HYDROGEN GAS SENSORS BASED ON NANOCRYSTALLINE SnO_2 THIN FILMS GROWN ON DIFFERENT SUBSTRATES USING SOL-GEL SPIN COATING METHOD

by

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LIST OF SYMBOLS

T	Absolute temperature
$\mathring{A}$	Angstrom
A	Area of Schottky contact
V	Bias voltage
K	Boltzmann constant
CB	Conduction band
D	Crystallite size
I_{air}	Current in the presence gas
I_g	Current in the presence gas
I-t	Current- time
I-V	Current-voltage
A^{**}	Effective Richardson constant
q	Electron charge
E_o	Electron energy in vacuum
E_g	Energy Band gap
E_f	Fermi level
B	Full width at half maximum
n	Ideality factor
d_{hkl}	Inter-plane distance
a,c	Lattice constants
ε_a	Lattice strain
hkl	Miller indices
I_o	Saturation current
Φ_B	Schottky barrier height

X_o	Semiconductor electron affinity
S	Sensitivity
VB	Valance band
V	Voltage
Φ	Work function
λ	X-ray wavelength

LIST OF ABBREVIATIONS

EDX	Energy-dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscope
FWHM	Full width at half maximum
MSM	Metal-semiconductor-metal
MBE	Molecular beam epitaxy
NC	Nanocrystalline
ppm	Part per million
PLD	Pulsed laser deposition
W	Saturated hydrogen electrode
SBH	Schootky barrier height
sccm	Standard cubic centimeters per minute
XRD	X-ray diffraction

PENDERIA GAS HIDROGEN BERASASKAN SAPUT NIPIS NANOHABLURAN SnO_2 DITUMBUHKAN DI ATAS SUBSTRAT BERBEZA MENGGUNAKAN KAEDAH SALUTAN PUTARAN SOL-GEL

ABSTRAK

Salutan putaran sol-gel adalah kaedah suhu rendah (di bawah 100 ^oC) dan berkemungkinan kaedah berkos paling rendah bagi pertumbuhan nanohabluran (NC) SnO_2 di atas pelbagai substrat. NC SnO_2 mempunyai potensi menambahbaik sifat-sifat penderiaan gas peranti juga secara ketara mengurangkan kos. Saput nipis SnO_2 sedia endap dan disepuh lindap mengalami keretakan yang muncul dpermukaan SnO_2 dan mempamerkan kesan tindak balas negatif ke atas prestasi peranti. Oleh itu, nisbah isipadu berbeza bagi gliserin (0:1, 1:12, 1:8) telah ditambah kepada larutan sol bagi mengatasi masalah keretakan. Saput nipis NC SnO_2 ditumbuh di atas tiga substrat yang berbeza iaitu, Si (100) tanpa salutan, SiO_2/Si dan Al_2O_3. Mekanisma pertumbuhan NC SnO_2 disiasat melalui pembelauan sinar-X (XRD), mikroskop imbasan elektron medan pancaran (FESEM), spektroskopi sebaran tenaga sinar-X (EDX) dan spektroskopi Raman. Nisbah isipadu gliserin terbaik ialah (1:12) yang menyingkirkan keretakan dan menambahbaikan penghabluran. Analisis pembelauan sinar-X menunjukkan sifat amorfus bagi saput nipis sedia endap. Sampel yang disepuh lindap pada suhu 400 ^oC selama 2 jam dalam udara mempamerkan puncak pantulan yang bersetuju dengan struktur rutil tetragonal bagi SnO_2 pukal piawai. Meningkatkan suhu sepuh lindap dari 400 ke 600 ^oC telah menambahbaikan penghabluran dan meningkatkan saiz habluran. Di samping itu, pengurangan dalam keterikan dan kecacatan hablur yang tercetus semasa penumbuhan lapisan seperti perkehelan yang berpunca daripada ketaksempurnaan larutan dehidrasi timah klorida di dalam larutan etanol tulen. Namun, imej FESEM menunjukkan pembentukan

aglomeratan di permukaan saput nipis NC SnO_2 apabila sampel disepuh lindap pada suhu 600 ^oC. Oleh kerana itu, larutan sol didedahkan dengan masa haba penuaan berbeza (24 jam pada suhu bilik (RT), dan 6, 8 dan 10 jam pada suhu 70 ^oC). Daripada pemerhatian EDX, apabila masa haba penuaan meningkat bersama peningkatan suhu sepuh lindap, kepekatan unsur bendasing klorin (Cl) dan karbon (C) menurun secara mendadak manakala kepekatan elemen Sn dan O meningkat. Mod getaran A_{1g} bagi NC SnO_2 menunjukkan anjakan biru yang lemah dengan peningkatan masa haba penuaan berbanding dengan anjakan biru yang ketara dengan peningkatan suhu penyepuh lindapan. Keputusan ini menunjukkan bahawa penghabluran tinggi saput nipis SnO_2 tanpa aglomeratan di atas substrat SiO_2/Si dan Al_2O_3 terjadi bagi larutan sol dengan penuaan 8 jam pada 70 ^oC dan sampel disepuh lindap pada 500 ^oC. Bagi saput nipis SnO_2 yang ditumbuhkan di atas Si (100) tanpa salutan, masa penuaan larutan sol yang terbaik ialah 8 dan 10 jam pada 70 ^oC dengan suhu sepuh lindap masing-masing pada 500 ^oC dan 400 ^oC. Peranti pengesan gas hidrogen logam-semikonduktor-logam (MSM) telah dihasilkan melalui pengendapan penyentuh palladium (pd) di atas permukaan selaput nipis NC SnO_2. Ciri-ciri sentuhan *I-V* Schottky bagi semua penderia gas, telah diukur pada RT. Sifat penderiaan bagi gas H_2 adalah bolehulang meliputi masa ujian (50 min) bagi kepekatan gas H_2 yang berbeza pada suhu operasi yang berbeza. Penambahan gliserin ke larutan sol meningkatkan keliangan pada permukaan NC SnO_2, apabila sampel terdedah kepada penyepuhlindapan di atas takat didih gliserin, yang mana penyejatan gliserin itu membawa kepada penghasilan lompang, yang menjana nisbah kawasan permukaan kepada isipadu yang tinggi. Akibatnya, keadaan ini membenarkan proses penyerapan/penyahnyerapan molekul H_2 dan O_2 di atas permukaan saput nipis NC SnO_2, yang menambahbaik kepekaan peranti yang telah

difabrikasi. Kepekaan bagi penderia pertama dan kedua yang ditumbuhkan di atas substrat Si (100) tanpa salutan masing-masing adalah 120% dan 90%, dengan kehadiran 1000 ppm H_2/ disambungkan dengan N_2 dan udara kering. Kepekaan penderia yang difabrikasi di atas substrat SiO_2/Si meningkat ke 600%, dan kepekaan penderia yang difabrikasi di atas substrat Al_2O_3 meningkat sehingga ke 2570% bagi kepekatan gas yang sama. Tambahan lagi, kebolehulangan dan kepekaan dipertingkatkan dengan peningkatan suhu operasi. Nilai kepekaan peranti pengesan gas H_2 berdasarkan selaput nipis NC SnO_2 yang ditumbuhkan pada substrat Al_2O_3 mengatasi peranti rekaan lain dan menunjukkan prestasi yang tinggi untuk mengesan perbezaan kepekatan H_2 (150-1000 ppm) pada suhu yang berbeza (suhu bilik, 75 dan 125 ^oC) .

HYDROGEN GAS SENSORS BASED ON NANOCRYSTALLINE SnO_2 THIN FILMS GROWN ON DIFFERENT SUBSTRATES USING SOL-GEL SPIN COATING METHOD

ABSTRACT

Sol–gel spin coating is a low-temperature method (below 100 ^oC) and possibly the lowest cost method for growing nanocrystalline (NC) tin dioxide (SnO_2) on various substrates. NC SnO_2 has potential to improve the properties of gas sensor device while also significantly lowering the cost. As-deposited and annealed SnO_2 thin films suffered from cracks that appeared on the surface of the SnO_2 thin films and they exhibited negative response effects of device performance. Therefore, different volume ratios of glycerin (0:1, 1:12 and 1:8) are added to the sol solutions to overcome the problem of cracks. NC SnO_2 thin films are grown on three different substrates, namely, bare silicon Si (100), silicon dioxide SiO_2/Si, and sapphire Al_2O_3. The growth mechanisms for the NC SnO_2 are investigated through X-ray Diffraction (XRD), field emission scanning electron microscope (FESEM), Energy Dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. The best glycerin volume ratio determined is (1:12), which eliminated cracks and improved the crystallization. X-ray diffraction analysis indicated the amorphous nature of the as-deposited thin films. The samples annealed at 400 ^oC for 2 h in air exhibited reflection peaks that agreed with the tetragonal rutile structure of standard bulk SnO_2. Increasing annealing temperatures from 400 to 600 ^oC resulted in improvement in the crystallization and increase in the crystallite size. In addition, we observed a reduction of strains and crystalline defects induced during growth of the film such as dislocations, which originated from the incomplete dissolving of tin (II) chloride dihydrate in pure ethanol. However, FESEM images showed the formations of

agglomeration on the surface of NC SnO_2 thin films when the samples were annealed at 600 ^oC. Therefore, the sol solutions were exposed to different aging heat times (24 h at room temperature (RT) and for 6, 8 and 10 h at 70 ^oC). For the EDX observation, when aging heat time increased in the presence of increasing annealing temperatures, the impurity concentrations of chlorine (Cl) and carbon (C) elements decreased sharply while the concentrations of Sn and O elements increased. The A_{1g} modes of the NC SnO_2 showed a weak blue shift with increasing aging heat times as compared with a noticeable blue shift with increasing annealing temperatures. The results showed that the high crystallization for SnO_2 thin films without agglomerations on SiO_2/Si and Al_2O_3 substrates occurred for sol solution time of 8 h at 70 ^oC and the samples annealed at 500 ^oC. For the SnO_2 thin films grown on bare Si (100), the best sol solution aging times are 8 and 10 h at 70 ^oC at annealing temperatures of 500 ^oC and 400 ^oC, respectively. Metal-semiconductor-metal (MSM) hydrogen (H_2) gas sensor devices have been fabricated through the deposition of palladium (Pd) contacts on the top surface of NC SnO_2 thin film. The *I-V* characteristics of all the gas sensors are observed at RT. The sensing properties of H_2 gas sensor are repeatable over the test time (50 min) for different H_2 gas concentrations at different operating temperatures. The addition of glycerin to sol solutions increased the porosity of NC SnO_2 film when the sample is exposed to an annealing temperature above the boiling point of glycerin, of which the evaporation of glycerin leads to a production of voids, which provide a high surface-area to volume ratio. Consequently, this condition allowed for easy adsorption/desorption processes of H_2 and oxygen (O_2) molecules on the NC SnO_2 films surface, which improved the sensitivity of fabricated devices The sensitivity of the first and the second sensors grown on bare Si (100) substrates are 120% and 90%, respectively, in the presence of

1000 ppm H_2/ balanced N_2 and dry air. The sensitivity of the sensor fabricated on SiO_2/Si substrate increased to 600%, and the sensitivity of the sensor fabricated on Al_2O_3 substrates increased by up to 2570% for the same gas concentrations. Furthermore, the repeatability and sensitivity are enhanced with increasing operating temperatures. The sensitivity value of H_2 gas sensor device based on NC SnO_2 thin film grown on Al_2O_3 substrate outperformed other fabricated devices and showed high performance for detection different H_2 concentrations (150–1000 ppm) at different operating temperatures (room temperature, 75 and 125 ^oC).

CHAPTER 1

INTRODUCTION

1.1 Overview

High performance gas sensors have received great attention because of their importance in various fields, especially in chemical industries, safety systems, environmental monitoring and chimerical flame detection [1, 2]. Tin dioxide (SnO_2) displays versatile characteristics such as chemical sensitivity to several gases, high chemical stability, low cost and flexibility in fabrication [3, 4]. Furthermore, SnO_2 can be potentially applied in other applications such as thin film electroluminescent displays, solar cells and heat reflectors [5, 6].

SnO_2 based gas sensor is commonly studied because of its wide direct band gap (~3.6 eV) at 300 K as well as SnO_2 is an n-type semiconductor that has a tetragonal rutile structure [7-10]. Metal oxide-semiconductor exhibits sensitivity to a variety of gases in the atmosphere because of variation in their electrical characteristics [11]. SnO_2 dominates over of all other metal oxide-semiconductors and is the most widely used in the gas sensor field because of its many advantages such as low cost fabrication, higher sensitivity, thermal stable structure and low operating temperature [12]. In 1971, Naoyshi successfully fabricated and patented the first gas sensor device for practical applications using SnO_2 as the sensitive material [13]; since then, studies on SnO_2 gas sensors have been extensively developed. SnO_2 has been successfully used to detect various gases, including hydrogen (H_2), hydrogen sulfide (H_2S), nitrogen dioxide (NO_2), carbon monoxide (CO), oxygen (O_2), methanol (CH_4O) and ammonia (NH_3) [14-18].

In the current global economy, H_2 has become an important subject for the development of new sustainable energy because it is an efficient and clean energy source that is widely used as replacement of oil in automobiles, aircraft, fuel cells, and chemical industries [19, 20]. H_2 is an odorless, colorless and highly volatile, inflammable and explosive gas when its concentration in dry air is beyond 4% [20]. Consequently, H_2 gas sensors that show good performance at room temperature (RT) are highly required in the chemical industries and in environment applications to detect the formation of potentially explosive mixtures with air. Therefore, the gas sensors help prevent the risks of explosions and fires [21-23]. Moreover, H_2 gas sensors operate at RT that have numerous benefits such as low power consumption and cost-effective [21, 24], ability to be used safely in inflammable and toxic gases [25] and long lifetime [26].

The improvement of the gas sensing properties for the SnO_2 nanostructure is affected by several factors such as morphology, operating temperature, adsorption/desorption process and porosity for sensor design. The control on the gas parameters improves the sensitivity and selectivity of nanocrystalline (NC) SnO_2 sensors. These improvements are achieved by enhancement of film porosity, tuning of annealing temperature, and the modulation of the sensor operating temperature [27, 28]. The Schottky contact formation is an effective method to obtain a large barrier height in the metal-semiconductor (MS) contact for high performance gas sensors.

1.2 Motivations and problem statements

SnO_2 nanostructures can be prepared by several methods such as sol-gel spin coating [29], pulsed laser deposition (PLD) [30], hydrothermal [31], molecular beam epitaxy (MBE) [32] and thermal evaporation [33]. The sol–gel spin coating method

has been selected for the preparation of NC SnO_2 thin films because of its several advantages compared with other methods. This method is operated at low reaction temperatures, easy to process and not expensive. The film thickness can also be easily changed by changing either the spin speed or the viscosity [34].

Thin films deposited onto different substrates through the sol–gel spin coating method suffer from cracks problem at RT and at different annealing temperatures. Cracks occurred when the liquid evaporates from the gels during the drying processes, which result in gel shrinkage [35]. Glycerin can be added to the sol solution to overcome these cracks [36]. Therefore, a study on the effect of adding glycerin to the sol solutions with different volume ratios is required to select the best volume ratio of glycerin that should be added to the sol solution. Determining this volume ratio can eliminate cracks problem, in which glycerin contains three hydroxyl groups that can produce hydrogen bonds with other atoms [37, 38], and could contribute to improving the characterization. Through enhanced dissolving of tin (II) chloride dihydrate in pure ethanol and the formation of voids during glycerin evaporation, the porosity of the surface of the nanocrystalline (NC) SnO_2 thin film increases, thereby providing a high surface-area to volume ratio. Other factors such as increasing the aging heat times of sol solutions and annealing temperature can enhance the crystallization of SnO_2 thin films that are produced by sol- gel spin coating method.

Several factors can improve the crystallization of SnO_2 thin films such as aging heat times and annealing temperatures, but can also generate agglomerations, wherein the nanoparticles can be clumped together. These agglomerations are undesirable because they decrease the performance of the devices. Consequently, a study on the effects of aging heat times and annealing temperatures is necessary to

select the best crystallization of the SnO_2 thin films without agglomerations. Generally, gas sensing tests are carried out at high operation temperatures. SnO_2 thin film H_2 gas sensor indicated low performance when tested at operation temperature near to RT. Therefore, different substrates are used to determine the best crystallization parameters and low fabrication cost of NC SnO_2 thin films, which can improve the sensitivity of the gas sensor.

1.3 Scope of study

This study focuses on the growth of SnO_2 thin films on bare silicon [Si (100)], silicon dioxide (SiO_2) layer formed on Si(100) substrate (SiO_2/Si) and sapphire (Al_2O_3) substrates at low temperature using the sol-gel spin coating method. Studying the effect of adding glycerin at different volume ratios (0:1, 1:12 and 1:8) to the sol-solutions on the characterizations of NC SnO_2 thin films. Selecting the best values for different aging heat time and annealing temperature is specified to avoid the formation of agglomerations and to produce high quality NC SnO_2 without cracks and agglomerations. Therefore, the sol solutions exposed to different aging heat times (24 h at RT, and for 6, 8 and 10 h at 70 ^oC), and the as-deposited thin films exposed to different annealing temperatures (400, 500 and 600 ^oC) are investigated. The structural properties and surface morphology of thin films are analyzed by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. The optimized NC SnO_2 thin films deposited on different substrates are selected to fabricate gas sensors, which showed a high ability to detect H_2 gas when exposed to different concentrations of H_2 at different operating temperatures.

1.4 Objectives of the research

The main objectives of this research are as follows:

1. To prepare high quality NC SnO_2 thin films without cracks through the sol-gel spin coating method by investigating the best volume ratio of glycerin that should be added to the sol solutions.
2. To obtain the optimal growth and high characterization of NC SnO_2 thin films without agglomerations by exploring the best values of aging heat time and annealing temperature at a constant volume ratio of glycerin.
3. To fabricate metal-semiconductor-metal (MSM) H_2 gas sensors based on optimized NC SnO_2 thin films on (bare Si (100), SiO_2/Si and Al_2O_3) substrates, which can show good detector performance at different operating temperatures, especially at RT for different gas concentrations.
4. To improve H_2 gas sensor performance, especially at RT as well as increase the sensitivity and stability by enhancing the process of adsorption/desorption of gas molecules.

1.5 Originality of the research

This research provides the following originality to solve the problems presented in Section 1.2:

1- Selection of the best glycerin volume ratio that should add to the sol solutions to eliminate cracks problem, enhance the crystallization and increase surface porosity.

2- Selection of the best value of aging heat time and annealing temperature that can be produced high quality NC SnO_2 thin films without agglomerations.

3- Fabrication H_2 gas sensors based on NC SnO_2 thin films grown on bare Si (100) substrates that can be operated at RT, 75 and 125 ^oC.

4- Fabrication of gas sensors based on NC SnO_2 thin film grown on SiO_2/Si and Al_2O_3 substrates with high detection ability for different H_2 gas concentrations at operating temperatures (RT, 75 and 125 ^oC).

1.6 Outline of the research

The organization of the present study is as follows:

Chapter 1 introduces a brief overview of SnO_2 nanostructures, motivations and problem statements, scope of study, objectives and finally the originality of this research.

Chapter 2 provides a literature review for growth of SnO_2 nanostructures and gas sensors based on SnO_2 nanostructures. In addition, the sol-gel spin coating method is also presented. The theoretical background of the structural properties of SnO_2, surface properties, metal-semiconductor (MS) contact, gas sensing properties and sensing mechanism of SnO_2 nanostructures are discussed.

Chapter 3 presents the details of methodology and instruments systems that used to prepare and measure the NC SnO_2 thin films, as well as introduces the fabrication steps and gas sensing system of the MSM H_2 gas sensors.

Chapter 4 discusses the results of the preparation and characterization of SnO_2 thin films grown on bare Si (100), SiO_2/Si and Al_2O_3 substrates that exposed to different growth parameters.

Chapter 5 focuses on the current-voltage *I-V* characteristics of the fabricated sensors based on NC SnO_2 that have been grown on bare Si (100), SiO_2/Si and Al_2O_3 substrates. The performance of these sensors when exposed to different H_2

gas concentrations at different operating temperatures is also discussed.

Finally, **Chapter 6** presents the conclusions of the study and possible future works.

CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Introduction

Several studies have been conducted on the use of SnO_2 as a gas sensor because of its large band gap, thermal stability and low cost. This chapter presents a summary and literature review of the previous studies performed on the preparation of SnO_2 nanostructure, the structural characteristics, surface morphology investigations, and gas sensing properties. The factors that could contribute to the improvement of the performance of the fabricated SnO_2 nanostructure sensor are discussed. Moreover, this chapter also discusses the theoretical background of the tetragonal rutile structure of SnO_2 thin films; basic equations and issues related to metal-semiconductor contact and gas sensing behaviour.

2.2 Nanomaterials

In the last two decades, nanoscience and nanotechnology have been vital subjects because of their use in different applications such as gas sensor devices, photodetectors and solar cells. Nanomaterials exist in a dimension of less than 100 nm [39]. Nanostructured materials can be classified into four types comprising 0-dimensional (0D) (quantum dots, nanoparticles, etc.), 1-dimensional (1D) (nanotubes, nanorods and nanowires), 2-dimensional (2D) (thin films and nanosheets) and 3-dimensional (3D) (nanospheres). Nanomaterials are crucial in modern applications because of their unique physical and chemical characteristics.

Several methods can be used to prepare the nanostructured materials. These methods involve the liquid phase methods, mixed phase syntheses and gas phase methods. Selection on a suitable method is significant to determine the failure or success of the prepared nanostructured materials, due to their physical and chemical characteristics, and the applications of nanomaterials are powerfully reliant on how they are fabricated. Moreover, the significance of choosing a suitable method in forming nanomaterials has been a motivating force for the development of new methodologies.

2.3 Literature review for the growth of SnO_2 nanostructures and gas sensors based on SnO_2 nanostructures

2.3.1 Growth of SnO_2 nanostructures

Generally, SnO_2 nanostructures can be prepared using different methods on different types of substrates such as sol-gel spin coating, thermal evaporation, chemical precipitation, PLD and hydrothermal methods. As well as SnO_2 nanoparticles powders can be prepared without substrates by sol-gel method. These methods produce different growth morphologies such as nanoparticles, nanowires, nanobelts, nanospheres, nanosheet and NC SnO_2 thin films [40, 41].

2.3.2 Sol-gel spin coating method

Sol-gel spin coating method has been used to produce uniform thin films on flat substrates, which have several benefits, such its ability to operate at low reaction temperatures, relatively low cost and easy process [42]. This method was used in the 1950s by Larson and Rehg when they deposited phosphor on the glass surfaces of color television tubes [43].

At the beginning, sol solution should be prepared by dissolving the source of material, which is usually a salt material in a suitable solvent. These solvents depend on the type of source material, which should be one of water, organic material, acidic or alkaline substance. For example, the suitable solvent for dissolving tin (II) chloride dihydrate ($SnCl_2.2H_2O$) is ethanol (C_2H_5OH) [36]. Practically, the precursor solution is stirred using a magnetic stirrer at the appropriate temperature for times ranging from 1 to 24 h to achieve good dissolving ability for the source of material in the solvent [44, 45].

Figure 2.1 (a) shows the spin coating system used to deposit the sol-gel solution based on different types of substrates. The mechanism of spin coating process can be divided into four steps [46, 47]. The first step is dropping the solution on the center of the substrate using a micropipette. The second step is to accelerate the substrate gradually until it reaches to the desired final spin speed. In this step, the spin speed increases by increasing the centripetal acceleration and some amount of solution will be ejected from the edge of the substrate. The third stage starts when the substrate spins with a constant spin speed and the net solution that flows from the edge of the substrate becomes negligible and viscous forces dominate solution thinning behavior and its attachment on the substrate [48, 49], as shown in Figure 2.1 (b),

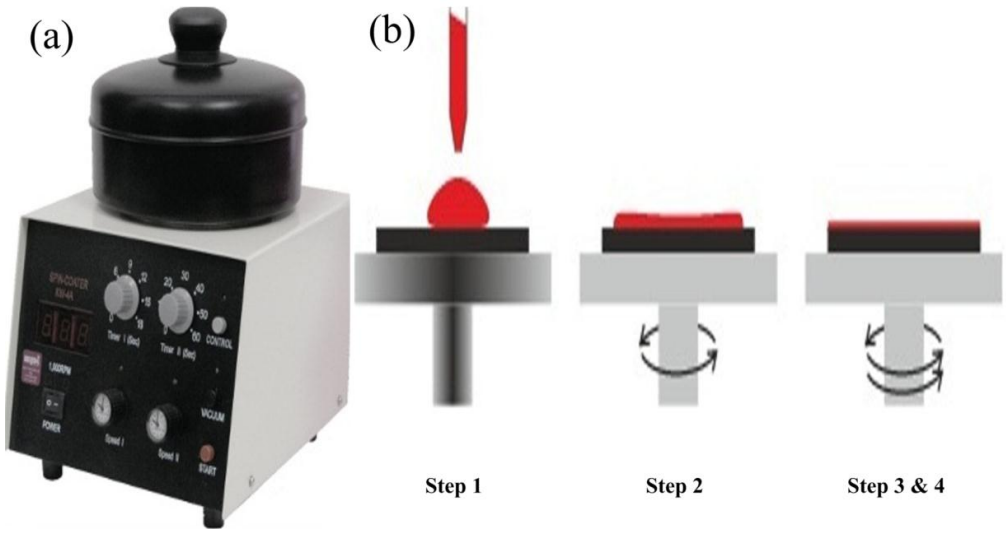

Figure 2.1: Spin coating process (a) spin coating system, (b) the four steps involved [50].

Finally, the fourth step begins during the spin-off when the spin speed of the substrate decreases gradually until it stops. During the spin-off, the substrate still spins, but the centrifugal outflow stops and further thinning of film occurs because of solvent evaporation. Then, the as-deposited thin film dried in an oven at a suitable temperature depending on the evaporation temperature of the solvent which ranging from 10 to 30 min [51] In addition, the vacuum pump device is part of the spin coating system that creates a vacuum and holds the film tightly to prevent it from slipping and breaking [52]. Spin speed should be slow to reduce the ejected amount of solution from the edge of the substrate in the second step. Thus, two spin speeds are used. The first spin speed should be slow, reaching approximately 500– 900 rpm, and last only for several seconds (applied in the second step). The second spin speed should be higher than the first spin speed, reach approximately 1500–5000 rpm, and last for a longer time to approximately 10–70 s (applied in the third step).

Film thickness depends on the nature of the sol solution such as viscosity, drying rate, percent solids (the concentration of material source) and surface tension.

Spin process factors can influence in the thickness of film such as spin speed, acceleration, amount of the delivered solution and spin time. Practically, the spin speed increases with increasing viscosity of solution. Fast spin speed and long spin time create thinner film [34]. The spin coating and drying operations should be repeated many times to increase the thickness of film [53].

Liu et al. [36] synthesized SnO_2 thin films on Al_2O_3 substrates through sol-gel spin coating method; the as-deposited thin films were amorphous. The samples were sintered in air at 550 ^oC for 2 h in order to obtain the crystallization of SnO_2 films. Glycerin was added to the sol solution to eliminate cracks. In addition, they studied the effect of cooling rate at 1800, 200, 100 and 25 $^oC/h$ and found the crystallite size was 21 ± 0.4 nm. Thus, they concluded that the cooling rate caused by the limitation influence on crystallite size of thin films, where the crystallites of SnO_2 ceases to grow up under the cooling process. Kose et al. [54] used the same method to synthesize SnO_2 thin films on glass substrates. The crystallization of thin films was achieved after the samples calcined in air at temperature reaching 600 ^oC at a heating rate of 2 ^oC /min. The formations of agglomerations were observed on the surface of films due to the increase of ethanol ratio with reduced glycerin ratio in the precursor solution that produced roughness of SnO_2 thin films. The adding glycerin leads to enhance film porosity and increased solution viscosity. XRD analysis indicated that the broadest (110) peak occurred because of the nanoparticles size became very small.

Sakai et al. [55] prepared SnO_2 thin films using spin coating method from a hydrothermal sol suspension on Al_2O_3 substrates. The samples were sintered at 600 ^oC for 3 h in air to obtain the crystallization of SnO_2 thin films. SnO_2 films with

thicknesses over 300 nm were selected and used to fabricate gas sensor devices. These thin films were selected because the cracks did not penetrate through the film down toward the bottom. The thickness of films increased steeply with increasing spin coating times. It was also found that the thickness of SnO_2 thin films ranged from 100 to 300 nm but the average size of grain was still of 6 nm on average.

Cha et al. [56] used spin coating method for the deposition of the washed gel of SnO_2 thin films on alumina substrate. Calcination temperatures affected grain size, morphology and microstructure of the films. XRD analysis showed improved crystallinity of SnO_2 thin films and increased grain size after increasing the calcination temperature from 500 to 900 ^oC. Surface morphology analysis demonstrated that cracks appeared on the surface of the films at different calcination temperatures and became larger at high calcine temperatures. This phenomenon decreased the stability of the mechanical attributes. Agglomerations also occurred in the grains during calcination.

Similar results were obtained by Esfandyarpour et al. [29] for SnO_2 thin films deposited on Si (100) substrates using sol-gel spin coating method. Superficial cracks appeared on the surface of SnO_2 films during calcination. However, they assumed that the superficial cracks did not penetrate via the film down to the bottom. Jeng [57] found that the as-deposited SnO_2 thin films on quartz glass substrates prepared by sol-gel spin coating method was amorphous. The crystallization of thin films was enhanced with increased annealing temperature in O_2 gas and in N_2 gas. SEM morphology showed a smooth surface for the as-deposited thin films. However, small nodules appeared on the surface of SnO_2 thin films after the films were annealed. Surface morphology changed from small to large nodules after annealing

temperature was increased from 300 to 500 ^{o}C. Izydorczyk et al. [58] successfully deposited SnO_2 thin films on SiO_2/Si substrates through sol-gel spin coating method. The crystallization and the diameter of nano-grains for different molar concentrations of the sol solution increased with increased annealing temperatures from 700 to 900 ^{o}C.

Similar method was used by Uysal and Arier [59] to prepare SnO_2 nano films on glass substrates with different concentration of water. They found that the crystallite size of SnO_2 increased from 6 to 22 nm with increasing annealing temperatures from 450 to 650 ^{o}C at volume ratio 1: 0.025 of $SnCl_2$: water.

Shoyama et al. [60] used same method to show that the addition of poly ethylene glycol (PEG) avoided the agglomerations of SnO_2 particles, which were deposited on Si (100) substrates. The topography images indicated that 3.3 wt.% of PEG is necessary to prevent the particle agglomerations of the SnO_2 particles, while the agglomerations of SnO_2 particles occurred in the PEG-free SnO_2 thin films. Furthermore, the thickness of the annealed thin films at 500 ^{o}C with the presence PEG 3.3 wt.% was around 600 nm and the particle size decreased from 30 to 10 nm after PEG was added to the sol solution. XRD analysis showed that the crystallinity of SnO_2 thin films improved with increased annealing temperatures from 500 to 800 ^{o}C.

Kaur et al. [61] used the same method to deposit SnO_2 nanoparticles on the float glass substrates. The degradation in the performance of the sensor based on these SnO_2 nanoparticles was noticed because of the agglomerations grown among nanoparticles. Indium-doped SnO_2 thin films with two different concentrations (5 wt% and 10 wt%) were used to resolve the problem of agglomerations of particles.

XRD analysis indicated that the full width at half maximum (FWHM) increased with increased in indium concentration in the SnO_2 films, thus, crystallite size decreased. Transmission electron microscope (TEM) micrographs demonstrated that the indium-doped SnO_2 thin films at concentration 10 wt% was suitable to prevent the problem of agglomerations of particles. Table 2.1 provides a list of NC SnO_2 thin films that were prepared by sol-gel spin coating method based on different types of substrates.

Table 2.1: Summary of the NC SnO_2 thin films prepared using sol-gel spin coating method.

Starting Materials	**Substrates**	**Ref.**
Tin (II) chloride dehydrate ($SnCl_2.2H_2O$), ethanol (C_2H_5OH) and glycerin ($C_3H_8O_3$)	Al_2O_3	[36]
Tin chloride ($SnCl_4$), alkohol (C_3H_8O) chloroplatinic acid ($H_2Cl_6Pt.6H_2O$)	Si (100)	[29]
Tin chloride pentahydrate ($SnCl_4.5H_2O$), antimony(III) acetate [$Sb(OAC)_3$] and ethanol (C_2H_5OH)	Quartz glass	[57]
Tin chloride pentahydrate ($SnCl_4.5H_2O$), and isopropanol (C_3H_8O)	SiO_2/Si	[58]
Tin cholide ($SnCl_2$), 2-methoxyethanol $CH_3OC_2H_4OH$ and poly ethylene glucol (PEG)	Si (100)	[60]
Tin chloride pentahydrate ($SnCl_4.5H_2O$), ethanol (C_2H_5OH) , water (H_2O) and indium chloride ($InCl_3$)	Float glass	[61]

2.3.3 Growth mechanism of SnO_2 thin films using sol-gel spin coating method

SnO_2 thin films can be prepared using sol-gel spin coating method operated at low reaction temperatures (below 100 ^oC) by dissolving tin (II) chloride dihydrate ($SnCl_2.2H_2O$) in pure ethanol (C_2H_5OH) for a few hours. Therefore, a solution containing compounds of tin (II) chloride ($SnCl_2$) and tin (II) hydroxide ($Sn(OH)_2$) is produced. This solution can be deposited on different substrates using spin coating system. Then, when the samples are exposed to anneal in air, the hydrogen atoms will start to be removed, chloride will evaporate and be replaced by oxygen atoms [38]. Given that the material tends toward stability, the oxygen atom creates a double bond with tin to produce tin dioxide (SnO_2); thus, the tin turn to tetravalent tin (IV).

Murugadoss et al. [62] found that, when $SnCl_2$ dissolved in the water solvent, uncontrolled $Sn(OH)_2$ nanoparticles may grow in the solution. That $Sn(OH)_2$ containing solution was deposited on a glass substrate and then annealed in air at 200 ^oC for 2 h, resulting in the formation of inhomogeneous SnO_2 nanoparticles by rapid oxidation.

The as-deposited and annealed SnO_2 thin films suffer from cracks [63]. Gaweł et al. [35] suggested that the cracks are generated due to the evaporation of the liquid from the gels during drying, which can cause gel shrinkage.

2.3.4 Glycerin as binding agent

Glycerin ($C_3H_8O_3$) is a colorless, odorless, viscous liquid and completely soluble in water and alcohol, the boiling point is 290 ^oC. Glycerin can be used to remove cracking during the drying processes of the gels [35]. This may be due to the existence of three hydroxyl groups that produce hydrogen bonds with a pair of acceptors (chlorine and oxygen), and donor (hydrogen) atoms [37, 38]. Therefore,

glycerin can prevent cracks through the physical interaction between the hydrogen atoms of hydroxyl group of glycerin and the two compounds $SnCl_2$ and $Sn(OH)_2$ as shown in Figure 2.2.

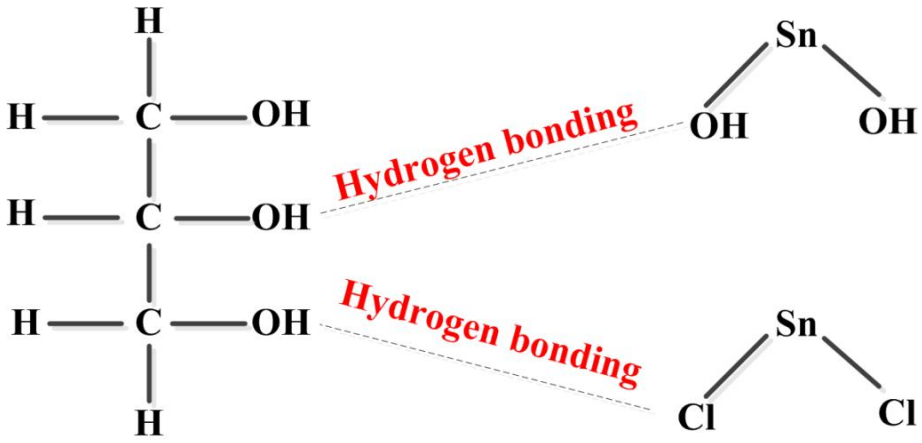

Figure 2.2 : Hydrogen bonding between glycerin and the compounds of $SnCl_2$ and $Sn(OH)_2$.

The solution can be deposited on different substrates and is exposed to air for annealing to obtain the SnO_2 thin films as explained in section 2.3.3. During the annealing step to a temperature above its boiling point, glycerin, similar to any organic compound, will turn to carbon dioxide (CO_2) and water vapor (H_2O) [64]. Therefore, voids will be formed after the removal of glycerin, leading to enhanced porosity of the annealed samples. Kose et al.[65] mentioned that the addition of glycerin leads to enhanced film porosity.

A diol such as methanediol ($H_2C(OH)_2$) with two hydroxyl groups can be a replacement for glycerin, however it dissolved only in water not in ethanol, thus glycerin is preferred.

2.3.5 SnO_2 morphology changes with annealing temperature

The annealing temperature is an important parameter that affect the surface morphology of SnO_2. The surface of the as-deposited thin film prepared using sol–

gel spin coating method exhibits a smooth and continuous morphology, as is in agreement with the amorphous nature of SnO_2 [66]. Thus, annealing is used to achieve crystallinity of the SnO_2 thin films. When the samples are annealed at an appropriate temperature to achieve crystallization, small nanoparticles can be obtained, and the surface appeared as polycrystalline. The particle size increased with increased annealing temperature. These results are attributed to the increased annealing temperature, which enhances crystallinity and defect reduction for thin films [58, 66]. At low annealing temperatures, the strong chemical bonds (covalent or ionic) dominate between primary particles. While at high annealing temperatures, weak bonds exist between primary particles, in which the particles are held together by the weak van der Waals forces to produce agglomerations [67-69]. These agglomerations are undesirable because they contribute to performance reduction for any device [70, 71].

Ansari et al. [72] and Sharma and Madau [73] mentioned that the sensing capability depended on both the ratio of the particle size and depletion width (L) of the material. When the crystallite size (D) is markedly larger than thickness of the depletion region ($D>>2L$), conduction electrons should move from grain to grain (conduction through the hopping of the electrons from grain to grain), across the potential barrier at each grain boundary (grain boundary control), and the height of the boundary varies according to the surrounding atmosphere. In this case, the sensitivity will be independent on the grain size. In addition, when D decreases to a closer degree to $2L$, the conduction electrons move through a channel penetrating each neck (neck control), which is normally formed by connecting the pores between the two neighboring grains. In this case, sensitivity is related to grain size through the neck size. When D is smaller than $2L$, the resistance of grains dominates, and the

gas sensitivity is controlled by grains themselves (grain control) and produces the largest gas sensor response. The other possible explanation for the increase in sensitivity with the decrease in particle size is the surface-to-volume ratio. Smaller diameter means higher surface-to-volume ratio and consequently, higher gas adsorption [74].

Jiang et al. [75] and Serventi et al. [76] showed that the porosity on the surface of SnO_2 samples could be extremely useful for sensing properties. Higher porosity increases surface to volume ratio of the materials. This enhances the gas diffusion inside the SnO_2 sample and thus improves sensitivity. Leem and Yu [77] and Li et al. [78] investigated the effect of annealing temperature on the properties of SnO_2 samples. They found that the increase in annealing temperature of the SnO_2 sample leads to improved crystallinity and increased porosity surface of SnO_2 sample, which enhance the sensing properties of the gas sensor.

2.3.6 Gas sensor based on SnO_2 nanostructures

Fields et al. [79] used thermal evaporation method to fabricate gas sensors based on SnO_2 nanobelts that were grown on SiO_2/Si substrates. PLD deposition method was utilized to deposit a thin film (~100 nm) of ruthenium oxide (RuO_2) onto the mask in order to obtain ohmic contact to the nanobelt. The sensor was tested for 20,000 ppm of H_2 gas at a temperature range 25-80 ^oC. The sensitivities of the SnO_2 nanobelts sensor was almost constant, as calculated by [$S=G_{gas} - (G_{air}/G_{air})$], where G_{gas} and G_{air} were the sensor conductance tested in gas and air, respectively. SnO_2 nanobelts sensor can be operated at RT with sensitivity about 60% and the response and recovery times were about 220 s.

Wang et al. [4] investigated H_2 gas sensing based on SnO_2 nanowires prepared via thermal evaporation method based on SiO_2/Si substrates with Cadmium – Gold (Cd-Au) combo-shaped interdigitating electrodes. The sensitivity increased with increasing H_2 gas concentrations and operating temperatures. The sensitivity toward exposure to 10 ppm H_2 was nearly 0.2 at an operating temperature of 200 ^oC and increased to 0.4 at 300 ^oC. When H_2 concentration reached to 1000 ppm, the sensitivity was nearly 0.7 at an operating temperature of 200 ^oC, which increased to 3.25 at 300 ^oC.

Ahn et al. [28] fabricated nanophase SnO_2 powder using inert gas condensation method (IGC). SnO_2 powder was milled and mixed to make a paste that was placed on Al_2O_3 tube and Palladium (Pd), was used as electrodes. The sensitivity of the H_2 gas sensor was presented at operating temperatures of (100, 150, 200, 250, 300 and 350 ^oC), at a constant H_2 pressure of 2500 ppm. Sensitivity results at different H_2 concentrations ranged from 100 to 10.000 ppm at a constant operating temperature of 250 ^oC. The sensitivity increased with increasing H_2 concentrations and operating temperatures. The highest sensitivity was obtained for the film sensor sintered at 600 ^oC with a sensitivity value of 96% for H_2 concentration of 2500 ppm at 250 ^oC. [S (%) = ((R_{air} - R_{gas})/R_{gas}×100)] where R_{gas} and R_{air} were the sensor resistances tested in gas and air, respectively.

Similar results were presented by Gong et al. [80], where the NC SnO_2 sensor prepared by sol-gel spin coating method on glass substrates with Platinum (Pt) electrodes showed 39% sensitivity [(S (%) = (($R_{air} - R_{gas}$)/R_{air}×100)] upon exposure to 1500 ppm of H_2 at operating temperature 200 ^oC and then increased to 40% at 250 ^oC. Lingmin et al. [81] studied the influence of the morphology of one-dimensional

SnO_2 nanocrystals prepared via thermal evaporation method on improving H_2 sensing performance. SnO_2 nanostructure powders were mixed with distilled water to create a paste that was placed on Al_2O_3 tube and platinum (Pt) was used as electrodes. The high response (R_{air} / R_{gas}) of SnO_2 nanowires sensor toward exposure to 500 ppm of H_2 gas was 24.35 at an operating temperature of 260 ^oC, while SnO_2 nanoclusters and nanorods produced responses of 19.30 and 12.40, respectively.

Doping is an effective method that is commonly used to enhance the sensing performance and stability of gas sensors. However, it is achieved through a long and complicated preparation steps that increases the cost of sensor device [82]. Kim et al. [83] successfully fabricated NC powder of SnO_2-Ag_2O-PtO_x composites through sol-gel method and screen printed on Al_2O_3 substrates with Pt electrodes. The composites showed that the highest response of H_2 gas was for SnO_2:Ag_2O: PtO_x= 93:5:2 in wt% ratio. At the operation temperature of 125 ^oC, the sensitivity (R_{air} / R_{gas}) at exposure to 500 ppm H_2 gas was 18.40 and the response and recovery times were about 8 and 10 s, respectively.

Kocemba et al. [84] demonstrated the H_2 sensing properties based on Pt-doped SnO_2 sensor with doping ratio 1 wt% of Pt at operating temperatures from 100 to 350 ^oC, was prepared via sol-gel method. Pt-doped SnO_2 was dispersed onto Al_2O_3 tube that was used as a substrate with Pt as electrodes. The sensor showed high sensitivity at increased operating temperatures and increased calcined temperatures of the Pt-SnO_2 nanoparticles. The maximum sensitivity (R_{air} /R_{gas}) to 100 ppm H_2 gas was approximately 5 at an operating temperature of 350 ^oC. Lin et al. [85] synthesized pure and the transition metal (TM) doped SnO_2 thin films using the sol-gel spin coating method on glass substrates and Pt used as electrodes. The sensitivity

(R_{air}/R_{gas}) based on pure SnO_2 toward exposure to 500 ppm of H_2 gas was 3.9 at an operating temperature of 250 ^oC and a recovery time of 84 s, whereas doping of at 5% tungsten (W) increased the sensitivity to 25.8 at the same operating temperature, while the recovery time was 72 s.

Previous studies have attempted to improve the sensitivity of devices without doping steps. Chen et al. [86] noted the significance of porosity for sensor design in the porous SnO_2 thin films using PLD method. In addition, Cantalini et al. [87] noted that a higher porosity in the SiO_2–Co_3O_4 films, which were prepared by sol-gel method, allowed for increasing the adsorption/desorption of gas molecules on the surface of a device.

Serventi et al. [27] investigated the contribution of porosity that appeared along the thickness of NC SnO_2 thin films in increasing the sensitivity toward exposure to carbon monoxide (CO) gas. The NC SnO_2 thin films were prepared by RF-sputtering method at substrate deposition temperature of 250 ^oC on Al_2O_3 substrates. The NC SnO_2 thin films showed higher porosity than the films prepared at RT. The high porosity of film permitted the gas diffusion inside the thin film. Thereby, high sensitivity was obtained by using the film that was deposited at the highest temperature of 250 ^oC. Consequently, the sensitivity increased from 175% to 375% toward exposure to 100 ppm of CO gas. Liu et al.[36] showed that the quenched NC SnO_2 thin film 1800 ^oC/h appears little response (R_{air}/R_{gas}) reach to 4.9 to 13.7 ppm H_2S gas at 100 ^oC , while the thin film with the slowest cooling rate 25 ^oC/h exhibits the highest response reach to 42.3 in the same atmosphere and operating temperature. Table 2.2 summarizes the sensitivity of SnO_2 nanostructures based H_2 gas sensor at various preparation methods and at different operating temperatures.

Table 2.2: Summary of the sensitivity, the response and recovery times for the SnO_2 nanostructure based gas sensor.

Materials	**Preparation Methods**	**Substrates**	**H_2 Concentrations (ppm)**	**$T_{opt.}$ (^oC)**	**S_{gas} (%)**	**Ref.**
SnO_2 nanobelts	Thermal evaporation	SiO_2/Si	20,000	RT	60	[79]
SnO_2 nanowires	Thermal evaporation	SiO_2/Si	1000	200	70	[4]
Nanophase SnO_2 powder	IGC	Al_2O_3 tube	2500	250	96	[28]
NC SnO_2 thin film	Sol-gel spin coating	Glass	1500	200	39	[80]
SnO_2 nanowires	Thermal evaporation	Al_2O_3 tube	500	260	2435	[81]
NC powder of SnO_2-Ag_2O-PtOx	Sol-gel	Al_2O_3	500	125	1840	[83]
Pt-doped SnO_2	Sol-gel	Al_2O_3 tube	100	350	500	[84]
1-SnO_2 thin films 2-W-doped SnO_2 thin films	Sol-gel spin coating	Glass	500 500	250 250	390 2580	[85]

2.4 Theoretical background

2.4.1 Structural properties of SnO_2

Tin (Sn) is a natural occurring element that emerges in group 14 (IV) [88] of the Periodic Table at the boundary between metals and nonmetals. The electronic configuration of the $_{50}$Sn element is $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6\ (3d)^{10}\ (4s)^2\ (4p)^6\ (4d)^{10}\ (5S)^2\ (5p)^2$ [89], whereas that of the $_8$O element is $(1s)^2\ (2s)^2\ (2p)^4$ [90]. Various types of organic and inorganic compounds may be formed with Sn. Depending on the name of the compound, divalent and tetravalent oxidation states may be labeled by using the names of stannous and stannic, respectively [91]. Another widely encountered nomenclature system, the stock oxidation-number system refers the divalent and tetravalent tin as Sn (II) and Sn (IV), respectively. Sn is a silver-white metal that is malleable and slightly ductile. At normal pressures, Sn has two allotropic forms that have a crystalline structure. One form has a cubic structure and the color is gray or α-Sn that exists for few temperatures less than 13.2 °C. The other form has a tetragonal structure and the color of gray Sn is changed to white or β-Sn at 13.2 °C. In compounds, tin can occur in the +2 or +4 oxidation states [92]. Sn (IV) dioxide is commonly called tin dioxide, stannic anhydride, or stannic dioxide has a formula SnO_2.

Tin dioxide (SnO_2) is a semiconductor and an anisotropic polar crystal that crystallizes into a tetragonal rutile structure. The unit cell contains six atoms, two for tin and four atoms for oxygen. The position of each tin atom is placed at the central of six oxygen atoms and surrounding at the corners of a regular somewhat deformed octahedron. Three tin atoms position are roughly placed at the edge of corners of an equilateral triangle surrounding every oxygen atom; this formation results in a 6:3 coordination as shown in Figure 2.3 [93].