Investigation of Metal Oxide Nanostructured Thin Films Based Optical Hydrogen Sensors

A thesis submitted in fulfilment of the requirements for
the degree of Doctor of Philosophy

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March 2012
Author’s Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work, which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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Mohd Hanif Yaacob

March, 2012
Acknowledgement

First and foremost, I would like to thank God for his guidance and spiritual comfort in making this quest of knowledge possible. A big thank you to my senior supervisor Prof. Wojtek Wlodarski for his invaluable support, guidance, encouragement, intellectual input and friendship for me in conducting this research to its success. I also would like to take this opportunity to express my sincerest love to my wife (and my soul); Zuraidah Zan and my two lovely princesses; Huda and Hannan for their unconditional love, support and patience. I thank my beloved parents, Mr. Yaacob Awang and Mrs. Rosnah Mahmood for their continuous support and encouragement.

A special gratitude as well to Assoc. Prof. Kourosh Kalantar-zadeh and Prof. Arnan Mitchell as my second supervisors for making my PhD program a truly fruitful experience.

I wish to thank to my colleagues Dr. Micheal Breedon, Dr. Mahnaz Shafei, Dr. Rashidah Arsat, Dr. Jerry Yu, Mr. Jian Ou, Mr. Muhammad Zamharir Ahmad, Dr. Rick Zheng, Dr. Chen Zhang, Dr. Audrey Chapelle, Mr Amin Kayani, Mr. Josh Campbell and Mr. Laith Al-Mashat for their help, good humour and providing a friendly and inspiring environment for conducting research. May the friendship lasts forever.

I would also like to pass my special thanks to Dr. Abu Z. Sadek, Dr. Matt Field, Dr. Ali Moafi, Dr. Glenn Matthews, Dr. Samuel Ippolito, Dr. Vijay Sivan, Dr. Gorgi Kovtoski, Dr. Muhammad-Bagher Rahmani, Mr Tanveer, Mr. Eike and Ms. Lilin Li for their support, friendship and encouragement.

My thanks extended to the academic and administrative members of the School of Electrical and Computer Engineering at RMIT University specifically Ms. Karen Hewitt for her help in the postgraduate matters. I am especially grateful to the technical and MMTC staffs of the school, Mr. Paul Jones, Mr. Yuxun Cao, Ms. Chi Pin Wu, Mr. Mahyar and Mr. Tristan for their assistance during my experiments.
I also would like to take this opportunity to thank several people, without whom part of this research would not be possible. My gratitude goes to Professor Jonhee Kang from University of Incheon, Korea, for providing me with the WO$_3$ nanorod samples, Dr Anurat Wisitsoorat from NECTEC, Thailand, for the sputtered NiO samples and Dr Vladimir Golovko and Mr. David Anderson from Canterbury University, New Zealand, for the gold nanoclusters. Special thank you also to Dr Olena Berger and Professor Wolf-Joachim Fisher from Dresden University of Technology, Germany, for preparing the WO$_3$ thin films with nanosphere.

Additionally, I would like to thank Dr. Johan du Plesis, Mr. Phil Francis, Mr. Peter Rummel and all microscopists of the Department of Applied Physics, RMIT University for their input and help in organising the material characterisations. Also thanks to Dr. Paul Spizziri of School of Physics, University of Melbourne for his assistance in the Raman characterisation.

I thank the Ministry of Science, Technology and Innovation of Malaysia (MOSTI) for awarding me the PhD scholarship and Universiti Putra Malaysia especially the staffs of the Department of Computer and Communication Systems Engineering for their continuing support.

Special thank you to my parent-in-law: Mr. Zan Dawam and Mrs Siti Aisah, and my sister and brothers for their endless encouragement, pray and support especially to Siti Farhana, Noor Alyani, Siti Zaharah, Nor Hafizah, Noor Hidayah, Nishrin, Nurul Amalina, Adidah and Fatin Nadiah for their help in taking care of my daughters.

My special thanks also to Mr. Asmadi Abdul Kadir and family, Mr. Nushi Mahfodz and family as well as friends and close-knitted Malaysian families of South Eastern and Melbourne for the wonderful friendship and togetherness. Representing my family, we are indebt with your support and kindness throughout our stay in Melbourne.

May peace be with you….

Mohd Hanif Yaacob
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Abstract

In this PhD research, novel metal oxide nanostructured thin film based optical H\textsubscript{2} sensors were developed and investigated. The nanotechnology enabled gas sensors had been reported to improve substantially their performance compared to the conventional sensors towards target analytes. Nevertheless, the previous investigations were mostly concentrated on the electrical based sensors and less focused on the optical based sensors. Therefore, the author embarked into this PhD research project to explore the sensing potential of the optical devices and comprehensively study a various kinds of metal oxide nanostructured thin films as the gas sensing layers. This was undertaken with the aspirations of enhancing the performance of the nanostructured thin film based optical sensors as compared to the conventional based sensors. To the best of author’s knowledge, the author developed several novel metal-oxide nanostructured based optical sensors with morphologies that have not been reported previously.

The nanostructured materials under investigation are tungsten trioxide (WO\textsubscript{3}), molybdenum trioxide (MoO\textsubscript{3}), titanium dioxide (TiO\textsubscript{2}) and nickel oxide (NiO). These metal oxides are known to have electrochromic and photochromic properties. However, their potentials in the gasochromic applications are yet to be fully explored especially in their nanostructure forms. The developed optical gas sensors require a thin (≈25Å) catalytic metal layer such as palladium (Pd), platinum (Pt) or gold (Au) to dissociate the H\textsubscript{2} molecules into the nanostructured thin films. The author deposited these catalysts and metal oxide nanostructures via different deposition techniques such as sputtering, electron beam, pulsed laser, acid etching, thermal evaporation, anodisation as well as spin coating. The optimisation of these deposition techniques resulted in various thin films consisted of unique structures such as WO\textsubscript{3} nanostructures (nanograins, nanospheres, nanorods and nanoplatelets), MoO\textsubscript{3} nanorods, TiO\textsubscript{2} nanopores and NiO nanograins. The gasochromic properties of these nanostructures were investigated towards H\textsubscript{2} with low concentration (<1%). Micro-nanocharacterisation techniques such as SEM, TEM, XPS, XRD, EDX, Raman and UV-vis-NIR spectroscopies were employed to
obtain complete structural properties of the nanostructured materials in order to fundamentally understand their functionalities with respect to the optical sensors’ performance.

The investigations of the H₂ sensing performance of the developed optical sensors were carried out in two stages. In the first stage, the metal oxide nanostructured thin films were deposited onto transparent substrates such as quartz and tested towards H₂ via absorbance measurement. Cumulative absorbance by integrating the response for a wavelength range was introduced. To the best of the author’s knowledge, this is a new approach in the optical sensor measurement to improve the sensitivity. The author also expanded the optical H₂ sensing mechanism of the metal oxide based films to include the formation of water during the coloration of the films due to the gas molecules and sensing layer interaction.

In the case of sputtered WO₃, the 500 nm films were deposited onto different transparent substrates consisting of quartz, glass, ITO and FTO conductive glasses to study the effect of the different WO₃ nanograin sizes on the H₂ sensing performance. The absorbance response increase of 110% was recorded for the Pd/sputtered WO₃ films with similar grain sizes (30 - 60 nm) on quartz, glass and ITO as compared to the small response (5% increase) for the films on FTO glass with large grains (300 – 500 nm) upon exposure to H₂ of 1% concentration. The H₂ sensing performance was also compared for the WO₃ films with different catalyst. Pd was proven to be highly efficient in improving the optical response as compared to Pt and Au. As a result, Pd was chosen to be the catalytic layer for the developed sensors in this research project.

For the first time, the author successfully developed optical sensors based on Pd/MoO₃ nanorod films and Pd/TiO₂ nanoporous films which are sensitive towards H₂ with low concentrations <1% at temperature below 120°C. The p-type metal oxide shows the opposite gasochromic properties than the n-type metal oxides which is proven by the Pd/400 nm p-type NiO nanostructured film reduced its absorbance by 6.5% towards H₂ of 1% concentration. It was found out that amongst the sensors investigated, the devices based on the Pd/WO₃ sputtered films and Pd/WO₃ nanoplatelet films produced the largest absorbance response compared to the other metal oxide nanostructured films by
increasing the response to 110% and 99%, respectively, towards H$_2$ with 1% concentration. The superior optical response exhibited by the Pd/WO$_3$ nanoplatelet films towards H$_2$ has never been reported before and thus, can be considered as a significant contribution to the body of knowledge.

In the second stage, the author deposited the Pd/WO$_3$ sputtered films and Pd/WO$_3$ nanoplatelet films onto different optical transducing platforms such as optical fiber and channel waveguide. The reflection measurement performed on the multimode fiber showed that the ones with WO$_3$ nanoplatelet films had a much larger response (18%) as compared to the fiber with the sputtered WO$_3$ films (5.6% response) when exposed to H$_2$ of 1% at 100°C. Finally, the author developed optical sensor based on single mode inverted rib polymer waveguide coated on top with Pd/WO$_3$ nanostructured thin films. According to the literature, this is the first time the single mode inverted rib polymer waveguide was developed for H$_2$ sensing applications. Using a beam profiler, the measured intensity of the light propagating in the waveguide was reduced when exposed to H$_2$ due to the change of evanescent field at the interface of the waveguide and the sensing layer. As a result of this PhD research project, several novel optical H$_2$ sensors based on the metal oxide nanostructured thin films were developed.
Chapter 1

Introduction

The first chapter of this thesis outlines the work carried out in this PhD research project. This includes the research motivation, objectives, the author's achievements as well as the organisation of this thesis.

1.1 Motivations

Hydrogen (H\textsubscript{2}) is one of the most used process gases in many industries such as petrochemical, electronics or semiconductor, metallurgy, food, glass and laboratory analysis [1]. Currently, the world H\textsubscript{2} industry is estimated to worth around USD39 billion [2]. With the introduction of H\textsubscript{2} powered vehicles in 2015, the consumption of the element is set to increase by 3.5% every year [2].

In the future, H\textsubscript{2} applications will be more diversified and accessible to the public than in the present time. The advances of H\textsubscript{2} powered fuel cells to generate energy allow the deployment of this technology in the automotive as well as the backup generator for the residential areas. The increase use of high-speed turbine generators in the power plants requires H\textsubscript{2} as the cooling agent to transfer heat in the generators. One of the feasible technologies for power generation in the future is nuclear. The growing constructions of nuclear reactors raise the need of H\textsubscript{2}-O\textsubscript{2} mixture to suppress inter-granular stress corrosion cracking in their cooling water system [3].

On the other hand, there are major safety concerns related to the properties of H\textsubscript{2}. Even though H\textsubscript{2} has higher auto-ignition temperature (585°C) as compared to the other type of fuels, its low mass and high diffusion coefficient (0.61 cm\textsuperscript{2}s\textsuperscript{-1}) makes it really difficult to contain [4]. It is also easily leaks out due to the smallest molecule size [5]. H\textsubscript{2} has wide flammability range (4-75%) and hence
easily combusted when mixed with air. The risk of explosion due to H₂ leakage is further increased with its small ignition energy (0.02 mJ) and large flame propagation velocity [1]. As shown in Fig. 1, H₂ has much larger window of flammability and smaller ignition energy as compared to gasoline and methane [6]. H₂ leak is very dangerous because common electrostatic discharge (ESD) is enough to be the source of ignition.

![Flammability Limits](image)

**Fig. 1.1 Flammability limits of H₂ in comparison to gasoline and methane (CH₄) [6].**

While H₂ is non-toxic, it is odourless, tasteless and burn with almost invisible flame making it difficult for the human detection [1]. Many studies [7-10] also identified that H₂ may cause the loss of mechanical stability in the corroded metals with the formation of brittle metal hydride. Therefore, it is extremely important to develop highly sensitive and reliable H₂ sensors to detect or monitor the gas as well as to prevent safety hazards.

The current standard in H₂ and its safety guidelines is based on American National Standards Institute (ANSI) G-095-2004 and International Organization for Standardization (ISO) TR 15916:2004. Apart from that, the Department of Energy (DOE), USA, has set several specifications for H₂ sensors to be considered relevant and commercially viable [11]. These specifications are compared with the automotive H₂ sensing requirements and outlined in the following table.
Table 1.1 \( \text{H}_2 \) sensor specifications and their requirements for the automotive applications.

<table>
<thead>
<tr>
<th>No</th>
<th>DOE Proposed Performance Specifications for ( \text{H}_2 ) Sensor</th>
<th>Automotive ( \text{H}_2 ) Sensing Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{H}_2 ) leakage concentration (%)</td>
<td>Between 0.1 - 10%</td>
</tr>
<tr>
<td>2.</td>
<td>Response time (seconds)</td>
<td>In seconds, preferably less than 1 s</td>
</tr>
<tr>
<td>3.</td>
<td>Operating temperature (°C)</td>
<td>More than -30°C, up to 80 – 100°C</td>
</tr>
<tr>
<td>4.</td>
<td>Accuracy (%)</td>
<td>±5%</td>
</tr>
<tr>
<td>5.</td>
<td>Selectivity</td>
<td>Only detect ( \text{H}_2 ) and no interference from other gases such as hydrocarbon, ( \text{CO} ) and ( \text{O}_2 )</td>
</tr>
<tr>
<td>6.</td>
<td>Reference ambient environment</td>
<td>Air with relative humidity from 10 – 98%</td>
</tr>
<tr>
<td>7.</td>
<td>Lifetime</td>
<td>More than 10 years</td>
</tr>
</tbody>
</table>

The \( \text{H}_2 \) storage solution especially in the automotive is perceived as inadequate by many critics due to the gas molecular properties as well as unreliable leakage detection system. According to the records[12], fourteen fatalities and substantial physical damages have been reported in the world mainly because of lack of \( \text{H}_2 \) monitoring equipments. This is one of the main challenges in promoting \( \text{H}_2 \) powered technologies to reduce pollutions and fossil fuel dependency in the community. If reliable \( \text{H}_2 \) sensor with the above specifications could not be achieved, it will be very difficult to convince the public to embrace the new technology. This can lead to over-reliance on the fossil fuel which is expected to be very expensive in the future. As a result, the community can be affected by the rising cost of living and inflation.

Sensing technologies for \( \text{H}_2 \) have been studied and several traditional sensing techniques are commonly used in the industry such as gas chromatography, mass spectrometry, catalytic bead and thermal conductivity [6]. Although these techniques enable accurate detection of \( \text{H}_2 \), their setup are mostly expensive, complex and unsuitable for in-situ applications [1]. Apart from that, solid state metal oxide based sensors have been developed and gained popularity as practical and highly sensitive devices towards chemicals with low concentrations. The semiconducting metal oxides are also known for their reliability towards high temperature applications. The solid state sensors are developed using various kind of transducing platforms such as conductometric, surface acoustic, piezoelectric and pyroelectric [1]. These electrical transducing platforms are widely deployed in developing \( \text{H}_2 \) sensors.
due to their simplicity, low cost and large dynamic range [1]. Other platform for H₂ sensing applications is optical transducer.

The development of optical sensors is relatively new and less endeavoured as compared to the electrical sensors. Nevertheless, the reduced cost in optical components which is driven by the large commercial telecommunication and optoelectronic markets creates opportunity in the implementation of the technology for sensing applications. The properties of the optical signal have many advantages as compared to the electrical signal and thus offer vast opportunity to the researchers to explore its potential in the sensing applications. Some of the unique properties of optical signal such as immunity to the electromagnetic interference (EMI) as well as resistance to the corrosive, reactive and flammable environments [13] making optical sensor a promising candidate for H₂ sensing applications. Optical sensors also allow remote and distributed sensing when they are integrated with the existing optical fiber networks. As a result, the author believes that by employing optical sensors in the volatile environments, the safety risks associated with the leakage of H₂ will be significantly reduced.

1.2 Nanotechnology Enabled Optical Hydrogen Sensors

In the past few years, the advances in the field of nanotechnology allow the design, fabrication and deployment of nanostructured solid state materials for the gas sensing applications. Nanostructured materials are defined as the materials with at least one dimension in the nanoscale range (<100 nm) [14]. Within this range, the physical, chemical, optical, mechanical, electronic and biological properties of the nanomaterials are normally unique and substantially different from those observed for bulk materials [14].

It has been reported that the nanotechnology enabled gas sensors improve substantially their sensing performances towards target analytes [14]. The nanostructured thin films have higher surface to volume ratio as compared to the amorphous films. The interaction between the gas molecules and the nanostructured layer of the gas sensor is enhanced significantly to produce maximum output signal. As a result, higher sensitivity and lower operating temperatures are normally expected for the
nanotechnology enabled gas sensors as compared to the conventional sensors. In addition, the nanostructures minimize the time taken for the analyte molecules to diffuse into and out of the films [14]. These fast response and recovery showed by the sensors with nanostructured thin films are very important in preventing a potential disaster. Combining the nanomaterials with the optical transducers results in the development of new generation of gas and vapour sensors with the significant advantages as mentioned before.

In optical sensor based on the thin films, these nanostructured materials are combined with various kind of transducing platforms such as transparent substrates, optical fiber or waveguides (planar and channel). For gas sensing applications, the optical techniques deployed to measure the response are based on the absorbance, reflectance, refractive index, surface plasmon resonance (SPR) and the luminescence change induced by the interaction between the nanostructured films and various gases and vapours molecules.

The first report on the optical sensor based on the thin films towards H₂ was published by Ito et. al in 1984 [15]. They developed gas sensor comprised of optical fiber or waveguide coated with metal oxide film sensitive towards H₂ or gasses with hydrogen such as ammonia (NH₃) and hydrogen sulphide (H₂S). The metal oxide film was combined with a catalytic metal layer such as palladium (Pd) or platinum (Pt). In the presence of H₂, the gas molecules are adsorbed on the metal surface and dissociated into H ions and electrons [5]. The ions diffuse into the metal oxide layer and as a result the change in its optical properties is observed. The absorbance of the film increases with the increase of H₂ concentrations. In other words, the film turns dark when exposed to H₂. In their work, Ito et. al observed the response for optical wavelength around 1400 nm.

A variety of optical sensors for gas sensing applications have been developed based on the results by Ito group. Hamagami et. al [16] reported that their sputtered molybdenum trioxide (MoO₃) film coated with Pd changed its transmittance when exposed to pure H₂ and H₂ of 0.1% in argon (Ar). Sumida et. al [17] successfully deposited Pt/tungsten trioxide (WO₃) amorphous films on the tip of
optical fiber and tested towards H\textsubscript{2} of 1\% concentration in nitrogen (N\textsubscript{2}) using optical time domain reflectometry (OTDR).

Nevertheless, most of the works were based on the bulk or amorphous films and measured at single optical wavelength towards H\textsubscript{2} within the 0.1 - 4\% concentration ranges [18, 19]. With the advances in the field of nanotechnology, different nanostructures are developed and thus creating opportunities in the investigation of optical performances of the metal oxide nanostructured thin films towards H\textsubscript{2} with low concentrations <1\% or 10,000 parts per million (ppm).

1.3 Objectives and Research Questions

The aim of this research program is to develop novel metal oxide nanostructured thin films based optical sensors for H\textsubscript{2} sensing applications. This includes:

- investigation of the semiconducting metal oxides with gasochromic properties.
- deposition or synthesis of the metal oxide nanostructured thin films onto suitable optical transducers.
- comprehensive study of the micro-nanocharacteristics of the nanostructured metal oxides to understand their influence on the optical sensor’s performance.
- investigation of the optical sensing performances (static and dynamic) of the developed sensors towards H\textsubscript{2} with low concentrations (<1\%).
- to understand and explain the gas molecules-sensing layer interaction mechanism of these optical sensors.

In order to achieve these objectives, the author outlined the following research questions:

- what are the metal oxides that change their optical properties when exposed to gas, specifically H\textsubscript{2}?

- what are the deposition techniques or synthesis methods available to produce novel metal oxide nanostructured thin films?
Chapter 1: Introduction

- how to integrate the nanostructured metal oxides with the optical transduction platforms for the optical sensor?

- which optical measurement techniques will be deployed to investigate the gasochromic response of the developed sensors towards H₂?

- how different are the optical sensing performances of the nanostructured metal oxides with different morphologies?

Based on these research questions, the author focused the investigation on a few kinds of semiconducting metal oxides (SMO) well-known for their electrochromic properties. It is also suggested that the nanostructured SMO have the potential to exhibit excellent gasochromic properties. With reference to this hypothesis, the author developed optical sensors based on nanostructured thin films using tungsten trioxide (WO₃), molybdenum trioxide (MoO₃), titanium dioxide (TiO₂), nickel oxide (NiO), combined with platinum (Pt), palladium (Pd) or gold (Au) as the catalysts. The nanostructured thin films were deposited onto different optical transducing platforms to analyse their gas sensing performance via different optical measurement techniques. The nanomaterial characterisation combined with the gas sensing performance contributes to the fundamental understanding of the gas interaction mechanisms in optical sensors.

1.4 Outcomes and Author’s Achievements

This PhD research has led to several novel and significant findings contributed to the body of knowledge in the field of gas sensor based on metal oxide nanostructured thin films. In this thesis, the author presents a comprehensive report on the experiments and the theoretical analysis of the developed optical sensors exposed to H₂ with low concentrations at room as well as elevated temperatures. The findings of this research program can be outlined as follows:

- several catalytic layer/metal oxide based optical sensors were successfully developed with excellent sensing performance towards H₂ with low concentration less than 1%.
Different nanostructured metal oxides combined with different catalytic layer demonstrated variable gas sensing performances at different operating temperatures.

- new measurement approach was introduced by integrating optical response over a range of wavelengths as compared to the single wavelength measurement commonly used in the previous studies. The cumulative measurement improves the sensitivity and allows the use of low cost broadband light source such as light emitting diode (LED).

- optical sensors coated with Pd catalytic layer were found to show excellent H$_2$ sensing performance as compared to the sensors coated with Pt or Au layers. The influence of the catalytic metal thickness on the gas response was also studied.

- novel optical sensors coated with Pd/WO$_3$ nanoplatelets, Pd/MoO$_3$ nanorods, Pd/NiO nanograins and Pd/TiO$_2$ nanoporous thin films were developed for the first time to the best of the author’s knowledge. These sensors exhibited optical response towards H$_2$ with concentration as low as 0.06%.

- the H$_2$ gas interaction mechanism was studied for the developed optical sensors. This study supported the theories developed by Deb et. al [20] and Georg et. al [21]. It is believed that the optical response is attributed not only due to the oxygen vacancies in the metal oxide layers created by the diffusion of H ions but also affected by the water vapour generated from the H$_2$ molecules-sensing layer interaction.

- it was proven, for the first time, that the H$_2$ response was observed for the inverted rib polymer waveguide coated with the Pd/metal oxide nanostructured thin films. Nevertheless, the response was irrecoverable and only suitable for H$_2$ leakage detection. Further investigation need to be carried out to improve the device sensing performance.
In summary, this PhD research program successfully fulfilled its objectives to investigate and develop novel H$_2$ optical sensors based on nanostructured thin films. Throughout this research, the author gained various achievements such as numerous publications and award. Research papers associated with this PhD program have been published in high impact refereed journals and presented at various established international conferences. These include four first author and five co-author publications in: Sensors and Actuators B: Chemical, Sensor Letters, Physical Chemistry Chemical Physics, Korean Physical Society and Journal of Biomedical Engineering. The details of the author’s journal publications are as follows:


The author’s also successfully published and presented personally and on his behalf, 18 research papers in highly established sensor conferences. Throughout the candidature, the author personally attended the following conferences:

- Nano Today Conference, Singapore, August 2-5, 2009
- The 8th IEEE Sensors Conference, Christchurch, New Zealand, October 25-28, 2009
- IEEE Australia and New Zealand Student Congress, Melbourne, Australia, November 24-26, 2010.

During the 2010 IEEE Australia and New Zealand Student Congress, the author received the best research project award. Throughout the course of this PhD program, the author was also invited to be a reviewer for Physica:E journal and International Conference on Photonics (ICP) 2010 and 2011 organised by IEEE Photonics Society of Malaysia. The author is also writing another research paper titled ‘Low Concentration Hydrogen Detection Using Inverted Rib Polymer Waveguide Coated with Pd/WO3 Nanostructured Thin Films” which will be submitted to Optics Communication journal. The complete list of the author’s publications is shown in Appendix A.
1.5 Thesis Organisation

This thesis consists of eight chapters and two appendices. The thesis presentation is outlined as follows:

- Chapter 1 is the introduction and overview of the author’s motivation in taking the research in the optical sensors for gas sensing applications. This includes the research objectives, significant contributions as well as the achievements of this study.

- Chapter 2 presents the research rationales and literature review of the optical sensor for H\textsubscript{2} employing different metal oxide nanostructured thin films. The optical properties of H\textsubscript{2} and the use of nanostructured materials such as WO\textsubscript{3}, MoO\textsubscript{3}, TiO\textsubscript{2}, NiO as well as the catalytic metals (Pd, Pt, Au) for gas sensing applications are also reviewed. This chapter also covers the optical measurement principles and the transducing platforms for optical sensors. The focus is on the measurement principles using absorbance and reflectance. The optical transducing platforms under reviewed in this chapter are spectrophotometer based as well as optical fiber and waveguides. In addition, the gas sensing mechanism for optical sensors deploying the metal oxide nanostructured thin films is also presented.

- Chapter 3 outlines the design and fabrication processes of the optical transducers. This includes the preparation of the transparent substrates and optical fibers used in this research. The design and fabrication processes of the channel waveguide are also presented.

- Chapter 4 discusses about the synthesis and deposition of the nanostructured materials. The different techniques employed for the physical deposition and chemical synthesis to produce various kinds of metal oxide nanostructured thin films act as the optical sensing layer are presented in details in this chapter.

- Chapter 5 reports the characterisation of the nanomaterials to be used as the sensing layer. The micro-nanocharacterisation results were obtained via many techniques such
as SEM, TEM, XRD, EDX, Raman spectroscopy, UV-Vis-NIR spectroscopy and XPS.

- Chapter 6 presents the different gas testing setups for the developed optical sensors. The discussion includes the setups to measure absorbance, reflectance and beam intensity for the waveguide based sensor. The gas chamber constructions as well as the testing procedure are also described.

- Chapter 7 presents the experimental results obtained from the developed optical sensors performance towards H₂. The effect of nanostructured materials’ morphology, the use of different catalytic metals, operating temperature and the different H₂ concentrations on the sensors’ performance is discussed in great details.

- Chapter 8 concludes the research findings and contributions. The suggestions for possible continuation and future work are also presented.
References


Chapter 2

Literature Review and Research Rationales

2.1 Introduction

The thesis first chapter outlined the motivation and the objectives of this PhD research. In this chapter, the author will present the rationale for developing optical sensor based on the metal oxide nanostructured thin films for H\textsubscript{2} sensing applications. This includes reviews on the nanomaterials deployed in the optical gas sensors. Later, the author presents the optical measurement techniques and transducers deployed in gas sensing applications. The discussion includes the H\textsubscript{2} interaction mechanism proposed by the author for the optical sensors developed in this project.

2.2 Review of Nanostructured Materials in Optical Sensors for Gas Sensing Applications

There are several major groups of nanomaterials that could be combined with optical transducers for gas sensing applications. In general, they can be divided into three major groups, namely, semiconducting metal oxides (inorganic), conductive polymers (organic) and composite materials. However, there are no evidences that all the materials are equally effective for gas sensors applications [1]. Therefore, with numerous types of nanomaterials, one of the main issues in the optical gas sensor development is the identification of the materials with the best gasochromic properties and sensing performance parameters.

In this research project, the author focused the investigation on the metal oxide nanostructured thin films. The metal oxide based gas sensors offer low cost, high sensitivity, high temperature operation, simplicity and can be easily combined with different types of transducing platforms [2-4].
The deployment of the metal oxides as the gas sensing materials was first reported in 1953 by Brattain and Bardeen [5]. It was demonstrated that the adsorption of gas on the surface of a semiconductor (Germanium) change the conductivity of the material. Since then, different types of metal oxides were investigated and identified to be sensitive towards different gases. It is commonly known that these materials can have either n- or p-type of conductivity [1]. The p-type materials accept and donate negative charges when exposed to oxidizing and reducing gases, respectively. In contrast, the n-type materials act in the opposite of their p-type counterparts when exposed to the similar gases [6]. Table 2.1 summaries some of the well-known metal oxides sensitive towards many gases.

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Gas Optimal for Detection</th>
<th>Operating Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>Reducing gases (CO, H₂, CH₄, etc)</td>
<td>200 – 400</td>
</tr>
<tr>
<td>WO₃</td>
<td>O₃, NO₂, H₂S, SO₂</td>
<td>300 – 500</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>O₂, CO</td>
<td>600 – 900</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>O₃, NOₓ</td>
<td>200 – 400</td>
</tr>
<tr>
<td>MoO₃</td>
<td>NH₃, NO₂</td>
<td>200 – 450</td>
</tr>
<tr>
<td>TiO₂</td>
<td>O₂, CO, SO₂</td>
<td>350 – 800</td>
</tr>
<tr>
<td>ZnO</td>
<td>CH₄, C₂H₁₀, O₃, NOₓ</td>
<td>250 – 350</td>
</tr>
<tr>
<td>CTO</td>
<td>H₂S, NH₃, CO, VOC</td>
<td>300 – 450</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Alcohol, CH₄, NO₂</td>
<td>250 – 450</td>
</tr>
</tbody>
</table>

Table 2.1 shows that the metal oxides based conductometric sensors for gases commonly operate with optimum temperatures more than 200°C. The advantage of having high operating temperatures is that it allows the use of the sensors in the harsh environments such as car engines and machines. However, the conductometric sensors’ selectivity is poor. It is difficult to identify the target gas for any leakage detection via conductometric sensors. In contrast, optical sensors are known to have better gas selectivity as compared to the other types of sensors [1]. However, the development of the optical sensors is limited by the availability of the materials with chromic properties.

Initially, it was presumed that almost any metal oxide could be used for gas sensing applications. In other words, it is sufficient to deposit this metal oxide on the intended transducing platform under certain surface control to induce gas response [1]. However, when the nature of the
gas molecules – sensing layer interaction is increasingly well-understood, the deployment of different metal oxides for different gas sensing applications was explored. This is because the metal oxides for gas sensors require specific combination of their physicochemical properties in order to exhibit response. Nevertheless, not every material possesses this combination [1, 4]. As a result, the metal oxides with excellent conductivity response towards certain gas are not necessarily show the same performance in their optical response.

It is also known that the sensing performance of the metal oxide based gas sensors, especially sensitivity, are controlled by three independent factors such as material properties, transducer function and variability of sensor construction [7]. The material properties provide the ability of the metal oxide surface to interact with the target gas and the transducer function provides the ability to convert the signal caused by chemical interaction of the metal oxide surface into readable signal [8]. Since the surface is responsible for receptor function of the gas sensors, the enhancement of the surface properties by depositing nanostructured metal oxides should considerably improve the sensor’s performances. In nanometre scales, most of the atoms are surface or near surface atoms which significantly increasing the effective number of sites available for reactions with target molecules.

Based on this information, the author focused the investigation on four different metal oxide nanomaterials, which are tungsten trioxide (WO₃), molybdenum trioxide (MoO₃), titanium dioxide (TiO₂) and nickel oxide (NiO). As mentioned in Table 2.1, most of these metal oxides were commonly deployed as the sensing layer for electrical based gas sensors and widely reported throughout the last decades. In contrast, limited studies were carried out on their deployment for optical sensor towards gases especially H₂. This is supported by the data retrieved from the well-known online publication database, Web of Science, which is developed by ISI Thomson as shown in Fig 2.1.
Based on the graph, the total publication record from 1991 – 2011 on the topic on the metal oxides based conductometric sensor towards H$_2$ is 159 articles. As opposed to this, only 59 articles had been published in the topic on the metal oxides based optical sensor towards similar gas. This trend provides strong rationale in the investigation of the metal oxides based optical sensors towards H$_2$.

The systematic investigation will be carried out initially on the nanostructured WO$_3$. The following subsection present in details the justification to deploy the WO$_3$ nanostructured thin films as the optical sensing layer towards H$_2$.

### 2.2.1 Tungsten Trioxide (WO$_3$)

Tungsten trioxide (WO$_3$) is the most extensively studied electrochromic material [10-14]. The material ability to sustain reversible and persistent changes of its optical properties under the action of a voltage was discovered in 1969 by Deb [15]. The coloration of the WO$_3$ from transparent to dark was found to be strongly demonstrated in the highly disordered thin films [15]. Since then, extensive technological developments were carried out on this material especially for smart window applications [13]. However, the first report on the material potential for the gasochromic applications was only published by Ito et. al in 1992 [16]. In his work, Ito coated a
thin layer of polycrystalline WO$_3$ with palladium (Pd) and exposed to H$_2$ with the concentration range of 0.1 – 1% in argon (Ar). The gasochromic response of the films towards H$_2$ has been suggested to be analogously similar to the electrochromic phenomenon in WO$_3$ [15].

Previously, the development of the WO$_3$ based optical gas sensor was focusing on the amorphous films. However, the response of the amorphous WO$_3$ films was found to be less sensitive as compared to their conductometric based counterparts [15]. A key solution to improve the optical sensitivity is by deploying nanostructured WO$_3$ films.

In some early works, Ando et. al [17] reported that their sputtered Pt/WO$_3$ composite films responded at a temperature of 200°C, and only in a fixed exposure of H$_2$ with 1% concentration in air. Shanak et. al [18] reported coloration in their sputtered Pt/WO$_3$ thin films when exposed to an undisclosed fixed H$_2$ concentration at room temperature. Both reported baseline stability issues, and recovery times were reported to be in the realm of 50 minutes. Ando et. al [19] also developed Pd/WO$_3$ based optical sensor with slightly improved response time of around 8 minutes at 200°C when exposed to H$_2$ of 1% concentration.

The author believes that these sensing performances can be significantly improved by deploying WO$_3$ nanostructured films as the sensing layer. The reduction from micro to nano dimensional crystallite size increases the surface area to volume ratio up to several orders of magnitude. The increased surface area of the nanostructured film also increases the number of available surface reaction sites for the adsorption of gas species, leading to fast sensor response and recovery. Recently, the development of novel WO$_3$ nanostructures such as nanorods, nanospheres and nanoplatelets provide very high surface area. If being deployed as the sensing layer, these nanostructures are anticipated to improve the optical response towards H$_2$ with very low concentration (<1%) and low operating temperatures (<100°C). Highly sensitive gas sensors with low operating temperatures are required in several critical applications such as hydrogen generation plants, vehicle H$_2$ tanks and volatile nuclear reactors which produce massive H$_2$ in the case of meltdown.
WO₃ is a wide bandgap n-type semiconductor with crystals has perovskite-like atomic configurations based on corner-sharing WO₆ octahedra. In agreement with the behaviour of most perovskites, the WO₃ single crystals structurally transform depending on the temperature [20]. Table 2.2 presents the different WO₃ crystal structures at different deposition temperatures.

<table>
<thead>
<tr>
<th>WO₃ Crystal Structure</th>
<th>Deposition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic</td>
<td>&lt; -43</td>
</tr>
<tr>
<td>Triclinic</td>
<td>-43 – 17</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>17 – 330</td>
</tr>
<tr>
<td>Orthorombic</td>
<td>330 – 740</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>&gt; 740</td>
</tr>
</tbody>
</table>

With reference to the table above, the WO₃ crystal phase transformation occurs in the following sequence: monoclinic, triclinic, monoclinic, orthorombic and tetragonal. Monoclinic WO₃ exists at below subzero temperature (-43°C) as well as at room temperature until 330°C. However, the crystal formation at the subzero temperature is very rarely encountered except in the laboratory and thus, the monoclinic crystals formation are normally referred to the ones exist at room temperature. It has been reported that the WO₃ crystal transition is partially reversible. When annealing at high temperature more than 330°C and 740°C, WO₃ transforms into orthorombic and tetragonal crystal structures, respectively as in Table 2.2. Despite of that, WO₃ is unable to retain these phases when it is returned to room temperature and commonly transformed into monoclinic structure [20]. As a result, monoclinic is known to be the most stable crystal phase for WO₃. Based on this characteristic, it is important for the author to control the deposition parameters of the WO₃ nanostructures to produce monoclinic crystal phase. By maintaining stable and similar crystal phase for the different WO₃ nanostructures developed, investigation of the nanomaterial gas sensing properties can be carried reliably. Szilágyi et. al [21] and Souza et. al [22] also found out that the asymmetrical monoclinic WO₃ improves the gas molecules adsorption/desorption rate.

Interest in the use of WO₃ for the chromic applications arose from its optical properties in the visible wavelengths region which are dominated by the absorption threshold [20]. The
threshold is defined by the WO$_3$ nanostructures bandgap energy ($E_g$) which is ranging from 2.60 – 3.25 eV. These properties make the WO$_3$ films generally transparent in nature. Nevertheless, light yellowish films were reported for the samples with $E_g$ at the low end due to some absorption of the blue spectrum and light greenish films were observed for the non-stoichiometric (WO$_x$) samples [23]. The refractive index of the material was reported to be around 2 – 2.5 [20].

The colour shift in the transparent WO$_3$ to dark bluish films (tungsten bronze) can be initiated by applying voltage (electrochromic) or exposing to reducing gas like H$_2$ (gasochromic) [15]. Different models have been proposed to explain the gasochromic phenomena and will be discussed in details in the later subsection (2.4). The electrochromic phenomena in the WO$_3$ would not be covered in details as it is beyond the scope of this research.

The coloration efficiency of the films is said to be highly influenced by the surface morphology [24]. The high surface area of the WO$_3$ nanostructured thin films is expected to interact strongly with the gas molecules and as a result, large optical response is observed. Furthermore, the open structure improves the molecules desorption rate from the surface and thus, lower response time than in their bulk structures. Nevertheless, a study on the electrochromic properties of WO$_3$ nanowires by Chen et. al reported that high surface irregularities and the effect of the WO$_3$ nanostructure size might suppress the optical response during the chromic interactions [25]. This creates opportunity to confirm the optical response of the different WO$_3$ nanostructured films developed for the gasochromic applications. Investigation should be carried out to determine the influence of the surface morphology for the WO$_3$ nanostructured films interaction with gas molecules instead of electrolyte (liquid) as in the electrochromic experiments.

The other nanostructured material investigated for its gasochromic properties towards H$_2$ is molybdenum trioxide (MoO$_3$).
2.2.2 Molybdenum Trioxide (MoO₃)

Molybdenum trioxide (MoO₃) is a well established metal oxide which has been studied for its electrochromic properties for many years [12, 26, 27]. In the periodic table, MoO₃ belongs to Group VI elements which include WO₃. Some studies reported that the electrochromic response of the MoO₃ films shows a stronger and more uniform absorption of light in its colored state as compared to WO₃. MoO₃ shows high coloration efficiency since the human eyes were found to be very sensitive towards the colour of the molybdenum bronze [28, 29]. The transition metal oxide electrochromic properties were identified by Deb et. al in 1966 [12] and since, extensive research was carried out to understand the material electrochromism. In 1992, Fujishima et. al made a major discovery by inducing the coloration in MoO₃ with visible light than UV as in conventional methods [30].

Similar to WO₃, few investigations have been carried out on the gasochromic response of MoO₃ towards H₂. Shortly after, the works by Fujishima group, Hamagami et. al [31] successfully proved the optical sensitivity in the visible wavelength range of Pd/MoO₃ films towards H₂ in 1993. They deposited Pd/MoO₃ films onto glass substrates via RF sputtering technique and exposed the samples to pure H₂ and 0.1% H₂ in argon (Ar). The films changed their transmittance when exposed to H₂. Nevertheless, they did not investigate vital sensing characteristics such as dynamic performance and repeatability of the Pd/MoO₃ amorphous films. With the limited knowledge on the gasochromic performance of MoO₃, detailed investigation on the films response towards H₂ will provide significant contribution towards the understanding of the nanomaterial gas sensing properties.

Commercial MoO₃ is a white or light gray-colored powder with energy band gap of 2.65 – 3.60 eV [32-34]. The bulk crystal of MoO₃ has an orthorhombic structure which consists of corner-sharing chains of MoO₆ octahedra that share edges with two similar chains to form layers of MoO₃ stoichiometry [35]. The orthorhombic and layered structures of MoO₃ were identified to be stable structures thermodynamically as well as receptive for ion intercalations [36]. Excellent chromic response observed when the MoO₃ films with these structures were connected to a
standard three-electrode system and subjected to -1 to +1 V [36].

The excellent electrochromic performance of the orthorombic MoO\(_3\) films provides motivation for the author to investigate the gasochromic response of the MoO\(_3\) nanostructured thin films. To the best of author’s knowledge, no work has been published in the investigation of the optical sensor based on the MoO\(_3\) nanostructured thin films towards H\(_2\). It is believed that the porous and high surface area of the MoO\(_3\) nanostructures improve the adsorption of H ions with the films, which result in a fast coloration process.

Another nanomaterial under investigation is titanium dioxide (TiO\(_2\)), which will be reviewed in the following subsection.

### 2.2.3 Titanium Dioxide (TiO\(_2\))

Titanium dioxide (TiO\(_2\)) is a wide bandgap (2.50 – 3.20 eV) metal oxide well-known for its applications in the photocatalysis, sunscreen, electrochromic and photochromic devices [37]. The photosensitivity of TiO\(_2\) was discovered by Fujishima and Honda in 1972 [38]. Ever since, the material was extensively studied for various kinds of applications including gas sensors. It was found that the TiO\(_2\) was highly sensitivity towards oxygen and has been so far successfully deployed as an electrical sensor (lambda sensor) in the internal combustion engine that control the air to fuel ratio [7].

Nevertheless, TiO\(_2\) deployment is very limited in the gasochromic devices towards H\(_2\). Macia and Opilski [39] coated Pd/TiO\(_2\) at the tip of an optical fiber and exposed to H\(_2\) of 0.5 – 3.0% concentrations. The TiO\(_2\) films were DC sputtered at room temperature and as a result, the films were amorphous. Optical response was observed only when the films were exposed to H\(_2\) with concentration higher than 1%. At room temperature, the reflectance increased only by 2% for the H\(_2\) with 1% concentration. The response time of their Pd/TiO\(_2\) is 2 mins. These sensing performances are expected to improve significantly if TiO\(_2\) nanostructures are to be deployed as the sensing layer. Another work was carried out by Manera et. al [40] on the Au/TiO\(_2\) nanocomposite films deposited via sol-gel technique. The films were tested towards volatile
organic compounds (VOC) such as ethanol, methanol and isopropanol. The film’s absorbance increase to approximately 1.5%, 5.5% and 1.5% towards 3000 ppm of ethanol, methanol and isopropanol, respectively. The response was minimal and assumed due to the physisorption rather than the chemisorption of the analytes.

TiO$_2$ is an n-type semiconductor with atomic configuration of TiO$_6$ octahedra chains, where each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions [38]. TiO$_2$ commonly exists in the form of rutile, anatase or brookite crystal structures. The most stable TiO$_2$ structure is rutile. In fact, anatase or brookite TiO$_2$ transforms into rutile structures upon annealing. In electrical based sensor, anatase TiO$_2$ was identified to adsorb more gas molecules as compared to rutile [41, 42]. Nevertheless, the crystals of the TiO$_2$ nanostructures have been proven to possess different characteristics than their bulk materials.

A comprehensive TiO$_2$ nanoparticles phase stability study by Bernard et. al [38] demonstrated that the surface hydrogenation induced significant changes in rutile, but not in anatase. They also demonstrated that the structure size at which the phase transition might be expected to increase dramatically when the uncoordinated surface titanium atoms were H-terminated. These findings provide useful information in the investigation of the TiO$_2$ nanostructured thin films as the optical sensing layer towards H$_2$. The author believed that the limited results published on the TiO$_2$ optical sensor towards H$_2$ might be due to the use of anatase TiO$_2$ as in the electrical (conductometric) based gas sensor. Therefore, in this project, the optical testing towards H$_2$ will be performed on both anatase and rutile TiO$_2$ nanostructured thin films.

The deposition of TiO$_2$ nanostructured thin films offers interesting study on their gas sensing properties. Apart from the increase of surface area, the transducer properties based on phonons or photons are also affected significantly by the size and geometry of the nanomaterials [43, 44]. In this project, the deposition of the TiO$_2$ nanostructures will be carried out via anodisation technique. There is no report yet on the H$_2$ sensor based on the optical properties of anodised TiO$_2$ nanostructured thin films. This investigation will provide more understanding on
the H₂ sensing characteristics of the TiO₂ nanomaterials.

In this PhD research, the final metal oxide investigated for its optical sensing properties towards H₂ is nickel oxide (NiO). The review on NiO is presented in the next subsection.

2.2.4 Nickel Oxide (NiO)

The nanomaterials considered previously are all n-type semiconducting metal oxides. The author completed the optical gas sensor investigation by using NiO, a p-type metal oxide which is also reported to be highly potential in electrochromism [45-47]. Apart from that, NiO is commonly used as an antiferromagnetic layer [47] and p-type transparent conducting film [48].

NiO is a semiconducting metal oxide with a wide band gap around 3.50 – 4.00 eV [49]. NiO films are normally greenish and the crystal structure is rhombohedral or cubic. The colour of the NiO is strongly dependent on the valence band of nickel. As such, the electrochromic property of NiO changes reversibly after the injection/extraction of ions and electrons upon potential applied. The electrochromic effect in NiO is yet to be fully understood. However, the widely acceptable explanation on the coloration is due to the charge transfer process between Ni²⁺ and Ni³⁺ ions [10]. The same process is used to describe the gasochromic effect in NiO which is limitedly investigated towards H₂.

A few studies have concentrated on NiO for optical gas sensing. In 1990, Kobayashi et. al [50] first identified the potential of NiO as an optical sensing layer when exposed to carbon monoxide (CO) at temperatures around 250 – 350°C in the visible-NIR range. The responses of the polycrystallined NiO films were reversible and associated with the decrease of hole density on the metal oxide surface due to the CO oxidation. Buso et. al [51] also reported that their Au/NiO films synthesised via sol-gel changed the absorbance upon exposure to H₂ and CO at 300°C. Nevertheless the reversible response was only observed for the films exposed to CO. Later, Della Gaspera et. al [4] fabricated silicon dioxide (SiO₂) porous films doped with Au/NiO nanoparticles synthesised via sol-gel and tested towards H₂ as well as CO of 1% concentration at 300°C. They
found that the film absorbance decreased and increased when exposed to H\textsubscript{2} and CO, respectively. The response obviously the opposite of the n-type semiconductors as discussed before. The films response time was excellent (≈1 min), but the dynamic response was performed only towards H\textsubscript{2} concentration of 1% with minor baseline drift for the alternating cycles of synthetic air and H\textsubscript{2}. In order to achieve stable optical response towards gases, most of the developed NiO film based sensors were operated at high temperatures around 250 - 300°C.

Meanwhile another work on H\textsubscript{2} sensor based on Pd/NiO films was reported by Maciak and Opilski [39]. They sputtered the tip of optical fiber with 10 nm Pd/150 nm NiO films and tested towards H\textsubscript{2} with concentration up to 3.5%. The NiO films were amorphous and showed good response at room temperature. However, the films suffered degradation and limited only towards a few gases cycles due to the room temperature deposition.

The existing studies on the gasochromic properties of NiO highlighted some of the improvements that can be made for the H\textsubscript{2} sensor using NiO nanostructured thin films. The author believed that the high operating temperatures around 250 – 300°C can be reduced by increasing the NiO films surface area, optimising the film’s thickness and deploying H\textsubscript{2} catalyst such as Pd or Pt. The deposition of the amorphous NiO films at low temperature resulted in the poor durability even though the films sensing performance was good. In order to solve this, the deposition of the NiO is suggested to be carried out at high temperatures to produce nanostructured thin films with high crystallinity as well as durability.

In order to develop optical sensor towards gas, the chosen metal oxides must be combined with the gas catalysts. This will be discussed in the following subsection.

2.2.5 Catalytic Metals (Pd, Pt, Au) in Optical Hydrogen Sensors

The investigation of the gasochromic response of the metal oxide nanostructured thin films towards H\textsubscript{2} is more complicated than their electrochromic response. In contrast with the electrochromic, the gasochromic response of the metal oxide films can only be induced when
combined with a catalytic material. The electrolyte deployed in any electrochromic device provides very efficient medium for ion intercalation and much stronger interaction with the metal oxide to induce coloration as compared to the gas molecules. In the gasochromic films, the coloration takes place only when the ion intercalated into the metal oxide layer from the dissociation of the gas molecules into atoms by the catalytic layer [18]. The catalytic metal layer promotes chemical reactions by reducing the activation energy between the film and the test gas. The metals are used in order to improve the sensitivity of the sensor as well as reducing the response and recovery times [52].

Previous literatures [52-54] had identified Pd, Pt and Au as the potential materials that can be used as a catalyst towards H₂. However, there are conflicting results on the effectiveness of the abovementioned metals to dissociate H₂ molecules. Ando et. al [19] coated amorphous WO₃ films with the three different catalytic metals and comparing their optical sensing performances towards H₂. They found out that only the WO₃ films coated with Pd and Au showed significant change of absorbance when exposed to H₂ with 1% concentration. Insignificant response from Pt/WO₃ was also reported by Young Shim et. al [55] when their films were exposed to many cycles of H₂. Meanwhile, Pt/WO₃ studies by Georg et. al [56], Shanak et. al [57] and Ghadiri et. al [58] were among the works that successfully proved the strong activation by the films when exposed to H₂. The variety on the response of the films coated with different kinds of catalytic metals provide opportunity for the author to investigate the influence of the noble metals on the optical sensor deploying metal oxide nanostructured thin films.

Brief introduction on the catalytic metal layer used in this project is presented as follows:

**Palladium (Pd)**

Pd is a soft metal with silvery-white in colour belong to Group 10 in the periodic table. The ability of Pd to highly absorb H₂ at almost 900 times its own volume has been well-studied [59]. The adsorption of H₂ into Pd was systematically investigated by Lundstrom and Salomonsson et. al for their Schottky based gas sensor [60, 61]. They identified that the H₂
adsorption occurs at the Pd surface as well as at the interface between the metal and the semiconducting metal oxides. Upon interaction with H₂, Pd transforms into palladium hydride (PdHₓ). The ratio between Pd and hydrogen atoms, which is characterised by the existence of two different crystallographic phases, α and β, depends on the hydrogen partial pressure and temperature [62]. In α phase, hydrogen is slightly absorbed into the lattice, which leads to a slight increase (≈0.4% in length) in the lattice parameter. As the hydrogen partial pressure increases, the transition from α to β phase occurs, resulting in a drastic lattice parameter increase (≈3% in length) [62]. This has been confirmed with the surface characterisation via atomic force microscopy (AFM) which revealed the Pd morphology alteration when the films exposed to H₂ and O₂ [63]. The transformation of the Pd catalytic layer leads to the change in the material electrical and optical properties.

The fact that Pd has fast H₂ adsorption/desorption kinetics, high solubility and selectivity towards H₂ making the catalyst a popular choice for optical sensing material towards H₂. Several researchers [62, 64-66] developed H₂ sensors by coating optical fiber with Pd layer. However, the use of single layer Pd-based H₂ sensors had been identified to have poor reliability due to material instabilities resulting from the large volume changes that occur during PdHₓ phase transition [66]. This can be solved by combining thin layer of the material with the metal oxide films which is well-known for their high reliability and strong structure stability.

**Platinum (Pt)**

Pt is a silvery-white element belongs to the same group as Pd in the periodic table (Group 10) and a well-known catalyst towards H₂. The material is the least reactive metal and hence commonly non-oxidised when interacts with the other elements. H₂ adsorption and dissociation on the Pt surface was found to be similar with the process on Pd [63]. However, as concluded by many studies [63, 67, 68], H₂ solubility in Pd was found to be much higher than in Pt. While hydrogen adsorbs and dissociates deep into the Pd layer reaching the interface of the metal oxide, most of the processes were found to occur only on the surfaces of the Pt layer. AFM
studies [63] also showed minimal changes in the Pt morphology upon exposure to H₂ and O₂. However, it was reported that the H₂ catalytic activity in Pt is more stable than in Pd [63]. It has been suggested that the high H₂ sensitivity of Pd films can increase the concentration of available adsorption sites at the Pd-metal oxide interface and as a result, nonlinear sensing performance. In contrast, the H₂ adsorption sites for Pt mostly concentrate at the surface and considerably less at the interface. Hence, the ion intercalations at the Pt-metal oxide interface are less but stable and might resulting in the linear sensing performance.

Despite the intensive works on the H₂ catalytic activity in Pd and Pt layers, the sensing performances especially in the optical domain of the catalytic metal/metal oxide nanostructured thin films are yet to be comprehensively studied. The different surface morphologies of the nanostructured thin films produce different interface coatings with the catalytic metal. The fact that the H₂ adsorption sites are highly influenced by the interface as well as the catalytic metal surface will provide important optical sensing performance analysis. As a result, the author plans to compare the sensing performances of metal oxide nanostructured thin films coated with different H₂ catalysts.

**Gold (Au)**

Apart from Pd and Pt, Au is also reported to have the ability to adsorp and dissociate H₂ [19, 51, 69]. Nevertheless there are only few studies dealing with the Au-H₂ interaction as compared to the other catalytic metals [67]. The main reason might be due to the low H₂ catalytic activity shown by Au as concluded in the previous studies. Furthermore, H₂ dissociation in the Au was found to be started only at higher temperatures as compared to the reaction in Pd and Pt [69, 70]. The H₂ adsorption was detected only at the surfaces of Au similar to the reaction in Pt. However, the concentration of the dissociated H atoms in Au was found to be less than in Pt [67]. Therefore, the H₂ catalytic activity is considered weaker in Au as compared to Pt.

There were several recent works on the metal oxide based gas sensors deploying Au as the catalytic layer. Ippolitto et. al [69] developed conductometric H₂ sensors based on Pt/WO₃ and
Au/WO₃ films. The operating temperature for Pt/WO₃ and Au/WO₃ films was found to be 70°C and 262°C, respectively. The H₂ response amplitude was observed to be higher in Pt/WO₃ than Au/WO₃. Nevertheless, the response in the Au/WO₃ films was more stable and linear as compared to Pt/WO₃. In the optical domain, Della Gaspera et al. [71] investigated gasochromic properties of Au/NiO films towards H₂. They found out that the film absorbance response changed around 8% when exposed to H₂ with 1% concentration at the operating temperature of 300°C.

Although some considerable works had been carried out on Au, it is still relevant to be investigated as the catalyst in the gas sensor especially with the current development of Au nanoparticles and nanoclusters. Recent studies had identified that the Au nanostructures show higher catalytic activity and are more selective towards H₂ than their bulk counterparts [67]. The author believed that the combination of the Au nanostructures with the metal oxide nanostructured thin films might significantly improve the gasochromic performance of such films towards H₂ especially by lowering the operating temperature and increasing the sensitivity.

In order to investigate the H₂ response of the developed optical sensor, the author needs to focus on the principles of the optical measurements in gas sensing applications. This will be discussed in the following subsections.

### 2.3 Optical Measurement Techniques in Gas Sensing

Gas sensing techniques may be divided into two different groups, namely, direct techniques which monitor the physical parameter of the target gas and indirect techniques which use chemical reaction in the gas sensitive material to indicate the concentration of the analyte [7, 72]. Each technique may be divided further into two domains, electrical and optical.

In this PhD research, the author focus is on the indirect optical spectroscopy techniques by deploying gas sensitive metal oxide layer. Eventhough the use of sensitive layer might expose to the risk of poisoning, the technique offers many advantages. Gas sensing systems based on indirect optical spectroscopy are simple, low cost, highly selective and sensitive with the use of a
suitable catalyst [72]. This is because most of the deposition techniques of the metal oxides are well-established and the measurement can be performed in the convenient wavelength ranges (visible-NIR) using inexpensive optical components such as LED, optical fiber as well as silicon photodiode.

Common optical spectroscopy techniques used for gas sensing applications are absorbance/transmittance, reflectance, refractive index, photo or chemi-luminescence and surface plasmon resonance (SPR). Absorbance and reflectance require less complicated setups than the other techniques and hence, become the preference throughout this project. In both techniques, the output signal is directly related to the gas concentration.

### 2.3.1 Absorbance, Transmittance and Reflectance

The absorption of optical signal occurs when atoms or molecules of an element take up the energy of a photon of the signal and thus, reducing the transmission of light as it passed the said element [73]. The intensity of the absorption is measured as a function of frequency or wavelength. Eventhough the measurement can be carried out for the whole electromagnetic spectrum, the common ranges are ultra-violet (UV), visible and infrared (IR). For chemical sensors, these ranges are important because the radiation energy is able to change the material atoms configuration and electronic states [73]. Table 2.3 lists the spectral region important for optical sensor.

<table>
<thead>
<tr>
<th>Range</th>
<th>Wavelength, ( \lambda ) (nm)</th>
<th>Wavenumber, ( \bar{\nu} ) (cm(^{-1}))</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet (UV)</td>
<td>200 – 380</td>
<td>50000 – 26000</td>
<td>6.2–3.3</td>
</tr>
<tr>
<td>Visual (Vis)</td>
<td>380 – 780</td>
<td>26000 – 13000</td>
<td>3.3–1.6</td>
</tr>
<tr>
<td>Near Infrared (NIR)</td>
<td>780 – 3000</td>
<td>13000 – 31000</td>
<td>1.6–0.4</td>
</tr>
<tr>
<td>Infrared (IR)</td>
<td>3000 – 50000</td>
<td>3300 – 200</td>
<td>0.4–0.025</td>
</tr>
</tbody>
</table>

The general setup to measure the absorption spectra is by having a light source radiates the signal onto a sample with sufficient transparency (Fig. 2.2). A light detection system is deployed on the other end of the sample to calculate the intensity of the radiation. Normally, the measurement is expressed in absorbance, a logarithmic ratio of the light intensity incident onto a
sample to the intensity that passed through the sample [73].

Based on Fig. 2.2, absorbance, \(A\), can be expressed as

\[
A = \log_{10} \frac{I_0}{T}
\]  

(2.1)

Another measurement associated with absorbance is transmittance, \(T\), which can be expressed as

\[
T = \frac{I}{I_0}
\]  

(2.2)

Therefore, in some cases, absorbance is also known as

\[
A = -\log_{10} T
\]  

(2.3)

Apart from absorbance and transmittance, the author is also interested in the reflection measurement. Reflection is defined as the change in the optical signal direction at an interface of two materials with different refractive indices so that the signal returns into the material its originally propagates. Reflection of light can be specular (the angle of incidence is equal to the angle of reflection) or diffuse (the angle of incidence is not equal to the angle of reflection) [74]. In this project, the measurement of the optical signal propagates in the optical fiber coated with the sensing layer at its tip includes both diffuse and specular reflection.

The optical spectroscopy measurements for gas sensing are derived from Beer-Lambert Law, which will be discussed in the next section.
2.3.2 Beer-Lambert Law

One of the most important transducing principles for optical sensing is Beer-Lambert law. This law relates the magnitude of the light absorption and the gas concentration. Lambert described first that the intensity of monochromatic light decreases when it crosses a light-absorbing element. The decrease is a logarithmic function of increasing length of the light path. Beer stated that the transparency of a coloured, light-absorbing solution is an exponential function of its solute concentration [73]. Beer-Lambert law is a combination of these relationships. Applying the law for gas sensing, the relationship can be addressed as

\[ A = \varepsilon CI \] (2.4)

where \( A \) is the absorbance, \( \varepsilon \) is the absorption coefficient, \( C \) is the gas concentration and \( l \) is the path length of the light through the sensing layer.

Based on Beer-Lambert law, the measured absorbance is linearly proportional to the gas concentration. This relationship is very important because the change of absorbance in the sensing layer can be concluded as a direct change in the gas concentration.

The absorbance response of the sensing layer is due to the change of the material electronic states when interact with the dissociated hydrogen ions. The author explained the gas sensing mechanism in the metal oxide nanostructured thin films based on the film’s optical response.

2.4 Gas Sensing Mechanism for Optical Sensors Based on Metal Oxide Nanostructured Thin Films

Despite the intensified research in the electrochromic phenomena of metal oxides, the coloration process is still not completely understood and several mechanisms have been proposed [75-77]. Most of them were explained for \( \text{WO}_3 \). Deb presented a comprehensive work on \( \text{WO}_3 \) and reported five different mechanisms, including his model, being suggested to describe the coloration [15]. They are oxygen vacancy, intervalence charge transfer (IVCT), polaronic
absorption, interband excitations and transitions from the valence band to split off the $W^{5+}$ state. Widely accepted mechanisms among them to describe the coloration are IVCT, polaronic absorption and oxygen vacancy.

Faughnan et. al [78] first introduced the IVCT or double injection model to describe the coloration in $WO_3$. They suggested that the coloration proceeds by the double injection of protons/electrons reducing $W^{6+}$ to $W^{5+}$ and as a result, the formation of the tungsten bronze ($H_xWO_3$). An alternative model is based on the concept of polaron formation introduced by Landau when he argued that displacing atoms or ions in a material from their carrier free equilibrium position produces a potential well that will bind a charge carrier by self-trapping [15]. Salje et. al [79] and Lehan et. al [80] supported this model by suggesting that the coloration is due to small polaron formation in $WO_3$. The suggestion was based on the observation that the film colour centre peak moves to high energy with increasing coloration density. Nevertheless, these two models did not include the critical role of oxygen vacancy, which has been identified to reduce the coloration efficiency. In oxygen vacancy model, the coloration process is believed due to the defect in the metal oxide films which contains positively charged oxygen vacancies formed during the preparation. Upon the ions intercalation, the positively charged vacancy exerts coulombic repulsion to the nearest W-ions. As a result, the neighbouring W-ions were displaced and the defect level shifted upward into the bandgap, thereby creating a colour centre [15].

Overall, the different models shared a common understanding that the coloration in the metal oxide take place with the insertion of ions changes the material electronic states. Some studies [56, 57] had also verified the formation of water on the film surface during the coloration. Therefore, the author decided to explain the $H_2$ gasochromic response in the catalytic metal/metal oxide films by expanding the double injection model to include the restoration of the film transparent state upon exposure to oxygen. This mechanism is developed based on the absorbance response of Pt/WO$_3$ nanostructured thin films towards $H_2$. The details of the film optical sensing performances are discussed in Chapter 7.
The gasochromic transition of Pt/WO$_3$ from transparent to a coloured state involves the following steps [81]:

1. Dissociative chemisorption of molecular hydrogen onto Pt, forming hydrogen ions and electrons:

   \[ H_2 \xrightarrow{\text{Pt}} 2H^+ + 2e^- \]  \hspace{1cm} (2.5) 

2. Reduction of W$^{6+}$ (transparent) centre in the WO$_3$ crystal lattice to W$^{5+}$ (blue colour) caused by the electrons generated in (1) in the process known as spill-over [57].

3. Formation of H$_2$O vapour resulting from the combination of 2H$^+$ with surface bound O$^-$ ions produced by the reduction of W$^{6+}$ to W$^{5+}$:

   \[ W_2O_6 + 2e^- + 2H^+ \xrightleftharpoons[k_2]{k_1} W_2O_5 + H_2O \]  \hspace{1cm} (2.6) 

   Forward reaction $k_1$, rate limited by $e^- + H^+$ supply

   Reverse reaction $k_2$, rate limited by H$_2$O

4. Reversal occurs when hydrogen gas is purged from the system at elevated temperatures with synthetic air, restoring the stoichiometry of the WO$_3$, i.e. W$^{5+} \rightarrow$ W$^{6+}$:

   \[ W_2O_5 + H_2O \xrightarrow{\text{Pt}} W_2O_6 + H_2 \]  \hspace{1cm} (2.7) 

   Steps 2 and 3 occur concurrently and simultaneously.

Generally, the transition steps in the proposed sensing mechanism might be used to explain the gasochromic response of the other catalytic metal/metal oxide thin films apart from Pt/WO$_3$ films. The difference probably will be in the electronic states of the metal oxides that determine the material coloration and transparent centres.
In the next section, the optical transducers deployed for gas sensing applications will be presented.

2.5 **Optical Transducers**

One of the main advantages of gas sensing in the optical domain is the vast choices of transducing platforms available for different sensing applications. In this research project, the author plans to combine the metal oxide nanostructured thin films with three kinds of optical transducing platforms, namely, transparent substrates for spectrophotometer system, optical fiber and waveguide.

2.5.1 **Transparent Substrates for Spectrophotometer System**

In the initial stage of this research project, the investigation of the gasochromic response of the metal oxide nanostructured thin films will be performed by depositing the materials onto transparent substrates and tested using the spectrophotometer system. The main advantage of the setup is its simplicity of the sample preparation and absorbance measurement. The depositions of the metal oxide nanostructures can be performed in batches of samples. Therefore, extensive sensing analysis can be carried out over a wide range of metal oxides with different nanostructures.

Five kinds of transparent substrates will be used in this project. They are quartz, glass, sapphire (\(\text{Al}_2\text{O}_3\)), indium tin oxide (ITO) and flourine doped tin oxide (FTO) conductive glasses. The different substrate surfaces are expected to grow different nanostructured thin films.

Quartz and glass substrates are made of fused silica. However, their structures are slightly different from each other due to the high impurities in the glass and the quartz surface is normally polished to reduce the light reflection. Compared to the polymer or organic transparent substrates, the silica substrates have very high melting temperature (≈1700°C) and generally non-reactive with chemicals. These characteristics make the substrates suitable to be used in the deposition and synthesis of metal oxide nanostructured films, which involve high temperatures and corrosive
chemicals. Their amorphous nature also minimise the crystal peak interference during the crystallographic characterisation of the nanostructured films.

Sapphire is fabricated from fused aluminium oxide and highly transparent substrate. It is also very strong material with polycrystalline structures and very efficient heat conductor. Therefore, sapphire is a suitable substrate to grow metal oxide nanostructures with its crystal interface as well as high temperature resistant [82].

ITO and FTO glasses are two inorganic thin films commonly used to provide high conductivity as well as optical transparency. Both conductive glasses typically consist of 90% indium oxide (In$_2$O$_3$) and 10% tin oxide (SnO$_2$) while in the FTO, the film was doped with small amount of fluorine ($\approx$5%) [83]. The surface of the transparent substrates is very different between ITO and FTO. The ITO substrate consists of grains in the sizes of 40 – 60 nm while FTO has larger structures in the sizes of 300 – 500 nm grains. Eventhough In$_2$O$_3$ is known to be sensitive towards ozone (O$_3$) and nitrogen oxide (NO$_x$), the metal oxide is not selective towards H$_2$ [1]. The variations in the surfaces of the transparent substrates provide interesting analysis on the growth of the metal oxide nanostructures for optical H$_2$ sensing. By normalising the absorbance spectra of the samples with their respective substrates, the measurements that will be recorded via the spectrophotometer are the actual responses from the nanostructured thin films.

Basically, the operation of the spectrophotometer system in measuring the absorbance and other optical parameters can be understood from the following schematic diagram in Fig. 2.3.
The optical signal from the sample will be received by the spectrophotometer via the optical fiber connected to the input port (1). Behind the input port is a slit (2), which is a piece of material with a rectangular aperture to regulate the amount of the signal that enters the instrument as well as control the spectral resolution. Apart from that, there is a filter (3) to restrict the optical radiation to predetermined wavelength regions. Both bandpass and longpass filters are available to restrict radiation to certain wavelength regions. The light entering the spectrophotometer will be focused and reflected off by the collimating mirror (4) onto the grating (5). The main function of the grating is to select the wavelength coverage and the resolution in the spectrophotometer by having different groove densities. The diffracted light from the grating will be received by the focusing mirror (6) and directed towards the charge coupled device (CCD) camera (8) via a set of lens (7) to reduce the effect of stray light. The camera convert the light signal into digital signal and the information on the sample spectrum will be displayed on computer via operating software.

Due to the time constraint, the author plans to prioritise the deployment of the optical fiber or waveguide as the transducing platform only for the metal oxide nanostructured films with excellent absorbance response towards H₂.

### 2.5.2 Optical Fibers

The most common transducing platforms in optical sensor technology are optical fibers. The advancement of low-loss optical fiber in the mid 1970s primarily for telecommunication industry also created momentous development in the gas sensing applications [85].

For application of optical and spectroscopic techniques in optical sensors, nearly exclusively the phenomenon of light conduction is utilised. The light conduction phenomenon means that the light propagates inside the fiber is guided based on the principle of total internal reflection (TIR). According to the TIR principle, the light propagating in a medium is confined and guided if the refractive index of the medium (n₁) is higher than that of the surrounding material (n₂). The medium is normally known as the core and the surrounding is the cladding. Fig. 2.4 shows the light propagation in the optical fiber based on the TIR principle. Incident light...
may travel in the core with TIR only if the incident angle is less than \( \theta_{\text{max}} \), which is given by \( \sin^{-1}(n_2/n_1) \). TIR phenomenon is valid for light guiding in the cylindrical medium as in optical fiber as well as planar shape waveguide medium as in the integrated optics.

![Fig. 2.4 Light conduction in optical fiber based on TIR principle [73].](image)

Optical fibers are made of fused silica (SiO\(_2\)) or polymer. If sensor use is restricted to visible light and intended for short distance, polymer fibers are sufficient. Fused silica is characterised by maximum spectral transparency and thus useful for light propagation over long distances [73]. Depending on the various possible patterns of propagating or standing electromagnetic fields, the theory of light propagation categorises two distinguished light guiding forms, namely, single mode and multimode. Fig. 2.5 illustrates the differences in the light propagating inside the single mode and multimode fibers.

![Fig. 2.5 Light propagation inside typical (a) single mode optical fiber, (b) multimode optical fiber, and the modes of propagation indicating evanescent wave in (c) single mode and (d) multimode [73].](image)

Fig. 2.5 shows the modes of the light propagates in the single mode optical fiber (a) with the core and cladding diameter of 8 \( \mu \)m and 125 \( \mu \)m, respectively. In the multimode optical
fiber (b), the core dimension is typically 65 µm and larger than that of the single mode fiber. The core size is one of the main factors to determine the mode of propagation [73]. As shown in Fig. 2.5 (c) and 2.5 (d), the total reflected light inside the core propagates in Mode 0 for single mode fiber and Mode 1, 2 or more for multimode optical fiber. Single mode fiber has higher sensitivity compared to multimode fiber. However, the large core in the multimode fiber provides more surface to deploy the sensing layer than the single mode ones. If the sensing layer is very sensitive when interact with the gas molecules, it is sufficient to use multimode fiber as the optical gas sensor. Based on this information, the author selected multimode fiber as the transducer.

When the light propagates in the optical fiber or waveguide with TIR, every reflection at the interface between the core and cladding generates an evanescent wave, which penetrates only a short distance from the interface but transfers energy to the cladding. To utilise the evanescent wave for optical fiber sensing application, a direct contact with the sample must be established by removing the cladding [86].

There are two types of sensing designs for optical fiber gas sensors, which are intrinsic and extrinsic. In the intrinsic design, the gas molecules interaction occurs within the elements in the fiber itself and modifies the light transmission properties [85]. In the extrinsic design, the optical fiber is used to direct the light, usually to and from the gas sensitive layer where the light beam is influenced by the layer’s chemical or physical change upon exposure to the gas analyte.

Typical configurations of optical fiber gas sensors are shown in Fig. 2.6 [86].

![Typical configurations of optical fiber gas sensors](image-url)
From the figure, A and B are extrinsic type sensors, C and D are intrinsic sensors, in which the gas molecules interaction with the membrane/sensing layer modifies the transmission characteristics of the fiber. Optical wave properties such as phase and amplitude alter, when compared to the light entering the fiber. The sensing layer can be placed on the tip of the fibre (A and B) or on the side (C). In other configurations, part of the cladding can be removed and leave the fibre core exposed to the gas medium (D). In this research, the author deployed the extrinsic fiber sensing design (A). The configuration is preferred due to the flexibility in the deployment of the sensing layer onto the fiber as well as strong optical response from the gas chemical reaction in that layer.

2.5.3 Optical Waveguides

Apart from optical fiber, gas sensors can be assembled of thin planar layers or waveguides. This type of optical sensors operate by taking the advantage of the change in the evanescent field, refractive index as well as light absorption/transmission caused by the interaction of gas molecules and metal oxide sensing layer. An important improvement of the optical waveguide is the substantially larger useful interface of the planar layer as compared to the optical fiber. Coating this interface with the gas sensitive layer provides better analyte-thin film interaction than the ones in the optical fiber.

Optical waveguides offer advantages like potential for integration with the optoelectronic components for compactness, robustness and ease in depositing gas sensitive layers [87]. Furthermore, some studies [88-90] reported that use of planar waveguides offers high gas sensitivity for gas detection. To provide high sensitivity, the waveguide is made thin enough to support only a single mode and is fabricated from high refractive index materials. Similar to the fiber, single mode waveguide has higher sensitivity than the multimode counterpart. Nevertheless, the fabrication of a single mode planar waveguide is more complicated than the multimode waveguide. The coupling of optical signal into the single mode waveguide is also difficult due to the very thin layer.
There are variety of waveguides such as slab, ridge, strip-loaded and rib for the diverse optical sensing applications. Basically, these waveguides can be categorised into two designs; planar and channel waveguides [91]. When a thin layer with a slightly increased refractive index is fabricated on top of a substrate, it functions as a planar waveguide. The thin layer becomes the core and the light transmitted into the waveguide layer with a small enough divergence will be guided perpendicular to the layer and unguided in the other direction. The waveguide layer may also be embedded between two cladding layers [92]. Fig. 2.7 (a) is an example of a planar waveguide.

Meanwhile, a channel waveguide has a guiding structure in the form of a stripe with a finite width [92]. This includes a ridge on top of the cladding structure or an embedded channel. Fig. 2.7 (b) and (c) are examples of a channel waveguide and optical sensor based on the waveguide coated with metal oxide layer, respectively.

![Fig. 2.7 Typical (a) planar waveguide, (b) channel waveguide and (c) channel waveguide coated with metal oxide sensing layer.](image)

The selection of waveguide to be used for the optical gas sensing applications has to consider various fabrication and measurement factors. The choice has to be made from considerations such as difficulty of fabrication, ease of light coupling with adjacent optical devices as well as type of waveguide and substrate materials to be used. Apart from that, the waveguide must be able to stand the high temperature and pressure during the deposition of the gas sensitive layer. These factors will be considered in details in the chapter related to the optical waveguide fabrication (Chapter 3).
The principle of optical waveguide sensor is based on the interaction of the evanescent wave of the guided mode in the core with the gas sensitive layer [89]. In order to achieve maximum interaction with the sensing layer on top of the waveguide, the penetration depth of the evanescent field should be determined.

The penetration depth, $d_p$, is defined as [93, 94],

$$d_p = \left( \frac{\lambda}{2\pi} \right) \left[ n_{\text{eff}}^2 - n_c^2 \right]^{1/2} \quad (2.8)$$

where $n_{\text{eff}}$ is the effective refractive index of the guided mode, $n_c$ is the refractive index of the cladding layer and $\lambda$ is the wavelength.

When the sensing layer interacts with $H_2$, its absorption coefficient, $\varepsilon$, and refractive index change. As a result, the evanescent wave at the interface of the sensing layer and the waveguide will change and affecting the intensity of the light propagates in the core [89]. This is valid provided that the change in the sensing layer occurs deep and reaching the interface of the waveguide. Therefore, the thickness of the sensing layer must be optimised to influence the response. The determination of the evanescent field penetration dept and the optimised thickness of the sensing layer will be discussed in the next chapter.

### 2.6 Summary

In this PhD research program, the author aims to develop highly sensitive optical sensors based on the metal oxide nanostructured thin films for $H_2$ sensing applications. In this chapter, an extensive review of the contemporary literature on the existing materials deployed in the optical gas sensors was presented. The author also justified the rationales to embark in the development of optical $H_2$ sensors based on the current research trends in the field of gas sensor. Consequently, the outcomes of the previous research outputs related to the development of the metal oxide nanostructured thin films with strong chromic properties including $WO_3$, $MoO_3$, $TiO_2$, $NiO$ were presented. This includes discussion on the importance of catalytic metals (Pd, Pt, Au) for optical $H_2$ sensors. This chapter also covers the optical measurement techniques and related theories for gas sensing applications. Gas sensing mechanism specifically for optical sensors is proposed to
provide better understanding on the sensor’s gasochromic response. Finally, the different types of optical transducers and their operation principles are presented.

In the next chapter, the design and fabrication processes of the optical transducers will be explained.
References


Chapter 3

Design and Fabrication of Optical Transducers

3.1 Introduction

As mentioned earlier in Chapter 2, typical transduction platforms for optical sensors are optical fibers, channel waveguides and transparent substrates for the spectrophotometer system. Each of the platforms utilised different optical signal properties to sense H₂ with different concentrations. In this chapter, the design and fabrication of the optical transducers will be presented.

This chapter is divided into four sections inclusive of Section 3.1: Introduction. Section 3.2 introduces the transparent substrates used in the spectrophotometer system. Section 3.3 explained the properties of optical fiber and its integration process with the sensing layer. Subsequently, it is followed by the discussion in Section 3.4 on the design and fabrication of optical waveguides for H₂ sensing. Finally, the summary is provided in Section 3.5.

3.2 Transparent Substrates for Spectrophotometer

This section explains about the types of transparent substrates chosen as the platforms for sensing layers for the optical measurement in the spectrophotometer system. This also includes the preparations carried out on the substrates before the deposition of the metal oxide nanostructured thin films. In this PhD project, the substrate selection was vital because the absorbance measurements performed with the spectrophotometer depend on the substrate transparency.

The selection of substrate is also very important for the growth of nanostructured thin films because lattice parameters and crystal structure differences between the material and the substrate strongly affects the nanostructured films. The lattice mismatch between the material and substrate
induces internal stresses causing the sensor poor stability. This produces disorders dominantly through the increase in the grain boundary density and thereby decreases in the crystallite size [1]. Therefore, in this project, the author fabricated different nanostructured thin films by having different transparent substrates as well as varying the deposition techniques.

### 3.2.1 Types of Transparent Substrates

Five different transparent substrates were chosen as the platforms to grow the metal oxide thin films. The substrates are fused quartz (SiO$_2$), sapphire (Al$_2$O$_3$), glass, indium tin oxide (ITO) and flourine tin oxide (FTO) glasses.

The main transparent substrate used by the author is the amorphous fused quartz. It was purchased from Lianyungang Haisheng Quartz Tech. Co. Ltd. (China) originally in the size of 70 mm diameter wafer. The thickness of the wafer is 0.9 mm and polished on both surfaces. The transparency of the quartz is 95% at 550 nm.

Another transparent substrate used in this project is sapphire (Al$_2$O$_3$). The substrate was supplied and used in the deposition of WO$_3$ via pulsed laser by the collaborator at the University of Incheon, South Korea. The thickness of the substrate is 0.5 mm with the transparency of 86% at 550 nm. However, the substrate was used only for the film characterisation.

The author also used microscope slide glass as the substrate for the sputtered WO$_3$. The glass was supplied by Knittel Glaser (Germany). The thickness of the substrate is 1 mm with the transparency of 90% at 550 nm.

Apart from that, two types of conductive transparent substrates were also deployed, namely ITO and FTO glass. The ITO and FTO glass were purchased from Sigma Aldrich. The surface resistivity of the ITO is 80 $\Omega$/sq with the thickness of 1 mm. The transparency of the ITO is typically 88% at 550 nm. Meanwhile, the surface resistivity of the FTO is 100 $\Omega$/sq with the thickness of 2 mm. The transparency of the FTO is also approximately 70% at 550 nm.
3.2.2 Substrate Cleaning and Dicing

Prior to the deposition of the thin films, the substrates were cleaned to remove particles and contaminants on the surface. Initially the substrates were washed in acetone for 3 min to remove organic impurities before rinsed in isopropanol (IPA) and methanol. Later, deionised (DI) water was used to soak the substrates from the solvents. Finally, the substrates were blown dry in nitrogen (N₂).

For the substrates originally in the form of wafer, the dicing process was carried out to produce samples that can fit into the holder of the customised gas chamber. Before the dicing process, thick photoresist (AZ1512) was spin-coated on the surface of the transparent substrates to protect the surface from any damage or scratch. The wafer was deluged with photoresist AZ1512, and then spun at 3000 rpm for 30 s to obtain a uniform layer photoresist of approximately 0.5 µm. After that, the soft baking process was performed at 90°C for 20 min. This is necessary to harden the photoresist by forming a cured protective film on the wafer. After soft baking, the wafer was left cool at room temperature for approximately 10 min.

The photoresist coated wafer was diced into typically 10 mm × 15 mm substrates using a DISCO DAD 321 automatic dicing machine. The dicing were carried out by the diamond tip blade at a speed of 0.1 mm/s and spindle revolution of 30000 rpm. The water flow rate was fixed at 1 l/min. After dicing, the photoresist was removed by immersing the diced wafers in an acetone bath for approximately 5-6 min. Then the prepared substrates were rinsed with methanol and DI water as well as blown dry with N₂. At this stage, the substrates were ready for the deposition of the gasochromic materials.

Apart from the transparent substrates, the optical testing was also carried out on the nanostructured thin films deposited on the tip of optical fiber.
3.3 Optical Fibers

As mentioned earlier in Chapter 2, there are two types of optical fiber, namely single mode and multimode. Commonly, the multimode optical fiber are made of silica (SiO$_2$) or plastic. In this PhD project, the author used multimode silica optical fiber as the transduction platform. The fiber core and cladding diameters are 62.5 µm and 125 µm, respectively. The fibers were purchased from AFW Technologies (Australia).

The main advantage of multimode optical fiber is its core has large diameter that allow stronger light interaction with the sensing layer at the tip as compared to the single mode fiber (typical diameter 8 µm). Furthermore, the multimode fibers are easily available for the sensing applications in the visible wavelength range. The silica fiber also has lower attenuation loss and much higher thermal resistant compared to the plastic fiber [2]. These characteristics are suitable for remote H$_2$ sensing applications and high temperature operation.

The preparation of optical fiber as the transducer includes the cleaving, stripping, cleaning and splicing processes. Initially, the fibers were cut using a fiber cleaver in the length of typically 7 cm. This is the maximum length for the fiber to fit into the sputtering chamber and the minimum length to be conveniently placed onto the splicing machine stage. Then, the thin plastic coatings of the bare fibers were stripped off with a fiber stripper. The fibers were cleaned with ethanol and blown dry with N$_2$ before being placed on the stage in the chamber for the deposition via sputtering.

Later, the fiber was spliced with a patchcord using a Fujikura FSM-40S (Japan) arc fusion splicer. Splicing is the process to fuse two fibers together in such a way that light passing through the fibers is not scattered or reflected. Fig. 3.1 shows the photos of the bare fibers, WO$_3$ coated fiber tips and the spliced fiber with the patchcord. The dark tips in (b) and (c) are the nanostructured thin films act as the gas sensing layers. Black carbon tape was used to hold the fibers in (a) and (b).
Fig. 3.1 The images of (a) bare fiber, (b) WO₃ coated fiber tip and (c) the fiber spliced to the patchcord.

The SEM image of the optical fiber tip coated with metal oxide nanostructured thin films is illustrated in Fig. 3.2. The core with the 62.5 µm diameter in the centre of the fiber could not be observed due to the films coating.

Fig. 3.2 Multimode optical fiber tip coated with metal oxide nanostructured thin films.

The fiber with the sensing layer on the tip was spliced to the patchcord as a part of the testing setup to analyse the optical sensing properties of the nanostructured thin films exposed to H₂. This configuration will be discussed in details in Chapter 6.
3.4 Optical Waveguides

Apart from transparent substrates and optical fibers, the other optical transduction platform used in this project is channel waveguides. As mentioned earlier in Chapter 2, there are variety of channel waveguides such as ridge, strip-loaded and rib for diverse optical sensing applications [3]. In order to produce channel waveguide specifically for gas sensing applications, the author identified the suitable type of waveguide as well as carried out its fabrication processes.

3.4.1 Type of Optical Waveguide Used in This Project

The author chose inverted rib channel waveguide as the optical transduction platform as shown in Fig. 3.3. To the best of author’s knowlegde, this is the first time the optical sensing properties of metal oxide nanostructured thin films on inverted rib waveguide towards H₂ were examined.

![Inverted rib channel waveguide](image)

Fig. 3.3 Inverted rib channel waveguide.

In contrast to the conventional rib waveguide, the inverted rib is embedded into the cladding. The optical signal propagates in the core layer (red region) which has higher refractive index than the cladding layer. The mode of the signal is mostly determined by the dimension of the rib. The main advantage of the inverted rib structure is that the rib is imprinted in the robust cured lower cladding, with little processing required on the core layer. The preservation of the rib minimises the attenuation as well as the light scattering. The inverted rib waveguide is also suitable for gas sensing applications because the structure allows the wide area coating of the sensing layer on top of the core and thus enhance its interaction with both the gas analytes as well
as the optical signal. Furthermore, it has been reported that the propagation loss is lower in the
inverted rib as compared to the conventional rib waveguides [4]. Commonly, silicon (Si) is used
as the waveguide substrate. The material is well known primarily for its low cost (due to abundant
resources), inert and very high thermal resistance [5].

In this project, the single mode inverted rib waveguide was fabricated. The use of single
mode waveguide as the transducing platform is to minimise the high nonlinearity effects
associated with the multimode polymer waveguide. In contrast, the effect is insignificant in the
multimode optical fiber based on silica [6]. Although its fabrication process is more difficult, the
single mode waveguide is also less susceptible to attenuation when the light propagates in its core
as compared to the multimode waveguide.

There are many stages involved in the design of the single mode inverted rib waveguide.
The first stage is to identify the waveguide material.

3.4.2 Waveguide Material

The type of materials used in the construction of the waveguides are one of the most
important factors to determine the modes of light propagation. In order to confine the light in the
waveguide, the material used as a core must always have higher refractive index than the cladding
($n_{\text{core}} > n_{\text{cladding}}$). Apart from that, the complexity of the fabrication processes also being
determined by the type of the waveguide materials.

In this project, the author used polymer as the waveguide material. The advantages of
polymer are low cost, flexibility and easiness to fabricate as well as high optical transparency
from visible to infrared wavelength ranges [7]. Two different types of polymers were used in the
waveguide fabrication. The polymers were SU-8 2002 and KMPR® (MicroChem Corp., USA) for
the core and cladding layers, respectively. The refractive index of the SU-8 2002 was found to be
1.592. Meanwhile the KMPR® refractive index is 1.566. Both values were measured at the
wavelength of 632.8 nm. The details of the materials specifications can be found in [8]. Once
cured, these polymers are highly resistant to solvents, acids and bases and have excellent thermal
stability. SU-8 polymer was chosen as the waveguide core material due to its relatively high refractive index and low loss over a wide visible wavelength range [9]. These characteristics suit very well for the optical transducer in gas sensing applications which operates in the visible range and at elevated temperatures. The waveguide structure was formed using nanoimprint lithography techniques [10].

After identifying the type of channel waveguide as well as its materials, the process was continued with the waveguide fabrication. This was carried out at the RMIT University clean room (Class-1000) to minimise the exposure to dust and contaminants which can severely affect the properties of the single mode optical waveguides.

### 3.4.3 Single Mode Waveguide Design

In this project, the fabrication process of the inverted rib waveguide began with the modelling to achieve single mode performance and the selection of appropriate mask to produce the waveguide master.

Based on the inverted rib channel waveguide in Fig. 3.3, the dimensions of the core and cladding were modelled to achieve single mode performance at the visible wavelength 633 nm as well as TE fundamental mode (TE\(_{0}\)) to enhance the guided light-sensing layer interaction. Based on the modelling, the SU-8 core and KMPR cladding thicknesses should be 2.5 and 40 µm, respectively. Meanwhile, the rib height was determined to be 0.3 µm for its width range of 3-7 µm to achieve single mode inverted rib waveguide at the visible wavelength. This is summarised by Fig. 3.4 below.

![Fig. 3.4 Single mode inverted rib waveguide dimension.](image-url)
Using these parameters, the penetration depth, $d_p$, of the evanescent field was estimated based on Equation 2.8 in Chapter 2. The calculation was carried out based on two different operating wavelengths of the available light sources which are 532 nm and 633 nm. The top cladding layer is air with refractive index of 1.

The penetration depth, $d_p$, is defined as,

$$d_p = \left( \frac{\lambda}{2\pi} \right)[n^2_{\text{eff}} - n^2_c]^{1/2}$$  \hspace{1cm} (2.8)

where $n_{\text{eff}}$ is the effective refractive index of the guided mode, $n_c$ is the refractive index of the cladding layer and $\lambda$ is the wavelength.

Taking SU-8 $n_{\text{eff}} = 1.592$, air $n_c = 1$,

At $\lambda = 532$ nm, $d_p = 105$ nm,

At $\lambda = 633$ nm, $d_p = 125$ nm,

The values above indicated that the evanescent field radiates around 100 nm and 125 nm above the interface of the waveguide if the wavelengths of the light propagates inside the SU-8 core are 532 and 633 nm, respectively. However, this is valid by taking air as the top cladding. Based on Equation 2.8, the higher the refractive index of the cladding, the lower the evanescent field radiation. The author must determined this factor when deciding on the metal oxide nanostructured thin films to be coated on top of the waveguide.

In order to fabricate the waveguide, the author chose a customised waveguide mask labelled EOPC – Optics Mk2 available at RMIT University. This mask consists of sets of strips (waveguides) with the widths range from 3.0 - 7.0 μm. The widths increment is in 0.1 μm steps. The individual waveguide was separated by approximately 40 μm to each other. The waveguides on this mask are defined by chrome strips, surrounded by transparent area (Fig. 3.5).
The waveguide patterns on the mask were transferred to a mold using photolithography. The process was described in the following subsection.

### 3.4.4 Waveguide Photolithography Process

Photolithography is a process of transferring the waveguide mask patterns onto the other material or photoresist that is sensitive to UV exposure. If the photoresist is of positive type, its area exposed to UV light becomes soluble to the photoresist developer. In contrast, if the photoresist is of negative type, the effect is the opposite.

In this project, the photoresists used are the negative type and based on epoxy polymer, namely, SU-8 and KMPR®. The negative photoresist is well known for its excellent adhesion to the Si substrate, low cost and strong chemical resistance [7]. The steps involved in developing a waveguide mold are explained based on the following Fig. 3.6.

![Photolithography process to develop waveguide mold.](image)

**Fig. 3.6** Photolithography process to develop waveguide mold.
Initially, a 3 inch Si wafer was cleaned with acetone and methanol. After being blown dry with N₂, the wafer was spin-coated with SU-8 2000.3 diluted with SU-8 2000.5 to achieve 0.3 µm thick of the SU-8 layer (Fig. 3.6(a)). The Karl Süss RC8 spin coater was set to 3000 rpm spin rate for the duration of 30 s and acceleration of 500 rpm/s. The spin coater is equipped with the edge-bead removal to take away the film portion that was built-up around the wafer. The edge-bead affects the flatness of the films which is very critical especially in developing a waveguide mold with 0.3 µm trench depth. Subsequently, the wafer was baked alternately at 65°C and 95°C for the duration of 1-2 mins to prevent dust from settling in the wet SU-8 films. Later, the wafer was placed beneath the mask and exposed to UV light of 12 mW/cm² for 5 s (Fig. 3.6 (b)). This was carried out using Karl Süss MA6 mask aligner. The wafer was baked for the second time with the same condition mentioned before. After that, the films were submerged in the SU-8 developer solution for 3 s to dissolve the unexposed area. This process produced a waveguide patterns as shown in Fig. 3.6 (c).

The material used for the waveguide mold is polydimethylsiloxane (PDMS), a type of polymer that is very transparent, inert, non-toxic and non-flammable with excellent rheological properties [11]. PDMS and its curing agent were mixed and degass in a vacuum chamber to remove the air bubbles. Later, the pre-treated PDMS mixture was poured onto the patterned wafer placed in a petri dish until the thickness reached approximately 1 cm (Fig. 3.6 (d)). A thick mold is desirable because it maintains good planarity during imprinting. The degass process was repeated again for a few minutes until no air bubbles appear in the mould. Afterwards, the mould was heated in a convection oven at 70°C for 2 hrs. Once cured, the PDMS waveguide mould with the ribs of 0.3 µm depth was peeled off from the wafer (Fig. 3.6 (e)). After cleaning with methanol, the PDMS waveguide mould was ready for imprinting to fabricate single mode inverted rib waveguide (Fig. 3.6 (f)).
3.4.5 Waveguide Imprinting Process

The final stage to fabricate single mode inverted rib waveguide is imprinting the rib (core) into the cladding layer (KMPR). Before that, another 3 inch Si wafer used as the substrate was cleaned with acetone and rinsed with methanol. The wafer was dehydrated by heating it at 120°C for 5 mins. In the meantime, the PDMS mold was baked at 95°C in the oven for 25 mins to remove any moisture as well as traces of solvents. The mold was left to cool down at room temperature before imprinting. The process is described based on Fig. 3.7 as follows:

After the Si wafer has cooled, KMPR 1035 was dispensed at the centre of the wafer placed in the spin-coater. The polymer was spun in two consecutive cycles. The first cycle was to spread the polymer throughout the wafer surface and carried out at 500 rpm spin rate with the acceleration of 100 rpm/s for the duration of 10 s. The second cycle was immediately executed afterwards at 2000 rpm spin rate with the acceleration of 300 rpm/s for the duration of 30 s. The purpose of this cycle is to thinning the KMPR cladding layer to 40 µm thick as suggested in Section 3.4.3 before. After the spin-coating of the KMPR on Si wafer was completed (Fig. 3.7 (a)), the imprinting step was immediately performed. The PDMS mold was imprinted on the KMPR layer along the direction of the waveguides (step 1 in Fig. 3.7(b)). The mold was rolled very carefully and slowly to avoid any air bubbles trapping in between the mold and the KMPR layer. After the mold completely rested on the KMPR layer, the wafer was left for 5 mins. Later, the wafer was baked in the convection oven at approximately 85 to 95°C for 20 mins. The
PDMS has a very large thermal expansion coefficient. Therefore, uniform heating is very critical and was performed in the oven instead of hotplate. The wafer was also verified to be fully levelled in the oven. This is important to avoid the mold from sliding away from the KMPR layer. Later, the wafer was exposed to UV light of 8 mW/cm² for 2 mins (step 2 Fig. 3.7 (b)). This step was performed quickly to minimise the shrinkage and stress in the sample. After UV exposure, the wafer was returned to the oven and baked at 95°C for 10 mins. The next step was to peel off the PDMS mold from the KMPR layer (Fig. 3.7 (c)). This was done slowly and carefully along the direction of the waveguides.

The next process in the fabrication of the waveguide is the coating of the core layer. Initially, the wafer with the KMPR cladding was baked on the hotplate at 65 and 95°C for the duration of one and 2 mins, respectively. This served the dual purposes of evaporating absorbed moisture as well as solvents that may have been trapped in the KMPR layer. Then, plasma treatment was performed on the KMPR surface for 5 mins to improve the surface adhesion. Subsequently, the SU-8 2002 core layer was spun onto the KMPR layer (Fig. 3.7 (d)). As same as the KMPR deposition, the coating of the SU-8 layer was carried out in two cycles. The spreading cycle was performed at the rate of 500 rpm with the acceleration of 100 rpm/s for 5 s. Consecutively, the thinning cycle was carried out at the rate of 2000 rpm with the acceleration of 300 rpm/s for 30 s. This resulted in the SU-8 core layer of 2.5 um thick. Later, the wafer was exposed to UV light of 8 mW/cm² for 30 s to cure the core layer. The process was finished with the sample baked on the hotplate at 65 and 95°C for the duration of one and 2 mins, respectively.

The single mode inverted rib waveguide fabrication was completed with the dicing of the wafer into 2.5 × 2.5 cm waveguides. This was performed using the DISCO DAD 321 automatic dicing machine. The dicing were carried out by the diamond tip blade at a speed of 0.1 mm/s and spindle rotation of 30000 rpm. The water flow rate was fixed at 1 l/min. This step is very critical to provide smooth endfaces for the light coupling into the waveguide. Fig. 3.8 shows the inverted rib waveguides fabricated on Si wafer. The good section of the waveguides with no air bubbles or distortions was diced along the dotted red line. The strips obvious in the image contains sets of
waveguides with different rib widths in the range of 3 – 7 μm.

![Inverted rib waveguide on Si wafer.](image)

Before depositing the nanostructured thin films on top of the core layer, the properties of the waveguides were analysed.

### 3.4.6 Optical Waveguide Properties

In this PhD project, SEM was used to observe the physical properties of the waveguide. As shown in Fig. 3.9, comparisons are made between the a rib in the waveguide mask and its imprinted waveguide on the KMPR layer. The imprinted rib was found to be slightly shrinked in the KMPR layer as compared to the rib width in the mask. The rib wall in the KMPR layer was also somewhat distorted as compared to its mask. Despite that, the overall dimension of the fabricated waveguides took the shape of the mask.
Fig. 3.9 SEM images of the rib in the waveguide mask and its imprint in the KMPR layer.

Meanwhile, a section of the waveguide endface is shown in Fig. 3.10. The SEM image on the left side clearly illustrates the SU-8 core layer, the inverted rib and the KMPR cladding layer of a waveguide channel. The width of the inverted rib was measured to be 7 µm.

Fig. 3.10 SEM image of the waveguide endface and its equivalent layers.

Fig. 3.11 shows the diced waveguides sample with a section of it was coated with the nanostructured thin films (grey colour). Using only one sample, the waveguide characteristics as well as the gas sensing performance with and without the sensing layer can be conveniently investigated. It also reduce the time to align the sample on the optical testing setup.
The insertion loss of the waveguide was also measured. Insertion loss is the light intensity loss caused by the introduction of any optical device in the setup. The insertion loss of the inverted rib waveguide was measured to be approximately 2 dB for the blank channel and 4 dB for the channel coated with the sensing layer.

### 3.5 Summary

In this chapter, the author presented in details the design and fabrication of the optical transducers, namely, transparent substrates, optical fiber and channel waveguide. This includes the preparation of the transducers which involves common processes such as cleaning and dicing as well as other steps unique to the different transducers.

The transparent substrates were used for the H$_2$ sensing applications based on the spectrophotometer. Five different transparent substrates were deployed such as quartz, sapphire, glass, ITO and FTO glasses. The lattice mismatch between the different substrate surfaces and the materials contributes to different nanostructured films. This provides interesting optical properties and as a result, excellent sensing performance from the films.

The author also employed multimode silica optical fiber as the transducer. The nanostructured thin films were deposited on the tip of the fibers. The large core, visible wavelength range operation and high thermal resistance made the multimode silica fiber a suitable
candidate for optical sensing. The fiber preparation steps involve cleaning and cleaving before depositing the films. After the deposition, the fibers were spliced to patchcords for H₂ testing.

The next optical transducer used by the author is the channel waveguide. Inverted rib single mode waveguide based on polymer was employed for the H₂ sensing applications. The waveguide based gas sensor is one of the novelties of this PhD project. The design and fabrication of the inverted rib waveguide involved various steps such as spin-coating, photolitography, heating, imprinting and dicing. Later, the waveguides were characterised to compare with the initial design.

In the beginning, variety of gasochromic metal oxide films were deposited or synthesised on the transparent substrates. Based on the sensing performance, the materials with the excellent response were chosen to be deposited on the optical fibers and channel waveguides.

After completing the design and fabrication processes of the optical transducers, the deposition and synthesis of the metal oxide nanostructured thin films were carried out. This will be presented in the following chapter (Chapter 4). The author used many deposition techniques to produce various kinds of nanostructures.
References


Chapter 4

Nanostructured Material Deposition and Synthesis

4.1 Introduction

In the previous chapter, the design and fabrication of the optical transducers for H₂ sensing were presented. This chapter will discuss in details the deposition and synthesis of the nanostructured optical sensing layers. The scope of the fabrication is only for the materials considered in the literature review (Chapter 2), namely, WO₃, MoO₃, TiO₂ and NiO. The discussion will also include the deposition methods of the catalytic metals (Pd, Pt and Au).

This chapter is divided into nine sections inclusive of Section 4.1: Introduction. Section 4.2 introduces the principles of the nanostructures growth. Section 4.3 explained in details the different deposition techniques and synthesis of the WO₃ nanostructures. This is followed by the presentation of the deposition of the other gasochromic nanostructured metal oxides such as MoO₃ (Section 4.4), TiO₂ (Section 4.5) and NiO (Section 4.6). Meanwhile, Section 4.7 discusses the different deposition techniques for the catalytic metals. Finally, the findings are summarized in Section 4.8.

4.2 Deposition and Synthesis of Nanostructured Materials

Nanostructured materials are defined as the materials with at least one dimension in the nano scale range (<100 nm). Depending on the dimension, nanomaterials can be categorised into a few classes [1, 2] such as:

- zero-dimensional nanostructures: nanoparticles;
- one-dimensional nanostructures: nanowires, and nanorods;
- two-dimensional nanostructures: thin films.
Nanomaterials are expected to have different properties than their bulk counterparts. In general, they might demonstrate unique mechanical, optical, electronic and magnetic properties significantly different from those observed for the bulk materials. This is due to material’s high surface to volume ratio, different surface energy and comparable dimensions with Debye length [1-3].

The two most common approaches to fabricate the nanostructured thin films are ‘bottom-up’ and ‘top-down’ [1]. The bottom-up approach is that by which a material is built-up from the bottom atom-by-atom, molecule-by-molecule or cluster-by-cluster [1]. It is also refers to controlled or directed self-assembly of atoms and molecules into nanostructures [4]. This is illustrated in Fig. 4.1.

![Fig. 4.1 Nanostructures growth via bottom up approach.](image)

This approach has shown the potential to obtain nanostructures with less defects and more homogeneous chemical composition [4]. It is also preferable because nanostructures with smaller dimension are normally achieved as compared to the top down approach [5]. In this PhD project, the author deployed different deposition techniques based on the bottom up approach like sputtering (RF and DC), electron beam, pulsed laser and thermal evaporation.

The top-down approach is considered when the bulk dimensions of a material are reduced until nanometer size features are achieved [1, 4]. Usually, this approach consists of at least one etching step to create nanostructures. This approach is described in Fig. 4.2. In this PhD project, acid etching and anodisation are among the techniques based on the top-down approach deployed by the author to deposit nanostructured thin films.
The different deposition and synthesis techniques create different nanostructure morphologies. The author deployed many of these techniques to achieve different metal oxide nanostructures especially for WO$_3$ which is the main candidate for the sensing layer due to its excellent chromic properties.

### 4.3 Deposition and Synthesis of WO$_3$ Nanostructured Thin Films

In this PhD project, the physical deposition techniques of the WO$_3$ nanostructured thin films used by the author are RF sputtering, electron-beam and pulsed laser. Meanwhile the chemical synthesis deployed is acid-etching. However, before any of the techniques was implemented, the substrates were prepared and cleaned from contaminants and dust as discussed in Chapter 3.

#### 4.3.1 RF Sputtering

Sputtering is a popular and well-known technique to deposit metal oxide films. In this technique, the WO$_3$ nanostructured thin films were deposited onto the substrates due to the oxidisation of the W atoms ejected from the metal target resulting from the collision with the ionised gas particles in the vacuum chamber at a suitable pressure. The gas ionisation in the sputterer can be generated either in direct current (DC) or radio frequency (RF) modes. In this project, the author mainly used RF sputtering because it is more common for oxide films deposition and flexible fabrication parameters as compared to the DC. A 99.95% tungsten target which was 4 inches in diameter, manufactured by
Target Materials Inc. was utilized for the deposition. Fig. 4.3 (a) and (b) illustrate the schematic of the RF sputterer and the planar RF magnetron sputtering system at RMIT University, respectively.

Fig. 4.3 RF sputtering system (a) a schematic diagram and (b) planar RF magnetron sputtering system at RMIT University.

The specifications of the sputtering process for the WO$_3$ nanostructured thin films are summarised in Table 4.1.

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Target to substrate distance</td>
<td>7.0 cm</td>
</tr>
<tr>
<td>2.</td>
<td>Sputtering power</td>
<td>80 W</td>
</tr>
<tr>
<td>3.</td>
<td>Process gas</td>
<td>90% O$_2$ / 10% Ar</td>
</tr>
<tr>
<td>4.</td>
<td>Process pressure</td>
<td>$2 \times 10^2$ Torr</td>
</tr>
<tr>
<td>5.</td>
<td>Deposition rate</td>
<td>5.3 nm/min</td>
</tr>
<tr>
<td>6.</td>
<td>Substrate temperature</td>
<td>100 and 260°C</td>
</tr>
</tbody>
</table>

The substrate temperature was varied depending on the transducers properties. Temperature of 260°C was used for quartz, glass, ITO and FTO glass substrates as well as optical fibers. For polymer waveguide transduction platform, the temperature was lowered to 100°C to avoid physical and chemical changes to the waveguide channels. As discussed in Chapter 2, the WO$_3$ nanostructures are still in the form of monoclinic for the temperature range of 30 - 300°C. For the deposition on the optical fiber tip, a special stage was used to hold the fiber vertically as
well as heating the tip. Throughout this project, WO$_3$ films with different thicknesses were sputtered by varying the deposition time. The film thickness was measured using an Ambios Technology XP-2 profilometer, and confirmed with cross sectional SEM. In terms of the film morphology, grains are typical of structures growth based on sputtering [6]. The detailed characterisation of the films will be discussed in the next chapter.

4.3.2 Electron Beam Deposition

In this project, another physical technique deployed to deposit WO$_3$ nanostructures is electron beam deposition. This technique has been known to deposit very smooth and uniform films. The thickness of the films can be controlled precisely down to resolutions of approximately one nanometer [4]. Compared to the solid disc W target used in RF sputtering, the electron beam deposition in this project used a small amount of the WO$_3$ powder as the target. The powder will be vaporised onto the substrate by the high energy electron beam under a very high vacuum. The schematic of the electron beam deposition system is illustrated in Fig. 4.4.

![Fig. 4.4 Schematic diagram of a typical electron beam deposition system.](image)

The WO$_3$ nanostructured thin films in this project were deposited via electron beam system in Dresden University of Technology, Germany. Different thickness of films were achieved on quartz substrates by varying the deposition time based on the following specifications. Commercially available 99.99% pure WO$_3$ powder manufactured by CERAC Inc. was used as the target. The e-beam deposition was carried out at room temperature with the
process pressure of $6.5 \times 10^{-7}$ Torr. The deposition rate was 0.2 nm/s. Later, the samples were annealed at 300°C in 99.95% O$_2$ to improve the structures crystallinity. The morphology of the WO$_3$ nanostructured films deposited via electron beam are very different from their sputtered counterparts. It is anticipated that this will affect the film’s optical sensing performance towards different H$_2$ concentrations. The following chapter will discuss thoroughly the characteristics of the e-beam deposited films.

### 4.3.3 Pulsed Laser Deposition

Apart from the physical deposition techniques discussed earlier, pulsed laser deposition (PLD) was also deployed in order to achieve different WO$_3$ nanostructures. PLD is a versatile deposition technique for growing thin films and can be applied to a very wide range of materials. A pulsed laser, usually in the ultra-violet (UV) wavelength, is periodically used to ablate the target material in a high vacuum. As a result, the solid material was transformed into plasma and generated a plume in the direction of the substrates. This plume condensed as it reaches the substrate to form nanostructured films [4]. A schematic diagram of the PLD system is illustrated in Fig. 4.5.

![Fig. 4.5 Schematic diagram of a PLD system.](image)

In this project, the WO$_3$ samples were fabricated using the PLD facility available at the University of Incheon, South Korea. The deposition was performed using ArF Excimer Laser operating at a wavelength of 193 nm. The short wavelength laser uses high energy photons and improves the films quality. The temperature of the substrate was 300°C and the oxygen pressure was maintained at $200 \times 10^{-3}$ Torr.
4.3.4 Acid Etching Synthesis

Recently, the WO$_3$ nanostructures synthesis via acid etching was first reported by Widenkvist et. al [7]. The high-temperature acid etching is considered as a fast and inexpensive synthesis process to form unique WO$_3$ nanostructures on large substrate areas. In this synthesis, W coated substrate is immersed in nitric acid solution at elevated temperature, resulting in the formation of nanostructured film of hydrated tungsten oxide or tungstite (WO$_3$•H$_2$O). Subsequently, the tungstite film is annealed at high temperature to obtain anhydrous WO$_3$ nanostructures. Widenkvist et. al used tungsten foil (99.95% purity) for the synthesis of the WO$_3$ nanostructures. Their films were composed of WO$_3$ platelet crystals with the edges directed out from the substrate surface. They investigated the effects of the deposition parameters such as acid concentration, temperature and immersion time on the shape and size of the platelets. According to them, the most important factor influencing the microstructure of the tungstite crystallite is the deposition temperature.

In this PhD project, the author modified the acid etching synthesis by using sputtered W films on transparent substrates instead of foil. Initially, the W films were deposited on the substrates via RF sputtering system. The substrates in the RF sputter chamber were adjusted to be at a distance of 65 mm from the W target (99.95% purity) in the presence of 100% argon (Ar). The base and process pressures of the sputtering chamber were fixed at $1.0 \times 10^{-5}$ and $2.0 \times 10^{-2}$ Torr, respectively. A constant 100 W RF power was applied during the deposition process and the substrates were heated to 300°C. The sputtering duration was 2 minutes. The film thickness was measured to be approximately 50 nm. These parameters were chosen to achieve transparent films after the acid etching process. After sputtering, the W films were placed in a reaction flask filled with 100 ml 1.5M nitric acid (HNO$_3$). A condenser was attached to the flask to maintain the solution concentration during the boiling process for 45 min. The flask was boiled at a constant temperature of 50°C in a bath. This process converted the W into tungstite (WO$_3$•H$_2$O). Later, the samples were annealed in air at 300°C for 120 minutes with a ramp rate of 2°C/min to remove the water and resulting in the transparent WO$_3$ nanostructured thin films.
The fabrication of the nanostructured thin films was also performed for the other gasochromic metal oxides. The nanostructured thin films must be transparent in order to analyse its absorbance properties when exposed to H₂. Therefore, the deposition techniques which allow to fabricate such films become the major concern in this PhD project.

### 4.4 Thermal Evaporation of MoO₃

Thermal evaporation is an effective technique used for depositing nanostructured thin films directly from the vapour of the materials under the supersaturating condition. It is one of the most versatile deposition techniques and does not require a precursor or catalyst. It is also a quick and effective technique without the need for vacuum atmospheres and can grow a vast selection of crystalline nanostructures in a single deposition [8-13]. Using thermal, the deposition is a physical process through material built-up on the substrates and it can also involve in-situ chemical process such as oxidation. The typical setup for a thermal evaporation apparatus is shown in Fig. 4.6.

![Fig. 4.6 Typical setup for thermal evaporation apparatus.](image)

The apparatus consists of a furnace to control the temperature of the fabrication chamber (quartz tube), material powder and the substrates to deposit the nanostructured thin films. The carrier gas is introduced to transport the material vapour from the source to the substrate. In some cases, apart from the carrier gas such as Ar, O₂ is also mixed for the material oxidation and to improve the crystalinity of the nanostructures. The technique important parameters that influence the growth of the nanostructured films are temperature, the partial pressure of the carrier gas and the vapour source, the source-substrate distance, the flow and type of gas and the growth time [4].
In this PhD project, the deposition was carried out by evaporating MoO$_3$ powder (99.99% purity, China Rare Metal Material Co.) onto quartz substrates. The MoO$_3$ powder was weighed at 10 mg and placed on an alumina boat inside the quartz tube (18.5 mm diameter and 680 mm length, Extech Equipment) at the main hot spot of the furnace. The quartz substrates were placed on alumina at a distance of 10, 15 and 20 cm from the powder. The evaporation temperature was increased by heating at rate of 2°C/min until 770°C was reached and maintained for duration of 30 min. The temperature was allowed to decrease at rate of 2°C/min until room temperature. A carrier gas mixture of 10% oxygen (O$_2$) and 90% Ar was allowed to flow through the quartz tube at a constant rate of approximately 800 sccm. The O$_2$ gas was added to the apparatus to improve the formation of fully oxidized MoO$_3$. The setup for the thermal evaporation deposition apparatus at RMIT University is shown in Fig. 4.7

![Thermal evaporation apparatus at RMIT University.](image)

The deposition of the MoO$_3$ nanostructured thin films on quartz at the different source-substrate distances produced different film morphology, thickness and transparency. These characteristics will be presented in details in Chapter 5.
4.5 Anodisation of TiO$_2$

Anodisation is a synthesis technique based on top-down approach. It is an electrochemical process to transform metal into its metal oxide. The typical setup for anodisation is shown in Fig. 4.8. In the anodisation, the metal coated substrate or metal foil is made the anode by connecting it to the positive terminal of a DC power supply. The cathode is connected to the negative terminal of the supply. The cathode is a Pt foil unreactive in the electrolyte. When the circuit is closed, electrons are withdrawn from the metal at the positive terminal, allowing ions at the metal surface to react with the electrolyte to form an oxide layer on the substrate or foil [14-17].

Anodisation is one of the most promising techniques to produce TiO$_2$ nanostructures [14, 18]. In this technique, titanium (Ti) in the form of a film or foil, is anodised in fluoride-ion-containing electrolytes to form nanopores/tubes. For foils, it has been reported that, by controlling the anodisation voltage and time, the nanotube/pore dimensions and aspect ratio can be varied to obtain diameters of about 10-150 nm and a length of up to several hundreds of microns [18-27].

Before the synthesis, Ti films were DC sputtered from a pure 99.99% Ti target (Target Materials Inc.) onto quartz substrates in the presence of argon (Ar) gas, at 600°C under a process pressure of 1 x 10$^{-2}$ Torr with a DC power of 100 W. This particular deposition temperature was chosen as it produced distinct crystallographic orientation which resulted in the formation of pores. After anodisation, the DC sputtered films deposited at low temperatures produced nanotubes with distinctly different crystal orientations as compared to the other techniques [17]. The sputtering time was set to be 70 min. The thickness of the films was measured to be 1 µm. The anodisation of Ti films was performed using a neutral ethylene glycol electrolyte containing 0.5% (wt) ammonium fluoride (NH$_4$F) at 5 V for 1 hour.
Fig. 4.8 Typical setup for anodisation technique.

After anodisation, the films were annealed at 800°C for 8 hours in a furnace with a ramp up rate of 2°C/min in air. This was carried out to fully transform the anodised Ti into TiO$_2$ nanostructured thin films as well as improve the films transparency. For comparison, a non-anodised film was also annealed at the same conditions. According to the literature, annealing at high temperature modifies the crystal structures of the TiO$_2$ films [14, 22, 24]. As a result, the gasochromic responses of the films were also changed. It is interesting to investigate the microcharacteristics of the TiO$_2$ nanostructured thin films and the gas sensing analysis which will be presented in Chapter 5 and 7, respectively.

### 4.6 RF Sputtering of NiO

In this PhD project, the author also investigated the gasochromic properties of the p-type metal oxide nanostructures. The nanostructured thin films deposited previously are all n-type metal oxides. One of the suitable candidates is NiO. The deposition of the NiO$_x$ films were carried out in the collaboration with Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center (NECTEC), Thailand. Initially, the NiO$_x$ films were RF sputtered onto quartz substrates in the presence of oxygen (O$_2$) and argon (Ar) gases with the ratio of 5:1. The process pressure and the RF power were set to 4.5 x $10^{-3}$ Torr and 200 W, respectively. The sputtering rate for this material is approximately 9 nm/min. The sputtering was performed to achieve NiO$_x$ films with the thicknesses of 100 nm and 400 nm. Later, the NiO$_x$ films were
annealed at 500°C for 180 min in 90% O₂ and 10% Ar with the furnace ramp rate was set to 2°C/min. This process converted the NiOₓ into NiO nanostructured thin films and improved the films’ crystallinity.

Subsequently, the metal oxide nanostructured thin films were coated with a catalytic metal layer to enhance the gasochromic properties. As discussed in Chapter 2, the catalytic metals were Pd, Pt and Au.

4.7 Deposition of Catalytic Metal Layers

As mentioned in Chapter 2, many studies have identified the requirement of the catalytic metal layer to improve the gasochromic properties of the metal oxides [28-34]. In the case of WO₃, the films coated with the catalytic metal layer change from transparent to dark blue upon exposure to H₂ [6, 35, 36]. The common model utilized to explain the gasochromic effect of WO₃ is the reduction of W⁶⁺ (transparent) centre in the WO₃ crystal lattice to W⁵⁺ (blue colour) facilitated by the transfer of H⁺ ions and electrons from H₂ molecules disassociated by the catalytic metal [6, 35].

In this PhD project, the author deployed different deposition techniques to deposit the catalytic metal layer onto the metal oxide nanostructured thin films.

4.7.1 Palladium (Pd)

The author deposited Pd catalytic layer using two different techniques: either DC sputtering or electron beam evaporation. The sputtering was carried out using a 2 inch Pd foil target (99.99% purity, ProSciTech), 30 W DC power in the 100% Ar process gas and operating pressure of 3.75×10⁻³ Torr at room temperature. The substrate-target distance was maintained at 2.5 cm. The rate of the Pd deposition was approximately 2.5Å/s. The SPI-Module™ DC sputtering system is shown in Fig. 4.9.
Meanwhile, for the Pd deposition via electron beam, Balzers™ system was used. The system deployed a one inch solid Pd target of 99.99% purity. During the deposition, the process pressure and the beam power were set at $3 \times 10^{-7}$ torr and 22W, respectively. The substrates were rotated to provide uniform and homogeneous coatings. The Pd deposition rate of the system is approximately 0.5Å/s.

For the Pd deposition onto quartz substrates, the author deployed either DC sputtering or electron beam evaporation. However, for the deposition onto optical waveguides or on the tip of the optical fibers, only DC sputtering system was used. This is because the sputtering system is more flexible to accommodate the fragile optical fiber and allow the protection of the polished waveguide endfaces from the Pd coatings as compared to the Balzers™ system.

The characterisation of the Pd catalytic layer deposited via DC sputtering and electron beam will be presented in the next chapter. The effects of the different Pd thicknesses on the gasochromic properties of the metal oxide nanostructured thin films were also investigated and presented in Chapter 7.
4.7.2 Platinum (Pt)

The deposition of the Pt layer was also carried out using a DC sputtering system. However, this system is different from the system used for Pd coating. A Gatan Precision Etching and Coating System (PECS™) model 682, designed for coating electron microscopy samples, was used to sputter Pt onto metal oxide nanostructured thin films. The PECS coating system is designed to slowly deposit electron transparent amorphous coatings of Pt with a built in thickness monitor. The sputtering was carried out by two penning ion guns. The guns were set to 612 µA aimed at the Pt target (99.99% purity), which provided an average deposition rate of 1.2 Å/s. The deposition was performed at an operating pressure of 6×10⁻⁵ Tor in Ar gas and the sample was rotated at 10 rpm to ensure a uniform coating. The PECS system is shown in Fig. 4.10.

![Fig. 4.10 PECS™ sputtering system for Pt deposition.](image)

The characterisation of the Pt coatings on the metal oxide films was only carried out using energy dispersion X-ray (EDX). It is not possible to directly image the amorphous Pt coatings via SEM as the PECS system used for Pt deposition is designed to deposit conductive coatings over samples that will not interfere with imaging.

4.7.3 Gold (Au)

In this PhD project, the Au nanoclusters were provided by the collaborator from the Canterbury University, New Zealand. The author developed a procedure to deposit the nanoclusters onto the sputtered WO₃ films. In this procedure, 11 mg of Au nanoclusters were
suspended in 430 µl chloroform solution. To provide homogenous suspension, the solution was sonicated in the ultrasonic bath for 60 min. Later, the suspension was transferred into a micropipette. The pipette was set to deliver 5 ml of the suspension onto the sample placed on the spin coater stage. Immediately, the sample was spun at 500 rpm for 30 s. Then, it was annealed at 200°C in air to remove the organic compound used in the formation of the Au nanoclusters.

The microcharacterisation of the metal oxide nanostructured thin films coated with Au layer was performed using SEM and EDX. The gasochromic analyses of the WO3 films coated with Au were also presented in Chapter 7.

4.8 Summary

In this chapter, the author presented in details the deposition techniques and synthesis steps of the metal oxides nanostructured thin films on optical transduction platforms. The depositions of the catalytic layers namely Pd, Pt and Au were also explained thoroughly.

As much as the main fabrication focus is on WO3 nanostructures, extensive works were also carried out to deposit other potential nanostructured metal oxides with gasochromic properties such as MoO3, TiO2 and NiO. In order to obtain different WO3 nanostructures, the author deployed variety of techniques such as sputtering, electron beam, pulsed laser and acid etching. Meanwhile, for the other metal oxide nanostructures, MoO3 was deposited via thermal evaporation, TiO2 via anodisation and NiO via RF sputtering.

These various kinds of deposition techniques have their own advantages and disadvantages in producing unique nanostructured thin films. Sputtering, electron beam and pulsed laser depositions are bottom up techniques that produce highly uniform and transparent thin films which are very critical for optical gas sensing. The high vacuum environment facilitated by these techniques ensured that the developed films are of minimum impurities with consistent nanostructures. On the other hand, the developed samples via these techniques are generally compact and require additional complicated processes to achieve porosity. Nanoporous thin films
are known to have very strong interaction with the gas molecules and thus, highly preferable for optical gas sensing applications. This can be achieved via top down techniques deployed in this project such as acid etching and anodisation. Even though these techniques are not as controllable as the bottom up techniques discussed earlier, the nanostructured films produced are extremely porous and unique. The author anticipates highly sensitive optical gas sensing performances from these nanoporous films.

Initially, the depositions of the metal oxide nanostructured thin films were carried out mainly on quartz and other transparent substrates such as sapphire, glass, ITO and FTO glasses. Then, the gasochromic properties of the films when exposed to H₂ with different concentrations were analysed. Afterwards, the film deposition onto established optical transducers such as optical fiber and planar polymer waveguides were carried out for the metal oxide nanostructures with excellent sensing performance. Further optical sensing analyses were performed on the optical fiber and waveguides coated with selected metal oxide nanostructured thin films.

Beforehand, the microcharacterisation of the deposited and synthesised metal oxide nanostructured thin films will be presented in the following chapter (Chapter 5). Understanding the properties such as crystal structure and the stoichiometry of the fabricated materials is highly important as it will help in realising the gas sensing performance, which will be presented in Chapter 7.
References


Chapter 5

Micro-Nano Characterisation Techniques and Results

5.1 Introduction

In Chapter 4, the synthesis and deposition of nanostructured materials for gaseous hydrogen sensing based on their optical response were presented. In this chapter, a thorough analysis of the nanostructures characterisation results will be provided. This is very important in gaining understanding on the materials' physical, chemical and optical properties. The material properties of the metal oxide nanostructured thin films such as crystal orientation and structure dimension are strongly dependant on the deposition technique and are known to vary considerably from their bulk materials [1]. Furthermore, the optical sensing performance of the nanostructured materials towards gasses is also determined by these properties.

This chapter is divided into four sections inclusive of Section 5.1 Introduction. Section 5.2 introduces the micro-nano characterisation techniques. Section 5.3 discusses the detailed characterisation of the materials under study. Finally, the findings are summarized in Section 5.4.

5.2 Micro-Nano Characterisation Techniques

The main characterisation techniques used in this project are Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV-Vis-NIR spectroscopy, Raman spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD), General Area Detector Diffraction System (GADDS) and Energy Dispersion X-Ray (EDX). In general, these techniques provide useful information on the morphology, crystal structure,
stoichiometry, composition and optical properties of the developed nanostructured thin films.

5.2.1 Scanning Electron Microscopy (SEM)

SEM is the main technique used in this project to characterise the morphologies of the materials. A scanning electron microscope consists of an electron optical column, a vacuum system and electronics [2]. As shown in Fig. 5.1, the column comprises of an electron source to produce electron beam, a set of lenses to focus the electrons into a fine spot onto the samples in the specimen chamber and a secondary electron detector to convert the scanned beam into electrical signal for image processing. These devices are encapsulated in a vacuum system which allows primary electrons movement in straight lines and operates in low or high vacuum modes. The electronic circuitries are mainly employed to control the voltages and currents for the electron source, magnetic lenses and the detector.

![Fig. 5.1 Schematic diagram of SEM.](image)

High resolution images can only be produced by SEM if the samples are conductive. Electric charging occurs for samples with minimum or no conductivity. This can be prevented by coating the samples with a thin layer of Pt or Au (≈ 10 - 50Å) via DC sputtering. In this project, a FEI Nova NanoSEM 200 at the Department of Applied Physics, RMIT University was used to analyse the material (Fig. 5. 2).
5.2.2 Transmission Electron Microscopy (TEM)

TEM is another important technique to examine materials morphology, crystallography, structure distribution and their elemental composition [3]. The image magnification provided via TEM is higher, approximately up to 1 million times as compared to 400 000 times for the SEM.

As in SEM, TEM consists of an electron optical column, a vacuum system and the microscope (Fig. 5.3). However, in TEM, the image of the material is projected onto the fluorescent screen by the electrons penetrating through the sample. The sample must be very thin (< 500 nm) to allow electrons to pass through. TEM has the capability to provide both images and diffraction patterns for the same region by adjusting the strength of the magnetic lenses [4]. By defocusing the condenser lens to produce parallel illumination at the specimen and using a selected area aperture to limit the diffracting volume, a selected area diffraction (SAED) pattern from an area as small as several hundreds to a few nanometers in diameter can be obtained. SAED results can determine whether the nanomaterials crystal structures are orthorhombic, tetragonal, hexagonal, cubic or others.
In order to investigate the morphology and the crystallography of the nanomaterials used in this project, a Jeol 1010 Transmission Electron Microscope (TEM) at the Department of Applied Physics, RMIT University was used (Fig. 5.4).
5.2.3 X-Ray Diffraction (XRD)

XRD is a characterisation technique used to identify the various crystalline phases in solid materials and powders [3]. In XRD analysis, the X-ray signals interact with the sample and diffracted with the X-ray diffractometer. The diffraction from the sample consists of pattern unique to certain material with certain crystal phases. Later, the material and its crystal phases are identified by comparing the diffractogram with those of internationally recognised databases that contain the reference diffractogram. The scientific organisation with the most recognised XRD database is International Centre of Diffraction Data (ICDD), based in Philadelphia, USA.

In this research project, XRD patterns of the nanostructured materials were collected at room temperature on a Bruker D8 ADVANCE powder X-ray diffractometer and Bruker AXS D8 Discover with General Area Detector Diffraction System (GADDS) at the Department of Chemistry, RMIT University as shown in Fig. 5.5. The instrument was fitted with a graphite-monochromated copper tube source (Cu-Ka radiation, \( \lambda = 1.5406 \) Å), and a scintillation counter detector.

Fig. 5.5 Bruker (a) D8 ADVANCE X-Ray Diffractometer and (b) D8 Discover with GADDS.
5.2.4 Energy Dispersion X-Ray (EDX)

Apart from XRD, the elemental composition of the materials under investigation can be identified via EDX technique. The EDX system is integrated in the Nova NanoSEM system described in Section 5.2.1.

In EDX, the SEM electron beam is transmitted onto the sample. The incident beam excites the electrons in the inner shell of the element atom and ejecting them from the orbit. The removal of the electrons from the shell creates vacancy which will be filled by the electrons from the outer shell. This is possible when the outer shell electrons are reducing some of their energy by emitting X-rays. The emitted X-rays are collected by the detector and their discrete energy is unique to atoms of every element in a sample. The EDX results are presented in the form of intensity peak versus beam energy spectrum.

5.2.5 Raman Spectroscopy

Raman spectroscopy is an analytical technique to investigate the qualitative and quantitative composition of materials [5, 6]. Discovered in 1923, this characterisation technique is widely used to investigate organic and inorganic materials.

Raman spectroscopy is based on the monitoring of the light intensity and wavelength that are scattered inelastically from molecules or crystals [3]. In this technique, visible or infrared signal is transmitted onto the sample. When striking the sample, the signal interacts with the bonding electrons of the sample molecules and inelastic (Raman) scattering is produced. The wavelength of the scattered signal will shift in reference to the wavelength of the transmitted light. Specifically, the Raman shift is due to the interaction of the photons with the phonons (molecular vibrations) which are unique to the chemical bond of the molecules. These molecules can be identified based on their Raman peak shifts. The measurement was carried out using a Renishaw RM1000 spectrophotometer with an argon ion laser of 514.5 nm as the excitation source in the Physics Department, University of Melbourne and an Oceanoptics QE65000-Raman spectrophotometer in the Microelectronic and Materials Technology Centre (MMTC), RMIT.
University. A 532 nm laser with a power of 5-500 mW was used as the excitation source. A notch filter was used to prevent measurements below 100 cm$^{-1}$.

5.2.6 X-Ray Photoelectron Spectroscopy (XPS)

XPS is another type of analytical technique to identify the material stoichiometric composition and empirical formulae [3]. XPS analysis is based on the photoelectric effect in which photoelectrons are ejected from the material surface when it was exposed to X-ray beam. The photoelectrons ejected from the material surface mainly due to the absorption of the photon energy from the X-ray beam. The properties of the ejected photoelectrons such as their amount and kinetic energy are measured and plotted as a spectrum of their binding energies. The spectrum peak positions and shapes correspond to the material’s electronic configuration and is unique to its elements and compounds. Later, the material characterisation is carried out by comparing the acquired spectrum with the spectra from the known databases. The measurement was performed by VG-310F instrument using Al non-monochromated X-rays (20 kV, 15 mA) with the hemispherical energy analyser set at pass energy of 100 eV for the survey spectrum and 20 eV for peak scans. The XPS facility is located at the Department of Applied Physics, RMIT University.

5.2.7 UV-Vis-NIR Spectrophotometry and Band Gap Analysis

Ultraviolet-visible-near infra red (UV-Vis-NIR) spectrophotometry is a characterisation technique based on the interaction of electromagnetic waves in the UV-Vis-NIR wavelength ranges and the material [3]. The magnitude of the absorbed or emitted electromagnetic waves by the materials is analysed against the wavelengths. Information on the material’s optical properties such as transparency and optical band gap can be extracted from this spectrum [7, 8].

The UV-Vis-NIR spectrophotometry system consists of light sources to produce light of a known intensity and wavelength ranges onto material and a spectrophotometer to measure the spectrum and intensity of the light exiting the material. In this project, the materials were examined using a spectrophotometric system consisting of a Micropack DH-2000 UV-VIS-NIR light source and an Oceanoptics HR4000 spectrophotometer. The analysis was performed using Spectrasuite
2007 edition software. This facility is located at the Sensor Technology Laboratory, School of Electrical and Computer Engineering, RMIT University. The author set the system up and fabricated a customised gas chamber by himself to perform the optical characterisation. The setup is shown in Fig. 5.6.

![Spectrophotometric system setup](image)

Fig. 5.6 Spectrophotometric system setup.

The absorbance spectra of a material measured using the spectrophotometric system can be used to estimate the optical band gap. According to Tauc equation, the band gap can be estimated from the following expression [9]:

\[
adhv = A(hv - E_g)^n
\]  

\[
(5.1)
\]

where \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant \( (1.69 \times 10^{-19}) \), \( v \) is the photon frequency \( (3 \times 10^8 \text{ ms}^{-1}) \), \( A \) is the dimensional constant, \( E_g \) is the energy band gap and \( n \) is 2 for indirect semiconductor such as WO\(_3\) [10]. Based on this equation, the estimation of the energy band gap was obtained by plotting \((adhv)^2\) versus photon energy \((hv)\). The estimated optical band gap is the value of the linear extrapolation of the plotted curve.

### 5.3 Micro-Nano Characterisations Results

The WO\(_3\) nanostructures were chosen for this PhD thesis due to their excellent photochromic properties as discussed in Chapter 2. The coloration of the WO\(_3\) films when exposed to UV radiation is significantly influenced by the films’ morphology [10]. Therefore, it is projected that the WO\(_3\) nanostructured films will exhibit excellent gasochromic properties towards
H₂ as compared to their amorphous counterparts. Microcharacterisation were performed to identify the quality of the WO₃ nanostructures which have been fabricated using different deposition techniques such as RF sputtering and electron beam. This includes the films that are combined with different catalytic metals onto different transparent substrates. The characterisations were also performed on the other prospective metal oxide nanostructures with gasochromic properties such as MoO₃, TiO₂ and NiO.

### 5.3.1 RF Sputtered WO₃

The WO₃ nanostructured films with different thicknesses were successfully deposited onto different transparent substrates (quartz, glass, ITO and FTO) via RF sputtering method. SEM micrographs of the WO₃ 1.2 µm thin films deposited on quartz substrates are shown in Fig. 5.7.

![SEM images of (a) RF sputtered WO₃ on quartz, (b) RF sputtered WO₃ surface at high magnification and (c) cross-sectional SEM (44° rotation) with the inset shows high magnification image of the columnar structures.](image)

Fig. 5.7 (a) and (b) show the compactness and homogeneous morphology of the RF sputtered WO₃ films. These films consist of nanotextured grains with approximately 100 – 200 nm in diameter. Upon closer inspection it is clear that these grains are agglomerates of smaller crystallites which are
estimated to be less than 50 nm in diameter. These images are in good correlation with the WO$_3$ thin films RF sputtered by Takano et. al [11] and Marsen et. al [12].

In order to observe the cross section of the sample, some parts of the films were removed via argon ion miller. The SEM of the cross section taken at 44° stage rotation angle as in Fig. 5.7 (c) revealed that the sputtered films initiate with small hemispherical grains which later progress into more columnar structures. The initial layer of hemispherical grains are formed due to the mismatch between the lattice constants and also the thermal expansion coefficients between the film and substrate during the deposition at elevated temperatures [13]. Beyond this preliminary region of mismatch and subsequent compensation, the sputtered WO$_3$ grew as columnar structures.

During the sample cross sectioning, the sputtered WO$_3$ was not completely removed, providing an observational insight into the growth mechanism of the thin film (Fig. 5.7 (c)). The smooth dark grey regions in the left hand side of the micrograph in Fig. 5.7 (c) show the morphology of the underlying quartz substrate, which has been rendered smoothly by argon ion milling. Moving away from this region, the nodular hemispherical foundations (enhanced by the argon ion milling) are exposed. Larger columnar structures sit atop these hemispherical foundations as seen in the inset of Fig. 5.7 (c). Also visible in Fig. 5.7 (c) are the rough nanostructures of the sputtered film. The rough structures provide high surface area and have many sites for gas molecules adsorption [14, 15]. From the cross-sectional image, the thickness of the sputtered WO$_3$ was determined to be approximately 1.2 µm.

Fig. 5.8 illustrates the TEM image of the sputtered WO$_3$ films. The image contrast revealed the dimension of the WO$_3$ grains and verified their sizes to be in range of 30 – 50 nm.

![TEM image of nanotextured WO$_3$ films.](image-url)
Apart from quartz, the WO$_3$ nanostructured films were also sputtered on different transparent substrates such as glass, ITO and FTO. Each substrate has a different surface structure as shown in Fig. 5.9. The approximate grain size for quartz, glass, ITO and FTO is 20 – 40, 10 – 30, 40 – 60 and 300 – 500 nm, respectively. The substrate grain dimension will influence the nucleation growth sites of the metal oxide atoms during the deposition. This initial nucleation process is strongly influencing the morphology and the crystallinity of the developed nanostructured films [16-21]. Therefore, the WO$_3$ films sputtered on the different transparent substrates are expected to have different morphologies and crystals. These surface characteristics will be one of the key factors for the optical sensor performance. A high surface area and certain crystal orientation are known to facilitate the chemisorption process in the films by increasing the gas adsorption and desorption rates [22, 23]. As a result, sensors coated with such films have high sensitivity and fast response.

![Fig. 5.9 SEM of transparent substrates surface; (a) quartz, (b) glass, (c) ITO glass and (d) FTO glass.](image)

Fig. 5.10 shows SEM images of WO$_3$ thin films sputtered on the different transparent substrates. The thickness of each film is 500 nm. The SEM in Fig. 5.10 (a) shows that the WO$_3$ thin films were comprised of fine nanotextured WO$_3$ of 30-50 nm grains on glass. This is similar to the films
sputtered on quartz in Fig. 5.7. The SEM image of sputtered WO$_3$ on ITO glass (Fig. 5.10 (b)) shows the grains are slightly larger than the ones deposited on the quartz or glass and in the range of 40-60 nm sizes. The sputtered WO$_3$ grains on FTO glass are the largest with the sizes of 300-500 nm as compared to the films deposited on other transparent substrates as illustrated in Fig. 5.10 (c). The results indicate that the size of the sputtered WO$_3$ nanostructures is influenced by the surface of the substrates. The WO$_3$ structures on FTO are very different as compared to the structures on the other substrates. The FTO films present larger grain sizes which generally indicate these films to have lower surface to volume ratio compared to the other small grain sizes WO$_3$ that exists on quartz, glass and ITO. This will provide interesting optical sensing analysis of such films towards H$_2$. The optical gas responses of the films will be presented later in Chapter 7.

Fig. 5.10 SEM of WO$_3$ thin films sputtered on different transparent substrates; (a) glass, (b) ITO glass and (c) FTO glass.

Fig. 5.11 shows the X-ray diffraction (XRD) analysis of the sputtered WO$_3$ films on the transparent substrates. The XRD peaks for WO$_3$ on quartz substrate are in good correlation with WO$_3$ ICDD card file no. [75-2072], with a predominant reflection corresponding with the (020) crystal plane.
of monoclinic crystal structure. Minor reflections were observed in the (021), (002), (022), (421) and (013) planes of crystallographic WO₃.

Fig 5.11 XRD spectrum of RF sputtered WO₃ films on transparent substrates.

This XRD pattern is in good agreement with other RF sputtered thin films reported by Takano [10]. The peaks on the ITO sample are related to primarily ITO (ICDD card file no. [74-1410]) and several minor peaks can be associated with WO₃ (ICDD card file no. [30-1387]). While the WO₃ peaks are of low intensity measured from those deposited on quartz and ITO, minimum peaks are visible for the films deposited on the glass substrate. A mixture of peaks can be observed in the samples on FTO substrate including tin oxide (SnO) and WO₃ correspond to ICDD card files no. [88-0287] and [46-1096], respectively. WO₃ is identified in almost all samples on the transparent substrates.

Raman spectroscopy was also utilised to study the RF sputtered WO₃ films. As illustrated in Fig. 5.12, the Raman spectrum of the sputtered WO₃ films correspond to hydrous WO₃•½H₂O with the bands presence at 155, 190, 255, 320, 680, 805 and 945 cm⁻¹ mixed with the monoclinic WO₃ phase (band at 434 cm⁻¹). This spectrum also in good correlation with the detailed Raman spectrum analysis on WO₃ films as observed by Daniel et. al [24]. The terminal ν(W=O) bond is indicated by band at 945 cm⁻¹ and the presence of ν(O-W-O) bond is verified by the bands at 680 and 805 cm⁻¹. The bands at 155, 190, 255 and 320 cm⁻¹ belong to the ν(W-OH₂) and ν(W-O-W) bonds, respectively. The
presence of $\frac{1}{3}\text{H}_2\text{O}$ phase is found to be in favour of the H ions diffusion in the films [25, 26]. Therefore, the sputtered WO$_3$ films with the $\frac{1}{3}\text{H}_2\text{O}$ phase will be promising for the development of the highly sensitive H$_2$ optical sensor.

![Raman spectrum of the sputtered WO$_3$ films on quartz.](image)

The sputtered WO$_3$ films were also characterised with the XPS characterisation. Fig. 5.13 (a) and (b) show the W(4f) and O(1s) XPS peaks of the sputtered WO$_3$ films.

![XPS spectrum of sputtered WO$_3$ films.](image)

The W(4f) orbital of the sample can be identified as W(4f5) and W(4f7) orbital levels, which are centered at 37.9 eV and 35.4 eV, respectively. The results indicate the sample is WO$_3$ without any evidence of substoichiometric tungsten oxide [27-29]. The O(1s) peak show a dominant component centered at 530.5 eV, which is assigned to the oxygen atom forming the strong W=O bond [28, 30].
5.3.2 RF Sputtered WO$_3$ Films Coated with Catalytic Metals (Pd, Pt and Au)

As discussed earlier in Chapter 5, catalytic metals such as Pd, Pt and Au were deposited onto the metal oxide nanostructured films to improve the films’ optical response when exposed to H$_2$. The deposition techniques used to coat the catalytic metals onto WO$_3$ films on quartz substrate are electron beam or DC sputtering for Pd, DC sputtering for Pt and spin-coating for Au. Fig. 5.14 shows the SEM images of the WO$_3$ films coated with the catalytic metals; (a) Pd via electron beam deposition, (b) Pd via DC sputtering and (c) Au via spin-coating.

![SEM images of WO$_3$ films coated with catalytic metals](image)

The metals were identified by the bright structures distributed over the entire surface of the sample. The Pd grains deposited via electron beam and DC sputtered are 30 – 40 nm and 5-10 nm in sizes, respectively. The electron beam deposition technique achieved a more compact Pd coating compared to the DC sputtering. This can be attributed to the high electron beam power and vacuum
pressure provided by the electron beam deposition system as compared to the DC sputtering system. Meanwhile, the Au clusters covered the WO$_3$ films are measured to be in the sizes of 10 – 40 nm. The Au distribution is more uniform compared to electron beamed Pd coating. It is not possible to directly image the Pt coatings via SEM as the DC sputterer used for Pt deposition is designed to deposit conductive coatings over samples that will not interfere with imaging [31]. However, the presences of Pt as well as other catalytic metals were detected when the films were characterised via EDX as shown in Fig. 5.15.

EDX analysis of the Pd/WO$_3$, Pt/WO$_3$ and Au/WO$_3$ films on quartz substrates verified the presence of the elements on the films. Strong peaks of W and O indicated the films are mainly consisted of WO$_3$. Low intensity peaks of Pd, Pt and Au clusters are in agreement with their small amount deposited on the films as mentioned in Chapter 4. The presence of silicon (Si) and carbon (C) peaks is caused by the quartz (SiO$_2$) substrates and the carbon tape used to fix the samples on the stage, respectively. The EDX analysis also indicates the overlapping peaks for W and Si elements.

![Fig. 5.15 EDX spectrum of the WO$_3$ films coated with (a) Pd, (b) Pt and (c) Au, deposited on quartz substrates.](image-url)
Chapter 5: Micro-Nano Characterisation Techniques and Results

Fig. 5.16 illustrates the absorbance spectra of WO$_3$, Pd/WO$_3$ and Pt/WO$_3$ nanostructured films on quartz. The measurement of the spectra have been normalised with the blank quartz substrate. The characteristic shape reflects the transparent state of the films that have been previously observed in the studies of WO$_3$ optical properties [32, 33]. The fringes in the spectrum of these partially transparent films was ascribed to the optical interference that occurs in the sputtered WO$_3$, due to the multiple reflections of optical rays as they pass through the thin film with the WO$_3$ thickness of 1.2 µm and the catalytic metals of 25 Å [31]. The measurement of the band gap can be complicated with the presence of the fringes. Reducing the thickness of the thin film to a few hundred nanometers eliminates the fringes as shown by the smooth absorbance spectra of WO$_3$ films with the thickness of 200 nm (Fig. 5.17). Except for the obvious absorbance curve around 500 nm wavelength, there is no fringe in the 200 nm thick WO$_3$ films’ spectra throughout the vis-NIR wavelength ranges. The depositions of the catalytic metals onto the films clearly change their absorbance spectra. The absorbance spectrum of Pt/WO$_3$ thin films has a slightly larger magnitude of absorbance compared to the Pd/WO$_3$ because of the amorphous Pt covered the whole films. In contrast, Pd/WO$_3$ films were coated dispersedly with Pd islands via electron beam deposition. Both Pt/WO$_3$ and Pd/WO$_3$ absorbance spectra were shifted towards blue region as compared to the original WO$_3$ spectrum. The spectrum shift is bigger for Pt/WO$_3$ than in Pd/WO$_3$.

![Absorbance spectra of WO$_3$, Pd/WO$_3$, and Pt/WO$_3$](image)

Fig. 5.16 Absorbance versus optical wavelength of 1.2 µm sputtered WO$_3$ coated with Pd and Pt on quartz substrates.
Fig. 5.17 Absorbance versus optical wavelength of 200 nm sputtered WO$_3$ coated with 25 Å Pd and Pt on quartz substrates.

Fig. 5.18 illustrates the absorbance spectra of 500 nm WO$_3$ films coated with Au. The fringes in the spectrum are observed in the films with 500 nm thick but not as many as in 1.2 µm thin films. The deposition of Au onto WO$_3$ films also slightly shifts the spectrum towards blue region as well as increases the absorbance magnitude.

Fig. 5.18 Absorbance versus optical wavelength of 500 nm sputtered WO$_3$ coated with Au on quartz substrates.
The change in the absorbance spectra of the WO₃ films coated with the catalytic metals indicates the modification of the optical band gap of the films. Based on the Tauc equation (Section 5.2.7), the optical band gap of the sputtered WO₃ films could be estimated with reference to their absorbance spectra measured at room temperature. The band gap estimation curves which were derived from the films absorbance spectra is shown in Fig. 5.19. The band gap is the value where the tangent to the curve intersects the band gap energy axis as shown by the extrapolation of the dashed lines in the figure.

![Fig. 5.19 Estimated optical band gap of sputtered WO₃ (3.36 eV), Pd/WO₃ (3.04 eV), Pt/WO₃ (3.09 eV) and Au/WO₃ (3.00 eV).](image)

It was observed from Fig. 5.19 that the optical band gap reduces when the WO₃ films were coated with the catalytic metals. Optical band gap of the single layer sputtered WO₃ was found to be 3.36 eV. This value is within the band gap of the sputtered WO₃ films which is in the range of 3.00 – 3.40 eV as reported in the literature [10]. After the WO₃ films were coated with Pd, Pt and Au, the band gaps reduced to 3.04, 3.09 and 3.00 eV, respectively. It has been suggested that the deposition of the catalytic metal layer onto the metal oxide film reduces the band gap as it forms additional intermediate electronic states residing between the top of the valence band and the bottom of the conduction band [34].
5.3.3 Electron Beam Deposited WO$_3$

The depositions of the WO$_3$ nanospheres on quartz substrates were carried out via electron beam with the parameters discussed in Chapter 4. Fig. 5.20 illustrates the SEM micrograph of the WO$_3$ nanospheres.

![SEM images of WO$_3$ nanospheres on quartz substrates with inset in (b) showing the high magnification sphere structures.](image)

The electron beam deposited WO$_3$ films were very uniform compared to the sputtered WO$_3$. As in Fig. 5.20, the SEM revealed that the electron beam deposited WO$_3$ films were comprised of homogeneous WO$_3$ nanospheres with diameter 10-20 nm. The WO$_3$ spheres are smaller compared to the sputtered WO$_3$ grains (30 – 50 nm sizes) on quartz.

As illustrated in Fig. 5.21, the electron beam deposited WO$_3$ films Raman characterisation measurements indicate that the WO$_3$ structures are monoclinic with the bands presence at 273, 327, 434, 715 and 807 cm$^{-1}$. The $\nu$(O-W-O) bond is indicated by the bands at 715 and 807 cm$^{-1}$. The presence of $\delta$(O-W-O) bond is verified by the bands at 273, 327 and 434 cm$^{-1}$. The band at 218 cm$^{-1}$ is associated with the $\nu$(W-O-W) bond. These characterisations were performed with reference to the detailed Raman spectrum analysis on WO$_3$ films investigated by Daniel et. al [24].
Fig. 5.21 Raman spectrum of the electron beam deposited WO₃ films.

The absorbance spectra of the 500 nm thick electron beam deposited WO₃ coated with Pd is shown in Fig. 5.22. Compared to the sputtered WO₃ with the same thickness (Fig. 5.18), the absorbance spectrum of the electron beam deposited WO₃ has fewer fringes. These results indicate better structure uniformity within the electron beam deposited WO₃ films as compared to the sputtered WO₃ films. It is possible that the uniform structures of the WO₃ nanospheres reduce the optical reflection in the films and thus, fewer spectrum fringes. It is also important to minimise the fringes to avoid them from overlapping with the critical absorbance peaks that may appear in the spectrum when the films are exposed to H₂. The deposition of the Pd also shifts the WO₃ spectrum towards the blue region and increases the film’s absorbance magnitude.

Fig. 5.22 Absorbance versus optical wavelength of 500 nm WO₃ nanospheres coated with Pd on quartz substrates.
Using the previous absorbance spectra, the band gap analysis of the WO₃ nanospheres is shown in Fig. 5.23. The band gap of the WO₃ nanospheres was found to be 3.26 eV. Upon the Pd deposition, the films band gap was reduced to 3.09 eV. The reduced band gap of the developed sample allows the transition of the electron with less energy to the conduction band than in the sample without the catalyst. The change of the electronic states of the material may change its optical properties.

![Fig. 5.23 Estimated optical band gap of WO₃ nanospheres (3.26 eV) and Pd/WO₃ (3.09 eV).](image)

5.3.4 Pulsed Laser Deposited WO₃

The deposition of WO₃ films onto quartz substrate via pulsed laser deposition (PLD) revealed very different nanostructures from the samples deposited via RF sputtering (Section 5.3.2) and electron beam (Section 5.3.3). The SEM micrographs of the pulsed laser deposited WO₃ (Fig. 5.24 (a) and (b)) show that the films consist of nanorods. They are highly homogenous in the sizes of 30-80 nm and grown in various upward directions. The TEM image (Fig. 5.24 (c)) shows that the WO₃ nanorods grown perpendicular to the substrate. The high magnification TEM cross-sectional image on the single rod shows a single crystal-like lattice structure (Fig. 5.24 (d)).
Fig. 5.24 SEM (a and b) and TEM (c and d) micrographs of the WO$_3$ nanorods deposited via PLD on quartz substrate.

Fig. 5.25 is the WO$_3$ nanorods XRD analysis revealed that peaks are in correlation with the monoclinic WO$_3$ ICDD card file no. [83-0947], with a predominant reflection corresponding with the (002) crystal plane.

Fig. 5.25 XRD of WO$_3$ nanorods.
Fig. 5.26 shows the Raman spectrum of the PLD WO₃ films deposited onto sapphire (Al₂O₃). The films structure corresponds to a combination of monoclinic and hydrous WO₃·⅓H₂O crystal with the bands presence at 255, 320, 645, 690, 715 and 807 cm⁻¹. The ν(O-W-O) bond for the monoclinic WO₃ is indicated by the bands at 715 and 807 cm⁻¹. The presence of δ(O-W-O) bond for the WO₃·⅓H₂O is verified by the bands at 255 and 320 cm⁻¹. The Raman peaks (378, 418, 451, 578 and 751 cm⁻¹) are associated with the sapphire substrate.

The absorbance spectra of the 170 nm thick WO₃ nanorod films coated with Pd is shown in Fig. 5.27. An absorbance peak is observed for the nanorod films around 700 nm. The deposition of the Pd shifts the WO₃ spectrum towards the blue region and increases the film’s absorbance magnitude.
Using the absorbance spectra, the band gap analysis of the WO$_3$ nanorods was performed and shown in Fig. 5.28. The band gap of the WO$_3$ nanorods was found to be approximately 2.88 eV. This obtained value is within the $E_g$ range of 2.60 – 3.25 eV as reported for the WO$_3$ nanostructures [35]. The band gap of the films reduced to 2.72 eV after coating with the Pd indicating low energy required for the electrons in the films to move to the conduction band.

![Graph of absorbance spectra](image)

**Fig. 5.28** Estimated optical band gap of WO$_3$ nanorods (2.88 eV) and Pd/WO$_3$ nanorods (2.72 eV).

### 5.3.5 Acid Etched WO$_3$

The microcharacterisation of the metal oxide nanostructured thin films were also performed on the WO nanoplatelet films synthesised via acid etching chemical method. Fig. 5.29 shows the SEM micrographs of (a) sputtered W film, (b) acid etched tungstite (WO$_3$.2H$_2$O), and (c) annealed WO$_3$ nanoplatelet film at 300°C.
Fig. 5.29 (a) shows the sputtered W film on quartz consists of dense and uniform W grains. During acid etching, W grains with sizes of 100-500 nm are transformed into tungstite plates with dimension 100-500 nm and thicknesses 20-60 nm (Fig. 5.29 (b)). The tungstite film was 150 nm thick. After annealing, the WO$_3$ crystallises and the distinctive lamellar shape is maintained (Fig. 5.29 (c)). It was observed that the annealing process refined the surface of the nanoplatelets and improved the homogeneity of their average thicknesses in the range of 20-30 nm.

Fig. 5.30 displays the XRD patterns for the as-deposited and annealed samples. The diffraction pattern of the as-deposited sample closely correlates the features for WO$_3$·2H$_2$O (ICDD card file no. [87-1203]). The patterns correlate the as-deposited sample with the presence of un-oxidised W (annotated #). As the WO$_3$·2H$_2$O sample was annealed at 300°C in air, a transition to monoclinic WO$_3$ (annotated *) of ICDD card file no. [83-0950] was observed. The growth in
favour (002) plane indicates this transition. The W peaks were observed to reduce in intensity for the annealed sample, which indicates a state of oxidation. Inset in Fig. 5.30 belongs to the XRD pattern of the sputtered W film (ICDD card file no. [47-1319]) before the acid treatment.

![XRD patterns of as-synthesised tungsite and 300°C annealed WO₃ nanoplatelets. Inset is the XRD of sputtered tungsten.](image)

Raman spectra of the as-deposited and annealed samples are shown in Fig. 5.31. For the as-deposited sample, hydrous tungstes of WO₃·H₂O peaks (253, 662 and 956 cm⁻¹) can be easily identified [24]. As the sample was annealed at 300°C, the original hydrous peaks at 253 cm⁻¹ assigned to δ(O-W-O) bending mode and 662 cm⁻¹ assigned to ν(O-W-O) stretching mode were shifted to 272 and 706 cm⁻¹, respectively. In addition, the peak at 956 cm⁻¹, which could be assigned to terminal ν(W=O) vibration, disappears and respectively, new monoclinic peaks appear at 185 and 327 cm⁻¹. It is suggested that the initial hydrous structure transform into monoclinic WO₃ after the annealing process [36].
The transmission spectra of the tungstite and annealed WO$_3$ nanoplatelet films are shown in Fig. 5.32. The annealing process at 300°C transformed the cloudy and yellowish tungstite into transparent WO$_3$ films. Based on Fig. 5.32, the average transparency of the tungstite films is around 25%. After annealing, it was increased to 60%. Even though the SEM show that the overall structure was maintained prior to and subsequently after annealing, their optical properties differed significantly caused by the removal of the water content.

The absorbance spectra of the annealed and Pd coated WO$_3$ nanoplatelet films shown in Fig. 5.33 reveal smooth spectra without any fringe. This is attributed by the minimum optical reflection from the highly uniform thin films preventing the light interference. The Pd coating turned the films slightly dark but did not introduce any absorbance peak.
Fig. 5.33 Absorbance spectra of annealed and Pd coated WO$_3$ nanoplatelet films.

Fig. 5.34 shows the band gap of as-deposited tungstite was estimated as 2.55 eV. The film that was subsequently annealed at 300°C and coated with Pd was found to have high band gaps of 2.70 eV and 2.66 eV, respectively. The as-deposited tungstite has lower band gap compared to the annealed films due to the presence of W metal in the sample as examined by the XRD (Fig. 5.30). The W causes additional level of electronic states residing between the valence band and the conduction band [34]. Annealing process in air transforms the remaining W metal into WO$_3$ and resulting in a wide band gap. On the other hand, the subsequent deposition of the Pd metal onto the annealed sample reduces the band gap.

Fig. 5.34 Estimated optical band gap of tungstite films (2.55 eV), WO$_3$ nanoplatelets (2.70 eV) and Pd/WO$_3$ nanoplatelets (2.66 eV).
The characteristics of the WO₃ nanostructured thin films on quartz studied in this thesis are summarised in Table 5.1.

<table>
<thead>
<tr>
<th>No</th>
<th>Material Characteristic</th>
<th>RF sputtered WO₃</th>
<th>Electron beam deposited WO₃</th>
<th>Pulsed laser deposited WO₃</th>
<th>Acid etched WO₃</th>
</tr>
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<td>1.</td>
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<td>nanosphere</td>
<td>nanorod</td>
<td>nanoplatelet</td>
</tr>
<tr>
<td>2.</td>
<td>Structure dimension (nm)</td>
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<td>10-20</td>
<td>30-80</td>
<td>100-500</td>
</tr>
<tr>
<td>3.</td>
<td>Crystal and its main phase</td>
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<td>monoclinic</td>
<td>monoclinic (002)</td>
<td>monoclinic (002)</td>
</tr>
<tr>
<td>4.</td>
<td>Film thickness (nm)</td>
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<td>500</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>5.</td>
<td>Transparency (%)</td>
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<td>80-90</td>
<td>70-95</td>
<td>20-80</td>
</tr>
<tr>
<td>6.</td>
<td>Band gap (eV)</td>
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<td>3.26</td>
<td>2.88</td>
<td>2.70</td>
</tr>
</tbody>
</table>

The different deposition techniques resulted in WO₃ nanostructured films with different morphologies as well as crystallographic structures. The films with the highest surface areas are the WO₃ nanospheres deposited via electron beam with average diameter between 10 – 20 nm. The main crystal structures of all the WO₃ films are monoclinic. As mentioned in Chapter 2, the formation of the monoclinic WO₃ occurs in the temperature range of 30 - 300°C. Monoclinic WO₃ is favourable for optical gas sensing as the sensing layer with this crystal structure exhibits high stability and excellent sensitivity towards gases as reported by Szilágyi et. al [37] and Souza et. al [38]. They found out that the sensing layer with asymmetrical monoclinic WO₃ improves the gas molecules adsorption/desorption rate.

The films deposited via RF sputtering and electron beam were found to have transparencies around 80 – 90% and band gaps of 3.20 – 3.30 eV at the 500 nm thickness. However, the same thickness could not be achieved for the pulsed laser deposited WO₃ films due to the fabrication equipment limitation. The maximum film thickness achieved via pulsed laser deposition technique is only 170 nm that shows transparencies of 70 – 95%. On the other hand, the WO₃ nanoplatelets synthesised via acid etching were found to have transparencies around 20 – 80% with a thickness of...
only 150 nm. The nanoplatelet films have very low transparency (<10%) for the thickness of 500 nm and thus, unsuitable to be used in the absorbance measurement.

The optical band gaps of the WO₃ films were found to decrease with the increasing nanostructured dimensions. WO₃ nanoplatelets with the largest dimension (100-500 nm) exhibit the lowest band gap (2.70 eV) as compared to the other counterparts such as nanograin (3.36 eV), nanospheres (3.26 eV) and nanorods (2.88 eV). It is suggested that the variation in the band gaps of the WO₃ samples are caused by the effect of quantum confinement. According to the quantum confinement theory, the reduction in the nanostructure dimensions increase the material band gap [39].

Apart from the nanostructure dimension, the optical band gap of the films is also reduced with the introduction of the metal catalysts. The deposition of the catalytic metal layer onto the metal oxide film introduces additional electronic states between the top of the valence band and the bottom of the conduction band of the metal oxide. The presence of the intermediate states reduces the minimum energy required by the electrons to move from the valence band into the conduction band. As a result, the band gap or energy difference between the valence and conductance bands is reduced.

The author believes that further work should be done on the optical properties of the WO₃ nanostructures such as nanorods and nanoplatelets for the H₂ sensing applications. The different morphologies of WO₃ nanostructured films deposited in this research project are shown to influence their gas sensing properties. The discussions and explanations will be presented in Chapter 7.

5.3.6 Thermally Evaporated MoO₃

Microcharacterisations were performed on the potential nanomaterials that exhibit advantageous properties for gasochromic applications. The author chose molybdenum trioxide (MoO₃), a metal oxide which can be easily formed from molybdenum (Mo), an element of (Group VI) of the periodic table similar to tungsten. The electrochromic response of MoO₃ shows a stronger and more uniform absorption of light in its coloured state compared to the WO₃ [40]. However, this MoO₃ response degrades above 300°C. In this PhD project, the deposition of the MoO₃ nanostructures on quartz was performed via thermal evaporation technique as discussed in the previous chapter.
SEM micrographs of the MoO$_3$ nanostructured films show uniform and homogeneous nanorods deposited on quartz (Fig. 5.35 (a)). These nanorods grow in random orientations with up to 3 µm lengths and 20-200 nm diameter crystallites (Figs. 5.35 (b) and (c)) and are unique compared to the MoO$_3$ structures like nanoplatelets, nanobelts and nanoflowers reported previously in the literature [41-43]. Based on the deposition parameters discussed in Chapter 4, the nanorods were formed at 15 cm distance between the MoO$_3$ powder and the substrate. At a shorter distance of 10 cm, MoO$_3$ platelets were observed on the quartz substrate (Fig. 5.35 (d)). However, these platelet films were thick (≈20 µm) and cloudy with low transparencies (<20%). Thin clusters of MoO$_3$ were grown sparsely when the source-substrate distance was 20 cm.

Fig. 5.35 SEM micrographs of (a) MoO$_3$ film surface (b) MoO$_3$ nanorods, (c) MoO$_3$ nanorods dimension and (d) MoO$_3$ platelets for deposition at 10 cm shows individual platelets.

Fig. 5.36 shows the XRD of MoO$_3$ peaks at 12.85°, 23.3°, 25.5°, 27.15°, 33.75°, 39.05° and 49.25° (2θ). These peaks correspond to the (020), (110), (040), (021), (111), (060) and (002) crystal planes which are in good correlation with the growth of orthorhombic MoO$_3$ according to ICDD card no. [05-0508].
Fig. 5.36 XRD spectrum of MoO$_3$ nanostructures.

Fig. 5.37 illustrates the Raman spectrum of the MoO$_3$ nanostructured films. Peaks observed at 284, 671, 821 and 995 cm$^{-1}$. The 284 cm$^{-1}$ peak represents bending of the double bond (Mo=O) vibration [44]. The 671 cm$^{-1}$ peak is assigned to the triple coordinated oxygen (Mo$_3$–O) stretching mode. The 821 cm$^{-1}$ peak is for the double coordinated oxygen (Mo$_2$–O) stretching mode and the peak at 995 cm$^{-1}$ is assigned to the oxygen terminal (Mo$^{6+}$=O) stretching mode. Other peaks at 339 and 381 cm$^{-1}$ can be assigned to Mo–O bending modes. Meanwhile, the peak at 477 cm$^{-1}$ represents the same mode as that at 671 cm$^{-1}$. In addition, the peak at 160 cm$^{-1}$ assigns to the lattice mode.

Fig. 5.38 shows the absorbance spectrum of the MoO$_3$ and Pd/MoO$_3$ films in the visible-NIR wavelength range. The transparent state of both films is indicated by the low absorbance magnitude and broad spectrum expanding in the visible-NIR range. However, as compared to the single MoO$_3$ films, Pd/MoO$_3$ films have higher absorbance magnitude due to the Pd coating.
Using the absorbance spectra, the band gap analysis of the MoO$_3$ nanostructures was performed and results are shown in Fig. 5.39. The band gap of the MoO$_3$ was calculated to be 3.50 eV. The films band gap reduced to 3.20 eV with Pd. The value is within the band gap of MoO$_3$ in the range of 2.65 – 3.60 eV as reported in literature [45-47].

**Fig. 5.39** Estimated optical bandgap of MoO$_3$ (3.50 eV) and Pd/MoO$_3$ (3.20 eV).
5.3.7 Anodised TiO$_2$

A nanomaterial which was also selected in this thesis for its gasochromic properties is TiO$_2$. It is one of the most efficient metal oxides for photochromic applications. Solar cell based on dye-sensitized TiO$_2$ films achieved very high solar-to-electrical energy conversion efficiencies when used in conjunction with liquid electrolytes [48, 49]. TiO$_2$ nanostructures are recognised highly promising for optical sensing applications.

In Chapter 4, the deposition techniques used to fabricate TiO$_2$ nanostructures are DC sputtering and anodisation. The SEM images of Fig. 5.40 (a) DC sputtered Ti film, (b) non anodised TiO$_2$ film annealed at 800°C for 8 hours, (c) anodised TiO$_2$ nanoporous film synthesised using an electrolyte and (d) anodised TiO$_2$ nanoporous film annealed at 800°C for 8 hours.

![SEM images of TiO$_2$ films](image)

Fig. 5.40 SEM images of a (a) DC sputtered Ti film; (b) non anodised TiO$_2$ film annealed at 800°C for 8 hours; (c) anodised TiO$_2$ nanoporous film produced using a electrolyte and (d) anodised TiO$_2$ nanoporous film annealed at 800°C for 8 hours.

As shown in Fig. 5.40 (a), the Ti film (1 µm thick) consisted of randomly distributed hexagonal grains with 200-500 nm dimensions. As the films were annealed at 800°C for 8 hours to convert Ti to TiO$_2$ [50] and as a result, the transparency increased. The surface morphology of
the annealed and non-anodised TiO$_2$ films are dense and nonporous with smaller grains (80-200 nm) as compared to the DC sputtered Ti film. Anodisation of the DC sputtered Ti film results in a granular morphology however retained a regular array of pores with diameters in the range between 15-25 nm (Fig. 5.40 (c)). As these films were annealed, the anodised TiO$_2$ structures crumbled and transformed into nanoporous films with nanograins (diameter 20-100 nm) as seen in Fig. 5.40 (d).

In order to characterise the morphology of the films and their potential for gas sensing applications, XRD (Fig. 5.41) and UV-vis-NIR spectrophotometry (Fig. 5.42) characterisations were performed. The XRD results show the anodised and annealed film consisted of a distinct rutile phase (ICCD card file no. [21-1276]). However, the non-anodised and annealed TiO$_2$ film is obviously anatase (ICDD card file no. [21-1272]). The films constructed with a strong preferred orientation for the [110] plane of anatase at 27.5°.

![XRD spectra of the anodised and non-anodised TiO$_2$ films annealed at 800°C.](image-url)

In Fig. 5.42, the UV-Vis-NIR absorbance spectra show that the anodised films have lower absorbance magnitude and thus a higher transparency as compared to non-anodised films. The high transparency of the anodised films is due to the formation of nanoporous TiO$_2$. 
Fig. 5.42 Absorbance spectra of the anodised and non anodised Ti films annealed at 800°C.

The band gaps extracted from the spectra resulted in different values for different states of TiO$_2$ films. The band gaps of non anodised, anodised and Pd/anodised TiO$_2$ films were found to be 2.50, 2.80 and 2.70 eV, respectively. Fig. 5.43 shows that the estimated bandgap of anodised films was larger as compared to the non anodised films which are attributed to the nanoporous surface. The presence of these nanopores widens the distance between the energy bands as shown by Lee et. al in their nanoporous silicon (Si) films [51]. The anodised TiO$_2$ film’s band gap reduced to 2.70 eV with the deposition of the Pd metal layer.

Fig. 5.43 Estimated optical bandgap of non anodised TiO$_2$ (2.50 eV), anodised TiO$_2$ (2.80 eV) and Pd/anodised TiO$_2$ (2.70 eV).
5.3.8 RF Sputtered NiO

The characterisations of the nanomaterials for optical sensing towards hydrogen were performed on the n-type metal oxides i.e. WO$_3$, MoO$_3$ and TiO$_2$. This section provides microcharacterisation results on the p-type nanostructured films based on NiO. Fig. 5.44 shows the SEM micrographs of the NiO$_x$ nanostructured films as deposited and NiO films after annealing. As shown in Fig. 5.44 (a), before annealing, the NiO$_x$ films consist of granular structures with sharp edges. The black NiO$_x$ grains are found to be 40-60 nm in sizes. After being annealed, the NiO$_x$ films transformed into transparent NiO films with particles dimension of 20-40 nm (Fig. 5.44 (b)). The sharp edges of the structures observed before annealing were also converted NiO grains after annealing.

Fig. 5.44 SEM micrograph of (a) NiO$_x$ films and (b) annealed NiO nanostructured films.

In Fig. 5.45, the XRD diffractogram shows the presence of NiO peaks at 37.36° and 43.41°. These peaks correspond to the (111) and (200) crystal planes which are in good correlation with cubic NiO according to ICDD card file no. [47-1049].

Fig. 5.45 XRD of NiO nanostructured films.
Fig. 5.46 is the transmittance spectrum of the NiO$_x$ films and annealed NiO films with thicknesses of 400 nm and 100 nm, measured in vis-NIR wavelength range. Before annealing, the NiO$_x$ films were very dark and showed minimal transparency. After annealing, the dark films increased transparency in the ranges of 40-80% and 70-80% for 400 nm and 100 nm films, respectively. The harmonic optical fringes in the spectrum for the 400 nm thick film are due to the multiple reflections of the light rays as they pass through the film [52]. This effect is eliminated when the film thickness is reduced to 100 nm.

![Transmission spectra of NiO$_x$ film (before annealing) and NiO film (after annealing).](image)

The band gaps of the annealed NiO films with and without Pd were estimated to be 3.42 and 3.04 eV, respectively (Fig. 5.47). These values were in accordance with literature, whereby band gap values in the range of 3.15-3.80 eV were reported by Sato et. al [53] and Subramaniam et. al [54].

![Estimated optical bandgap of NiO (3.42 eV) and Pd/NiO (3.04 eV).](image)
The microcharacterisation results presented in this research provide important information on the material properties related to their optical gas sensing performances. The rough and porous structures of the metal oxide films are suitable for gas molecules adsorption/desorption. This allows strong optical response and fast recovery from the developed sensor upon exposure to H₂ gas. The crystals of the WO₃ nanostructured films were identified to be monoclinic, a type of crystal structure that is known to exhibit high temperature stability and sensitivity towards gases. These two characteristics are important in the development of the optical gas sensors for harsh and volatile environments. The MoO₃ nanorod films were observed to show higher surface area and optical transparency as compared to the MoO₃ platelet films. Similar high surface area and transparency were observed in the anodised TiO₂ nanoporous films and annealed NiO films. These nanomaterial characteristics are desirable for optical gas sensing. It is anticipated that the high surface area will increase the material-gas molecules interactions and the highly transparent films allow their absorbance change dynamically upon exposure to the gas.

5.4 Summary

In this chapter, the micro-nano characterisations carried out on the metal oxides nanostructured films provide important findings to identify the potential nanomaterials for highly sensitive H₂ optical sensors design. The material characterisation techniques used in this project include SEM, TEM, XRD, EDX, XPS, Raman and visible-NIR spectroscopies. The material characterisation results of the WO₃ nanostructures as well as other potential metal oxides such as MoO₃ nanorods, TiO₂ and NiO nanograins were presented.

SEM characterisations of the nanostructured materials were conducted to understand the nanomaterials in terms of morphology, dimension and orientation, uniformity as well as porosity of the films. These parameters can significantly affect the performance of the optical sensor. Other characterisation techniques such as TEM, XRD, EDX, Raman and vis-NIR spectroscopies were also employed to obtain the materials structure information and thus, their influence on the optical gas sensing performance which will be presented later.
The key outcomes of the material microcharacterisation results can be listed as follows:

- **RF sputtered WO$_3$**
  - Using SEM and TEM microscopy, the WO$_3$ nanostructured films deposited via RF sputtering consist of nanograins with different sizes highly dependent on the type of transparent substrates used in this project (quartz, glass, ITO and FTO conductive glasses). The XRD and Raman analysis revealed the main crystal phase is monoclinic with the existence of hydrous WO$_3$•$\frac{1}{3}$H$_2$O. The transparency of the 500 nm sputtered films on quartz was in range of 88-95% when measured via vis-NIR spectroscopy. The band gap was calculated to be 3.36 eV. The band gap was significantly reduced to 3.04, 3.09 and 3.00 eV when the films coated with different catalytic metal layer such as Pd, Pt and Au, respectively.

- **Electron beam deposited WO$_3$**
  - The morphology of the electron beam deposited WO$_3$ films characterised with SEM consist of nanospheres in the sizes of 10-20 nm. The XRD could not be performed due the insignificant intensity reflections from the smooth and uniform films. However, Raman analysis revealed the films to be monoclinic. The 500 nm thin film transparency and optical band gap were found to be around 80-90% and 3.26 eV, respectively. Upon Pd deposition, the band gap was reduced to 3.09 eV.

- **Pulsed laser deposited WO$_3$**
  - The SEM revealed that the WO$_3$ films deposited via pulsed laser were consisting of nanorods with the size of 30-80 nm. The XRD diffractogram indicated the nanorod crystal phase is monoclinic. Raman peaks supported this finding by confirming the crystals matched monoclinic phase which exists at temperature range of 30 - 350°C. The nanorod films with the thickness of 170 nm are highly transparent (98-99%). The optical band gap extrapolated...
from the spectrum measured via vis-NIR spectroscopy was found to be 2.88 eV and reduced to 2.72 eV when coated with Pd.

- **Acid etched WO$_3$**
  
  o The WO$_3$ films synthesised via acid etching technique consist of nanoplatelets. The typical plate dimensions are 100-500 nm length with thickness of 10 nm. The XRD diffractogram indicated that the films consist of monoclinic crystal structures. The films thickness was measured to be 150 nm with transparencies of 20-80%. The band gaps were 2.70 and 2.66 eV for the WO$_3$ nanoplatelet films with and without Pd, respectively.

- **Thermally evaporated MoO$_3$**
  
  o The MoO$_3$ nanorods were observed under SEM for the films deposited via thermal evaporation. The size of the nanorods is in the range of 20-200 nm with the length of up to 3 µm. The crystal phase analysed by the XRD is orthorombic. The Raman spectrum confirmed the films consist of MoO$_3$ without any substoichiometry. The transparency was between 70-90% for the film with thickness of 1.3 µm. The optical band gap of the MoO$_3$ films was estimated to be 3.50 and 3.20 eV with and without Pd, respectively.

- **Anodised TiO$_2$**
  
  o After annealing, the anodised TiO$_2$ were transformed into highly porous film with the 20-100 nm grain sizes as observed under SEM. The XRD diffractogram shows that the TiO$_2$ nanostructure crystal phase changes from anatase to rutile after annealing at 800°C. The 300 nm thick films have transparency around 30-90% with the estimated band gap of 2.80 eV. After Pd coating, the band gap was reduced to 2.70 eV.
**RF sputtered NiO**

- The SEM revealed that the RF sputtered NiO nanostructured films consist of nanograin with the size of 20-40 nm. The XRD highlighted the NiO films have cubic crystal phase. The transparency is around 40-80% for the film with the thickness of 400 nm. The estimated band gap was found to be 3.42 eV. After coating with Pd catalytic layer, the band gap was reduced to 3.04 eV.

In general, the metal oxide nanostructured films developed for optical H₂ sensor have high transparencies up to 90%. This was achieved by reducing the film thickness typically less than 500 nm except for MoO₃ with the thickness around 1.3 µm. The high transparency films are desirable for optical gas sensing. It is expected that the highly transparent films can show stronger absorbance or reflection change upon exposure to gas molecules as compared to the films with low transparency.

In this chapter, the potential nanomaterials for optical H₂ sensor were characterised. Optical sensing performance analysis of the nanostructured films towards H₂ will be presented in Chapter 7. Beforehand, the optical testing setup for the developed sensor will be presented in the subsequent chapter (Chapter 6).
References


Chapter 6

Measurement Setups for Optical Sensors Testing

6.1 Introduction

The micro-nano characterisation of the metal oxide nanostructured thin films discussed in the previous chapter provides useful information in the understanding of the optical sensing performance of the materials. In this project, the nanostructured thin films were deposited onto different transducers. For the transparent substrates, optical fibers and inverted rib waveguides, the measurement are based on the absorbance, reflection and beam intensity, respectively. The principles of these transducing platforms had been presented in Chapter 2.

This chapter will discuss in details the measurement setups for the optical sensor testing. It is divided into three main sections. The first section is Section 6.1: Introduction. The second section is Section 6.2: Optical Measurement Setups for the different optical transducers. The third section is Section 6.3: Gas Chamber Construction that discusses the construction of the gas chambers for the different optical setups as well as the testing procedure. Finally, the results are summarised in Section 6.4.

6.2 Optical Measurement Setup

In this project, different setups were constructed by the author to measure or characterise the properties of the developed optical sensors. These setups are summarised in the following table:
Table 6.1 Setups for properties measurement and characterisation of optical sensors.

<table>
<thead>
<tr>
<th>No</th>
<th>Designation</th>
<th>Measurement Technique</th>
<th>Transducing Platform</th>
<th>Focus of Measurement</th>
<th>Main Equipments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Setup 1</td>
<td>Absorbance</td>
<td>Transparent substrates</td>
<td>Optical sensing performance and characterisation</td>
<td>Source: Halogen Detector: spectrophotometer</td>
</tr>
<tr>
<td>2.</td>
<td>Setup 2</td>
<td>Reflectance</td>
<td>Optical fibers</td>
<td>Optical sensing performance</td>
<td>Source: Halogen Detector: spectrophotometer</td>
</tr>
<tr>
<td>3.</td>
<td>Setup 3</td>
<td>Mode profile</td>
<td>Optical waveguides</td>
<td>Optical characterisation</td>
<td>Source: Laser (635 nm) Detector: CCD camera</td>
</tr>
<tr>
<td>4.</td>
<td>Setup 4</td>
<td>Beam intensity</td>
<td>Optical waveguides</td>
<td>Optical sensing performance</td>
<td>Source: Laser (532 nm) Detector: Beam profiler</td>
</tr>
</tbody>
</table>

The constructed setups will be discussed in details in the following subsections.

6.2.1 Absorbance Measurement Setup

Most of the author’s investigation were based on the absorbance spectra of the gasochromic materials on the transparent substrates. The absorbance spectra of the materials were measured using Setup 1 as shown previously in Section 5.2.7 (Chapter 5). The measurements were carried out in the custom gas testing chamber as shown in the Fig. 6.1.

![Fig. 6.1 Setup 1: Absorbance measurement and gas testing setup.](image-url)
Setup 1 was attached to a gas calibration system with a computer controlled mass flow controllers (MFC) regulating flow rate at 200 sccm. In this system, the multi-channel gas calibration setup (MKS Instrument 647B, USA) was based on the volumetric mixing of gases. Certified gas cylinders of high purity dry synthetic air and H₂ of 1% concentration in synthetic air (Coregas Ltd., Australia) were used. Each gas cylinder was connected to a computer controlled MFC. The H₂ gas could be further diluted in synthetic air by simply adjusting the flow rates of each MFC.

Based on Fig. 6.1, the absorbance (A) is calculated using the following equation:

\[
A = -\log_{10}\left(\frac{l_0 - l}{l_0}\right)
\]  

(6.1)

The measurement was normalised with respect to the sample substrate. Therefore, the absorbance spectra measured are of the sensing layer.

### 6.2.2 Reflection Measurement Setup

The author constructed a different setup to measure the gas sensing response of the metal oxide nanostructured thin films coated at the tip of the optical fiber. It is based on the optical reflection measurement (Setup 2) as shown in Fig. 6.2.
Setup 2 is similar to the absorbance measurement setup (Setup 1) except for the configuration of the spectrophotometer and the use of a 2×1 multimode optical coupler (or splitter) with 50:50 coupling ratio (AFW Technologies, Australia). In Setup 2, the input optical signal, $I_0$, transmitted into the fiber via the optical coupler and reached the fiber tip coated with the metal oxide nanostructured thin films. The fiber tip was positioned onto a heater. During the operation at elevated temperature, the film’s refractive index changes when the sensing layer is exposed to the H$_2$ with different concentrations. Due to the differences in the core and the thin films refractive indices, the signal was reflected and splitted by the coupler into the spectrophotometer. The intensity of the reflected optical signal measured by the spectrophotometer varies accordingly to the concentrations of the H$_2$.

In Setup 2, the measurement is the total of the specular and diffuse reflections. With the 50:50 splitting ratio, the reflected signal measured by the spectrophotometer, $I$, is halved of its actual intensity. The reflection at any wavelength, $R$ (in percentage) is calculated by the spectrophotometer using the following equation:

$$R = \left( \frac{I}{I_0} \right) \times 100\%$$  \hspace{1cm} (6.2)

Where:

$I$ = the sample intensity

$I_0$ = the initial reference intensity

For the gas testing setup in Fig. 6.2 (Setup 2), the reflection of the thin films on the fiber tip was measured relative to the reflection from a standard reference (blank fiber tip). Therefore, the system measured the change of reflection ($\Delta R$) instead of absolute $R$.

### 6.2.3 Waveguide Based Sensor Testing and Measurement Setup

As discussed in Chapter 3, the channel waveguides fabricated in this project are single mode inverted rib polymer waveguides. The waveguides were characterised in order to determine
the mode profile before being tested towards H₂ with different concentrations. For the waveguide characterisation, the setup is shown in Fig. 6.3 (Setup 3).

Based on the figure, the characterisation was carried out by coupling the light into the endface of the waveguide. The light that emerged from the opposite endface was observed via a camera. The image captured by the camera is the optical power distribution within the waveguide, which is known as a mode profile. The determination of the mode profile was carried out on the waveguide fixed onto a micro-alignment stage. The stage allows three-axis movements in 100 µm radius. This feature is very critical to align the light into the waveguide channel with dimension < 3 µm. At the first waveguide endface, class 3B HeNe laser (Model 105-1, Spectra Physics) with 635 nm wavelength and 10 mW power was used as the light source. An attenuator and a polariser were positioned just after the light source to modify the light intensity and polarity, respectively. The light was coupled into the waveguide using an objective lens (20×, Olympus) on a micropositioning stage. At the second endface, another objective lens (20×, Olympus) fixed on a micropositioning stage was used to focus the light emerging out of the waveguide onto a CCD camera (Philips SPC900NC).

Meanwhile, the gas testing of the channel waveguide optical sensor was carried out based on the setup in Fig. 6.4 (Setup 4).
The main differences between Setup 3 and Setup 4 are the selection of light source and the detector. The channel waveguide gas testing setup used a 532 nm green laser (Shanghai Dream Laser Technology, China) class 3A with 500 mW maximum power as the source. The green laser was selected because it has higher output power that can be varied as compared to the red laser. The detector is a Beamage CCD12 beam profiler (Gentec, Canada) which operates in the visible wavelength range. The profiler provides more information such as the beam width, relative intensity, divergence and spatial modes as compared to the conventional camera. A gas chamber with inlet and outlet ports was made from PDMS or teflon and sealed on top of the waveguide. The waveguide was placed on a heater on the micropositioning stage.

The channel waveguide transducing mechanism is based on the change of the evanescent field at the interface between the waveguide core and the sensing layer. H\textsubscript{2} interaction with the sensing layer on top of the waveguide changes the layer refractive index and absorbance property. This resulted in the change of the evanescent field at the boundary of the waveguide core and the sensing layers. The intensity and the beam width of the light propagated in the waveguide affected by these changes and thus, recorded by the beam profiler. This sensing mechanism had been discussed in details in Chapter 2.
6.3 Gas Chamber Construction

There are two types of gas chamber constructed for this project. The first chamber is for the gas testing of the metal oxide nanostructured thin films on transparent substrates and optical fiber tip (Setup 1 and 2). The second chamber is for the testing of the thin films on the single mode inverted rib polymer waveguide (Setup 4).

6.3.1 Gas Chamber for Transparent Substrates and Fiber Based Sensors

The author constructed the following gas chamber to test the films on the transparent substrates as well as the optical fiber tip.

![Gas chamber for transparent substrates and fiber based transducers.](image)

The chamber consisted of an aluminium box with quartz windows in two of its sides. The chamber consists of two ports for gas inlet and outlet, two electrical connectors for a heating plate and an input for a thermocouple. Teflon was used to seal the chamber from gas leakage. Inside the chamber, a teflon block and a piece of alumina (Al₂O₃) were used to mechanically support the quartz, with the later acting as a thermal insulator (effectively isolating the heating plate and the chamber). A sample holder frame with a wide base was utilized to mount the substrate during testing and ensure uniform heat distribution. The chamber was fixed on to a stage with two optical fiber SMA adapters for the connection with the light source and the spectrophotometer.
6.3.2 Gas Chamber for Waveguide Based Sensors

The gas chamber for the waveguide based transducers was constructed based on the schematic in Fig. 6.6.

![Schematic diagram of the gas chamber for the waveguide based transducers.](image)

The chamber was sealed on top of the waveguide coated with the sensing layer. Two types of materials were used for the chambers such as PDMS and teflon. PDMS gas chamber was fabricated with the same method used for the waveguide mold discussed in Chapter 3. Meanwhile, teflon chamber was made by machining the teflon block. Silicone based sealant was used to seal the chamber as well as the gas pipes. The materials used in the gas chamber design were identified to be stable when the waveguide based sensor was exposed to its typical operating temperature approximately <120°C. The photos of the PDMS and teflon based gas chambers on waveguides are shown in Fig. 6.7. Inset is the teflon chamber space.
6.3.3 Gas Testing Procedure

In this research, the author tested the performance of the developed optical sensors towards H\textsubscript{2}. Depending on the material and the type of the sensor, each of them was tested at several operating temperatures. A sequence control computer was utilized to automate the pulse sequence of the target gas with different concentrations. Initially, the synthetic air was maintained for 60 min. Then the first cycle of the target gas was given for 10 min, followed by another 60 min purge of synthetic air. The sensors were exposed to a few cycles of H\textsubscript{2} and synthetic air to stabilise the baseline. Only after the baseline gas was stable, the measurements were started by purging the sequences of the gas with different concentrations.

6.4 Summary

In this chapter, the author discussed in details the testing and measurement setups of the optical sensors coated with metal oxide nanostructured thin films. The author deposited the thin films onto three optical transducers such as transparent substrates, multimode fibers and single mode inverted rib waveguides. The gas testing and measurements were carried out on the different optical sensors based on different properties. Four different setups were constructed to perform the measurements and characterisations.

The absorbance measurement setup (Setup 1) was constructed for the gas testing of the nanostructured thin films on the transparent substrates. This includes the design and development
of a customised gas chamber. This chamber consists of an aluminium box with quartz windows, heating plate, sample holder, thermocouple, power supply and gas inlet and outlet. The setup configuration also includes the light source, spectrophotometer and multi-channel gas calibration system.

For the gas testing of the thin films on the multimode fiber tip, the reflection based measurement setup (Setup 2) was constructed. The setup and gas chamber was similar to the absorbance measurement except for the use of optical coupler to channel the reflected signal into the spectrophotometer.

Meanwhile, the waveguide based sensor required different setups and gas chamber. Setup 3 was constructed to characterise the waveguide mode profile. Setup 4 was used to measure the relative intensity and the width of the beam propagated in the channel when the sensing layer on top of the waveguide was exposed to gas. The measurement and gas testing setup (Setup 4) for the sensing layer on the waveguide transducer consists of laser sources, camera and beam profiler, objective lenses, attenuator, polariser, micropositioning stages and another customised gas chamber. Two chambers were built using PDMS and teflon. The gas testing and measurements were carried out based on a certain procedure to verify the reliability of the sensing results.

Once the construction of the setups were completed, extensive gas testing and measurements were performed on the optical sensors. The optical sensing performance of the metal oxide nanostructured thin films will be presented in the following chapter (Chapter 7).
Chapter 7

Gas Sensing Results

7.1 Introduction

In the previous chapter, the author presented the measurement setups for the optical sensors testing towards gases with different concentration. Three different setups were constructed for three different transduction platforms which are transparent substrates, optical fibers and inverted rib waveguides. Each of them were subjected to different optical measurements such as absorbance, reflection and beam intensity.

This chapter presents detailed discussions on the gas sensing performance of the developed optical sensors. As the sensors were exposed to H₂ gas of different concentrations, at elevated temperatures, their response and recovery times were measured. The results from each type of sensors are presented in their respective subsections.

To conclude this chapter, the sensors static and dynamic performance are discussed in the summary. The analysis will complete the investigation on the metal oxide nanostructured thin films based optical sensors in this thesis.

7.2 Hydrogen Sensing Results Based on Absorbance Measurement

In this project, the author deposited variety of gasochromic materials on the transparent substrates. Different nanostructured thin films combined with various catalytic metals were grown on the substrates using different deposition techniques. The absorbance response of the films were measured towards H₂ with different concentrations. The films’ dynamic and static performances were analysed and compared. Apart from the response and recovery time, the author also analysed two other important static characteristics which are sensitivity and repeatability.
The sensitivity (relative response) is determined by the formula:

\[
\text{Sensitivity} = \frac{R_o - R_g}{R_o} \tag{7.1}
\]

where \(R_o\) is the absorbance response in synthetic air and \(R_g\) is the absorbance response in H\(_2\). The repeatability is the sensor’s ability to produce the same response for successive measurement of a few cycles of H\(_2\) with different concentrations, when all operating and environmental conditions remain constant [1-3]. In this project, the repeatability is measured by the standard deviation (%) relative to the average absorbance response for H\(_2\) with different concentrations repeated up to three cycles.

After thorough analysis, the gasochromic material with the most promising sensing performance was chosen to be deposited onto the optical fiber tip and waveguides.

7.2.1 Pt/Sputtered WO\(_3\) Nanostructured Thin Films

In this section, the gasochromic response of Pt/sputtered WO\(_3\) nanostructured thin films on quartz substrate is presented and discussed. The investigations were carried out for 25 Å Pt/1.2 µm sputtered WO\(_3\) samples.

Fig. 7.1 shows the absorbance versus optical wavelength of the Pt/WO\(_3\) films exposed to H\(_2\) with 1% concentration in synthetic air, at room temperature (21°C) for a period of 10 minutes (Exposure 2).
A significant increase of the magnitude of absorbance was observed for the whole visible-NIR spectrum, indicating that the transparent thin films became dark and the $W^{6+}$ ions in WO$_3$ were reduced to coloured $W^{5+}$ ions. The detailed sensing mechanism of the optical sensor based on the metal oxide nanostructured thin films had been discussed in Chapter 2. The magnitude of absorbance increases with the wavelength. No change of magnitude or wavelength shift occurred when WO$_3$ thin films without Pt coatings were exposed to H$_2$ at room temperature.

It was also found that the recovery of the nanotextured WO$_3$ films after exposure to the H$_2$ of 1% concentration was slower at room temperature, than at elevated temperatures. It is hypothesised that during the reduction process, the adsorption of H$^+$ occupying defects in the thin films surface is fast compared to the desorption. However, during the oxidation process, the desorption of H$^+$ and the adsorption of O$_2^-$ is slow due to the small thermodynamic barrier of H$^+$. An elevated temperature can be used to overcome the thermodynamic barrier, effectively allowing for faster adsorption/desorption of ions onto the nanotextured WO$_3$ film [4]. The simultaneous reduction and oxidation processes that occur on the Pt/WO$_3$ thin films produce water on the surface as stated in the introduction on the coloration of WO$_3$. It has been widely suggested that the accumulation of water on the surface reduces the available surface sites on the WO$_3$ surface for the oxidation reaction to occur [5]. As such, the accumulation of water vapour on the surface of WO$_3$ affects the rate of oxidation after thirty minutes of synthetic air exposure. After this period, the absorbance spectrum decreased by a factor of two of the elevated Pt/WO$_3$ spectrum as shown in Fig. 7.1 (Exposure 3). Approximately ten and a half hours later, the Pt/WO$_3$ absorbance spectrum returned to its initial state (Fig. 7.1 – Exposure 1). Georg et. al [6] also found out that the recovery is incomplete and slow in their sputtered WO$_3$ and concluded this was a consequence of water blocking the reactive surface during the coloration process.
Fig. 7.2 shows the change of cumulative absorbance versus temperature of the thin film for H$_2$ with 0.06% concentration in synthetic air exposed for five minutes.

Cumulative absorbance was measured using the spectrophotometer and integrating the response curve from 500 – 800nm. This integration, measured the cumulative changes in absorbance and wavelength observed upon exposure to H$_2$ over the visible spectrum. The curve in Fig. 7.2 shows that the maximum sensitivity for the Pt/WO$_3$ sensor is observed at an operating temperature of 70°C. The low operating temperature could be due to the enhanced effective dissociation of H$_2$ [7]. However, it was found that the recovery was very slow for the operating temperature below 100°C due to the water blocking the reactive surface as discussed earlier. It was also observed that above the water boiling point (100°C), the response and the recovery were equivalently very fast (<100 s). Nevertheless, the magnitude of absorbance decreased with increasing temperature as seen in Fig. 7.2.
Fig. 7.3 shows the dynamic responses of the WO$_3$ (1.2 µm), Pt (2.5 nm) and Pt/WO$_3$ thin films towards H$_2$ with different concentrations in synthetic air at 100°C measured over the wavelength range of 500 – 800 nm. H$_2$ in a synthetic air balance was pulsed into the testing chamber to induce coloration, and regenerated to a transparent state with synthetic air.

Comparison of the WO$_3$, Pt and Pt/WO$_3$ thin films on quartz responses confirmed that the single layer of WO$_3$ or Pt thin films were not sufficient enough to induce significant changes in absorbance, and as such, are not suitable for optical gas sensing applications. It was found that absorbance changes increase progressively with increasing H$_2$ concentration. Concentrations as low as 0.06% resulted in an absorbance increase of 24% with respect to the baseline. Meanwhile, H$_2$ with 1% concentrations resulted in 120% absorbance increase. The introduction of H$_2$ gas to the Pt/WO$_3$ thin films resulted in a change of surface colour intensity, and hence the absorbance spectrum. The response was very fast and stable, as was the recovery. The film response and recovery time or $T_{90\%}$ (the time to achieve 90% of the maximum change) induced by H$_2$ of 1% concentration in synthetic air was measured to be 86 s and 76 s, respectively. This performance is better than for Pd/WO$_3$ based H$_2$ optical gas sensors operating at 200°C, developed by Ando et. al (response time = 500 s and recovery time = 300 s) [8].
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Fig. 7.4 illustrates the dynamic response of the Pt/WO₃ thin films towards H₂ of different concentrations in a synthetic air at 100°C measured at a single wavelength of 660 nm.

![Graph showing dynamic response of Pt/WO₃ thin films](image)

**Fig. 7.4 Dynamic response of the Pt/WO₃ thin films exposed to different concentrations of H₂ at 100°C for a single wavelength 660 nm.**

The magnitude of the response for a single wavelength was smaller compared to the response integrated over a range of wavelengths. However, the dynamic performance is very similar. There is a direct correlation between Figs. 7.3 and 7.4, which confirms the consistency and stability of the thin film. Both results indicate that H₂ saturation occurs at concentrations over 0.5%.

The deposited Pt/WO₃ thin films on quartz substrates operate at low temperatures and are capable of repeatedly responding to H₂ concentrations of 0.06% which is well below explosive thresholds at 100°C with high stability, and fast recovery. Ando et. al [8, 9] reported that their sputtered Pt/WO₃ composite films responded at a temperature of 200°C, and only in a fixed exposure of 1% H₂ in air. Shanak and Schmitt [10] reported coloration in their sputtered Pt/WO₃ thin films when exposed to an undisclosed fixed H₂ concentration at room temperature. Both reported baseline stability issues, and recovery times were reported to be in the realm of 50 minutes.
Fig. 7.5 represents the plots of cumulative absorbance change as a function of H\textsubscript{2} concentration for Pt/WO\textsubscript{3} thin film at 100°C for a wavelength range of 500 – 800 nm. The error bars represent the maximum and minimum deviations of the films absorbance response, when exposed to three cycles of H\textsubscript{2} with different concentrations.

![Graph showing cumulative absorbance change as a function of H\textsubscript{2} concentration](image)

Fig. 7.5 Cumulative absorbance change as a function of H\textsubscript{2} concentration for Pt/WO\textsubscript{3} thin film at 100°C for a wavelength range of 500 – 800 nm.

From the figure, the response is rising proportionally with the increase of the H\textsubscript{2} concentrations. However, the response approaches saturation for the concentration above 0.5%. The response deviation is also spreading with the increase of H\textsubscript{2} concentrations as shown by the magnitude of the error bars. This indicates that the sensor repeatability is declining for the increasing H\textsubscript{2} concentrations. However, the trend does not change the proportionality of the response with respect to the H\textsubscript{2} concentrations. The average standard deviation relative to the mean cumulative absorbance change is ±9.5%. Overall, the Pt/WO\textsubscript{3} nanostructured film shows good sensitivity when exposed to multiple cycles of H\textsubscript{2} with different concentrations.
7.2.2 Pd/Sputtered WO$_3$ Nanostructured Thin Films

The H$_2$ testing was continued for 25Å Pd/1.2 µm WO$_3$ nanostructured thin films on quartz. Fig. 7.6 shows the absorbance versus optical wavelength of the Pd/WO$_3$ films exposed to H$_2$ with 1% concentration in synthetic air for a period of 10 minutes at room temperature.

![Absorbance versus optical wavelength](image)

**Fig. 7.6 Absorbance versus optical wavelength for Pd/WO$_3$ films exposed to 1% H$_2$ at room temperature.**

For the same film’s thickness and upon 1% H$_2$ exposure, the increase of absorbance for the Pd/WO$_3$ films is much higher than for the Pt/WO$_3$ films as shown in Fig. 7.1. Both Pt and Pd are well-known catalysts for H$_2$ [7, 11, 12]. It was reported that, even though Pd and Pt belong to the same group in the periodic table, their interaction mechanism with H$_2$ is different to each other. Yamauchi et. al [13] did extensive works on H$_2$ interaction with Pd and Pt nanoparticles. They reported that their Pd nanoparticles stored and interacted with H$_2$ strongly inside the Pd lattice. Nevertheless, the Pt nanoparticles strongly absorbed H$_2$ at the surface and less in the Pt lattice [13]. Based on this, it is assumed that the H$_2$ molecules absorbed by the Pd lattice interact stronger with the WO$_3$ layer than the molecules absorbed by the Pt surface. These features seem to influence the transfer of the H$_2$ ions into the WO$_3$ layer. As a result, Pd/WO$_3$ films turned darker and shown higher absorbance as compared to Pt/WO$_3$ when exposed to H$_2$. The dynamic response of the Pd/WO$_3$ films in the following Fig. 7.7 supported this assumption.
Fig. 7.7 illustrates the dynamic response of the Pd and Pd/\text{WO}_3\) nanostructured films exposed to \text{H}_2 with different concentrations at 100°C measured over the wavelength range of 500 – 800 nm.

![Graph](image)

**Fig. 7.7 Dynamic response of the Pd and Pd/\text{WO}_3\) nanostructured films exposed to different \text{H}_2 concentrations at 100°C.**

Fig. 7.7 clearly shows that the single layer of 2.5 nm Pd did not induce any obvious optical response towards \text{H}_2. In contrast, Pd/\text{WO}_3\) films exhibited significant dynamic performance when exposed to \text{H}_2 with different concentrations. For 0.06% and 1% \text{H}_2 exposure, the film’s absorbance response with reference to the baseline, was approximately increased to 80% and 120%, respectively. This is huge as compared to the response shown by Pt/\text{WO}_3 films. However, the Pd/\text{WO}_3\) dynamic response started to saturate for the \text{H}_2 concentrations above 0.25%. The film T90% response and recovery times induced by \text{H}_2 of 1% concentration in synthetic air was measured to be 120 s and 180 s, respectively. This is slower as compared to Pt/\text{WO}_3 films. The author believed that the 1.2 µm thick WO_3 layer contributed to the response saturation and sluggish sensing performance. The sensing layer is too thick and resulted in the strong \text{H}_2 adsorption but weak desorption when purged with synthetic air at elevated temperature. Therefore, the investigation of the gas testing was continued on the Pd/\text{WO}_3 and Pt/\text{WO}_3 films with reduced thickness of 200 nm.
Fig. 7.8 illustrates the absorbance versus optical wavelength of 25 Å Pd/200 nm WO$_3$ and 25 Å Pt/200 nm WO$_3$ films exposed to H$_2$ with 1% concentration in synthetic air at 100°C.

![Absorbance versus optical wavelength of 25 Å Pd/200 nm WO$_3$ and 25 Å Pt/200 nm WO$_3$ films exposed to H$_2$ with 1% concentration in synthetic air at 100°C.](image)

A significant increase of the magnitude of absorbance was observed over the whole visible-NIR spectrum, indicating that the transparent thin films became dark and the W$^{6+}$ centres in WO$_3$ had been reduced into coloured W$^{5+}$ centres. The absorbance magnitude increases with the wavelengths. The Pd/WO$_3$ films show larger absorbance shifts compared to Pt/WO$_3$ films when exposed to H$_2$ with 1% concentration at 100°C.

The dynamic sensing performance of the 200 nm films revealed interesting characteristics when the films were exposed to H$_2$ with different concentrations at 100°C (Fig. 7.9). The measurements were carried out over the wavelength range of 500 – 800 nm.

![Dynamic response of (a) Pd/200 nm WO$_3$ and (b) Pt/200 nm WO$_3$ thin films towards H$_2$ at 100°C.](image)
It was observed that the Pd/WO$_3$ thin films show superior gasochromic responses when compared with Pt/WO$_3$ thin films. The cumulative absorbance response in 500 – 800 nm range increased by approximately 5% when exposed to H$_2$ with 0.06% concentration in synthetic air for Pd/WO$_3$ samples. Meanwhile, only 0.5% increase was observed in Pt/WO$_3$ samples exposed to the H$_2$ with the same concentration. Pd/WO$_3$ T$_{90\%}$ response towards H$_2$ with 0.06% concentration in a balance of synthetic air was 30 s at 100°C. Similarly, higher H$_2$ concentrations of 1% can be sensed in as little as 20 s for Pd/WO$_3$ films. Pd/WO$_3$ thin films were highly sensitive, providing stable and repeatable responses towards H$_2$ of low concentrations, with typical response and recovery times of <60 s. Pt/WO$_3$ thin films were also sensitive but experienced baseline drift. It was found that the Pt/WO$_3$ T$_{90\%}$ response towards H$_2$ with 0.06% concentration in a balance of synthetic air was 70 s at 100°C. For H$_2$ concentrations of 1%, Pt/WO$_3$ films can provide a T$_{90\%}$ response in 40 s. Moreover, the dynamic performance of the 200 nm WO$_3$ films shown significant and proportional response for H$_2$ with high concentrations as compared to the 1.2 µm WO$_3$ films.

The plots of cumulative absorbance change as a function of H$_2$ concentration for Pd/WO$_3$ and Pt/WO$_3$ thin films at 100°C for a wavelength range of 500 – 800 nm as in Fig. 7.10 revealed different static performances between the two sensing layers.

![Fig. 7.10 Cumulative absorbance change as a function of H$_2$ concentration for (a) Pd/WO$_3$ and (b) Pt/WO$_3$ thin films at 100°C for a wavelength range of 500 – 800 nm.](image-url)

The trends of the cumulative absorbance change were almost similar for the Pd/WO$_3$ and the Pt/WO$_3$ films when exposed to H$_2$ with different concentrations. Both films proportionally increased their absorbance towards the increase of H$_2$ concentrations. However, the Pd/WO$_3$ films
show higher sensitivity and distinguished rise in the response as compared to Pt/WO$_3$. When exposed to three cycles of H$_2$ with different concentrations, the Pd/WO$_3$ films outperformed the Pt/WO$_3$ by indicating better repeatability. The average standard deviation relative to the mean cumulative absorbance change for Pd/200 nm WO$_3$ and Pt/200nm WO$_3$ is ±2.1% and ±14.8%, respectively. The bars also indicated more stable sensing performance from Pd/WO$_3$ as compared to Pt/WO$_3$ films which experience fluctuating responses for the repeated cycles of H$_2$.

Based on these dynamic and static performances, it is clear that the developed gasochromic sensing films based on Pd/WO$_3$ nanostructures were more sensitive, had faster response and recovery as well as more stable baseline compared to Pt/WO$_3$. The Pd layer was proven to be a better H$_2$ catalyst as compared to the Pt. The investigation of the gas sensing performance of the Pd/sputtered WO$_3$ was continued with the films deposited onto different transparent substrates.

### 7.2.3 Pd/ Sputtered WO$_3$ on Glass and Conductive Substrates (ITO and FTO)

As discussed in the micro-nano characterisation chapter (Chapter 5), the WO$_3$ films sputtered on the different transparent substrates have different morphologies. These features contributed to the different surface to volume ratios which will alter the surface interactions with the gas analyte molecules [14-19]. The investigation of the gasochromic dynamic performance of the Pd/WO$_3$ films on the different transparent substrates provides promising results.
Fig. 7.11 shows the dynamic responses of the 25Å Pd/500 nm WO₃ nanostructured thin films sputtered on the different transparent substrates towards H₂.

Fig. 7.11 Dynamic performances of Pd/500 nm WO₃ thin films exposed to H₂ at 100°C for different transparent substrates; (a) quartz, (b) glass, (c) ITO glass and (d) FTO glass.

The gasochromic response of the WO₃ films was measured based on the cumulative absorbance over a range of wavelengths between 500 – 800 nm. It was observed that Pd/WO₃ thin films deposited on all transparent substrates show excellent gasochromic response except for the films on FTO glass. The cumulative absorbance response in 500 – 800 nm range increased by around 110% compared to the baseline (synthetic air) when Pd/WO₃ films on quartz, glass and ITO glass were exposed to H₂ of 1% concentration. The films on the three transparent substrates were highly sensitive, providing stable and repeatable responses towards H₂. Their response and recovery times were measured to be <180 s. By comparison, the films on FTO glass only show 5% increase in the cumulative absorbance when exposed to H₂ with the same concentration. Overall, Pd/WO₃ thin films on FTO glass were still sensitive towards H₂. However, the baseline
drift was observed and the sensitivity for H2 with the concentration of 0.06% is very low for the films on FTO glass. This is supported by the static performances of the films as shown in Fig. 7.12.

Fig. 7.12 illustrates the cumulative absorbance change as a function of H2 concentration for Pd/500 nm WO3 nanostructured thin films sputtered on different transparent substrates at 100°C for a wavelength range of 500 – 800 nm.

![Graphs showing cumulative absorbance change](image)

Fig. 7.12 Cumulative absorbance change as a function of H2 concentration for Pd/500 nm WO3 nanostructured thin films sputtered on (a) quartz, (b) glass, (c) ITO glass and (d) FTO glass substrates.

Generally, the films static performances supported the results of the dynamic performances in such away that the cumulative absorbance change proportionally with the H2 concentrations. Nevertheless, the optical responses measured at 100°C for the films on the quartz and ITO glass substrates indicate sign of saturation for H2 with concentrations above 0.75%. As shown by the magnitude of the cumulative absorbance change, the most sensitive films were the ones deposited onto quartz and followed by the glass and ITO substrates. The films sputtered onto FTO glass shows low sensitivity towards H2 as compared to the other substrates. When exposed to three cycles of H2 with different concentrations, the films on quartz and glass substrates indicating
better repeatability than the ones on the ITO and FTO substrates as shown by the error bars. The films on the FTO glass also show less stability as compared to the films on the other substrates.

The dynamic and static optical sensing performances show direct correlation with the films morphologies on the different transparent substrates. It was reported in Chapter 5 that the sputtered WO$_3$ films are uniform with the grain sizes on quartz, glass and ITO glass almost similar in the range of 30 – 60 nm. In contrast, the films deposited on the FTO glass consist of grains much larger than for the films on the other transparent substrates with the sizes of 300 – 500 nm. As a result, the surface to volume ratio is higher for the films on quartz, glass and ITO glass as compared to the films on FTO glass. Subsequently, more H$_2$ molecules were adsorbed in the Pd/WO$_3$ films deposited on the other transparent substrates than the ones on the FTO glass. This is supported by the increase in the films’ sensitivity which is around 110% for the ones on the quartz, glass and ITO glass and only 5% for FTO glass towards H$_2$ of 1% concentration. It is believed that the large WO$_3$ grains sputtered on the FTO glass also contributed to the trapment of some H$_2$ molecules in the films even when the synthetic air was purged during the recovery process at elevated temperatures. That is the reason for the baseline drift instability and increasing as shown in the dynamic response of the films on FTO glass.

This investigation proved that the optical sensing performance of the sputtered WO$_3$ nanostructured thin films towards H$_2$ with different concentrations is highly dependent on the film morphology. The films were sputtered in the same batch with the same conditions but on the different transparent substrates. The Pd/WO$_3$ films consist of smaller nanograins (30 – 60 nm) which give higher surface to volume ratio, showed better dynamic performance and sensitivity as compared to the films with larger grains (300 – 500 nm) when exposed to H$_2$.

Later, the author performed the H$_2$ testing on the WO$_3$ nanostructured thin films coated with Au catalytic layer on quartz substrate. This is important to compare the influence of Au on the gasochromic performance of the WO$_3$ nanostructures with the other catalytic metal layers studied previously.
7.2.4 Au/Sputtered WO₃ Nanostructured Thin Films

As mentioned in the literature in Chapter 2, Au is another noble metal commonly used as a catalyst apart from Pd and Pt. Many studies reported significant improvement in the sensing performance towards H₂ for the conductometric based sensors coated with Au [7, 20]. However, only few studies were carried out on the effect of the Au catalytic layer for optical gas sensing applications especially with the development of Au nanoparticles. In this project, the author deposited Au nanoclusters of 2 – 5 nm in diameter on the 500 nm sputtered WO₃ films on quartz. The gasochromic response of the Au/WO₃ films were tested towards H₂ with 1% concentration. Fig. 7.13 revealed the absorbance response of the films when exposed to the gas at 200°C.

![Fig. 7.13 Absorbance versus optical wavelength for Au/WO₃ films exposed to 1% H₂.](image)

Interestingly, no absorbance change was observed for the Au/WO₃ films exposed to the 1% H₂ at room temperature as compared to the films coated with Pd or Pt. Significant response was measured only at elevated temperature of 200°C. The magnitude of the change is also small and significant only in the NIR region (> 750 nm). Ando et. al [21] reported almost similar absorbance response for their DC sputtered Au on WO₃ films when exposed to H₂ of 1% concentration at 200°C and measured at 900 nm wavelength.
The author believed the low gasochromic response of the Au/WO₃ films as compared to the other catalytic metals is mainly due to the nature of the H₂ adsorption in the Au nanoparticles. It was reported that the gas adsorption in Au concentrates on the surface atoms similar to the adsorption in Pt [11, 22]. According to Bus and Bokhoven [22], H₂ chemisorbs only at the corner and edge atoms of these two catalytic metal particles. However, they also identified that the H₂ interaction with Pt is stronger than with Au. This is because the Pt corner and edge atoms can adsorb more than one hydrogen atom as compared to Au [23]. This can be understood via illustration in Fig. 7.14.

![Illustration of the H₂ adsorption in (a) Au atoms and (b) Pt atoms.](image)

The fact that a few Au surface atoms interact with the hydrogen atoms resulted in the weak H ions transfer into the WO₃ layer to induce coloration at high operating temperature (>200°C). Therefore, the gasochromic response of the Au/WO₃ films towards H₂ is not as significant as the response of the Pt/WO₃ and Pd/WO₃ films. Further investigation on the Au/WO₃ dynamic performance supported this conclusion.
Fig. 7.15 illustrates the dynamic performance of the Au/WO₃ nanostructured thin films exposed to H₂ with different concentrations at 200°C. The measurements were carried out over the wavelength range of 800 – 1000 nm.

It was observed that the films’ cumulative absorbance response in 800 – 1000 nm range increased by approximately 2.5% when exposed to 0.06% H₂ in synthetic air. The dynamic performance of the Au/WO₃ nanostructured thin films were repeatable towards H₂ with low concentrations, with typical response and recovery times of <5 min. Au/WO₃ T₉₀% response time towards H₂ with concentrations of 0.06% and 1% in a balance of synthetic air were 180 and 120 s, respectively. The sample T₉₀% recovery time was found to be approximately 5 min when exposed to H₂ concentrations of 0.06% and 1%. The thin films were sensitive only at higher temperature (200°C) and experienced delay in the recovery more than the Pd/WO₃. For that reasons, the author maintained the use of Pd as the main catalytic metal layer to investigate the gasochromic response of the metal oxide nanostructured thin films.

Fig. 7.16 shows the cumulative absorbance change as a function of H₂ concentration for Au/WO₃ films at 200°C for a wavelength range of 800 – 1000 nm. The film exposure to the three cycles of H₂ revealed proportional rise of cumulative absorbance upon the increase of the gas
concentrations.

![Graph showing cumulative absorbance change as a function of H₂ concentration for Au/WO₃ nanostructured thin films at 200°C for a wavelength range of 800 – 1000 nm.]

It is observed that the response trends show saturation for the H₂ concentrations above 0.5%. Nevertheless, the Au/WO₃ films on quartz substrate indicate good repeatability and stability by having only small deviation for the repeated H₂ cycles. The average standard deviation relative to the mean cumulative absorbance change is ±4.7%. By comparison, the films sensitivity is lower than the Pd/WO₃ films with the same thickness on quartz substrate as in Fig. 7.12 (a).

It is clear that the gasochromic response of the WO₃ films coated with Au catalyst is not as good as Pd/WO₃ when exposed to H₂. Therefore, Pd was selected as the catalytic layer for the other nanostructured thin films. The investigation on the gasochromic materials were continued for the WO₃ nanostructured thin films deposited via electron beam deposition.

### 7.2.5 Pd/Electron Beam Deposited WO₃ Nanostructured Thin Films

In this project, the gasochromic response of the metal oxide nanostructured thin films was carried out for the 25Å Pd/500 nm WO₃ films deposited onto quartz substrates via electron beam deposition.
Fig. 7.17 shows the absorbance spectrum of the Pd/WO$_3$ films exposed to synthetic air and H$_2$.

![Absorbance spectrum](image)

**Fig. 7.17 Absorbance spectrum of Pd/ electron beam deposited WO$_3$ films exposed to synthetic air and H$_2$ of 1% at room temperature.**

The spectrum indicates that the films became dark when exposed to H$_2$. The magnitude of absorbance increase with the wavelengths move towards NIR region. The response observed in the NIR wavelength range is obviously higher than in the visible range. The same feature was observed for the response of the sputtered WO$_3$ films (Fig. 7.6). It has been reported that broad and distinct absorption bands with typical peak around $\lambda = 1033$ nm were observed for WO$_3$ films deposited under high vacuum (>0.8 mTorr). This absorption bands were identified to be responsible for the electrochromism of the WO$_3$ [24, 25]. In this project, the films deposited via sputtering and electron beam techniques were carried out at high vacuum. The author believes that the significant increase in the gasochromic response as the wavelengths increase can be attributed to the similar strong absorption bands identified in the electrochromic WO$_3$. As discussed in Chapter 2, one of the by products of the WO$_3$ gasochromism is water vapour. In literature, the water vapour high absorption was found to be in the NIR region of 1000 – 1200 nm [26, 27]. Thus, it is assumed that the higher absorbance response observed in the NIR as compared to the response in the visible range during the coloration of the WO$_3$ films exposed to H$_2$ is also may be
contributed by the water vapour on the surface. Above 100°C, the removal of the water vapour from the film’s surface occurred rapidly and thus the decrease in the absorbance response.

Fig. 7.18 shows the dynamic responses of Pd/WO₃ films towards H₂ with different concentrations at 100°C for a wavelength range 500 – 800 nm.

The response as in Fig. 7.18 is measured by integrating the absorbance for 500 – 800 nm wavelength range. The cumulative absorbance response increased by around 5% and 17% compared to the baseline (synthetic air) when the Pd/electron beam deposited WO₃ films were exposed to H₂ with the concentrations of 0.06% and 1%, respectively. The films show excellent optical sensing performance for low H₂ concentrations. Pd/WO₃ T₉₀% response time towards H₂ with 0.06% and 1% concentrations at 100°C was approximately 60 s and 120 s, respectively. Meanwhile, the T₉₀% recovery time was found to be 120 s for both 0.06% and 1% of H₂ concentrations. The sensing performance measured in real time for the wavelength range is consistent with the performance at single λ.
Fig. 7.19 shows the dynamic responses of the 25Å Pd/500 nm WO₃ films towards H₂ with different concentrations at operating temperature 100°C and measured at single wavelength, $\lambda = 500$ nm and 1000 nm.

![Graph showing dynamic responses](image)

**Fig. 7.19 Dynamic response of Pd/500 nm electron beam deposited WO₃ films towards H₂ at 100°C and measured at a single wavelength, $\lambda = 500$ and 1000 nm.**

The dynamic performance of the 500 nm films in Fig. 7.19 supported the observation previously shown in Fig. 7.17 on the higher absorbance response in the NIR range as compared to the visible wavelengths upon H₂ exposure. In fact, the response at the NIR wavelength of 1000 nm was measured to be three times higher than the response at the visible wavelength of 500 nm for H₂ concentration of 1%.

Meanwhile, Fig. 7.20 illustrates the cumulative absorbance change as a function of H₂ concentration for Pd/electron beam deposited WO₃ film at 100°C for a wavelength range of 500 – 800 nm.
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Fig. 7.20 Cumulative absorbance change as a function of H₂ concentration for Pd/electron beam deposited WO₃ film at 100°C for a wavelength range of 500 – 800 nm.

The trend of the curve for the Pd/500 nm electron beam deposited WO₃ films was observed to be similar with the one for Pd/sputtered WO₃ films of the same thickness on quartz in Fig. 7.12 (a). The response was amplifying with the increase of the H₂ concentrations. However, the film response started to saturate for the H₂ concentrations above 0.75%. As indicating by the small margin of the error bars, the Pd/electron beam deposited WO₃ films have very good repeatability when exposed to many cycles of H₂. The average standard deviation relative to the mean cumulative absorbance change is found to be ±3.3%.

Overall, the Pd/electron beam deposited WO₃ nanostructured thin films on quartz is sensitive and as stable as the Pd/sputtered WO₃ films when exposed to H₂ with different concentrations. The films response and recovery are also very fast (<120 s).

Next, the author investigated the gasochromic response of the Pd/pulse laser deposited WO₃ nanostructured thin films.

### 7.2.6 Pd/Pulsed Laser Deposited WO₃ Nanostructured Thin Films

As discussed in the micro-nano characterisation section (Chapter 5), pulsed laser deposited WO₃ films consist of nanorods. This nanostructures are quite different from the WO₃
grown via RF sputtering and electron beam deposition techniques. The author investigated the gasochromic response of the WO$_3$ nanorod films coated with 25Å Pd on quartz substrate. Due to the limitation of the deposition technique, the typical film thickness was achieved only around 70 - 170 nm. The Pd/WO$_3$ nanorod films were exposed to H$_2$ with different concentrations at 100°C.

The absorbance spectrum versus wavelength of the 170 nm thick films exposed to H$_2$ with 1% concentration at room temperature was shown in Fig. 7.21.

![Absorbance spectrum versus wavelength of the 25Å Pd/170 nm WO$_3$ nanorod thin films exposed to H$_2$ with 1% concentration at room temperature.](image)

The magnitude of the absorbance spectrum of the Pd/WO$_3$ nanorod thin films increased substantially when the films were exposed to H$_2$ with 1% concentration. The response increases with the wavelengths. This is similar to the response of the other Pd/WO$_3$ nanostructured thin films discussed previously. The spectrum also obviously shifted towards the blue-region indicating the films turned dark when exposed to H$_2$.

The dynamic performance of the Pd/WO$_3$ nanorod films towards H$_2$ with different concentrations is shown in Fig. 7.22. The testing was carried out at 100°C and measured for a wavelength range of 500 – 800 nm.
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Fig. 7.22 Dynamic performance of the Pd/WO$_3$ nanorod films towards H$_2$ with different concentrations at 100°C for a wavelength range of 500 – 800 nm.

The cumulative absorbance response in 500 – 800 nm range of the Pd/WO$_3$ nanorod films was increased by approximately 5% and 11% when exposed to H$_2$ with the concentrations of 0.06% and 1%, respectively. The T$_{90\%}$ response time towards H$_2$ with 0.06% concentration was calculated to be 240 s at 100°C. The film’s T$_{90\%}$ recovery time for the H$_2$ with the same concentrations was approximately 420 s. For the H$_2$ concentrations of 1%, the film’s T$_{90\%}$ response and recovery times were determined to be 120 s and 360 s, respectively.

Fig. 7.23 shows the cumulative absorbance change as a function of H$_2$ concentration for Pd/WO$_3$ nanorod films at 100°C for a wavelength range of 500 – 800 nm.

The Pd/WO$_3$ nanorod films show signs of response saturation for the H$_2$ concentration
above 0.75%. Despite of that, the plot indicates good sensor repeatability especially for H₂ with concentrations less than 0.25%. This is supported by the average standard deviation relative to the mean cumulative absorbance change of the films which is ±5.8%.

Overall, the developed sensors were sensitive, providing stable and repeatable responses towards H₂ with low concentrations up to 0.06%. However, the sensing recovery was slower as compared to the other Pd/WO₃ nanostructured thin films discussed previously. This is due to the rate of the desorption of H⁺ which was reduced by the ion thermodynamic desorption barrier and the water molecules produced on the surface of the Pd/WO₃ nanorod films. The operating temperature of 100°C was not sufficient for the WO₃ nanorod films to achieve fast recovery. It is probably because of the nanorod films were compact with typical surface dimension of 30 – 80 nm. This gave a lower surface area as compared to the other WO₃ films deposited in this project with typical nanostructures of 10 – 50 nm.

Apart from H₂ testing on the WO₃ nanostructured thin films deposited via physical deposition techniques, the optical testing was also carried out on the WO₃ nanostructures developed via chemical synthesis, namely, acid etching.

### 7.2.7 Pd/Acid Etched WO₃ Nanostructured Thin Films

The WO₃ nanostructured thin films synthesised via acid etching on quartz substrate consist of nanoplatelets. The acid etching synthesis to develop WO₃ nanoplatelets was introduced recently by Windekvist et. al [28] and their gasochromic properties are yet to be reported. To the best of the author’s knowledge, this is the first report on the absorbance response of the WO₃ nanoplatelet films towards H₂.

In this project, the WO₃ nanoplatelet films were successfully synthesised onto quartz substrate and their thickness was optimised for optical testing. The 150 nm films were coated with 25Å Pd and tested towards H₂ with different concentrations at 100°C.
Fig. 7.24 shows the absorbance response of the annealed films exposed to H\textsubscript{2} of 1\% concentration at room temperature.

Fig. 7.24 Absorbance spectrum versus wavelength of the annealed 25Å Pd/150 nm WO\textsubscript{3} nanoplatelet thin films exposed to H\textsubscript{2} with 1\% concentration at room temperature.

The magnitude of the absorbance spectrum of the Pd/WO\textsubscript{3} nanoplatelet thin films clearly increased in the wavelengths above 700 nm (NIR range) when the films were exposed to H\textsubscript{2} with 1\% concentrations. Interestingly, the absorbance marginally decreased for the spectrum below 600 nm (visible range) when the films were exposed to the H\textsubscript{2} with similar concentration. The wavelengths significantly shifted towards the blue-region indicating the films turned dark when exposed to H\textsubscript{2}. The investigation on the optical sensing performance of the Pd/WO\textsubscript{3} nanoplatelet films was continued with the dynamic performance as in Fig. 7.25.

Fig. 7.25 Dynamic performance of the Pd/WO\textsubscript{3} nanoplatelet films towards H\textsubscript{2} with different concentrations in the wavelength range of 800 – 1000 nm at 100°C.
The cumulative absorbance response was measured in the 800 – 1000 nm wavelength range based on the initial observation of the films sensing characteristic in Fig. 7.24. At 100°C, the Pd/WO₃ nanoplatelet films response was increased by approximately 45% and 99% when exposed to H₂ with the concentrations of 0.06% and 1%, respectively. These results show that the 150 nm WO₃ nanoplatelet films are very sensitive towards H₂ and comparable with the sensitivity of the WO₃ sputtered films with higher thickness (500 nm) which give 110% response increase when exposed to H₂ of 1% concentration (Fig. 7.11 (a)). The film T₉₀% response and recovery times towards H₂ with 0.06% concentration was calculated to be 60 s and 180 s, respectively. The same durations were calculated for the film T₉₀% response and recovery towards H₂ with concentrations of 1%. The Pd/WO₃ nanoplatelet films on quartz substrate show a very stable dynamic performance. The investigation was continued with the film static performance as illustrated in Fig. 7.26.

![Graph showing cumulative absorbance change as a function of H₂ concentration for Pd/WO₃ nanoplatelet films at 100°C for a wavelength range of 500 – 800 nm.](image)

Fig. 7.26 Cumulative absorbance change as a function of H₂ concentration for Pd/WO₃ nanoplatelet films at 100°C for a wavelength range of 500 – 800 nm.

The plot in Fig. 7.26 supported the films excellent dynamic performance as shown in Fig. 7.25. The film cumulative absorbance change increased proportionally with the increase of the H₂ concentrations. The WO₃ nanoplatelet films also show the highest sensitivity towards H₂ with 0.06% concentration as compared to the other WO₃ nanostructures deposited in this project eventhough the film thickness was measured to be the lowest (150 nm). The small error margins
in the graph indicating the good repeatability of the Pd/WO$_3$ nanoplatelet films exposed to three cycles of H$_2$ with different concentrations. The average standard deviation relative to the mean cumulative absorbance change was found to be $\pm 4.4\%$. Similar to the dynamic performance, the film static performance point out the sign of saturation when the films sensed the H$_2$ with concentrations above 0.75%. In general, the films were sensitive, providing stable and repeatable responses towards H$_2$ with low concentrations of up to 0.06%.

The author believes that the excellent gasochromic performance of the Pd/WO$_3$ nanoplatelet films is due to their morphology. Based on the micro-nano characterisation of the WO$_3$ nanostructures in Chapter 6, the nanoplatelets have very different structures than the other WO$_3$ films developed in this project. The random oriented nanoplatelets were grown in the size of 100 – 500 nm as compared to the 20 – 80 nm structures for the other thin films deposited via sputtering, electron beam and pulsed laser deposition techniques. The individual nanoplatelets were distributed homogeneously on the substrate and has edges and corners of 20 – 60 nm thick. Nevertheless, the nanoplatelet films are very porous and less dense as compared to the other WO$_3$ nanostructured thin films. As a result, the WO$_3$ nanoplatelet films have the higher surface area as compared to the other deposited films. Generally, the high surface area provides numerous gas adsorption/desorption sites and thus increase in the sensitivity. The fact that the nanoplatelets as well as the other deposited nanostructured thin films have similar monoclinic WO$_3$ crystal structure with (002) orientation indicates that the strong gasochromic response in the nanoplatelet films is mainly due to their rough and porous structures.

Apart from the WO$_3$ nanostructures, the author investigated the gasochromic response of the MoO$_3$ nanostructures which is another promising material in the same group of periodic table.
7.2.8 Pd/Thermal Evaporated MoO$_3$ Nanostructured Thin Films

In this work, the gasochromic performance of Pd/MoO$_3$ nanostructured thin films upon exposure to H$_2$ with different concentrations (0.06 - 1%) in synthetic air was investigated. To the best of the author’s knowledge, only one work was reported on the gasochromic performance of nanostructured Pd/MoO$_3$ films towards H$_2$. Since MoO$_3$ being discovered as a potential photochromic material induced in visible wavelength range by Yao et. al [29], Hamagami et. al [30] reported that their sputtered Pd/MoO$_3$ films changed the transmittance when exposed to H$_2$ of 100% and 0.1% concentrations in argon (Ar). However, the Pd/MoO$_3$ nanostructured thin films deposited by the author on quartz via thermal evaporation technique shown more significant gasochromic sensing performance compared to the amorphous films.

Fig. 7.27 illustrates the absorbance spectrum Pd/MoO$_3$ nanostructured thin film exposed to synthetic air and H$_2$ with 1% concentration in the visible-NIR wavelength ranges at room temperature.

![Absorbance spectrum Pd/MoO$_3$ nanostructured thin film exposed to synthetic air and H$_2$ with 1% concentration in the visible-NIR wavelength ranges at room temperature.](image)

As shown in the figure, the magnitude of the absorbance was increased significantly when the film was exposed to H$_2$ with 1% concentration in synthetic air. The transparent film became dark. The response was also notably higher in the NIR wavelength range ($\lambda > 750$ nm) as compared to the
absorbance change in the visible region (400 nm < \( \lambda \) < 750 nm). These findings support the results by Hamagami et. al [30] which reported that their sputtered Pd/MoO\(_3\) thin films changed the transmittance at NIR wavelength of 780 nm upon exposure to H\(_2\). The response was observed only for the MoO\(_3\) films deposited at a distance of 15 cm from the alumina boat containing the MoO\(_3\) powder. The films at this distance have a thickness of 1.3 µm with transparency of 79 – 90% and consisted of nanorods. Meanwhile, the films deposited at a distance of 10 cm have a thickness of more than 3 µm with transparency of less than 20% and consisted of platelets. The MoO\(_3\) platelet films did not show any gasochromic response towards H\(_2\). Based on the MoO\(_3\) micro-nano characterisation results presented in Chapter 5, the MoO\(_3\) nanorod films have higher surface to volume ratio as compared to the platelet films. As a result, it is believed that the interaction between the gas molecules and the MoO\(_3\) nanorods are stronger than with the platelets. In addition, the low transparency of the MoO\(_3\) platelet films (<20%) indicated that the films are too thick for the gasochromic application. Vitry et. al [31] reported that the response magnitude of the metal oxide films is rising proportional with a certain increase in the film thickness. Above the optimum thickness, the film gasochromic response is saturated or ceased. No response was also detected when individual layer of MoO\(_3\) films exposed to H\(_2\) with 1% concentration.

The gasochromic response of the Pd/MoO\(_3\) film towards H\(_2\) can be explained with a model proposed by Deb [32] and Yao et. al [29] for the photochromic phenomena in the transition metal oxides in the visible wavelength range. Based on this model, the dissociative chemisorption of molecular hydrogen onto catalytic Pd forms hydrogen ions and electrons. The generation of electrons ‘spill over’ into the MoO\(_3\) layer and reduces the Mo\(^{6+}\) centre in the MoO\(_3\) crystal lattice to Mo\(^{5+}\) (blue colour). Simultaneously, water (H\(_2\)O) vapour was formed resulting from the combination of 2H\(^+\) with surface bound O\(^{2-}\) ions produced by the transition. When the H\(_2\) gas was purged out by the synthetic air at elevated temperature, the stoichiometry of the MoO\(_3\) was restored from Mo\(^{5+}\) to Mo\(^{6+}\).
Fig. 7.28 illustrates the dynamic response of the Pd/MoO$_3$ nanostructured film towards H$_2$ with different concentrations in a synthetic air at optimum operating temperature of 120°C.

The gasochromic response of the MoO$_3$ film was measured based on the cumulative absorbance over NIR range of wavelengths of 840 – 1020 nm. The measurement was also carried out at a single 900 nm wavelength as shown in Fig. 7.28. There is a direct correlation between Figs. 7.28 and 7.29, which confirms the consistency and stability of the thin film.
It was found that the cumulative absorbance response in 840 – 1020 nm range was increased by approximately 16% when exposed to H₂ with 1% concentrations in synthetic air for Pd/MoO₃ sample. The film T₉₀% response time towards H₂ of 0.06% in synthetic air was 70 s at 120°C. Similarly, H₂ with higher concentrations of 1% can be sensed at a short duration of 30 s. Meanwhile, T₉₀% recovery time towards H₂ with 0.06% concentration in synthetic air was 600 s at 120°C. For H₂ concentrations of 1%, the recovery time was 480 s.

Fig. 7.30 represents the cumulative absorbance change as a function of H₂ concentration for Pd/MoO₃ nanostructured film at 120°C for (a) wavelength range of 840 – 1020 nm and (b) a single wavelength of 900 nm. The error bars represent the maximum and minimum deviations of the films absorbance response, when exposed to three cycles of six different H₂ concentrations (0.06 – 1.0%).

It can be seen that the response is increasing linearly when exposed to H₂ with concentrations of up to 0.25%. Above this concentration, the response starts to saturate. It was found that the cumulative absorbance response deviation reduced with the increase of H₂ concentrations except for H₂ of 0.06% concentration (Fig. 7.30 (a)). However, the absorbance response deviation is almost constant for H₂ with different concentrations except for 0.25%, when the film sensing performance was analysed at a single wavelength of 900 nm as shown by the error bars in Fig. 7.30 (b). The average standard deviation relative to the mean absorbance change measured for the 840 – 1020 nm wavelength range and at a single wavelength of 900 nm is ±14%
and ±11.2%, respectively. Overall, the Pd/MoO₃ nanostructured film indicates moderate repeatability when exposed to multiple cycles of different H₂ concentrations.

The optical sensing investigation was carried out further with TiO₂ nanostructured thin films. This material is widely used for the photochromic applications. However, to best of the author’s knowledge, there is no report on the TiO₂ gasochromic response specifically towards H₂.

### 7.2.9 Pd/Anodised TiO₂ Nanostructured Thin Films

In this project, many deposition techniques and processes were performed to produce TiO₂ nanostructures suitable for gasochromic applications. However, the optical response towards H₂ was only observed for the anodised and annealed TiO₂ nanostructured films coated with Pd. Fig. 7.31 shows the absorbance spectrum of the 25Å Pd/1.0 μm TiO₂ anodised and annealed films when exposed to synthetic air and H₂ of 1% concentration at room temperature.

![Absorbance spectrum](image)

**Fig. 7.31** Absorbance spectrum of the Pd/TiO₂ anodised and annealed films when exposed to synthetic air and 1% H₂ in synthetic air at room temperature.

It was found out that the absorbance of the films is increased upon H₂ exposure which is similar to the response of the n-type metal oxides discussed previously. The magnitude of the absorbance response is notably increased for the optical wavelengths from visible to NIR range.
However, the response of the Pd/TiO$_2$ anodised and annealed films is obviously not as significant as shown by the Pd/WO$_3$ and Pd/MoO$_3$ nanostructured films responses. To the best of author’s knowledge, this is the first time the gasochromic response towards H$_2$ was observed in the TiO$_2$ nanostructured thin films developed via anodisation technique. Manera et al. investigated the gasochromic response of their TiO$_2$ films synthesised via sol-gel method doped with Au nanoparticles towards methanol at 200°C [33]. When exposed to methanol of 6000 ppm, their Au/TiO$_2$ films showed the absorbance response across the visible-NIR wavelength range as similar as in Fig. 7.31.

No absorbance change was observed for the Pd/TiO$_2$ films that were annealed or anodised when exposed to H$_2$. As reported in Chapter 5, the morphology are vastly different for the films undergone three stages of treatments (annealed, anodised, anodised and annealed). The author believes that the response shown only in the anodised and annealed TiO$_2$ films is mainly due to the films’ high surface area. The anodised and annealed porous films consist of nanograins in the size of 20 – 100 nm with rutile crystal lattice provide higher surface area and suitable sites for the H$_2$ adsorption as compared to the other TiO$_2$ films developed in this project. Many studies identified that the rutile TiO$_2$ has better sensitivity towards H$_2$ as compared to the other crystals such as anatase [34, 35]. Nevertheless, no gasochromic response was recorded for the dense rutile TiO$_2$ films consisted of 80 – 200 nm grains achieved solely via annealing. The fact that the response was only observed for the anodised and annealed films indicated the importance of the rutile crystal phase, small nanograins as well as high porosity of the TiO$_2$ films to function as the optical sensing layer towards H$_2$.

Fig. 7.32 shows the dynamic optical gas sensing performance of Pd/TiO$_2$ anodised and annealed films towards H$_2$ at optimum temperature of 60°C for the wavelength range of 500 – 950 nm. It was observed that the nanoporous anodised and annealed films show significant absorbance response when exposed to H$_2$. 
Fig. 7.32 Dynamic response of the Pd/TiO$_2$ nanoporous films annealed at 800°C exposed to H$_2$ with different concentrations at 60°C for the wavelength range of 500 – 950 nm.

As shown in Fig. 7.32, the cumulative absorbance in 500 – 950 nm wavelength range was increased by approximately 1.5% and 5% towards H$_2$ with concentrations of 0.06% and 1%, respectively. Overall, these are considerably lower than the sensitivity shown by the Pd/WO$_3$ and Pd/MoO$_3$ thin films. The T$_{90%}$ response and recovery times of the films towards H$_2$ with concentrations of 0.06% as well as 1% are approximately similar around 120 s and 180 s, respectively. The investigation was carried out further with the cumulative absorbance change as a function of H$_2$ concentration for Pd/TiO$_2$ nanoporous film at 60°C for a wavelength range of 500 -650 nm as shown in Fig. 7.33.

Fig. 7.33 Cumulative absorbance change as a function of H$_2$ concentration for Pd/TiO$_2$ nanoporous film at 60°C for a wavelength range of 500 – 650 nm.
Based on the figure, the response is increasing linearly when exposed to H\textsubscript{2} with concentrations of up to 0.25%. Beyond this, the film response saturates. The average standard deviation relative to the mean cumulative absorbance change for the films is ±8.1%. Eventhough the film shows acceptable repeatability when exposed to three cycles of H\textsubscript{2} with different concentrations, the overall magnitude of the cumulative absorbance change is very low. This indicates that the sensitivity of the Pd/TiO\textsubscript{2} films is much lower than the Pd/MoO\textsubscript{3} and Pd/WO\textsubscript{3} films.

The author suggests that the small optical response in the Pd/TiO\textsubscript{2} films towards H\textsubscript{2} might be caused mainly by the adsorption of the gas molecules onto the thin catalytic layer transforming Pd into PdH. The intercalation of the ions into and out of the TiO\textsubscript{2} layer probably too weak to induce large transition of Ti\textsuperscript{4+} into Ti\textsuperscript{3+} [36, 37]. As a result, the change in the film’s optical property is small as compared to the change in the other metal oxide films when exposed to H\textsubscript{2}.

So far, the optical sensing results presented are for the n-type nanostructured metal oxides. In this project, the investigation of the gasochromic nanostructured materials also includes p-type metal oxide such as NiO.

### 7.2.10 Pd/Sputtered NiO Nanostructured Thin Films

In this project, the author investigated the gasochromic properties of NiO nanostructured thin films coated with 25Å Pd. Based on the literature, this is the first time it was proven that the Pd/NiO films turned transparent when exposed to H\textsubscript{2}. The gas testings were carried out on the sputtered NiO films with the thicknesses of 400 nm and 100 nm.
Chapter 7: Gas Sensing Results

Fig. 7.34 shows the absorbance spectra of Pd/NiO films when exposed to synthetic air and H\textsubscript{2} with 1% concentrations at room temperature.

![Absorbance spectra of Pd/NiO films with the thickness of (a) 400 nm and (b) 100 nm, when exposed to synthetic air and H\textsubscript{2} with 1% concentrations.](image)

According to the figure, the Pd/NiO films absorbance is reduced when exposed to H\textsubscript{2} with 1% concentrations and indicating that the film became more transparent than the initial condition. The response is the opposite of the n-type gasochromic metal oxides such as WO\textsubscript{3}, which turns dark when exposed to H\textsubscript{2}. Only the magnitude of the absorbance reduced for the whole vis-NIR wavelength range and no wavelength shift occurs when the film was exposed to H\textsubscript{2}. Overall response magnitude is larger for the 400 nm thin film (20%) as compared to the 100 nm thin film (5%).

The gasochromic response of the Pd/NiO film towards H\textsubscript{2} can be explained with the sensing mechanism proposed by Hotovy et. al [38], Biju and Khadar [39] and M. Schönnenbeck et. al [40] for their conductometric based Pt/NiO sensor. Based on this mechanism, the dissociative chemisorption of molecular hydrogen onto catalytic Pd forms hydrogen ions and electrons. As discussed before, the spill over of the electrons in the n-type semiconducting metal oxides reduces their conductivity. In contrast, the spill over of the hydrogen electrons in the p-type NiO layer oxidises the Ni\textsuperscript{2+} to Ni\textsuperscript{3+}. According to Biju and Khadar, each Ni\textsuperscript{2+} vacancy in the lattice causes the transition of two adjacent Ni\textsuperscript{2+} ions into Ni\textsuperscript{3+} ions to acquire charge neutrality and this transition induces a local lattice distortion. Simultaneously, water vapour was formed resulting from the combination of 2H\textsuperscript{+} with surface bound O\textsuperscript{2-} ions produced by the transition. Obviously, the change in the NiO stoichiometry or the lattice distortion alter the
optical properties of the NiO films by increasing the films transparency. When the H$_2$ gas was purged out by the synthetic air at elevated temperature, the stoichiometry of the NiO was restored from Ni$^{3+}$ into Ni$^{2+}$.

Fig. 7.35 shows the dynamic responses of Pd/NiO films towards H$_2$ with different concentrations at the wavelength, $\lambda = 900$ nm for the film thicknesses of (a) 400 nm and (b) 100 nm. The testing was carried out at the operating temperature of 170°C. This can be considered low and within the typical optimum temperatures (150 - 320°C) for H$_2$ sensing reported elsewhere for conductometric based NiO films [39, 41, 42].

![Fig. 7.35 Dynamic response of Pd/NiO films towards H$_2$ at optical wavelength, $\lambda = 900$ nm for films thicknesses of (a) 400 nm and (b) 100 nm.](image)

It was observed that the response and recovery of the 100 nm film are faster than the 400 nm film even though the response magnitude is stronger for 400 nm film as mentioned before. $T_{90\%}$ response and recovery times towards H$_2$ with 0.06% concentrations at 170°C for 100 nm Pd/NiO film were approximately 160 s and 250 s, respectively. For the same H$_2$ concentration, 400 nm film $T_{90\%}$ response and recovery were calculated to be approximately 240 s and 480 s, respectively. The films responses were obviously saturated when exposed to H$_2$ with concentration above 0.5%.
Fig. 7.36 illustrates the dynamic response of Pd/NiO films towards H₂ at 170°C for films thicknesses of (a) 400 nm and (b) 100 nm measured at a wavelength range of 500-800 nm.

![Graph of dynamic response of Pd/NiO films towards H₂ at 170°C](image)

**Fig. 7.36** Dynamic response of Pd/NiO films towards H₂ at 170°C with films thicknesses of (a) 400 nm and (b) 100 nm, measured for a wavelength range of 500-800 nm.

The response in Fig. 7.36 is measured based on cumulative absorbance by integrating the absorbance for 500 – 800 nm in real time. Since the film responses towards H₂ throughout the vis-NIR spectrum, the measurement based on the cumulative absorbance obviously increase the films sensitivity towards H₂ with low concentrations of up to 0.06%. This is proved with the response magnitude shown in Fig. 7.36 measured for a wavelength range (500 – 800 nm) as compared to the measurement at a single wavelength (900 nm) as in Fig. 7.35. The film T₉₀% response and recovery times towards H₂ with 0.06% concentrations at 170°C for 400 nm Pd/NiO films were found to be around 240 s and 12 min, respectively (Fig. 7.36 (a)). The 100 nm thick film performed better than that with its T₉₀% response and recovery being approximately 120 s and 240 s, respectively, for the same H₂ concentration and temperature (Fig. 7.36 (b)). Meanwhile, the 400 nm films T₉₀% response and recovery times towards H₂ of 1% concentrations in 180 s and 9 min, respectively. This is slower than the response and recovery times for the 100 nm films which are 60 s and 7 min, respectively. The 100 nm thin film also showed a stable baseline as compared to the drifted baseline in the 400 nm film. The long sensing recovery for the 400 nm thin film is probably due to the slow H₂ adsorption and desorption on the NiO layer at that particular thickness [43].
Fig. 7.37 illustrates the cumulative absorbance change as a function of H₂ concentration for Pd/NiO nanostructured thin films at 170°C for a wavelength range of 500-800 nm.

Fig. 7.37 Cumulative absorbance change as a function of H₂ concentration for Pd/NiO nanostructured thin films of the thicknesses (a) 400 nm and (b) 100 nm at 170°C for a wavelength range of 500-800 nm.

From the figure, the response is increasing linearly when exposed to H₂ with concentrations of up to 0.25%. For the concentrations higher than that, the film response starts to saturate. The magnitude of the Pd/NiO response is also much lower than of the Pd/WO₃ films. When exposed to a few cycles of H₂ with different concentrations, the 100 nm NiO films indicate better repeatability than the 400 nm films. The average standard deviation relative to the mean cumulative absorbance change for the films with the thicknesses of 100 nm and 400 nm is ±7.3% and ±11.4%, respectively.

In conclusion, the author successfully proved that the Pd/NiO nanostructured thin films show promising gasochromic response towards H₂ with low concentrations of up to 0.06%. The p-type Pd/NiO films response is the opposite of the n-type metal oxides by turning transparent when exposed to the gas. The annealed Pd/NiO sputtered films have high surface area and based on the SEM images, they consist of 20 – 40 nm nanograins. However, the films clearly have low H₂ chemisorption. This is shown by their slow response and recovery even at the operating temperature that is higher than for any Pd coated metal oxides films used in this project.
### 7.2.11 Summary of the Gasochromic Response of the Metal Oxide Nanostructured Thin Films Based on Absorbance Measurement

In this PhD project, the gasochromic response of four different metal oxides nanostructured thin films towards H₂ based on absorbance measurement were successfully measured. The metal oxides are WO₃, MoO₃, TiO₂ and NiO. There are existing works on the chromic properties of these materials. However, most of the literatures on the materials were concentrated either on their electrochromic and photochromic properties or based on the gasochromic properties of their polycrystalline structures. In this research, the author focused on the gasochromic properties of the metal oxides nanostructured thin films. The nanostructured films’ morphologies are different from their polycrystalline counterparts and more critical for gas sensing applications as compared to the other applications due to their major influence in the gas molecules–surface interaction.

The main gasochromic material under investigation is nanostructured WO₃. Initial stage of investigation was to compare the optical sensing performance of the WO₃ sputtered films coated with different catalytic metal layers, namely, Pt, Pd and Au towards H₂ with different concentrations. The analysis was summarised as in Table 7.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Material Characteristic</th>
<th>Pt/RF sputtered WO₃</th>
<th>Pd/RF sputtered WO₃</th>
<th>Au/RF sputtered WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Thickness (nm)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>2.</td>
<td>Operating Temperature (°C)</td>
<td>100</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>3.</td>
<td>Sensitivity (%) towards 0.06% H₂</td>
<td>+0.5%</td>
<td>+5%</td>
<td>+2.5%</td>
</tr>
<tr>
<td>4.</td>
<td>Response Time* (s)</td>
<td>40</td>
<td>20</td>
<td>120</td>
</tr>
<tr>
<td>5.</td>
<td>Recovery Time* (s)</td>
<td>100</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td>6.</td>
<td>Repeatability (% ave. standard deviation)</td>
<td>±14.8%</td>
<td>±2.1%</td>
<td>±4.7%</td>
</tr>
</tbody>
</table>

* Taken for 1% H₂
Based on Table 7.1, the sputtered WO₃ films coated with Pd layer show superior optical sensing performance towards H₂ as compared to the films coated with other catalytic layer. Based on these findings, Pd was selected as the catalyst for all the metal oxide nanostructured thin films investigated throughout this project.

The WO₃ nanostructured thin films deposited via RF sputtering consist of nanograins. The gasochromic response investigation were continued for Pd/500 nm WO₃ sputtered films on different transparent substrates (quartz, glass, ITO and FTO). The aim of this investigation is to identify the effect of the substrate surface on the growth of the WO₃ nanostructures and on the film gasochromic response. The films deposited on the quartz, glass and ITO substrates consist of the smallest WO₃ nanostructures (30 – 60 nm grains) as compared to the ones on the FTO (300 – 500 nm grains). The maximum gasochromic response towards H₂ was observed to be similar for the films on quartz, glass and ITO substrates with the 110% increase of sensitivity and fast response and recovery (<180 s) when exposed to H₂ with 1% concentrations at 100°C. However, among these three transparent substrates, the best repeatability was indicated by the ones on quartz and glass substrates with the relative standard deviation of <±13%.

In the next stage, the author investigated the gasochromic response of the different WO₃ nanostructured thin films on quartz substrate. Various kinds of WO₃ nanostructures were deposited via RF sputtering, electron beam and PLD deposition techniques as well as acid-etching synthesis method. 25Å Pd layer was coated onto the nanostructured films and later exposed to H₂ with different concentrations.
Their gasochromic performance was summarised in Table 7.2.

**Table 7.2 Summary of the gasochromic response of the Pd/WO$_3$ nanostructured thin films.**

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Morphology</td>
<td>nanograin</td>
<td>nanosphere</td>
<td>nanorod</td>
<td>nanoplatelet</td>
</tr>
<tr>
<td>2</td>
<td>Film Thickness (nm)</td>
<td>500</td>
<td>500</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>Operating Temperature ($^\circ$C)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Sensitivity* (%)</td>
<td>+110%</td>
<td>+17%</td>
<td>+11%</td>
<td>+99%</td>
</tr>
<tr>
<td>5</td>
<td>Response Time* (s)</td>
<td>60</td>
<td>120</td>
<td>120</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Recovery Time* (s)</td>
<td>120</td>
<td>120</td>
<td>360</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>Repeatability (% ave. standard deviation)</td>
<td>±13%</td>
<td>±3.3%</td>
<td>±5.8%</td>
<td>±4.4%</td>
</tr>
</tbody>
</table>

* Taken for 1% H$_2$

Based on this summary, the Pd/WO$_3$ sputtered films show sensitivity of nearly ten times higher than for the Pd/WO$_3$ films deposited via electron beam technique with the same thickness of 500 nm. Even though they indicated lower repeatability, the Pd/WO$_3$ sputtered films have faster response than the Pd/electron beam deposited WO$_3$ films.

Meanwhile, the sensing performance results for the pulsed laser deposited and acid etched films are inconclusive to be comprehensively compared due to the different thicknesses achieved. This is caused by the limitation in the fabrication equipment for the former and low transparent films for the latter at the thickness of 500 nm. However, overall optical sensing performances indicate the superiority of the Pd/WO$_3$ nanoplatelet films synthesised via acid etching technique. These nanoplatelet films show sensitivity of nearly 100% when exposed to H$_2$ with 1% concentration even their thickness (150 nm) is the lowest of all the WO$_3$ thin films developed in this project. This sensitivity is approximately ten times higher than the WO$_3$ films deposited via PLD technique with the thickness of 170 nm. The nanoplatelet films also outperformed the PLD films by having faster response and recovery as well as better repeatability indication when exposed to H$_2$. 
Chapter 7: Gas Sensing Results

In the meantime, the investigation was also carried out on the gasochromic response of the other potential metal oxide nanostructured thin films. Various deposition techniques were deployed to produce the metal oxide nanostructured thin films. Later, the Pd coated films were subjected to comprehensive investigation on their gasochromic properties by varying the thickness and operational temperature. However, the author would like to highlight that the results presented in the following table are only for the metal oxide nanostructured thin films that shown their most significant gasochromic response when exposed to H$_2$.

The summary of the gasochromic performance of the MoO$_3$, TiO and NiO films coated with 25Å Pd layer is presented in Table 7.3.

Table 7.3 Summary of the gasochromic response of the Pd/Metal oxide nanostructured thin films.

<table>
<thead>
<tr>
<th>No</th>
<th>Material Characteristic</th>
<th>Thermal Evaporated MoO$_3$</th>
<th>Anodised TiO$_2$</th>
<th>RF Sputtered NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Morphology</td>
<td>nanorod</td>
<td>nanograin</td>
<td>nanograin</td>
</tr>
<tr>
<td>2</td>
<td>Film Thickness (nm)</td>
<td>1300 nm</td>
<td>1000 nm</td>
<td>400 nm</td>
</tr>
<tr>
<td>3</td>
<td>Operating Temperature (°C)</td>
<td>120°C</td>
<td>60°C</td>
<td>170°C</td>
</tr>
<tr>
<td>4</td>
<td>Sensitivity* (%)</td>
<td>+16%</td>
<td>+5%</td>
<td>+6.5%</td>
</tr>
<tr>
<td>5</td>
<td>Response Time* (s)</td>
<td>30 s</td>
<td>120 s</td>
<td>180 s</td>
</tr>
<tr>
<td>6</td>
<td>Recovery Time* (s)</td>
<td>480 s</td>
<td>180 s</td>
<td>540 s</td>
</tr>
<tr>
<td>7</td>
<td>Repeatability (% ave. standard deviation)</td>
<td>±14%</td>
<td>±8.1%</td>
<td>±11.4%</td>
</tr>
</tbody>
</table>

* Taken for 1% H$_2$

As much as the results above are inconclusive to be compared to each other mainly due to the vast different film thicknesses, overall gasochromic performances of these metal oxide nanostructured thin films are less superior than the WO$_3$ nanostructured thin films. The sensitivity of Pd/1.3 µm MoO$_3$ for H$_2$ of 1% is only 16% as compared to 120% for the Pd/1.2 µm WO$_3$ sputtered films as shown in Fig. 7.7. Eventhough Pd/MoO$_3$ films show impressive 30 s response time relative to 120 s for the Pd/1.2 µm WO$_3$ sputtered films, the former recovery time of 480 s is slower as compared to 180 s for the latter.
Meanwhile, Pd/anodised TiO$_2$ films of 1 µm thick have very low operating temperature than any metal oxide nanostructured thin films investigated in this project. Nevertheless, the films sensitivity of only 5% towards H$_2$ with 1% concentrations is much less than of the Pd/1.2 µm WO$_3$ sputtered films. Similarly, for the thicknesses of 400 nm and 100 nm, the Pd/NiO films sensitivity (<7%) is still very low relative to the Pd/WO$_3$ films towards H$_2$ of 1% concentrations. By comparison, the Pd/150 nm WO$_3$ nanoplatelet films show sensitivity of almost 100% towards H$_2$ with the same concentrations. In general, the Pd/WO$_3$ nanostructured thin films also perform better than Pd/NiO films by having lower operating temperature as well as faster recovery.

Based on the findings, the author concluded that the most promising gasochromic metal oxide nanostructured thin films investigated in this project towards H$_2$ were Pd/WO$_3$. In particular, the Pd/WO$_3$ films deposited via RF sputtering and synthesised via acid etching techniques have higher sensitivity, faster response and recovery as well as stable repeatability than the other metal oxide nanostructured thin films developed in this project when exposed to H$_2$. Due to this, the author continued the research by developing the optical fiber sensor coated with the Pd/WO$_3$ sputtered thin films and Pd/WO$_3$ nanoplatelet films towards H$_2$ with low concentrations.

To the best of the author’s knowledge, this is the first reported investigation on the gasochromic response of optical fiber coated with Pd/WO$_3$ nanoplatelet thin films towards H$_2$. The investigation was carried out based on the optical reflection measurement.
7.3 Hydrogen Sensing Results Based on Reflection Measurements

7.3.1 Optical Fiber Tip Coated With Pd/RF Sputtered WO$_3$

Fig. 7.38 shows the reflectance spectra of the optical fiber tip sputtered with Pd/200 nm WO$_3$ film exposed to synthetic air and H$_2$ with 1% concentration at room temperature.

![Reflectance spectra of optical fiber tip sputtered with Pd/200 nm WO$_3$ films exposed to synthetic air and H$_2$ of 1% concentrations at room temperature.](image)

It was found out that the reflectance of the optical fiber sensor is reduced for the visible-NIR wavelength ranges except between 660 – 740 nm upon the H$_2$ exposure. As mentioned in Chapter 2, the reflectance response is the opposite of the absorbance. As shown in the previous section, the Pd/WO$_3$ films increased their absorbance when exposed to H$_2$. In contrast, the reflectance measured from the fiber tip coated with the Pd/WO$_3$ films decreased when exposed to the same gas. The sensing mechanism can be described as follows. The light propagates inside the fiber and interacts with the Pd/WO$_3$ films on the tip. Due to the differences in the refractive indices of fiber core and the film, the light is reflected and then measured by the spectrophotometer. The Pd/WO$_3$ film becomes dark and its refractive index changes when exposed to H$_2$. The higher the H$_2$ concentration, the darker the films and thus, the lower the reflected light intensity. Based on Fig. 7.38, the intensity of the reflected light was reduced as well as shifted towards the blue region of the spectrum.

The magnitude of the reflectance response is stronger in the NIR wavelength range as compared in the visible range. This response characteristic similar to the Pd/WO$_3$ films...
absorbance change. Discussion about this characteristic have been presented in Section 7.2.5.

Fig. 7.39 shows the optical sensing performance of optical fibers sputtered with Pd/WO$_3$ film towards H$_2$ with 1% concentrations for WO$_3$ of thicknesses 100 and 200 nm. The measurement was carried out at the operating temperature of 100°C for the wavelength range of 750 – 900 nm.

It was clearly observed that the optical fiber coated with Pd/200 nm WO$_3$ films demonstrated larger changes in reflectance as well as superior response and recovery when compared with the Pd/100 nm WO$_3$ coatings. This is in agreement with the findings by Shanak and Schmitt [10] on the coloration of the WO$_3$ films. They reported that the optimised thickness in their sputtered WO$_3$ films to induce coloration is between 200 – 500 nm. According to them, for the films with the thickness less than 200 nm, the response was minimal with slower response and recovery as compared to the films with higher thickness.
Fig. 7.40 shows the dynamic sensing performance of the optical fiber sputtered with 200 nm thick Pd/WO$_3$ film towards H$_2$ at 100°C for the wavelength range of 750 - 900 nm.

The cumulative reflectance in 750 – 900 nm wavelength range was reduced by approximately 1.7% and 5.6% when exposed to H$_2$ with 0.06% and 1% concentrations, respectively. The T$_{90%}$ response towards H$_2$ with 0.06% concentration was less than 90 s while the recovery time was less than 100 s. When exposed to H$_2$ with 1% concentrations, the films T$_{90%}$ response and recovery were calculated to be approximately 60 s and 120 s, respectively. The optical fiber sensor shows excellent and significant response towards H$_2$ with low concentrations. Nevertheless, the sensor performance indicated some baseline drift which was raising with the increase of the H$_2$ concentrations. The author believed that the drift was due to the residual charge on the films as reported by Shanak and Schmitt [44]. The purging with the synthetic air after the H$_2$ exposure does not remove all the H$^+$ from the WO$_3$ film. These small amount remains in the film are responsible for residual charges [45]. The residual charges build up in the film depend on the level of the H$_2$ concentrations. The higher the concentration, the more the residual charges remained in the film. The synthetic air purged before another H$_2$ cycles removes some of the residual charges and the majority of the present H$^+$ from the preceding H$_2$ exposure. Due to this, the baseline drifted.

Fig. 7.41 represents the cumulative reflectance change as a function of H$_2$ concentration for the optical fiber sputtered with the Pd/WO$_3$ film at 100°C for wavelength range of
750 – 900 nm. The error bars represent the maximum and minimum deviations of the films reflectance response when exposed to a few cycles of different H₂ concentrations.

The graph of the optical fiber sputtered with the Pd/WO₃ nanostructured films exposed to H₂ with different concentrations indicate the sensor excellent static performance. The film cumulative reflectance increased linearly with the increase of the H₂ concentrations. The small error margins in the graph indicate the good repeatability of the optical fiber sensor exposed to many cycles of H₂ with different concentrations. The average standard deviation relative to the mean cumulative reflectance change was found to be ±2.48%. No sign of saturation were observed for the sensor response when exposed to H₂ with concentrations up to 1% in synthetic air. In general, the optical fiber sensor response was sensitive, fast and repeatable towards H₂ with low concentrations up to 0.06%.

The author continued the investigation on the gasochromic response based on reflection measurement with the optical fiber coated with Pd/acid etched WO₃.

### 7.3.2 Optical Fiber Tip Coated With Pd/Acid Etched WO₃

Before the gasochromic investigation on the optical fiber coated with the Pd/acid etched WO₃ films was performed, the fiber tip with the nanoplatelet films was annealed from 300°C to 480°C in air for the duration of 120 min. The annealing process converted the tungstite films into monoclinic WO₃ nanoplatelet films. The details on the WO₃ synthesis method was discussed.
previously in Chapter 4.

Fig. 7.42 shows the reflectance spectra of the optical fiber tip coated with the 25Å Pd/150 nm WO₃ nanoplatelet film exposed to synthetic air and H₂ with 1% concentrations at room temperature.

![Reflectance spectra of optical fiber tip coated with Pd/150 nm WO₃ nanoplatelet films exposed to synthetic air and H₂ of 1% concentrations at room temperature.](image)

It was observed that the reflectance of the optical fiber sensor is increased slightly in the visible range (470 – 670 nm) and significantly reduced for the visible-NIR wavelength ranges (700 – 950 nm) upon the H₂ exposure. The observed response is in the reflectance magnitude change as well as in the wavelength shift towards the blue-region. The fiber coated with the Pd/WO₃ nanoplatelet films exhibits larger reflectance change in the NIR region compared to the ones coated with the Pd/WO₃ sputtered films when exposed to H₂. According to the results described in the micro-nano characterisation section (Chapter 5), thermal treatment of the samples in high temperature enhances its monoclinic crystal phase and completely oxidizes the remaining W metal. The author believed that the improved crystallographic order of the sample could increase the available sites for H⁺ intercalation based on the findings by Georg et. al [6, 46, 47].
Fig. 7.43 shows the dynamic sensing performance of the optical fiber coated with the Pd/WO$_3$ nanoplatelet films towards H$_2$ at 100°C for the wavelength range of 750 - 900 nm.

The cumulative reflectance in 750 – 900 nm wavelength range was reduced by approximately 9% and 18% when exposed to H$_2$ with 0.06% and 1% concentrations, respectively. These results show that the fiber coated with Pd/WO$_3$ nanoplatelet films have much better sensitivity than the ones coated with the Pd/WO$_3$ sputtered films. The fiber sensor with the Pd/WO$_3$ nanoplatelet films $T_{90\%}$ response and recovery were calculated to be approximately 60 s and 120 s, respectively, when exposed to H$_2$ with 0.06% concentrations. For the sensing towards H$_2$ with 1% concentrations, the films $T_{90\%}$ response and recovery times were less than 60 s. These sensing performances were impressive and outperformed the performances exhibited by the sensor with the sputtered WO$_3$ films. Even though the 150 nm WO$_3$ nanoplatelet films on the fiber tip is with the thickness less than the WO$_3$ sputtered films (200 nm), they shows excellent and larger response towards H$_2$ with low concentrations. The fiber sensors with the WO$_3$ nanoplatelet films also have stable baseline except for a slight drift when sensing H$_2$ with 1% concentration. The author believed that the fiber sensor with the WO$_3$ nanoplatelet films responded stronger than the one with the WO$_3$ sputtered films due to their surface morphology. The nanoplatelet films are rough, porous and consist of (002) monoclinic crystal structures. As a result, the films have higher surface area and provide more sites for the H$_2$ adsorption/desorption as compared to the densed and predominantly (020) monoclinic sputtered films.
Fig. 7.44 represents the cumulative reflectance change as a function of H₂ concentration for the optical fiber coated with the Pd/WO₃ nanoplatelet film at 100°C for wavelength range of 750 – 900 nm.

The static performance of the optical fiber coated with the Pd/WO₃ nanoplatelet films exposed to H₂ with different concentrations indicate higher sensitivity than the sensor with the sputtered WO₃ films. The cumulative reflectance also increased linearly with the increase of the H₂ concentrations and showing no sign of saturation. The average standard deviation relative to the mean cumulative reflectance change was found to be ±5.4%. This indicates a slightly reduced repeatability for the nanoplatelet films relative to the sputtered films. In conclusion, the developed fiber sensor shows large response, fast recovery and stable repeatability towards H₂ with low concentrations.

Finally, the author completed project by investigating the gasochromic response of the WO₃ nanostructured thin films towards H₂ on the different transduction platform than transparent substrates and optical fiber, namely, inverted rib single mode polymer based optical waveguide. This is another novelty of the PhD research since no literature has been reported regarding the investigation.
7.4 Hydrogen Sensing Results Based on Beam Profile Measurements

In this project, the author completed the gasochromic investigation of the metal oxide nanostructured thin films towards H\(_2\) by observing the sensing performance of the waveguide based optical sensor coated with the WO\(_3\) sputtered films. On the other hand, the synthesis of the WO\(_3\) nanoplatelet films onto the waveguide could not be performed successfully because the method was found to affect the waveguide structure especially the endfaces. The details on the single mode polymer waveguide specifications are already presented in Section 3.4.3 (Chapter 3). In order to preserve the integrity of the polymer waveguide channels, the endfaces were covered and the top of the waveguide was RF sputtered with WO\(_3\) films at 100\(^\circ\)C. This is lower than the sputtering temperature for the films on quartz and optical fiber which is 260\(^\circ\)C. However, the film morphology was still mostly monoclinic WO\(_3\) nanograins of 30 – 60 nm sizes. This is in agreement with many previous works which identify that the monoclinic WO\(_3\) nanostructures exist within the temperature range of 17 - 330\(^\circ\)C [48]. Later 25Å Pd layer was DC sputtered on the WO\(_3\) nanostructured thin films at room temperature.

Fig. 7.45 illustrates the waveguide mode profile observed for (a) uncoated inverted rib channel and (b) Pd/WO\(_3\) films coated inverted rib channel via horizontally polarised optical signal.

![Waveguide mode profile](image)

Fig. 7.45 Polymer waveguide mode profile observed for (a) uncoated inverted rib channel and (b) Pd/30 nm WO\(_3\) films coated inverted rib channel.

The waveguides used for the gas testing applications were 25 mm in length. The setup used for the mode profile of the fabricated waveguide was explained in Chapter 6. A 635 nm laser was selected as the input light source and the mode profile was captured via CCD camera (Philips...
SPC900NC). TM polarisation was adjusted by tuning the fiber polariser.

Fig. 7.45 (a) shows the image of the mode profile of the uncoated inverted rib channel at the endface of the waveguide. The well-localised mode profile with a single intensity maximum shows clearly waveguide single mode operation. It is obvious that the fundamental mode is taking the v-shape of the inverted rib channel waveguide. In contrast, the coating of Pd/WO$_3$ layer on top of the waveguide changes the mode profile as in Fig. 7.45 (b). The mode becomes broader upward and there are approximately two maximum intensity spots were observed in the channel when compared to the mode in the uncoated channel. It is believed that the two intensity sites indicate that the light propagated in the channel was also coupled slightly into the thin sensing layer on top of the waveguide with the presence of more than one mode. The refractive index of the WO$_3$ layer is in the range of 2.0 – 2.6 [49]. This is higher than the refractive indeces of the waveguide core (1.592) as well as the cladding (1.566). Therefore, the light is guided not only in the core but also propagates into the WO$_3$ thin layer. Stankova et. al successfully coupled the light into the waveguide based on the 500 nm thick WO$_3$ films and reported the light propagation inside the films has high scattering due to the rough structures [50]. The mode profile in Fig. 7.45 (b) is for the Pd/WO$_3$ layer with the thickness of 30 nm coated on the waveguide. The thin Pd/WO$_3$ layer minimised the light from being fully coupled into the layer and mostly still guided in the channel. As shown in Fig. 7.46, it was observed that the mode profile in the waveguide coated with Pd/WO$_3$ layer of 50 nm thick shows worsen light scattering with no obvious guided mode than for the 30 nm WO$_3$ layer.

![Polymer waveguide mode profile observed for the Pd/50 nm WO$_3$ films coated inverted rib channel.](image)

Due to the above reasons, the author decided to investigate the gasochromic response of
the waveguide coated with the 25Å Pd/30 nm WO$_3$ films towards H$_2$. The thin layer of WO$_3$ was deposited within the penetration depth, $d_p$, of the evanescent wave estimated in Chapter 3 which is approximately less than 100 nm for optical signal wavelength of 532 nm. The gas testing setup was outlined as in Fig. 6.4 (Chapter 6). A 532 nm green laser (500 mW, Shanghai Dream Laser Technology, China) and Beamage CCD12 beam profiler (Gentec) were utilised as the source and the detector, respectively. Fig. 7.47 shows the intensity profile of the 532 nm optical signal propagates in the inverted rib waveguide channel coated with the Pd/WO$_3$ films when exposed to (a) synthetic air and (b) H$_2$ with 1% concentrations for 5 min at 100°C. The figure incorporates the intensity profile outlines in the bottom and left quadrants indicating the intensity patterns detected along the cross hairs (x and y axis).

![Intensity profile of the 532 nm optical signal propagates in the inverted rib waveguide channel coated with Pd/WO$_3$ films when exposed to (a) synthetic air and (b) H$_2$ with 1% concentrations at 100°C.](image)

The beam image of the 532 nm optical signal out of the inverted rib channel coated with the Pd/WO$_3$ films revealed two distinct intensity sites. Similar to the mode profile observed in Fig. 7.45 (b), the top and the bottom intensity sites indicated the light propagated in the Pd/WO$_3$ sensing layer and the channel, respectively. However, the intensity of the light in the channel is much stronger and focused than in the sensing layer. It is suggested that the light is scattered by the rough WO$_3$ nanostructured thin film layer. Fig. 7.46 clearly shows that the intensity diminishes when the Pd/WO$_3$ sensing layer on top of the waveguide was exposed to H$_2$ with 1% concentrations. This indicates that the light propagated in the channel was absorbed by the sensing layer.
The intensity profile outlines in Fig. 7.48 below provide detailed information on the effect of the H₂ to the light propagated in the channel waveguide.

![Fig. 7.48 Intensity profile outlines observed at horizontal (x) and vertical (y) axis of the beam in the inverted rib waveguide channel coated with Pd/VO₃ when exposed to synthetic air and H₂ of 1% concentrations at 100°C.](image)

The graphs in Fig. 7.48 represent the intensity profile outlines observed at horizontal (x) and vertical (y) plane of the beam in the inverted rib waveguide channel coated with Pd/VO₃ when exposed to synthetic air and H₂ of 1% concentrations at 100°C. The x-axis is the position of the light measured at the beam profiler interface. The y-axis represents the intensity of the light converted by the beam profiler analog-to-digital converter (ADC). The 14-bit ADC be able to convert the analog light intensity into the maximum 16384 relative levels.

As shown by the x-profile graph, the light intensity in the waveguide channel is reduced to approximately 50% when the Pd/VO₃ films on top of it was exposed to H₂. From the vertical axis as shown by the y-profile, the light intensity is reduced only by 25%. The profile outline from the vertical axis also shows two major intensity peaks which are belong to the light guided in the channel (right peak) as well as some portion in the Pd/VO₃ sensing layer (left peak). The inverted rib waveguide used in this project was designed in such a way that the interaction between the light (TM fundamental mode) in the channel and the sensing layer is optimised. As a result, the reduction in the light intensity observed from the horizontal profile is more than the reduction observed from the vertical profile when the waveguide exposed to H₂.
The gasochromic response shown by the waveguide based sensor is in accordance with the response reported earlier for the Pd/WO₃ nanostructured thin films on the transparent substrates and the optical fiber. The H₂ interaction with the Pd/WO₃ films on top of the waveguide turned the films dark and highly absorbed the light. The change of the films optical property also affecting the light propagates in the waveguide. More signal was absorbed into the Pd/WO₃ films resulting in the decrease of the light intensity as measured by the beam profiler.

It was found out that the film was only sensitive towards H₂ with 1% concentrations. Eventhough the light intensity was reduced for H₂ with only 1% concentrations, the response was also irreversible. Therefore, the dynamic performance of the sensor could not be observed. The author suggested that the 30 nm WO₃ films is too thin to induce reversible coloration when exposed to H₂ with different concentrations. The thin films posses much less oxygen vacancies than thicker films, whereas the gasochromic response of the WO₃ strongly depends on the defect or the oxygen vacancies in the metal oxide films [12]. As reported by Shanak and Schmitt for their DC sputtered WO₃ films, the coloration due to H₂ exposure was very minimal for the film with the thickness of 20 nm as compared to the thickness of 1 µm. They also found out that the optimum thickness of the sputtered WO₃ films to induce coloration is between 200 – 450 nm [10]. However, based on the current waveguide design, it is not possible to deposit the WO₃ sensing layer with the thickness previously recommended. This is because, the light propagates in the waveguide channel will be completely coupled into the sensing layer and thus, no proper guided light will be observed and measured with the beam profiler.

The author proposed some improvements to the existing inverted rib waveguide design to enable sensitive and reversible gasochromic sensing performance towards H₂. These will be presented in the next chapter on the conclusions and future works.
Based on the results of the three different sensors developed on different transducer setups, general evaluation on their attributes are compared in Table 7.4. The reference sensing layer is Pd/sputtered WO$_3$ thin films.

Table 7.4 Comparison of optical H$_2$ sensor attributes using different transducer setups with reference to Pd/sputtered WO$_3$ films.

<table>
<thead>
<tr>
<th>No</th>
<th>Transducer Setup Attribute</th>
<th>Absorbance Setup (Transparent Substrate)</th>
<th>Reflection Setup (Optical Fiber)</th>
<th>Beam Profile Setup (Waveguide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sensitivity</td>
<td>high</td>
<td>Medium</td>
<td>low</td>
</tr>
<tr>
<td>2.</td>
<td>Sensing speed</td>
<td>fast</td>
<td>fast</td>
<td>slow</td>
</tr>
<tr>
<td>3.</td>
<td>Cost</td>
<td>medium</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>4.</td>
<td>Sensor complexity</td>
<td>low</td>
<td>Medium</td>
<td>high</td>
</tr>
<tr>
<td>5.</td>
<td>Setup complexity</td>
<td>medium</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>6.</td>
<td>Product viability</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

The comparison on the general attributes of the optical H$_2$ sensors developed in this project indicates unique advantages for different transducer setups especially for absorbance and reflection setups. The developed H$_2$ sensors based on the absorbance response of the transparent substrates show high sensitivity and viability as well as fast sensing response towards H$_2$ with low concentrations. The fabrication of the sensing layer on the transparent substrate is also simple with low complexity. Nevertheless, its testing setup requires additional optical fibers and thus, incurring extra cost and unsuitable for remote sensing. Meanwhile, the developed sensors based on the reflection of the optical fiber show moderate sensitivity as compared to the absorbance based sensor. However, the sensing results proved that the fast response and high viability of the optical fiber sensor are equivalent with the performance of the absorbance based sensor. The fabrication of the sensing layer is also more complicated on the optical fiber as compared to the transparent substrate. On the other hand, the sensing application based on reflection measurement require single optical fiber and less complex than the other techniques. Therefore, the developed H$_2$ sensor based on reflection measurement is more suitable for remote sensing and requires simpler setup as compared to the absorbance measurement. It was found out that the H$_2$ sensor
using waveguide has lower sensitivity and response than the other devices. The waveguide sensor implementation is also more complex compared to the other setups. This is due to the process of coupling the light into the small waveguide channel requires high precision. As a result, the $\text{H}_2$ sensor using waveguide is more costly relative to the other sensors. More works should be explored to improve the waveguide sensor.

By taking the sensing performance, cost and setup complexity into the consideration, the author recommends $\text{H}_2$ sensor based on the optical fiber coated with Pd/WO$_3$ nanostructured films as the suitable device for remote gas sensing applications outlined in this project.

### 7.5 Summary

In this chapter, the author explained in details the gasochromic sensing performance of the developed optical sensors coated with metal oxide nanostructured thin films towards $\text{H}_2$. The author deposited the thin films onto three optical transducers, namely, transparent substrates, multimode optical fibers and single mode inverted rib waveguides. The investigation of the gasochromic sensing performance were carried out on the different optical sensors based on different optical measurements.

The investigation of the $\text{H}_2$ sensing response based on absorbance measurement was carried out on the metal oxide nanostructured thin films on the transparent substrates. Various kinds of potential metal oxides nanostructures were deposited and tested towards $\text{H}_2$ with different concentrations. They are nanostructured WO$_3$, MoO$_3$, TiO$_2$ and NiO. The highlights of the investigations that significantly contribute to the understanding of the gasochromic material characteristics towards $\text{H}_2$ are as follows:

- Different WO$_3$ nanostructures produce different gasochromic response when combined with the catalytic metal layer. Eventhough the $\text{H}_2$ response of the WO$_3$ sputtered films has been reported before, the author extended the investigation on the WO$_3$ films sputtered on different transparent substrates. The gasochromic sensing performance was determined to be the more stable for the films on quartz,
glass and ITO substrates with the similar small nanograin morphology as compared to the films with large nanograins on FTO substrate.

- The influence of the catalytic metal layer on the films gasochromic response was investigated by comparing the H\textsubscript{2} sensing performance of the films coated with Pt, Pd or Au. The analysis in this project supported the findings that the Pd layer is the most efficient catalyst to dissociate the H\textsubscript{2} molecules in order to induce the coloration in the metal oxide thin films as compared to the other noble metals.

- In this project, the author introduced new approach to measure the gasochromic response by integrating the response over a range of optical wavelengths as well as at a single wavelength in real time. This is important to accommodate the low cost light source which normally has broad linewidths or operates for a wavelength range rather than at a single wavelength. The measurement of the cumulative response was also identified to increase the sensitivity of the films towards H\textsubscript{2} with low concentrations.

- To the best of the author’s knowledge, this is the first time the absorbance sensing performance towards H\textsubscript{2} was reported for the WO\textsubscript{3} nanoplatelet thin films synthesised via acid-etching technique. The nanoplatelet films static and dynamic sensing performances were found to be significant than most of the other WO\textsubscript{3} nanostructured thin films developed in this project as presented in Table 8.2.

- The investigation on the response of the MoO\textsubscript{3}, TiO\textsubscript{2} and NiO nanostructured thin films towards H\textsubscript{2} revealed that the responses of these films were strongly dependent on the film morphology. In the case of TiO\textsubscript{2} films, the sputtered and annealed films did not show any response towards H\textsubscript{2}. However, when the TiO\textsubscript{2} films were anodised and annealed as well as coated with Pd layer, the response was observable towards H\textsubscript{2}. These findings are interesting because the only results reported in the present literature is on the response of TiO\textsubscript{2} towards ethanol. The
gasochromic response was detectable only for the Pd/MoO$_3$ nanorod films deposited via thermal evaporation technique at the 15 cm substrate-MoO$_3$ powder distance. The Pd/MoO$_3$ nanoplatelet films deposited via the similar technique but at a closer substrate-powder distance (10 cm) did not show any significant optical response towards H$_2$.

- Meanwhile, the gasochromic sensing performance of the p-type NiO nanostructured thin films coated with Pd was proven to be the opposite of the n-type semiconducting metal oxides such as WO$_3$. However, the operating temperature of the Pd/NiO films were found to be higher than any other metal oxides thin films developed in this project. Generally, the WO$_3$ gasochromic sensing performance is superior compared to these metal oxides nanostructured thin films upon H$_2$ exposure. Their sensitivities was measured to be less than 20% as compared to more than 100% for the WO$_3$ sputtered films towards H$_2$ with 1% concentrations.

In the case of the optical fiber sensors, their tips were coated with the sensing layers that were identified to provide the most well-balanced gasochromic performance when measured towards H$_2$ via absorbance measurement. The two types of the sensing layers are Pd/WO$_3$ sputtered thin films and Pd/WO$_3$ nanoplatelet thin films. The gasochromic performances of the fiber sensor coated with the Pd/WO$_3$ nanostructured thin films were investigated based on their reflection response. It was established that the optical fiber coated with the Pd/150 nm WO$_3$ nanoplatelet thin films shows better sensitivity than Pd/200 nm WO$_3$ sputtered thin films when exposed to H$_2$ with different concentrations. The high surface area due to the porous and rough morphology of the WO$_3$ nanoplatelet films were suggested to provide efficient sites for the H$_2$ adsorption/desorption and thus, stronger sensing performance than the WO$_3$ sputtered films.

The investigation on the gasochromic response of the single mode inverted rib polymer waveguide coated with Pd/WO$_3$ sputtered thin films was performed towards H$_2$. The response was
measured based on the intensity of the beam propagating in the waveguide channel. The WO$_3$ films were found to have higher refractive index than the SU-8 polymer used as the waveguide channel. Due to this, the deposition of the WO$_3$ nanostructured thin films on top of the waveguide was limited to 30 nm only to avoid the light propagation in the channel from completely coupling into the WO$_3$ layer. The beam intensity was reduced to 50% when the film on top of the waveguide was exposed to H$_2$ with 1% concentrations. Nevertheless, the response is irreversible and insensitive towards H$_2$ with the lower concentrations than 1%. This is believed due to the very thin WO$_3$ films having less oxygen vacancies to induce reversible coloration when exposed to H$_2$.

This waveguide based optical detector is useful for the early detection system towards H$_2$, which is odourless, colourless and highly flammable gas with low ignition energy [51]. It has been reported that the H$_2$ lower explosive level (LEL) threshold is only 4% [52, 53]. Minor leaks from H$_2$ storage tanks in enclosed environments can quickly reach this potentially explosive concentration. Therefore, the early warning detection system that is sensitive to H$_2$ with lower concentrations than its LEL are of great demand. This is also important especially in the volatile and flammable environment where the deployment of the electrical based system may pose high risk due to the electromagnetic interference and electrostatic.

In this project, the author successfully investigated the gasochromic response of the metal oxides nanostructured thin films towards H$_2$. Based on their excellent sensing performances, the optical sensors coated with the Pd/WO$_3$ nanoplatelet or sputtered thin films were identified as the best candidates for H$_2$ sensing applications as compared to the other metal oxide nanostructured thin films investigated throughout this research program.
Chapter 7: Gas Sensing Results

References


Chapter 7: Gas Sensing Results


Chapter 8

Conclusions and Future Works

The final chapter of this PhD thesis concludes the research results presented by the author. A summary of the outcomes and the author's suggestions for possible future work is also discussed.

8.1 Conclusions

The aim of this PhD thesis was to investigate the gasochromic response of the metal oxide nanostructured thin films based optical H₂ sensor. To achieve this, the author deposited and characterised various kinds of metal oxide nanostructured thin films on different optical transduction platforms. Generally, the developed optical sensors exhibited excellent static and dynamic performances towards H₂ with low concentration range of 0.06 – 1% in synthetic air. The work presented in this thesis has contributed to the body of knowledge in the gas sensing applications, specifically in the optical sensor technology which is new domain as compared to the well-established electrical based sensors.

This thesis presents the evolution of the author’s research, which can be summarised as follows:

- deposition and synthesis of metal oxide nanostructures promising for the gasochromic applications towards H₂. This includes WO₃ nanograins, WO₃ nanospheres, WO₃ nanorods, WO₃ nanoplatelets, MoO₃ nanorods, TiO₂ nanopores and NiO nanograins.
- deposition of catalytic metal layer (Pd, Pt, Au) and their combination with the metal oxide nanostructured thin films.
- development and fabrication of optical sensors incorporating the above H₂ sensitive thin films and different transduction platforms, namely, transparent substrates, multimode optical fiber and inverted rib polymer waveguide. The transparent substrates consist of quartz, glass, ITO and FTO glasses.
- investigation of the H₂ sensing performance of the optical sensors.
- determination of a sensing mechanism for the H₂ interaction with the developed optical sensors.

Based on the micro-nanocharacterisation and the gas sensing performance results, the major findings of this research are highlighted as follows:

- the Pd catalytic layer was identified to have greater influence to improve the optical sensing performance of the WO₃ nanostructured thin films when exposed to H₂ as compared to the films coated with Pt or Au catalysts. This was proven with the increase of sensitivity up to 5% for Pd/500 nm WO₃ sputtered films response towards H₂ with 0.06% concentration. The increase of sensitivity of the Pt/500 nm WO₃ and Au/500 nm WO₃ films was only 0.5% and 2.5%, respectively, towards H₂ with similar concentrations. The operating temperature for the WO₃ films coated with Pd or Pt was found to be 100°C as compared to 200°C for the films coated with Au. These results supported the previous works on the excellent performance of the Pd as H₂ catalyst and storage.
- the optical sensing performance of the sputtered WO₃ films towards H₂ were found to be significantly affected by the WO₃ nanograin sizes largely due to the improve in the surface area available for H₂ interaction. This was confirmed by the increase of response up to 110% towards H₂ with 1% concentration for the 500 nm films sputtered onto quartz, glass and ITO consist of 30 – 60 nm grains. In contrast, the response of the 500 nm thick films sputtered onto FTO consisting of 300 – 500 nm grains was increased by only 5% towards H₂ with similar concentration.
the H₂ testing on the Pd/WO₃ thin films with different nanostructures had identified that the 500 nm WO₃ sputtered films and 150 nm nanoplatelet films produced the largest response compared to the 500 nm e-beam deposited and 170 nm pulsed laser deposited films. Exposed to H₂ with 1% concentration, the absorbance responses of the Pd/WO₃ sputtered films and Pd/WO₃ nanoplatelet films increased by 110% and 99%, respectively.

the H₂ testing on the Pd/MoO₃ nanostructured thin films had showed that the films produced significant absorbance response in the NIR wavelength range at 120°C. The MoO₃ nanorod films were able to sense H₂ with concentration as low as 0.06%. The nanorod films are more sensitive than the Pd/MoO₃ films reported previously which operated towards H₂ with concentration range >1%.

for the first time, the H₂ testing on the Pd/TiO₂ nanoporous films showed that the films produced absorbance response in the visible-NIR wavelength range. Nevertheless, the optical response of the films was minimal with 5% increase towards H₂ of concentration around 1%. This is believed mainly due to the transformation of Pd into PdH instead of the large transition in the TiO₂ nanostructured thin films when exposed to H₂. The optical response of the Pd catalytic layer towards H₂ has been reported in the literature but very minimal as compared to the response of the Pd/metal oxide films.

the H₂ testing on the Pd/NiO sputtered films revealed that the absorbance response is reduced when the films are exposed to H₂ with different concentrations. To the best of author’s knowledge, the testing results are novel and successfully proved that the n-type metal oxide shows the opposite gasochromic properties as compared to the p-type metal oxides. The Pd/400 nm NiO films became transparent with 6.5% absorbance response decrease towards H₂ of 1% concentration.

the H₂ testing on the optical fiber tip coated with Pd/WO₃ nanostructured thin films produced excellent reflection response when exposed to H₂ with different
concentrations. The optical fiber tip sputtered with Pd/WO$_3$ nanograin films showed a 5.6% change in the reflection when exposed to H$_2$ of 1%. Meanwhile, the fiber tip coated with Pd/WO$_3$ nanoplatelet films had a larger response (18% reflection change) as compared to the tip with the WO$_3$ nanograins towards H$_2$ with the same concentration. These results highlighted the different sensing performance of the optical fiber sensor coated with different WO$_3$ nanostructures when exposed to H$_2$.

- the H$_2$ sensitive inverted rib polymer waveguide coated with 25Å Pd/30 nm WO$_3$ nanostructured thin films was successfully developed and tested towards H$_2$ with low concentrations of 1% at the operating temperatures of 100°C. The intensity of light propagating in the waveguide reduced significantly by 50% when exposed to H$_2$. Nevertheless, the response was irrecoverable and more investigation needs to be carried out to improve the device performance. These results provide an excellent platform for further research in low concentration H$_2$ leakage detection.

Based on the abovementioned findings, the main contributions of this PhD research can be highlighted as follows:

- developed optical sensor based on new nanostructured WO$_3$ such as nanospheres, nanorods and nanoplatelets towards H$_2$ with low concentrations up to 0.06%.
- introduced cumulative absorbance measurement by integrating the response for a wavelength range to improve sensitivity towards H$_2$ with low concentrations up to 0.06%.
- proved the high sensitivity of the developed sensors based on WO$_3$ nanostructured films deposited on different optical transducers such as transparent substrates and optical fibers compared to the other metal oxides when exposed to H$_2$ with concentrations as low as 0.06%.
- proved the optical response of p-type NiO nanostructured thin films is the opposite of the response of the n-type metal oxide films when exposed to H$_2$. 
• proved that the Pd/MoO$_3$ nanostructured thin films has higher sensitivity as compared to the Pd/MoO$_3$ amorphous films towards H$_2$.
• proved that the optical sensing response towards H$_2$ was larger for the WO$_3$ nanostructured thin films as compared to the other nanostructured metal oxides such as MoO$_3$, TiO$_2$ and NiO.
• developed optical fiber sensor based on novel WO$_3$ nanostructures (nanoplatelets) with excellent sensitivity towards H$_2$.
• developed H$_2$ sensitive optical polymer waveguide coated with Pd/WO$_3$ nanostructured thin films.

In summary, this PhD research program yielded a number of novel and significant contributions to the filed of optical sensors based on nanostructured thin films for H$_2$ sensing applications. Throughout this research, the author gained various achievements such as numerous publications and award. Research papers associated with this PhD program have been published in refereed journals and presented at various established international conferences. These include four first author and five co-author publications in: Sensors and Actuators B: Chemical, Sensor Letters, Physical Chemistry Chemical Physics and Korean Physical Society. Currently, the author preparing another research paper titled ‘Low Concentration Hydrogen Detection Using Inverted Rib Polymer Waveguide Coated with Pd/WO$_3$ Nanostructured Thin Films’ which will be submitted to Optics Communication journal. The author also successfully published or presented 18 research papers in highly established conferences. During the IEEE Australia and New Zealand Student Congress 2010 in Melbourne, Australia, the author received the best project award. Throughout the course of this PhD program, the author was also invited to be a reviewer for Physica:E journal and International Conference on Photonics (ICP) 2010 and 2011 organised by IEEE Photonics Society of Malaysia. The list of the author's publications is shown in Appendix B.
8.2 Future Work

This PhD research has presented some major advancement in the field of optical sensor based on nanostructured thin films for gas sensing applications. Throughout the course of this research, several areas of interest, which has tremendous research potential, have been identified.

Therefore, the author highlights the future recommendations to researchers whom seek to follow with these research:

- development of optical sensor based on polymer waveguide towards H₂. The author successfully showed that the polymer waveguide coated with Pd/WO₃ film was sensitive towards H₂ of 1% concentration. In a bid to improve the device repeatability and sensitivity towards H₂ with different concentrations, investigation should be carried out on the optical waveguide design, operating wavelength range and the sensing layer thickness on the waveguide.

- development of optical fiber sensor based on photonic crystal fiber for gas sensing applications. The current availability of the photonic crystal fiber with pores surrounding the core provides interesting opportunity for H₂ sensing applications. The deposition of the nanostructured thin films in the pores could provide a new path in enhancing the response of the gas sensor based on optical fiber.

- investigation of novel gas sensor based on the optical properties of the conductive polymer nanostructured thin films. The conductometric based sensors coated with conductive polymers such as polyaniline and polypyrrole were widely reported to show excellent sensing performance towards H₂ at room temperature. These polymers were also identified to have chromic properties and deployed as the sensing layer for optical sensor towards NH₃. The author believes that the optical sensor based on the conducting polymer can be made sensitive towards H₂ by deploying nanostructured thin films.

- optimisation of the developed optical sensors specifically in terms of long term stability and humidity effect was not possible due to the limited time frame of this
Having such an analysis will provide comprehensive performance of these sensors for the harsh environments.

The author believes the presented promising results could provide opportunities in developing next generation optical H\textsubscript{2} sensors deploying nanostructured thin films. Further optimisation of the developed sensors to improve their performance could lead to them being commercialised and deployed in various applications. The diverse and increasing use of H\textsubscript{2} particularly in the locations that are public accessible require these highly sensitive sensors. The rising deployment of H\textsubscript{2} powered fuel cells to generate primary or backup electricity for remote residential areas must be equipped with a reliable sensor system to avoid disasters. The H\textsubscript{2} sensor based on optical fiber allows central monitoring of the power generator from the main office in the city. The lightweight fiber sensor can also be easily integrated with the existing communication link in the H\textsubscript{2} powered vehicle to detect any leakage in the fuel tank. The availability of the reliable optical H\textsubscript{2} sensor increases the confidence of the public in the safe H\textsubscript{2} management. As a result, the utilisation of the H\textsubscript{2} based technologies can be intensified and becomes significant in reducing the fossil fuel dependency.
Appendix A

Author’s Publication List

A.1 Refereed Journal Articles:


A.2 Reviewed Conference Proceedings:


