Tungsten Oxide (WO$_3$) Thin Films For H2S Sensor Application In Energy Systems

Satya Kiran Gullapalli

University of Texas at El Paso, skgullapalli@miners.utep.edu

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TUNGSTEN OXIDE (WO$_3$) THIN FILMS FOR H$_2$S SENSOR APPLICATION IN ENERGY SYSTEMS

SATYA KIRAN GULLAPALLI
Department of Mechanical Engineering

APPROVED:

________________________________________
Ramana. V. Chintalapalle, Ph.D., Chair

________________________________________
Jack Chessa, Ph.D.

________________________________________
Vinod Kumar, Ph.D.

________________________________________
Jianmei (Jenny) Zhang, Ph.D.

Patricia D. Witherspoon, Ph.D.
Dean of the Graduate School
Dedicated to my Parents
TUNGSTEN OXIDE (WO₃) THIN FILMS FOR H₂S SENSOR APPLICATION
IN ENERGY SYSTEMS

by

SATYA KIRAN GULLAPALLI

THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
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of the Requirements
for the Degree of

MASTER OF SCIENCE

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THE UNIVERSITY OF TEXAS AT EL PASO
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Abstract

The sulfur containing emissions in coal gasification systems to produce energy are devastating and hostile to the requirements of clean, environmental friendly, efficient, and economical energy. Therefore, hydrogen sulfide (H$_2$S) emissions in coal gasification plants must be monitored, controlled and effectively removed before the syngas is used for energy production. The present research focuses on the development and utilization of tungsten oxide (WO$_3$) thin films and nanostructures for H$_2$S application in the coal gasification systems. As a part of that overall goal, the present work was performed with a specific objective of understanding the effect of growth temperature on WO$_3$ nanocrystalline films fabricated by reactive magnetron sputtering. WO$_3$ films were grown under varying deposition temperatures in the range of 30 (RT)–500 °C. The effect of growth temperature on the crystal structure, surface/interface morphology, chemical quality and electronic properties is investigated in detail. Characterizations on the WO$_3$ materials were performed using a wide variety of analytical tools viz., X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray spectrometry (EDS), UV-VIS-NIR double-beam optical spectrophotometer, and electrical resistivity measurements. XRD and SEM analyses indicate that the WO$_3$ films grown at RT were amorphous while those grown at higher temperatures are nanocrystalline. The grain size ranged from 12-62 nm as the temperature increased from 100 to 500 °C. It was observed that the films exhibited a smooth morphology below 300 °C and a rough morphology above 300 °C. XRD results indicated that the films grown at 100-300 °C were monoclinic while those grown at higher temperatures exhibited a tetragonal phase. Optical properties of the WO$_3$ films indicate that, as the growth temperature is increased, the transmittance of the films decreases. The band gap determined from optical measurements showed quantum confinement effects due to
reduction in crystallite size. The band gap decreased from 3.25 eV to 2.92 eV with increasing temperature from RT to 500 °C. The electrical measurements indicate that with an increase in substrate temperature the resistivity of the films decreases. A direct correlation between microstructure and electronic properties is derived. The results and implications for technology are discussed along with a recommendation of future directions.
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Publications


Chapter 1: Introduction

Currently there is enormous global interest in the energy production, storage, conversion, utilization, and management. Most importantly, energy systems capable of delivering clean and efficient energy are increasingly receiving attention in recent years.

Energy utilization for transportation, industry and domestic purposes is significant in the United States. The consumption rate of energy in the US is almost a quarter of the world’s energy. The majority of the energy (about 80%) comes from the fossil fuels, mostly coal which is a widely available fossil fuel. The rest of the energy comes primarily from the hydro and nuclear power plants. It is estimated that the coal reserves of the US are capable of supplying for several hundreds of years. Since a majority of the energy needs in the US are met by the fossil fuels, there is a need to develop and address the critical issues of the systems for efficient use of fossil fuels for clean energy production, conversion, and utilization.

The emphasis in this research topic is towards energy production from coal, one of the fossil fuels, and associated technologies. Coal is commonly used in energy production through the gasification process. Gasification, which is a thermal conversion process in which solid fuel is converted to a gaseous fuel (syngas, which can be subsequently converted into energy), was first developed around 1780 and commercialized in the early 1900’s. Gasification offers industry the opportunity to develop unique combinations of advanced technologies that offer low cost, reliable, and highly efficient energy options and for meeting a broad range of market applications. Gasification-based systems are capable of utilizing all carbon-based feedstock’s, including coal, petroleum coke, biomass, municipal and hazardous wastes, etc., and is the prime generation technology capable of meeting the demands of current and emerging market requirements. Gasification-based systems are the most efficient and environmentally friendly
technologies for the production of low-cost electricity and other products and can be readily adapted for concentrating and sequestering CO₂. These gasifiers are mainly classified into three types based on their flow geometry. They are:

1. Entrained flow gasifiers, in which pulverized coal particles and gases flow concurrently at high speed. They are the most commonly used gasifiers for coal gasification.
2. Fluidised bed gasifiers, in which coal particles are suspended in the gas flow; coal feed particles are mixed with the particles undergoing gasification.
3. Moving bed (also called fixed bed) gasifiers, in which gases flow relatively slowly upward through the bed of coal feed. Both concurrent and counter-current technologies are available but the former is more common.

One of the advanced energy systems is an Integrated Gasification Combined Cycle (IGCC), which uses coal for the production of syngas which in turn is used for generation of electricity. The details of IGCC are discussed below.

1.1 Integrated Gasification Combined Cycle (IGCC)

An IGCC is a gasification plant (Figure 1.1) combined with both gas turbine and a steam turbine. In this process, the coal is reacted with steam and air at very high temperatures and pressures to produce a combustible gas called syngas. The syngas is produced at various stages. The first stage involves the temperature control part. In this stage, the syngas is passed through a series of cooling (heat exchanger) process, where its temperature is brought down and the water is converted into steam. The second stage involves purification. The syngas after the temperature control stage is then passed through a solid removal phase, where any solid impurities (if
present) are removed. In the third stage, the syngas is gas treated for removal of sulfur and any other sulfur compounds.

Once the syngas is clean, it is then sent to the gas turbine where it is combusted to produce electricity. The products of combustion from the gas turbine are then passed through a heat exchanger, where it exchanges heat with water to produce steam. This steam produced from both the syngas heat exchanger and the exhaust products heat exchanger is used to run a steam turbine which generates electricity. The electricity produced from these turbines is then supplied to the grid.
Figure 1.1: Schematic of an IGCC [1]
1.2 Need for hydrogen sulfide (H\textsubscript{2}S) sensors in coal gasification plants

The release of sulfur compounds, however, is a major concern since the production of electricity from coal by gasification or combustion produces the undesirable sulfur compounds. The gasification results in emission of hydrogen sulfide (H\textsubscript{2}S) while combustion leads to the production of sulfur oxides (SO\textsubscript{2} and SO\textsubscript{3}). These sulfur containing emissions are devastating and hostile to the requirements of clean, environmental friendly, efficient, and economical energy. In an IGCC plant, even trace amount of sulfur compounds are harmful and decrease the efficiency. Since H\textsubscript{2}S is corrosive in nature, these small traces need to be detected and removed from the syngas before its use in combustion in gas turbines. Otherwise, it might corrode the turbine components reducing their life and efficiency. Therefore, for a better control and optimal operation of coal gasification process, the power production necessitates on-line detection and monitoring of H\textsubscript{2}S by a reliable and real-time sensor, which can operate at high-temperatures and can survive the harsh and chemically corrosive atmosphere within the coal gasifier.

1.3 Metal oxides for sensors

Chemical sensors based on metal oxide semiconductors are most promising for sensor device technology due to their small dimensions, low cost, low power consumption, on-line operation, high compatibility with microelectronic processing, and ease of integration into nanotechnology and portable device technology [2-9]. However, the choice of a specific material(s) for application as H\textsubscript{2}S sensor(s) in gasification plants necessitates understanding the operational principle of a sensor, which is outlined in Figure 1.2. The chemical detection is based on the principle that the changes in the atmosphere or chemical composition alter the material properties of sensor in a characteristic way. Specifically, the material selectively and
quantitatively responds to the surrounding chemical species by altering its electronic properties. The changes in electronic structure are converted into a measuring signal to detect the nature and amount of gas. The choice of sensing material used for H$_2$S gas detection is, therefore, a very important designing parameter.

One of the major disadvantages of the available H$_2$S sensors is their lack of selectivity; they normally respond to a large number of gases, such as NO$_2$, CO and methane, or NH$_3$ and H$_2$S. Research and development at the level of fundamental science (to elucidate the materials’ behavior) is still needed which in turn require development of new materials and discovery of new phenomena based on nanoscience and nanotechnology. Furthermore, besides a poor discrimination of chemical species, the commonly used sensors have other disadvantages such as slow response time, long-term instability, morphological disorders, and poisoning by the chemical substances that need to be detected. Thus, the objective of this proposed research is

![Figure 1.2: Sensor working principle](image)
linked to the acute demand of advancements in sensor performance for \( \text{H}_2\text{S} \) detection in the coal-gasification process, with a particular emphasis towards improving their selectivity and sensitivity. It is proposed to investigate the atomic/chemical structure, surface/interface microstructure, stability, electronic structure, and sensor performance of \( \text{WO}_3 \) thin-film nanostructures grown by various physical methods for their utilization in sensor devices to effectively monitor and detect the \( \text{H}_2\text{S} \) emissions in coal-gasification processes.

1.4 **Tungsten oxide thin films and nanostructures for \( \text{H}_2\text{S} \) sensors**

\( \text{WO}_3 \) is a wide band gap semiconductor [10]. For n-type semiconductor (Figure 1.3), the sensor resistance decreases in the presence of reducing species and increases in the presence of oxidizing species. Hence, \( \text{WO}_3 \) is a promising material for gas sensing due to its electrical conductivity and excellent sensitivity and selectivity [11-21]. It has high sensitivity to many kinds of gases such as \( \text{O}_3 \) [11], \( \text{O}_2 \) [12], \( \text{NO}_2 \) [13], \( \text{NO} \), \( \text{NH}_3 \), \( \text{H}_2\text{S} \) [14], \( \text{H}_2 \) [10, 15] and ethanol [16]. However, the electrical properties and, hence, the sensor performance are highly sensitive to the microstructure of \( \text{WO}_3 \) nanomaterials. Therefore, a careful choice of preparation conditions in order to have the controlled growth and microstructure which is stable over the specific gas composition and temperature ranges is desired.
1.5 History of tungsten oxide

Tungsten oxide occurs naturally in the form of hydrates. It can be prepared in several different ways. CaWO₄ or scheelite is allowed to react with HCl and form tungstic acid which decomposed to WO₃ and water at high temperatures.

\[
\text{CaWO}_4 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{WO}_4 \quad \ldots \ldots (1)
\]

\[
\text{H}_2\text{WO}_4 + \text{heat} \rightarrow \text{H}_2\text{O} + \text{WO}_3 \quad \ldots \ldots (2)
\]

It has a melting point of 1473° C and is very insoluble in water. The most common phase of WO₃ in monoclinic.

Tungsten oxide thin films have been the topic of interest for researchers for more than a decade considering their electrochromic properties. The electrochromic property of a material is the ability to change its optical properties when a voltage is applied across it and the original should be recoverable when the polarity of the voltage is changed [22]. Similarly the optical
properties change when exposed to a gas containing hydrogen which is considered to be a gasochromic property [23]. These properties of tungsten oxide make it applicable in various optical devices like information display, smart windows, variable reflectance mirrors, hydrogen sensors, etc.

In general, \( \text{WO}_3 \) is a complicated material with respect to crystal structure and thermal stability due to several structures, such as monoclinic, triclinic, tetragonal, orthorhombic, cubic, and hexagonal for pure and oxygen deficient \( \text{WO}_3 \) [22,24-28]. The important phases of \( \text{WO}_3 \) are listed in Table 1.1.

Table 1.1: \( \text{WO}_3 \) crystal phases

<table>
<thead>
<tr>
<th>PHASE</th>
<th>SPACE GROUP</th>
<th>TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>P1</td>
<td>30 °C</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>P2(_1/c)</td>
<td>330 °C</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Penb</td>
<td>740 °C</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>P4/ncc</td>
<td>&gt;740 °C</td>
</tr>
</tbody>
</table>

The ideal \( \text{WO}_3 \) crystal structure can be represented as a cubic \( \text{ReO}_3 \) structure [25]. In fact, the polymorphs of \( \text{WO}_3 \) can be described as distortions from the cubic \( \text{ReO}_3 \) structure [26-28]. Therefore, the structure is built up from three-dimensional network of corner-sharing \( \text{MO}_6 \) (\( M=\text{W} \) or \( \text{Re} \)) octahedra (Figure 1.4). The octahedral environment of \( \text{W} \) is shown in Figure 1.4B. The crystal structure of \( \text{WO}_3 \) can be viewed as alternating O and \( \text{WO}_2 \) (Figure 1.4B) planes, which can be viewed as placed normal to the respective crystallographic direction.
1.6 Objective(s)

It is clear that WO$_3$ is a promising material for gas sensor applications. Considering the excellent properties, it is intended to develop WO$_3$-based sensors to detect very small amounts of H$_2$S in the coal gasification systems. The following are the specific objectives of the work:

1. To deposit high quality WO$_3$ thin films by RF magnetron sputtering for H$_2$S sensor application in coal gasification systems.

2. Characterizing the films grown for their structural, morphological and electronic properties.

3. Understanding the effect of growth temperature (RT – 500 °C) on the structure and morphology along with the effect of size reduction effects.

4. Optimizing the conditions to grow high quality WO$_3$ thin films suitable for H$_2$S sensors.
Chapter 2: Experimental

2.1 Substrate cleaning

The substrates used for all the experiments were p-type Si (100) wafers with the measured sheet resistance of 1.3 – 10 $\Omega$-cm (measured by four point probe technique). Quartz and glass substrates were used in some of experiments. In order to avoid contamination during deposition and to achieve high performance of devices fabricated, the silicon wafers are cleaned with RCA cleaning procedure to remove organic, inorganic and metal particulate contaminants. The procedure has three major steps:

- SC1- Removal of insoluble organic contaminants using 5:1:1 H$_2$O/H$_2$O$_2$/NH$_4$OH solution
- SC2- Removal of ionic and heavy metal atomic components using a solution of 5:1:1 H$_2$O/H$_2$O$_2$/HCl solution
- Removal of native oxide by buffered oxide etches solution.

The SC1 solution was prepared by heating 50 ml of Deionized water (DI) water to a temperature of 100 $^\circ$C and then adding each 10 ml of NH$_4$OH and H$_2$O$_2$ to the DI water. SC2 solution was prepared by 10ml each of H$_2$O$_2$ and HCl to 50ml of water. The silicon substrates were soaked for 10 min in each solution and followed by 5 min of DI water rinse after each soak. Finally the silicon substrates were treated with BOE to remove any native oxide on it.

The glass and quartz substrates were used in some experiments, especially optical characterization, along with silicon substrates. These substrates were cleaned in an ultrasonic bath of methanol (semiconductor grade), acetone (semiconductor grade), and DI water. The
ultrasonic cleaning was carried out for 10 min in each step followed by a DI water rinse and then dried with nitrogen.

2.2 Thin film synthesis

WO₃ thin films in this work were grown employing radio-frequency (RF) magnetron sputtering. The sputter process (Figure 2.1) involves bombardment of target material by ionized atoms, usually Ar⁺ ions. The target material (called sputter target) is placed on a cathode and a negative voltage is applied to the cathode. The chamber is evacuated to high vacuum, usually 10⁻⁶ Torr and Ar gas will be injected into chamber at low pressures. The Ar gas will be ionized to create Ar⁺ plasma. Ar⁺ ions accelerate towards cathode, under the influence of cathode voltage, and bombard the target ejecting a target atom. The target atom will be deposited on to the substrate placed above the target. In this research RF magnetron sputtering was employed. In this type of sputtering a RF voltage of 13.56 MHz was applied to the target and the sputter cathode was equipped with a magnet.

A Kurt J Lesker sputter deposition system (Figure 2.2) has been used for the deposition. All the substrates were thoroughly cleaned and dried with nitrogen before introducing them into the vacuum chamber, which was initially evacuated to a base pressure of ~ 10⁻⁶ Torr. Tungsten (W) metal target (Plasmaterials Inc.) of 3 in. diameter and 99.95% purity was employed for reactive sputtering. The W-target was placed on a 3 in. sputter gun, which is placed at a distance of 8 cm from the substrate. A sputtering power of 40 W was initially applied to the target while introducing high purity argon (Ar) into the chamber to ignite the plasma. Once the plasma was ignited the power was increased to 100 W and oxygen (O₂) was released into the chamber for reactive deposition. The flow of the Ar and O₂ and their ratio was controlled using as MKS mass
flow meters. Before each deposition, the W-target was pre-sputtered for 10 min using Ar alone with shutter above the gun closed. The deposition was carried out for 1 h. The samples were deposited at different temperatures varying from RT to 500 °C. The substrates were heated by halogen lamps and the desired temperature was controlled by Athena X25 controller.

Figure 2.1: Sputtering process

Figure 2.2: Kurt J Lesker thin film sputter deposition system
Table 2.1: Deposition conditions

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample No.</th>
<th>Ar/O₂ ratio</th>
<th>Ar Pressure</th>
<th>Total Pressure</th>
<th>Substrate Temp( °C)</th>
<th>Power (Watt)</th>
<th>Deposition Time(min)</th>
<th>Substrate to target distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>W13</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>RT</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
<tr>
<td>2.</td>
<td>W14</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>100</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
<tr>
<td>3.</td>
<td>W15</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>200</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
<tr>
<td>4.</td>
<td>W16</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>300</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
<tr>
<td>5.</td>
<td>W17</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>400</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
<tr>
<td>6.</td>
<td>W19</td>
<td>1:6</td>
<td>1.2*10⁻³</td>
<td>7.5*10⁻³</td>
<td>500</td>
<td>100</td>
<td>60</td>
<td>8cm</td>
</tr>
</tbody>
</table>

2.3 Characterization

The WO₃ thin films obtained were characterized using High Resolution Scanning Electron Microscope (HRSEM), X-ray diffraction (XRD) and Optical Spectroscopy.

2.3.1 Surface morphology and interface analysis

The films obtained have been characterized using a HRSEM for surface morphology and interface analysis. Surface morphology of the films gives information about the microstructure of the films while the interface analysis gives information regarding the films interaction with the substrate. The HRSEM used here was a Hitachi S-4800 electron microscope (Figure 2.4).

Scanning electron microscope (SEM) uses an electron source with filament and anode. The microscopic column is contained in a vacuum envelope. As shown in the schematic below Figure 2.3, the incident electron beam is collimated, and then focuses onto the sample surface in a small spot. Then blanking and scanning coils are used to raster the spot across the sample. The
signal from each spot on the surface is imaged at the display, keeping the same raster position as the spot on the sample. In this way an image is formed from the interaction of the incident electron beam at each position on the sample surface. Magnification is achieved by rastering over a smaller area and displaying the smaller raster area on the entire screen. Incident beam size and the interaction area at the surface determine the resolution. Secondary electrons emitted from the sample surface as a result of collisions with the incident electron beam are used to form the image. The contrast in the image arising from the secondary electrons is due to the yield of the secondary electrons from each point probed on the sample surface. A particular point on the surface may contain atoms that yield more secondary electrons from an incident electron dose than an adjacent spot, and this spot will have a brighter image than the adjacent spot.

Figure 2.3: Schematic sketch of an SEM showing major components [29]
To obtain the image of the surface the sample is placed on a stage with its film surface facing the beam. For the interface image, the sample is placed in such a way that both the film and the substrate (cross-section) face the beam. The grain size and thickness of the film can be determined from the images by using image analysis software.

Figure 2.4: Hitachi S-4800 Scanning Electron Microscope

### 2.3.2 Structural characterization

A Bruker D8 Advance X-Ray diffractometer (XRD) (Figure 2.5) has been used for the structural characterization. The crystal structure, preferred crystallographic information (if any), crystallite size, and the phases were determined from XRD patterns. XRD is an analytical technique in which x-ray beam hits the surface of a substrate at various incident angles scattering preferentially oriented x-rays into detector which collects them to generate crystallographic
information about the sample such as lattice parameter, d-spacing, film orientation. XRD principle is based on Bragg’s law

\[ \lambda = 2dsin\theta \]  

(1)

where \( \lambda \) = wave length of X-ray, \( d \) = inter planar distance and \( \theta \) = Bragg’s angle.

Figure 2.5: Bruker D8 Advance X-ray diffractometer

2.3.3 Optical characterization

The samples obtained have been characterized using a Cary 5000 UV-VIS-NIR optical spectrophotometer (Figure 2.6) in the wavelength range of 200–2000 nm. The optical characterization is usually performed on highly transparent and semi-transparent thin films deposited on transparent substrates such as glass, quartz and sapphire.
The transmittance data obtained for the samples is used for calculating the band gap. First, the absorption coefficient $\alpha$ is determined using the thickness of the film ($t$) and transmittance data ($T$) from the formula

$$\alpha = \frac{-\ln (T)}{t} \quad \text{..................................(2)}$$

The energy of the photons $h\nu$ is calculated at every wavelength ($\lambda$) of light using the equation

$$h\nu = \frac{1240}{\lambda} \quad \text{..................................(3)}$$

The band gap of the films is then measured using the equation

$$\alpha h\nu = B(h\nu - E_g)^2 \quad \text{..................................(4)}$$

Where $B$ is a proportionality constant and $E_g$ is the band energy, the band gap of the films are calculated by plotting a graph between $(\alpha h\nu)^{1/2}$ vs $h\nu$. The transmittance data can further be used to calculate the extinction coefficient $k$, refractive index $n$ and dielectric constants.
Chapter 3: Literature Review

Minchener [1] discussed the development and deployment of various coal gasification technologies used for power generation. The advantages and disadvantages of coal gasification technologies along with the need for R & D in specific technologies like, advanced materials, sensors and controls were discussed.

Parreira et al. [30] deposited WO$_3$ coatings by sputtering at various oxygen concentrations. XRD patterns proved that WO$_3$ formed at oxygen atomic concentration greater than 75% were nanocrystalline in nature. With increase in O content, position of diffraction peak moves to lower diffraction angles. This means that O is allocated in the interstitial positions in the lattices which lead to higher latter parameter and induces compressive residual stresses. From mechanical characterization it was found that with increase in oxygen content the hardness and Young’s modulus of the film decreased.

Li-ge-Wang et al. [31] discussed the effect of oxygen content on the electrochromism of the WO$_3$ films deposited by mid-frequency dual target magnetron sputtering. It was observed that films with abundant oxygen is looser and has more pores which make electrochromism better. Electrochromism decreases due to irreversible flow of electrons and ions.

Ramana et al. [25] found that the phase transformation in WO$_3$ films occurs in a sequence as the temperature is increased from RT to 500 °C.

Chawla et al. [49] discussed the effect of sputtering gas pressure on the structural and optical properties of nanocrystalline tungsten oxide films deposited by RF magnetron sputtering. From XRD results, it was evident that at low oxygen pressure the film formed was a randomly oriented mixed phase (W and WO$_3$) while with an increase in pressure a single phase WO$_3$ film
is formed. Optical properties proved that the transmittance of WO$_3$ thin films increases with increase in oxygen partial pressure which was attributed to the fall in the density of oxygen ion vacancies in the oxygen rich films. The band gap increased with the increase in oxygen partial pressure.

Washizu et al [36] discussed the effect of substrate temperature on the WO$_3$ films formed by RF reactive sputtering. The XRD pattern of the film deposited at RT is very broad, which indicates that the structure of the film is amorphous. XRD peaks due to orthorhombic WO$_3$ crystal are clearly seen at substrate temperatures above 200 °C, with the width of the peaks decreasing with increasing substrate temperature, indicating that crystal grain growth is promoted by increasing substrate temperature. Transmittance of films at 500 °C is very low for which light scattering due to crystal grains is thought to be the reason for low transmittance. The larger band gap energies observed are thought to be the result of quantum size effects due to the small WO$_3$ cluster size. Shivakumar et al [50] also discussed the effect of substrate temperature on tungsten oxide films deposited by e-beam technique. From his experiments it was discussed that at higher substrate temperatures say $T_{\text{sub}} = 100 \, ^\circ\text{C}$ and 200 °C, the crystalline WO$_3$ film is obtained, due the complete coalescence formation followed by perfect growth alignment of WO$_3$ particles on the substrates. The reduction in the values of band gap from room temperature to higher substrate temperature may be due to the formation of more oxygen ion vacancies in the film during deposition at higher temperatures. Filipescu et al [51] also discussed the effect of substrate for films grown by laser ablation.

Stankova et.al [18] discussed the influence of annealing and operating temperatures on the gas sensing properties of WO$_3$ thin film sensors. They observed that it was the annealing temperature rather than the operating temperature, the most important parameter that affected the
sensitivity of the sensor. Xie et. Al. [19] also discussed the effect of annealing temperature on sensors in the range of 300 °C – 600 °C and reported that it has better response at 500 °C.
Chapter 4: Results and Discussion

The emphasis in this work is to characterize the growth behavior, microstructure, and electronic properties of sputter-deposited WO$_3$ materials as a function of growth temperature ($T_s$) and establish the conditions to produce materials for H$_2$S sensor application. For this purpose, WO$_3$ films were grown at various deposition conditions and studied their morphological, structural, optical and electrical properties. Samples were grown at varying temperature by maintaining a constant reactive gas ratio of 1:6 to study the effect of temperature. The results obtained are presented and discussed below in the following sequence. The crystal structure and phase analysis is made based on the XRD results and their analysis. The compositional or phase stability of WO$_3$ films is examined considering the EDS data. Subsequently, the focus is on SEM data to discuss the effect temperature on the grain structure and morphology. Finally, the observed dependence of optical and electrical properties on the growth temperature is explained on the basis of the relative structural changes in the oxide films. An attempt is made to establish a correlation between growth conditions, microstructure, and electronic properties of the grown WO$_3$ materials which can provide a road-map to select the specific conditions for H$_2$S sensor applications.

4.1 Crystal structure

The XRD patterns of WO$_3$ films are shown in Figures 4.1 and 4.2 as a function of $T_s$. The respective of XRD patterns of bulk WO$_3$ phases considered to index the observed peaks and assign the corresponding phase are also shown. The XRD curve (Figure 4.1) of WO$_3$ films grown at RT did not show any peaks indicating their amorphous (a-WO$_3$) nature. The XRD peak
corresponding to monoclinic WO\(_3\) (m-WO\(_3\)) phase appears when the \(T_s=100\) °C. However, the peak (at 23.1°) is rather broad indicating the presence of very small nanoparticles. It is evident (Figure 4.1) that the intensity of the peak, at 23.1°, which corresponds to diffraction from (002) planes increase with increasing \(T_s\). This is indicative of an increase in the average crystallite-size and preferred orientation of the film along (002) with increasing \(T_s\). The latter is dominant for WO\(_3\) films grown at \(T_s\geq200\) °C. Also, a structural transformation occurs at \(T_s=400\) °C. XRD peaks due to tetragonal (t-WO\(_3\)) phase are clearly seen for WO\(_3\) films grown at \(T_s\geq400\) °C (Figure 4.2). In fact, it can be seen in the XRD curve obtained for WO\(_3\) films grown at 300 °C that an overlap of (001) peak corresponding to t-WO\(_3\) and (002) peak corresponding to m-WO\(_3\) indicating the onset of phase transformation but not complete. Perhaps, the temperature is just sufficient to induce a phase change in nanoscale m-WO\(_3\) films but not fully favorable to complete the process. High-temperature t-WO\(_3\) formation at 400 °C seems to be the effect of phase stabilization at the nanoscale dimensions. The preferred c-axis orientation could be due to the growth process minimizing the internal strain-energy in the film. Anisotropy exists in crystalline materials and the strain energy densities will typically be different for different crystallographic direction. The growth will favor those orientations with low strain energy density. Therefore, increasing \(T_s\) favors the preferred orientation along (001) while minimizing the strain-energy in the WO\(_3\) film.
Figure 4.1: XRD pattern of amorphous and monoclinic WO$_3$ phases

Figure 4.2: XRD pattern of tetragonal WO$_3$ phase
4.2 Surface morphology

The high resolution SEM images of WO$_3$ films as a function of substrate temperature are shown in Figures 4.3 and 4.4. The effect of temperature on the surface morphology of WO$_3$ films is remarkable. As it is evident from these images, the SEM data of WO$_3$ films can be divided into two categories where the morphology differences are significant. The first category contains the set of WO$_3$ films grown at temperatures $\leq 200$ °C (Figure 4.3). The second is the set of WO$_3$ films grown at temperatures $>200$ °C (Figure 4.4). No features can be seen for WO$_3$ films grown at RT even at very high magnifications (Figure 4.3a). This observation is in agreement with the XRD results indicating the complete amorphous nature of the samples. If temperature is low such that the period of the atomic jump process of adatoms on the substrate surface is very large, the condensed species may stay stuck to the regions where they are landing thus leading to an amorphous WO$_3$ film. The adatom mobility on the surface increases with increasing temperature. The small, dense particles spherical in shape can be noticed in SEM images (Figures 4.3b and 4.3c) for WO$_3$ films grown at 100–200 °C. The fine microstructure and uniform distribution characteristics of the particles are evident in the micrographs (Figures 4.3b and 4.3c). The average particle size is 10–14 nm. The SEM data along with appearance of diffraction peaks in XRD clearly indicate that 200 °C is the critical temperature to promote the growth of nanocrystalline WO$_3$ films with particles in spherical shape. For the given set of experimental conditions, a temperature of 200 °C is, therefore, favorable to provide sufficient energy for WO$_3$ crystallization.
Figure 4.3: SEM images of WO$_3$ samples grown at temperatures ≤ 200° C
Figure 4.4: SEM images of WO$_3$ samples grown at temperatures $>200^\circ$ C
The XRD and SEM results suggest that a further increase in temperature beyond 200 °C results in changes in the crystal structure and morphology. WO3 films continue to show preferred growth along with an increase in average particle size with increasing temperature. It can be seen in SEM images (Figure 4.4) that increasing temperature above 200 °C results in size > 20 nm. The highest particle size (62 nm) is measured for WO3 films grown at 500 °C. However, it can be also seen in the images that the distribution of particles become random with increasing temperature. The spherical morphology noticed for WO3 films grown at ≤ 200 °C is also changed with increase in temperature above 200 °C. A functional relationship obtained between the average particle size ($L$) and the temperature is shown in Figure 4.5. At a constant partial pressure (Ar:O$_2$=1:6), the temperature-size (T-L) data fit to an exponential growth function (Figure 4.5). The data support thermally activated growth process of nanocrystalline WO3 thin films. Therefore, similar to the diffusion coefficient equation [32], $L$ can be expressed as:

$$L=L_0 \exp (-\Delta E/k_B T) .................................................. (5)$$

Where $L$ is the average particle size, $L_0$ is a pre-exponential factor or proportionality constant which depends on the specific film, substrate material, $E$ the activation energy, $k_B$ the Boltzmann constant, and $T$ the absolute temperature. The data analysis and Arrhenius plot are presented in Figure 4.6, where the data points and a linear fit to the data are shown. It is important to recognize the functional linear relationship which is an indicative of thermally driven growth of nanocrystalline WO3 films.
The activation energy derived from the slope of the linear fit (Figure 4.6) is ~ 0.15 eV. A direct comparison of this value with any other reports is not possible at this time since the data or such analysis is not available for nanocrystalline WO$_3$ films grown by sputtering or any other physical/chemical vapor deposition methods. However, this value is rather small, but expected for nanocrystalline films, when compared to the data of some of the microcrystalline transition metal oxide thin films [30, 33].

Figure 4.5: Grain-size variation with temperature for sputter deposited WO$_3$ thin films. The experimental data are shown with solid circles while the line is an exponential fit. The data fit to an exponential growth function indicating thermally activated growth process of nanocrystalline WO$_3$ thin films.
4.3 Interface analysis

The cross-sectional SEM images of WO$_3$–Si interfaces for WO$_3$ films grown at various temperatures are shown in Figure 4.7. The WO$_3$ film and Si-substrate regions are as indicated. The cross-sectional SEM images indicate that the WO$_3$ films grow in a columnar structure on Si surfaces. A sharp interface, within the limits of the resolution of instrument, is seen between the Si substrate and the oxide layer for all WO$_3$ films. The cross-sectional imaging analysis indicates that there is no reaction leading to compound formation at the Si–WO$_3$ interface even at the highest temperature (500 °C).
4.4 Chemical quality

The energy-dispersive X-ray (EDS) spectra of representative WO$_3$ films as a function of growth temperature are shown in Figure 4.8. The spectra indicate the characteristic x-ray peaks (as labeled in Figure 4.8) corresponding to W and O atoms present in the sample. The absence of any other peaks except those due to W and O indicate that the sample consists exclusively of W-oxide phase. It is well known that the x rays generated are characteristic of the atoms [47, 48]. Therefore, the detection of x rays emitted from the sample as a result of sample-electron beam interaction provides the identification of the atoms present in the crystal. The emitted x-ray peaks
detected are only from W and O while the peak due to Si substrate is serving as a reference. No other elements were detected, which is a sign of high purity WO₃ and without any elemental impurities incorporated from chemical processing or post preparation handling. However, it can be seen in the spectra that the peak intensity of O is slightly decreased when the temperature is increased to 500 °C. This could be due to formation a small fraction of oxygen vacancies at higher deposition temperatures.

Figure 4.8: EDS spectra of WO₃ films grown at various temperatures. The X-ray peaks due to W and O atoms present in the grown films are as labeled.

4.5 Optical properties

The optical transmittance (T) spectra of WO₃ films are shown in Figure 4.9. The dip noticed in the spectra is due to interference. The spectra reveal two important characteristic features. (1) All the WO₃ films show a very high transparency in the spectral region except where the incident radiation is absorbed across the band gap (Eₔ). This observation indicates the
high-quality and transparent nature of WO$_3$ films with almost zero absorption losses. (2) A decrease in T with increasing T$_s$. However, the decrease is not significant for T$_s < 300$ °C, whereas a clear distinction is seen for T$_s \geq 300$ °C.

It is well known that the optical absorption below E$_g$ follows an exponential behavior [34]. The absorption, therefore, is exponentially dependent on the energy (hv) of incident photon in that region. For WO$_3$, in the E$_g$ region (high absorption) or above the fundamental absorption edge, the absorption follows a power law of the form [22, 35-37]:

$$\alpha hv = B(hv - E_g)^2$$

Figure 4.9: Optical transmittance spectra of WO$_3$ films. The curves indicate that WO$_3$ films are highly transparent.
Where $h\nu$ is the energy of the incident photon, $\alpha$ the absorption coefficient, $B$ the absorption edge width parameter, $E_g$ the band gap. The optical absorption coefficient, $\alpha$, of the films is evaluated using the relation [34, 36-38]:

$$\alpha = \frac{1}{t} \ln\left[ \frac{T}{(1 - R^2)} \right]$$

Where $T$ is the transmittance, $R$ is the reflectance and $t$ is the film thickness. The absorption data and the plots obtained for WO$_3$ films are shown in Figure 4.10. It is evident that $(\alpha h\nu)^{1/2}$ vs $h\nu$ results in linear plots in the high absorption region, $\alpha > 10^4$ cm$^{-1}$, suggesting indirect allowed transitions across $E_g$ of WO$_3$ films. The $E_g$ values determined by extrapolating the linear region of the plot to $h\nu = 0$, decreases from 3.25 to 2.92 eV with increasing $T_s$.

Figure 4.10: $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots for WO$_3$ films. Linear fits of the absorption data indicate the indirect band gap of WO$_3$ films. The extrapolation of the linear region to $h\nu=0$ to determine $E_g$ values is as indicated with lines. The arrow indicates the shift in $E_g$ as a result of size reduction leading to QC effects.
The possibility of direct allowed transitions is ruled out since similar procedure results in 
$E_g \sim 4 \text{ eV}$, which is not reasonable for WO$_3$. The functional relationship obtained between $T_s$ and 
$E_g$ is shown in Fig.4.11. It is clear that the $T_s$-$E_g$ data exhibits a linear inverse relationship 
(Figure 4.11). The size-phase-property relationship in nanocrystalline WO$_3$ films can be derived 
based on the observed results and taking the simultaneous effect of size and structural 
transformations into account. The results indicate that the microstructure has significant effect on 
the optical properties of nanocrystalline WO$_3$ films. In WO$_3$, $E_g$ corresponds to electronic 
transitions from the top of valence band (formed by the filled O 2$p$ orbital’s) to the conduction 
band (formed by the empty W 5$d$ orbital’s) [36, 39]. $E_g$ (WO$_3$ bulk) = 2.62 eV [40]. $E_g$ widening 
in WO$_3$ films with relatively smaller size is mainly due to quantum-confinement (QC) effects. 
The shift in $E_g$ due to the size-effect can theoretically be described based on the two QC regimes, 
strong and weak [41, 42]. The former is a case where the electrons and holes are independently 
confined when the size of a nanocrystal ($R_n$) is much smaller than the size of Bohr radius ($R_B$) 
[41-43]. In the later case of weak QC, the energy is dominated by the Coulomb term and 
quantum effects arise from quantization of exciton motion. The $E_g$ shift is relatively smaller in 
the latter case [43, 44]. WO$_3$ nanocrystals exhibit a weak QC effect [44]. This accounts for the 
observed $E_g$ widening and shift by 0.58 eV. The highest $E_g$ (3.25 eV) at $T_s$=RT is due to 
formation of a-WO$_3$ phase. The effect of a-WO$_3$ to m-WO$_3$ transition is not significant; $E_g > 3$
eV for nanocrystalline m-WO$_3$ films can be attributed to the size reduction. Most importantly, it 
is very interesting to note that the $T_s$-$E_g$ data exhibits a direct, inverse linear relationship where 
the combined effect of size increase and structural transformation is evident. Such a size-$E_g$ 
inverse relationship, which was attributed to QC effects, was also reported in CdS [42], CdTe–
TiO$_2$ [43], ZrO$_2$ [45], ZnO [46] and most recently in WO$_3$ [44]. A drop in $E_g$ by $\sim 0.25$ eV for
WO₃ films grown at Tₛ=300 °C could be due to size (30 nm) and phase transition to t-WO₃. Surface roughening can be accounted for a decrease in transmittance (Figure 4.9) at higher Tₛ.

Figure 4.11: Tₛ-E_g relationship in WO₃ films. A direct inverse relationship is evident; a line is provided not only to guide the eye but also to indicate the linear fit.

The random distribution of the grains makes the surface rough and results in the increased light scattering losses. Furthermore, an increase in the scattering coefficient would decrease the optical transmittance in the UV and visible region [45]. This feature was clearly observed in the optical spectra (Figure 4.9) with increasing Tₛ which supports the idea of scattering losses due to surface roughening.
4.6 Electrical properties

The room temperature electrical conductivity variation of WO$_3$ films with $T_s$ is shown in Figure 4.12. It can be seen that the electrical conductivity increases with increasing $T_s$. The conductivity is reported to decrease with grain size reduction due to the increasing grain boundary volume and associated impedance to the flow of charge carriers [52, 53]. If the crystallite size is smaller than the electron mean free path, grain boundary scattering dominates and hence the electrical conductivity decreases. The electrical resistivity is also very sensitive to lattice imperfections in solids, such as vacancies and dislocations which are reported to be present in nanocrystalline materials. In addition to that, lattice strain and the distortions can affect the motion of charge causing decrease in conductivity [54-56]. The room-temperature conductivity data and its variation with $T_s$ observed for WO$_3$ can be explained taking these factors into consideration. WO$_3$ films grown at RT are completely amorphous as evidenced in XRD studies. The randomness or disordered structure of the films, therefore, accounts for the observed low conductivity of a-WO$_3$ films. Appearance of diffraction peaks in the XRD curves, an increase in the average crystallite size along with a preferred orientation of the film along (002) is clearly seen with increasing $T_s$. Therefore, increase in conductivity with increasing $T_s$ can be attributed to the increasing crystalline nature and preferred orientation of the film along (002). In addition, a decrease in strain energy of the growing WO$_3$ film, as discussed using the XRD results, with increasing $T_s$ also causes the increase in conductivity. The observed jump in the electrical conductivity for WO$_3$ films grown at 400 °C seems to be a result of combined effect of the grain-size increase and phase transformation from m-WO$_3$ to t-WO$_3$. The observed variation in electrical conductivity is in correlation with optical properties, where we found enhancement in the band gap for a-WO$_3$ films and continuous decrease in the band gap with
increasing temperature or grain size. A comparison of the data obtained in the present work with that reported in the literature is presented in Table 4.1.

Table 4.1: Resistivity data comparison

<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Room temperature resistivity value (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Sputtering (Present case)</td>
<td>~10^2</td>
</tr>
<tr>
<td>RF Sputtering (reported) [57]</td>
<td>~10^2</td>
</tr>
<tr>
<td>Pulsed Laser Deposition [58]</td>
<td>~10^3</td>
</tr>
<tr>
<td>Spray Pyrolysis [59]</td>
<td>~10^2</td>
</tr>
<tr>
<td>Thermal Evaporation [60]</td>
<td>~10^5</td>
</tr>
</tbody>
</table>

Figure 4.12: Variation of electrical resistivity of WO₃ samples with growth temperature
Chapter 5: Summary and Conclusions

WO$_3$ films were fabricated onto Si and quartz substrates using RF magnetron sputtering. The effect of growth temperature (RT-500 °C) on the structure, surface/ interface morphology, chemical quality, and optical and electrical properties of WO$_3$ films was investigated. XRD and HRSEM results indicate that the effect of growth temperature on the WO$_3$ films is significant. Samples grown at RT are amorphous while those grown at higher temperatures were nanocrystalline. The grain size varied from 12-62 nm with increase in T$_s$ from 100 °C to 500 °C. XRD results indicate that as the temperature is increased, the WO$_3$ films show a phase change. At T$_s$=100 °C, the film transforms from amorphous to monoclinic phase exhibiting a (002) preferred orientation. A further increase in T$_s$ above 300 °C transforms the films to tetragonal phase. Therefore, it is concluded that the crystal-size and specific phase can be obtained by carefully controlling the growth temperature.

The effect of T$_s$ was significant on the optical characteristics of WO$_3$ films. The crystal size effects were remarkably evident in the optical spectra and band gap analysis. The transmittance of the films decreased with the increase in size which may be attributed to the light scattering at the grain boundaries. The wide band gap of WO$_3$ films (3.25-3.17 eV; RT-200 °C) is due to the size reduction leading to quantum confinement. The band gap decreases to 2.92 eV at 500 °C. The corresponding electrical resistivity ($\rho$) of the samples decreased with increase in T$_s$ which is due to improvement in the crystal structure. The direct, inverse linear T$_s$-E$_g$ and T$_s$-$\rho$ relationships found for WO$_3$ films suggest that the electronic structure can be tuned by achieving control over the size and phase. A direct correlation between growth conditions, microstructure and electronic properties as noted in this work is quite useful to design WO$_3$ films for H$_2$S sensors. WO$_3$ films grown at T$_s$=200-400 °C could be useful for developing H$_2$S sensors.
Chapter 6: Future Work

The scope for the future work and some directions are as listed below.

1. The optimized conditions from this work can be used to develop WO$_3$-based H$_2$S sensors.
2. Pure WO$_3$ films can be tested for the sensitivity in a controlled H$_2$S environment. The parameters related to sensor performance can be derived.
3. The long-term stability and poisoning of the materials under exposure to H$_2$S can be tested.
4. Doping with some metals like Ti, Pt and Al can be considered to further improve the sensor characteristic performance.
5. The materials packaged to develop H$_2$S sensors can be finally tested for online monitoring in the coal gasification systems.
References


Curriculum Vita

Satya Kiran Gullapalli was born on October 14th, 1987 in Gudivada, Andhra Pradesh, India. The first son of Venkata Subbaiah Gullapalli and Kamala Gullapalli, he graduated from Jawaharlal Nehru Technological University with a bachelor’s degree in Mechanical Engineering. He then travelled to El Paso, Texas to pursue his master’s degree from the University of Texas at El Paso in Mechanical Engineering. During his master’s, he worked as a teaching assistant and research assistant in the department of mechanical engineering. He is a member of the cSETR center in the department of Mechanical Engineering. In summer 2010, he graduated with a Master of Science degree in Mechanical Engineering and proceeded further to pursue his Ph.D in the ESE program at UTEP.

Permanent Address: C-104, Keerthi Apartments,

Behind Saradhi Studios, Yellareddyguda,

Hyderabad, India - 500073