for the synthesized nano-sized SrTiO_3 oxygen sensors to the interference reducing gases such as CO, H_2 , hydrocarbons etc. are recommendation

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work. In addition, improving the response time for material by dopants is also an important research direction. There have been some references on improving the response properties and sensitivities for other materials [108, 166, 167].

The different mole ratio of Ti to Sr in deviating stoichiometric SrTiO_3 material series is possibly related to the quantity of the single-charged “O⁻” ions in the lattice oxygen in the materials, and hence it will affect the sensing properties of the SrTiO_3 material series. The detail micro-structure, XPS measurements, the sensing properties and electrical conduction properties of this material series are highly recommended as the extending works.

AUTHOR'S PUBLICATIONS

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